A Theoretical and Synthetic Investigation
of New Donors for Organic Electro-Optic Chromophores:
Understanding the Effects of Structure and Substituents on Donor
Strength

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Abstract

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Understanding of the intricate connection between shape, structure and property has allowed many challenges facing the adoption of organic chromophores for electro-optic (EO) applications to be overcome. Still, there is much to be learned about designing donors that localize electron density in the ground state, but not in the electronically polarized state to allow for enhanced charge transfer, and thus, large first-order molecular hyperpolarizability (β). To address this, density functional theory has been used to evaluate a large number of potential donors based on alkyl, aryl, saturated and unsaturated heterocycles. These were coupled to the tricyanopyrroline (TCP) acceptor by a simple vinylic bridge to identify new high β, high number density materials. Saturated heterocylces were found to off the largest improvements over traditional dialkyl donors, with the predicted systems rivaling much longer polyene-based chromophores with a trifluoromethyl, phenyl-tricyanofuran (CF_3PhTCF). Other potential candidates where based on diaryl amines donors which are a natural progression from previous heteroaryl chromophores. These systems were typified by a greater degree of localized electron density – by as much as 20% – at the donor and were found to exhibit characteristics that might described as a double-donor. Several novel chromophores based on these new donors were synthesized to verify the theoretical results and evaluate their potential for use in EO devices.

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NOMENCLATURE

List of Abbreviations

LiNbO$_3$ Lithium Niobate

CF3Ph-TCF 5-trifluoromethyl-5-phenyl-tricyanonofuran

DAAP 4-(diarylamino)phenyl

DATPA Diaminotriphenylamine

DFT Density Functional Theory

DNTPA Dinitrotriphenylamine

EO Electro-Optic

KDP Potassium Dihydrogen Phosphate

MN Malononitrile, CH$_2$(CN)$_2$

MND Malononitrile dimer, 2-Amino-1,1,3-propenetricarbonitrile

MPA Mulliken Population Analysis

NLO Nonlinear Optics

ONLO Organic Nonlinear Optics

OTN Optical Transport Network

TBDMS tert-butyldimethylsily

TBDPS tert-butyldiphenylsilyl

TCF 5,5-dimethyl-tricyanonofuran

TCP 5-trifluoromethyl-5-phenyl-tricyanonofuran

Physical Symbols

β_{ijk} First molecular hyperpolarizability, usually denoted as β_{vec} or β_{zzz} to indicate that it is in the direction of the dipolar axis

ΔE_{ge} Transition energy from the ground to the excited state.

$\Delta \mu_{ge}$ $\mu_{ee} - \mu_{gg}$

μ_r Relative permeability of a material

μ_{ee} Excited state dipole moment

μ_{ge} Transition dipole moment

μ_{gg} Ground state dipole moment

ε_r Relative permittivity of a material

r_{ij} Linear electro-optic coefficient

V_π Half-wave voltage, the voltage required to induce a phase change of π

n   Index of refraction

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I would like to thank Brandon Henry for his constant friendship and support, the undergrads I have worked with and the staff of the Chemistry department. I would also like offer a special thanks to Dr. Delwin Elder. He has been a great mentor and font of knowledge as I worked through some rather tricky synthetic issues. He has tirelessly, and graciously, offered his time in assisting with characterizing many of the molecules presented in this work, and for that I am eternally grateful.

DEDICATION

To Malia, you keep me (mostly) sane

and

to my mother,

who taught me the importance of an education.

Chapter 1

INTRODUCTION TO ORGANIC ELECTRO-OPTICS AND CHROMOPHORE DESIGN

1.1 Beyond textiles: Organic Dyes and Photonics

1.1.1 Synthetic dyes and Photonics
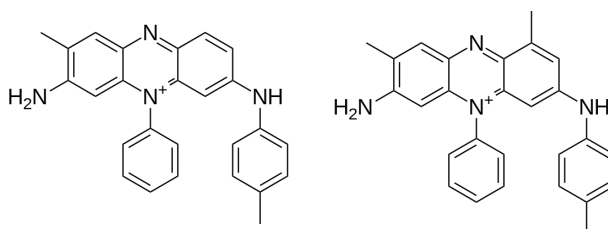
Fig. 1.1 Skeletal structure diagrams of Mauvine A(left) and Mauvine B(right), dyes synthesized by Sir William Henry Perkin in 1856 while trying to synthesize quinine from aniline.

The first synthetic dye was discovered in 1856[1,2]. It was synthesized from aniline (and isomeric toluidine impurities found in aniline) while trying to synthesize the antimalarial drug, quinine[3]. This marked the beginning of the synthetic dye industry, the reaches of of which have had impact far beyond the textile industry. Organic dyes have been used in medicine[4,5], sensing[6], optical recording[7] and power generation[8,9]. One thing that all of these applications have in common is the use of light; be it for the acquisition, storage, transmission and processing of data or for conversion into electricity, all of these applications fall under the broader field of photonics.

Photonics is the optical equivalent of electronics, where light and photons are used in place of electricity and electrons. As transistors become smaller, packing density starts to become an issue as interconnect crosstalk and power demands increase. Photonic offer one

possible way to overcome the inherent limits of electronics[10–12]. One industry that relies heavily on photonic devices is the telecommunications industry.

1.1.2 Photonics in Telecommunications

Telecommunications has become an integral part of modern business and society. Growth is being seen across all sectors and in all markets[13] as technological advances fundamentally change how traditional services are delivered. By the year 2020, the average internet household is predicted to generate 117.8 gigabytes of traffic per month and global IP traffic will reach an annual run rate of 2.3 zettabytes[13]. Most telecommunication networks have seen their older,copper-based, transmission lines replaced by optical fibers, but these networks are limited by the hardware used to transduce electrical signals on to optical carriers. These devices operate under the principle of the electro-optic effect.

1.1.3 The Electro-Optic Effect

The electro-optic effect (EO) is a change in the optical properties of a material by an electric field[14]. This change may be a change in absorption or a change in permittivity[15,16], but for the purposes of this text, the latter shall remain the focus. We can define the refractive index of a material as

$$n = \sqrt{\varepsilon_r \mu_r}, \tag{1.1}$$

where ε_r is the relative permittivity of the material and μ_r is the relative permeability[17]. For most cases, the relative permeability can be ignored for materials at optical frequencies – as they are non-magnetic so $\mu_r \approx 1$ – so the index of refraction can be expressed as $\sqrt{\varepsilon_r}$. For an electro-optic material, the index of refraction is a function of the applied electric, which changes very little with the elecetric field, E. We can then expand this in a Taylor's series about $E = 0$ such that,

$$n(E) = n + a_1 E + \frac{1}{2} a_2 E^2 + \cdots, \tag{1.2}$$

and the coefficients of expansion are $n = n(0)$, $a_1 = (dn/dE)|_{E=0}$ and $a_2 = (d^2n/dE^2)|_{E=0}$. We can now define the two new coefficients, r and K, as

$$r = -\frac{2a_1}{n^3}, \tag{1.3}$$

and

$$K = -\frac{a_2}{n^3}, \tag{1.4}$$

and recast equation 1.2 as

$$n(E) = n - \frac{1}{2}rn^3E - \frac{1}{2}Kn^3E^2 + \cdots . \tag{1.5}$$

We have now defined our linear EO coefficient, which corresponds to the Pockels effect, and the quadratic EO coefficient, which corresponds to the Kerr effect[1].

Both the Pockels coefficient and the Kerr coefficient are tensors, so the direction of the applied electric field is important in determing the change in the refractive index. The Kerr effect occurs in all materials and has no special symmetry requirements so it will be ignored cite(Boyd:2013aa). For an applied field, $E\,(E_x, E_y, E_z)$, the change in refractive index is

$$\Delta\left(\frac{1}{n^2}\right)_i = \sum_{j=1}^{3} r_{ij}E_j, \tag{1.6}$$

and $i = 1, \ldots, 6$ and $j = 1, \ldots, 3$. In a centrosymmetric crystal, all of the tensor elements r_{ij} are zero. For a non-centrosymmetric crystal, such as $LiNbO_3$, many of the off-diagonal elements vanish due to symmetry leaving only a few that are non-zero. From this, we learn that for a material to show a linear EO effect, it must be asymmetric or have a non-centrosymmetric crystal. Lithium niobate is a uniaxial crystal where $n_x = n_y = n_o$, $n_z = n_e$[2], and the important electro-optic coefficients are $r_{33} = 30.9\,\text{pm/v}$ and $r_{13} = 9.6\,\text{pm/v}$. Thus,

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[1]There is also a magneto-optic effect[18] that shares the same name. This refers strictly with the electro-optic Kerr effect.

[2]n_o and n_e are the ordinary and extraordinary refractive indices and the birefringence of a material is given as $\Delta n = n_e - n_o$

if an electric field is applied parallel to the E_z axis, a change in the refractive index will occur in either $n_z \propto n_e r_{33} E_z$ or $n_x = n_y \propto n_o r_{13} E_z$. For optimal device performance, it is advantageous to orient the crystal such that linearly polarized light is parallel to the optical axis.
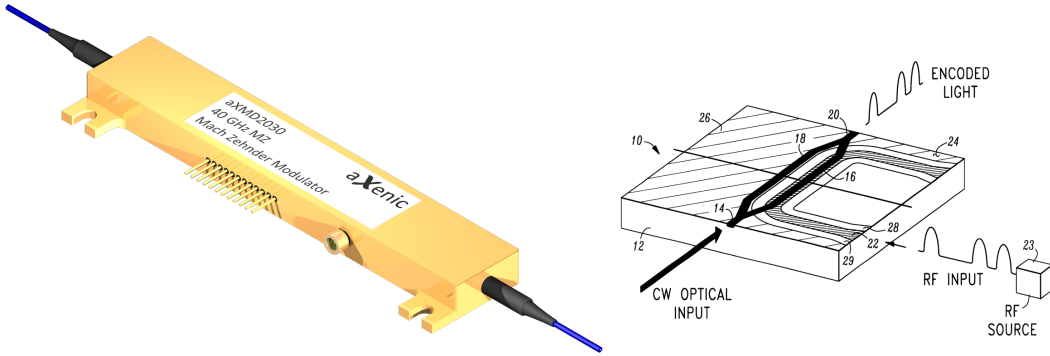
Fig. 1.2 A commercial Mach-Zehnder modulator based on gallium arsenide that operates at 40 GHz (source: aXenic) and Basic electro-optic modulator based on a Mach-Zehnder interferometer. Source: ref.[19]

One of the devices commonly used to transduce light onto optical carriers is a Mach-Zender modulator. This is shown in figure Fig. 1.2. They operate by splitting light from a single source into two arms. In a simple configuration(right side of figure Fig. 1.2), one arm allows the light to pass unperturbed. The other arm is passed through an EO material and depending on the applied voltage, passes unperturbed or has an induced phase change of π. When the two arms recombine, there is either constructive or destructive interference resulting in an optical 1 or 0. The half-wave voltage, V_π, is the voltage required to induce a phase change of π and is defined as

$$V_\pi = \frac{\lambda_0 d}{n^3 r L}, \tag{1.7}$$

where λ_0 is the operating wavelength, d is the active material thickness and L is the length of the active material. There is a trade-off between minimizing V_π and keeping optical losses at a minimum. Figure Fig. 1.3 shows typical half-wave voltages for EO modulators. Devices based on inorganic crystals have relatively low EO coefficients, necessitating longer
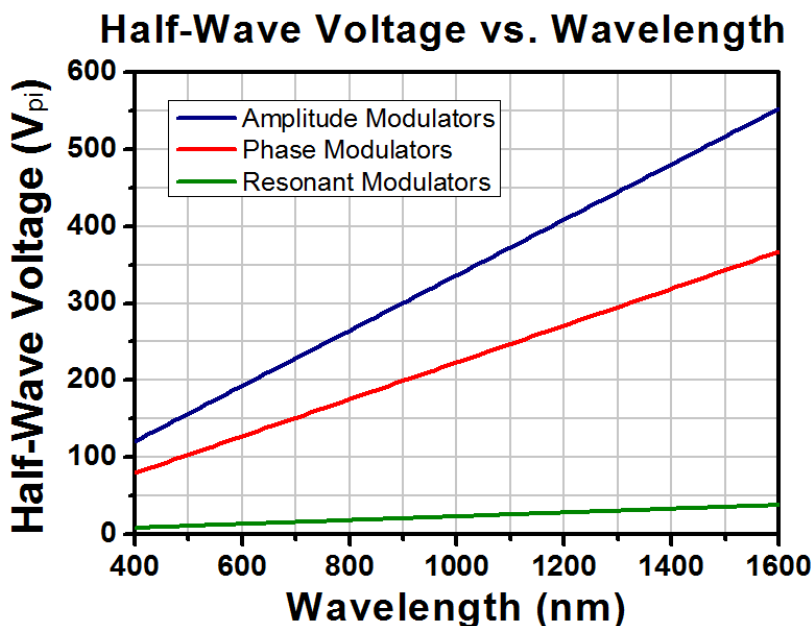
Fig. 1.3 The half-wave voltage of EO modulators based on inorganic crystals from Thor Labs.

devices and high half-wave voltages. Synthetic organic dyes have been shown to have high EO coefficients[11,12], high operating frequencies[20–22], and low half-wave voltages.[11] These attributes make organic dyes ideal candidates for replacing inorganics in EO applications.

1.2 Organic Electro-Optic Materials

1.2.1 Nonlinear Polarization in Organic Molecules

Before discussing what makes a good dye for use in EO applications, one must first know how the nonlinear optical (NLO) response in organic dyes arise[3]. Light is composed of both electric and magnetic components that are orthogonal to each other. The electric field is capable of interacting with electrons in organic molecules such that

$$p_i = \alpha_{ij} E_j, \tag{1.8}$$

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[2]The units for equations in this section are assumed to be in cgs or atomic units, unless stated or generally understood to be otherwise. Many of the equations are missing a factor of ε_0 that must be added if SI units are desired.
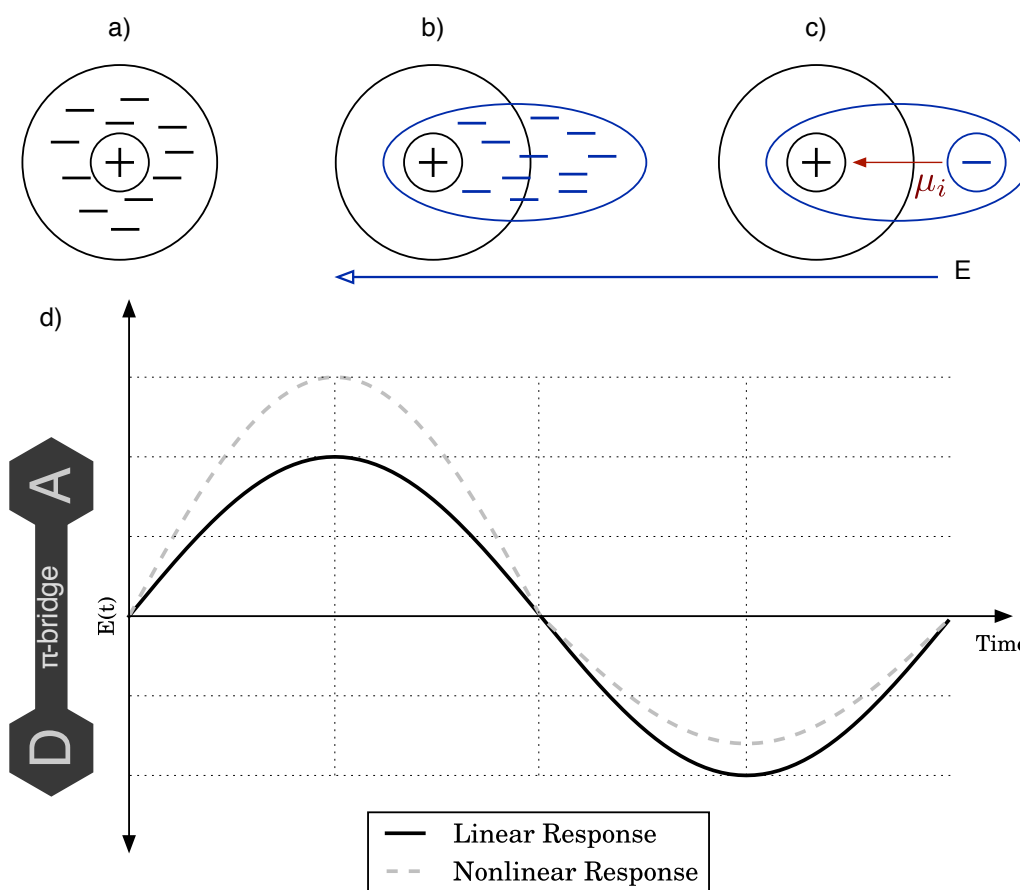
Fig. 1.4 Classic dielectric model of electric field interaction with an atom (top, a–c) and the linear and nonlinear response of π-conjugated system with electron donating and withdrawing end groups. a) Neutral atom in the absence of an electric field. b) As an electric field is applied, the electron cloud shifts in a direction opposite of the field. This leads to c) an induced dipole, μ_i, that is in the same direction as the electric field. The electric field is denoted by the blue arrow and the dipole by the red arrow. d) Following excitation by an optical field, an asymmetric electronic response arises due to polarization. The electron cloud favors the acceptor (A) end over the donor (D) end, resulting in a transition dipole and the nonlinearity.

where P_i is the induced polarization, α_{ij} is the linear polarizability, and i and j refer to coordinates in the molecular frame. Shown in figure Fig. 1.4, we see the results of polarization on a simple atom under the classic dielectric model. In the absence of an eternal field, the electrons are arranged around the positive atom core. When the atom is placed in a field, the electron cloud shifts in a direction opposite of the field to form an induced dipole. This induced dipole is equal to the polarization so equation 1.8 becomes

$$\mu_i = p_i = \alpha_{ij} E_j, \tag{1.9}$$

which is linearly proportional to the strength of the electric field. This holds true for cases of low intensity light, but as the intensity is increased, so to does the strength of the electric field and nonlinearities start to appear. The induced dipole is then a function of the field strength and we can express the nonlinear dependence with a Taylor expansion of equation 1.9:

$$\mu_i(E) = \mu_{g,i} + \alpha_{ij} E_j + \frac{1}{2!}\beta_{ijk} E_j E_k + \frac{1}{3!}\gamma_{ijkl} E_j E_k E_l + \cdots \tag{1.10}$$

We now have the first hyperpolarizability, β, and the second hyperpolarizability, γ, of the molecule. We can also define the linear and nonlinear susceptibilities as

$$P = P_0 + \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \cdots . \tag{1.11}$$

The first hyperpolarizability and second-order nonlinear susceptibility are at a maximum along the dipolar axis of the molecule, which we will define as the z-direction. We can now define the linear EO coefficient as

$$r_{33} = \frac{2f(\omega)}{n^4} \rho_N \beta_{zzz} \left\langle \cos^3(\theta) \right\rangle, \tag{1.12}$$

where $f(\omega)$ is the local field arising from the host dielectric permittivity, n is the refractive index, ρ_N is the molecular number density, β_{zzz} is the first molecular hyperpolarizability and $\left\langle \cos^3(\theta) \right\rangle$ is the accentric order parameter. Or course, this is assuming that the assumptions in the oriented-gas model hold true[23]. Our focus will be on improving r_{33} by improving β_{zzz} and possible ρ_N in small organic dyes that we will refer to as EO or nonlinear optical (NLO) chromophores so as to distinguish them from other uses.

1.2.2 Electric Field Poling
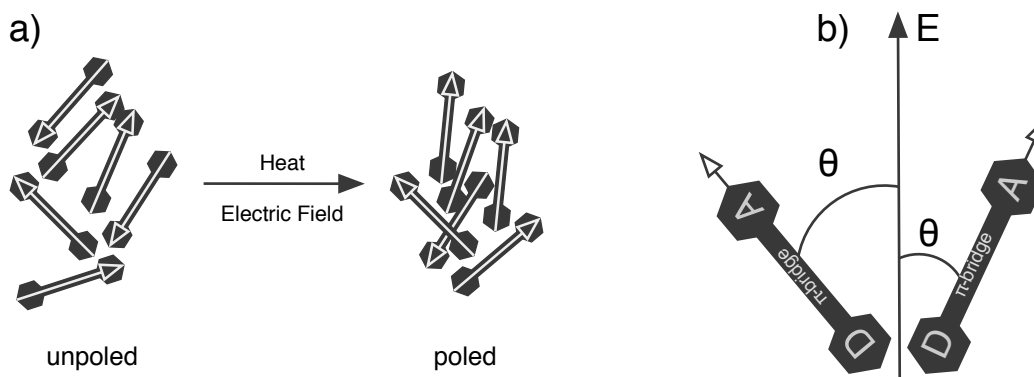
Fig. 1.5 a) In an unpoled systems, the molecules are randomly arranged and the EO activity is negligible. Upon applying heat and an electric field, the molecules are able to move so that their dipolar axis can align with the electric field. b) The amount of alignment is expressed in the term $\langle \cos^3(\theta) \rangle$ where θ is the angle between the dipolar axis and the external electric field.

As discussed before, the linear EO response requires noncentrosymmetric symmetry. To achieve this, a technique known as electric field poling is used. In figure Fig. 1.5 is a simple schematic showing the results of poling. First, the system is unordered with all the dipolar axes of the molecules pointing in random directions. Due to strong dipole-dipole interactions, many of these molecules are likely to be aligned antiparallel to minimize the overall energy of the ensemble. These interactions may be mitigated with shape engineering, guest-host polymer systems[24–27], binary systems[28] and side-chain interactions[29], among others. The unordered system is heated to allow for movement of the molecules. This temperature is typically just above the glass transition temperature and an external electric field is applied. A typical field strength is $100\,\mathrm{V}/\mu\mathrm{m}$ and once poling is complete, the achieved order is retained by allowing the system to cool. Activity may be measured by Teng and Man simple reflection ellipsometry[30,31], second harmonic generation[32], attenuated total reflection (ATR)[33,34], Fabry-Perot interferometry[35,36], and Mach-Zehnder interferometry[37,38].

1.2.3 Nonlinear Optical Chromophores
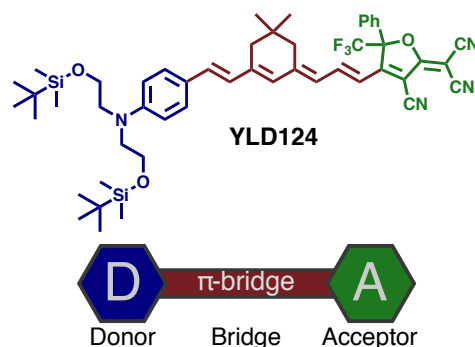
Fig. 1.6 The chromophore, YLD124, and a schematic showing the asymmetric donor-π-acceptor motif generally followed when designing neutral ground-state dyes for use in EO applications.

Dipolar, push-pull, chromophores for EO applications come in numerous shapes and sizes[39–48]. They may be be either a neutral ground state(NGS) or be zwitterionic(ZWI) molecules. Regardless, these chromophores share many similarities such as a rod-like design with a donor and acceptor connected by a π-conjugated bridge. We have shown a simple schematic of this D-π-A structure in figure Fig. 1.6 along with the structure for the chromophore YLD124. It is composed of a dialkyl donor and CF3-PhTCF acceptor linked by a CLD-type polyene bridge. The CLD polyene bridge in YLD124 and similar chromophores was developed to improve the loss in photo- and thermal stability often associated long, conjugated chains[49–53]. By incorporating the ring-locked isophorone unit in the bridge, the bridge length was extended to provide better charge separation. Another popular bridge is the FTC bridge, based on a thienyl-vinylene linker between the donor and acceptor. Chromophores based on this bridge often possess higher thermal and photo stabilities than their CLD counterparts, but at the cost of lower β[28,52,54]. These bridge moieties, along with several permutations, are shown in figure Fig. 1.7.
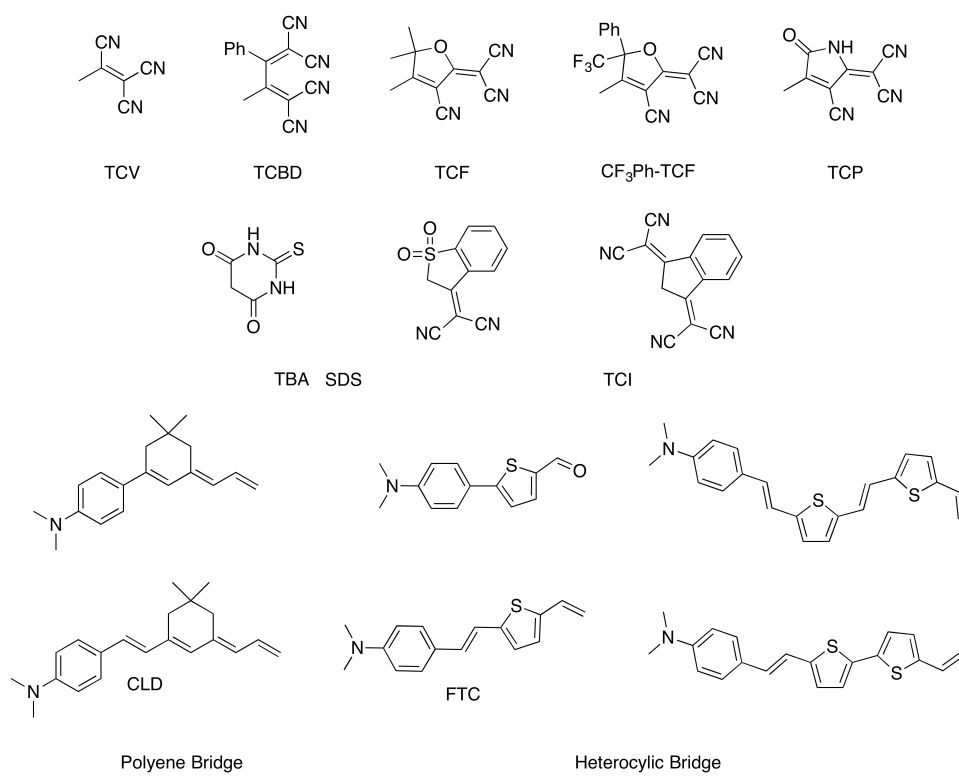
Fig. 1.7 Several acceptors (top) and donor-bridges (bottom) used in $D - \pi - A$ chromophores.

1.2.4 Structure and the effects on hyperpolarizability

The Two-State Model

Many early attempts at improving chromophore performance were based on permutations of 4-(*N,N*-dimethylamino)-4'-nitrostilbene (DANS). Oudar and Chemla put forth that the hyperpolarizability was dominated by a single intramolecular charge transfer process, greatly simplifying the sum-over-states(SOS) approach developed by Ward[55,56]. The SOS approach takes into account the admixing of the ground state and charge transfer state that arises from polarization caused by an external electric field. It accounted for all states and not just the dominant charge transfer state. But Oudar and Chemla were able to show that the contributions from the other states were neglible and that in these small $D - \pi - A$ systems, only the frontier orbitals made any significant contribution to the electric field polarized state. From this model,

$$\beta_{vec} \propto \frac{(\mu_{ee} - \mu_{gg})(\mu_{ge})^2}{(\Delta E_{ge})^2}, \tag{1.13}$$

where β_{vec} is the element of the hyperpolarizability tensor in the direction of the dipolar axis, μ_{gg} and μ_{ee} are the ground state and excited state dipole moments, μ_{ge} is the transition dipole moment and ΔE_{ge} denotes the difference between the ground and first excited state orbitals. The terms ΔE_{ge} and μ_{ge} may be obtained from UV-Vis absorption spectroscopy; μ_{ge} is related to the oscillator strength, ε, and ΔE_{ge} can be found from the onset of the low energy absorption(the ICT band). This simplified model gave much needed structural insight into chromophore design. As only the frontier orbitals makes major contributions to the polarized state, attention could be given to lowering the lowest occupied molecular orbital(LUMO) by increasing the acceptor strength and raising the highest occupied molecular orbital(HOMO) by increasing donor strength. This would lower ΔE_{ge} and an increase in β_{vec} according to equation 1.13. But if ΔE_{ge} is too low and the transition dipole, μ_{ge}, high, there will be significant electron density localized along the bridge. This would subsequently lower the term $(\mu_{ee} - \mu_{gg})$, hinting at the underlying structure-property relationship.

Bond-Length Alternation
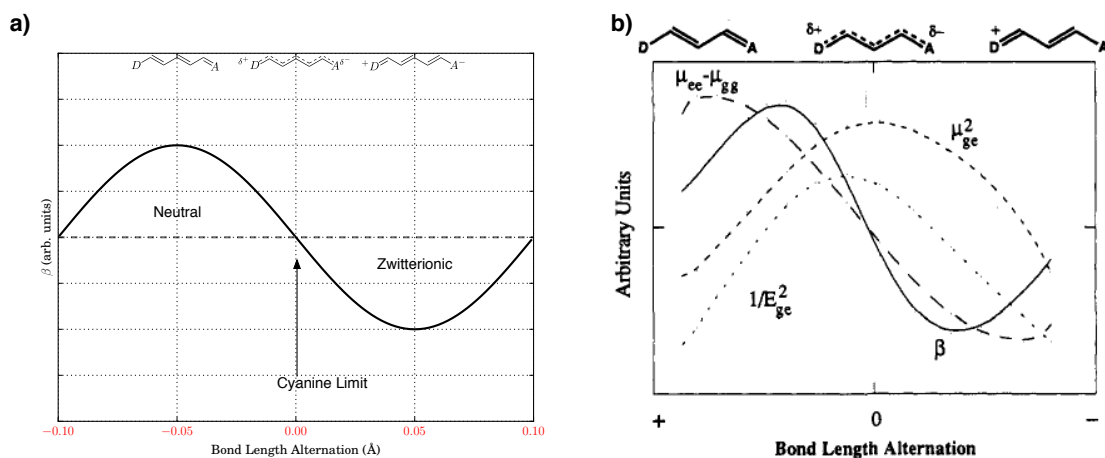
Fig. 1.8 a) Bond-length alternation as described by Marder *et al.*. For any given donor/acceptor pair, there is a certain amount of alternation between single- and double-bonds that maximizes the molecular hyperpolarizability. There also exist a point where both the bond-length alternation and molecular hyperpolarizability will be zero and this is referred to as the cyanine limit. b) The relationship between bond length alternation and β (——), $(\mu_{ee} - \mu_{gg})$(— — —), $(\mu_{ge})^2$(- - -) and $1/\Delta E_{ge}$ ($\cdot \cdot \cdot$) from equation 1.13.

Expanding upon the notion of the structure-property, Marder *et al.*, who showed that there was a mutual exclusion between the admixing of the HOMO and LUMO levels and the charge localization of the ground and polarized states. This was shown through the concepts of bond-length alternation(BLA) and bond-order alternation(BOA)[45]. Using a simple polyene system and varying the strength of an external electric field, Marder showed that β followed a sinusoidal dependence on the ground state polarization. Under this theory, the average difference between adjacent carbons in a polyene chain is calculated. For a molecule such as acetylene, the BLA should be $(+11\,\mathring{A})$, a carbon sp^2–sp^2 single bond is $1.45\,\mathring{A}$ and a double bond is $1.34\,\mathring{A}$. This system would have a β of zero, but as acceptors and donors are added to the polyene chain, the degree of bond length polarization changes and there exist an optimal amount of ground state polarization to maximize β. If the ground state is too polarized, you reach the cyanine limit and β is minimized before crossing over

into a zwitterionic ground state regime. This is shown in figure Fig. 1.8 and demonstrates the importance of the structure-property relationship.

Dewar's Rule and Chromophore Engineering
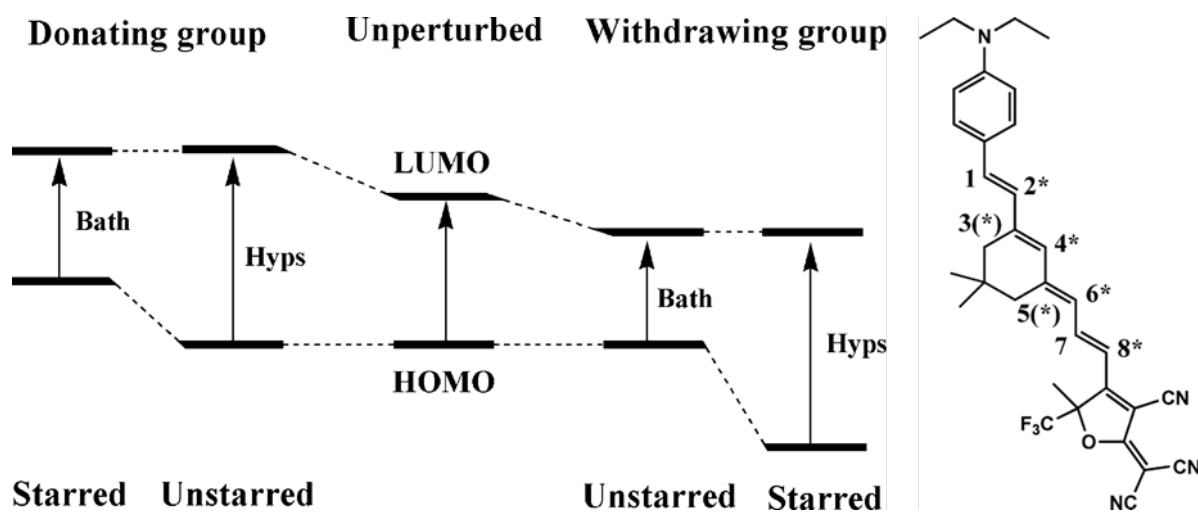
Fig. 1.9 The left is a schematic description of the effects of substituents to the HOMO and LUMO levels according to Dewar's rules. A CLD-type chromophore is shown on the right with substitution positions on the conjugated backbone. These are divided into starred and unstarred groups with the positions 3(*) and 5(*) denoting substitution of the isophorone ring.

Bond-length alternation has been helpful in optimizing chromophore design[57], but some have shown that it may not be applicable to all chromophore designs[58]. In attempts to engineer better chromophores, many schemes have been attempted. These attempts have run the gamut, from exotic shapes[59,60], modified bridges[61–63] and donors[64,65] to mixed-state and bichromophore systems[64,66,67]. Most modifications have centered around attempts to provide better site-isolation while minimizing the effects on β.

One promising paradigm are chromophores based on Dewar's rules[68]. He found that for $D - \pi - A$ type molecules, there was a pattern of alternating electronegativities along the $\pi-$conjugated backbone. As shown in Fig. 1.9, he proposed that this behavior can be used to predict the effects of substituents on the molecular energy levels based on the nature

of the substituent and location of the substitution. His work was based on pertubational molecular orbital theory, but in 2008, Chafin and Lindsay examined a polyene dye scaffold using density functional theory[69]. From their work, they found that the optimal pattern for optimizing the first molecular hyperpolarizability was substitute electron donating groups at the odd-numbered methine carbons and electron withdrawing groups at the even-numbered methine carbons. Their results mirrored Dewar's finding. Following the guidance on where to place substituents and what types of substituents to substitute has allowed chromophores to be synthesized that exhibit higher hyperpolarizabilities and thermal stabilities than their unsubstituted counterparts[70–73].

1.3 Aim and scope of this thesis

The research described in this thesis aims to understand the structure-property relationship of donor groups, and by doing so, improve upon donor design for inclusion in EO chromophores. While much attention has be given to the π-conjugated bridge and acceptors[74], there have been few systematic studies of electron donors[75]. That is not to say that donors beyond dialkyl amines do not exists in the literature, but they often arise as a consequence of trying to optimize other parts of the chromophore and are oft-times, neglected.

This works aims to remedy this, in part, by investigating a large body of donors with small perturbations. In doing so, a better understanding of the role of substituents on donor strength may be gleamed. Much like how the work of Chafin and Lindsay[69] offered guidance in how and where to substitute polyene bridges, this work aims to offer insight in to how and where to substitute donors. In doing so, better donors may be designed and current worst practices may be avoided in the future. Beyond that, this works aims to identify new potential donors that move beyond dialkyl and diaryl systems.

Much emphasis has been placed on the shape engineering of chromophores, but not necessarily on functional shape engineering. By functional, it is meant that substituents, if possible, should aid in the function of localizing the electron density at the donor in the ground state while not impeding overall polarization of the molecule. The molecular

hyperpolarizability of organic chromophores is dependent upon electron motion along the dipolar axis of the material from the donor, in the ground state, to the acceptor in the acceptor in the electronically excited state. Using density functional theory, donor structures will be investigated to discover how the molecular hyperpolarizability is affected by variations to i) how it is substituted and ii) how it is structured. Attempts will be made to identify trends that will lead to improvements in β and apply that to lessons learned from shape engineering. When possible, theoretical results will be compared to experimental work and attempts to synthesize new donors based on the study results shall be made.

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Chapter 2

UNDERSTANDING THE EFFECTS OF STRUCTURE AND SUBSTITUENTS ON DONOR STRENGTH

2.1 Introduction

A rigorous investigation of the structure-property relationship of donors by purely synthetic means would be daunting undertaking given the near endless possibilities of what is currently achievable current synthetic knowledge. For the affect of substituents on donor strength to be truly sussed out, many permutations would have to be explored making very minor changes with each iteration. Thankfully, there are other methods available to explore this structure-property relationship: namely computational chemistry. Given the advancements in modern computers, the matter of interrogating a large number of molecules bearing minor differences becomes almost trivial.

To study the structure-property relationship at the molecular level, Density functional theory (DFT)[1,2] has become an valuable tool as one can gain insight on both the linear and nonlinear properties of the target molecule[1–5]. For larger ensembles, Monte-Carlo simulations have been proven to lend insight in to how structural differences affect bulk properties[1,6]. It should also be mentioned that pioneering work by Kerry Garrett on small clusters–orientations obtained from both crystal structures and Monte-Carlo similations–using DFT has offered insight into what might expected from bulk systems of EO chromophores[2].

Typical EO chromophores contain a substituted amine attached to an aromatic ring[8–12]. While variants of this scheme exist, most donors still contain an aniline-like structure. This is, perhaps, best exemplified by the donors studied by Kwon *et al.* and shown in Fig. 2.1[7]. These structures have consistently been found to offer the best performance in EO applications and can be categorized in to one of four groups: alkyl (DA), ring-locked (RL), ring (R)
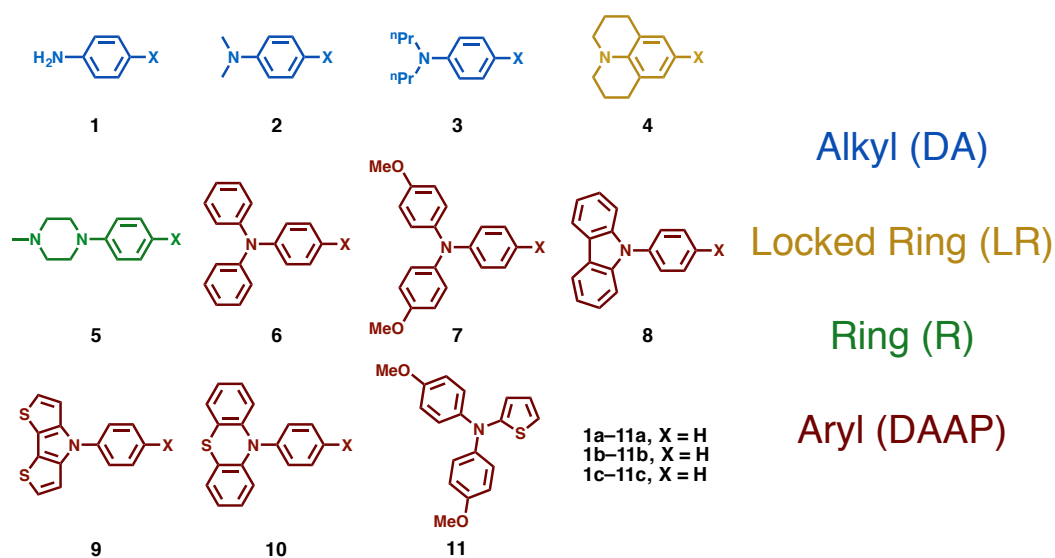
Fig. 2.1 Donors studied Kwon *et. al.*[7], seperated into 4 basic donor structures: Alkyl (DA), Locked Ring (LR), Ring (R) and Aryl (DAAP). These basic structure types will serve as the basis for all structures investigated in this study.
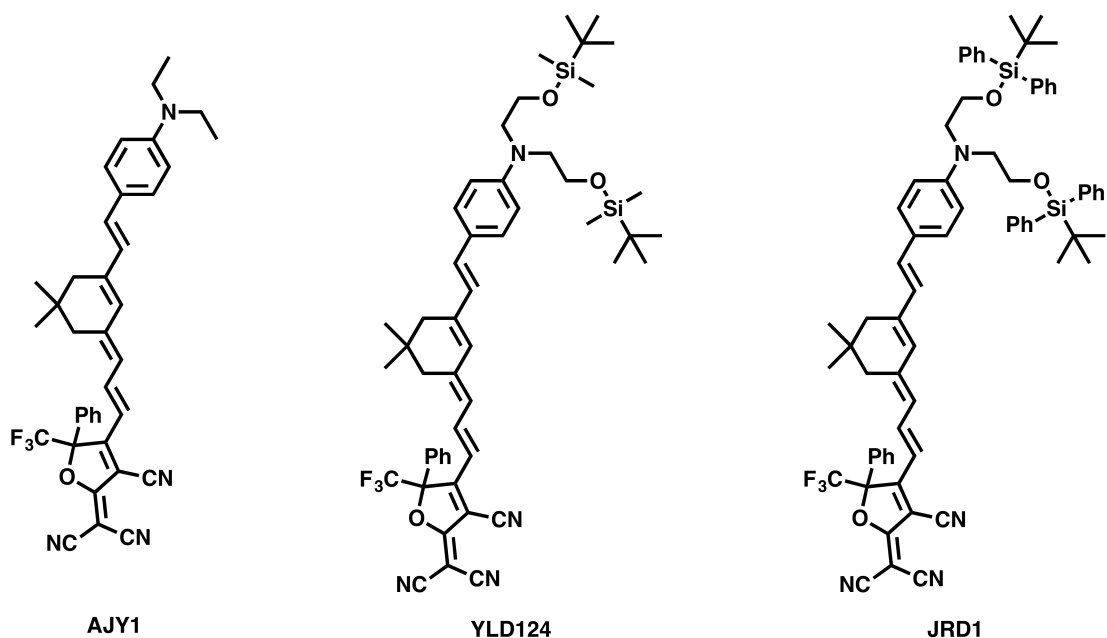
Fig. 2.2 The structures of three CLD chromophores with the CF3Ph-TCF acceptor and different donors.

and aryl (DAAP). During this study, they concluded that akly donors were the overall better better choice for use with EO chromophores[7]. This conclusion was based partly on the C—X (where X is either O or N) bond distances of their CHO or CN acceptors. They used the C—X bond distance as a measure of the donors ability to contribute to the charge-separated structure and they found a linear correlation between the C—O and C—N distances for 10 of the 11 molecules in the test set[7]. Due to sterics, many of the aryl donors were inferior to alkyl donors, despite being more thermally stable[13–16]. They did suggest that an aryl donor based on bis(4-methoxyphenyl)amine might be a workable compromise as it would offer the thermal stability of aryl donor with a donor strength similar to N,N-dimethylaniline[7].

Alkyl donors have been the most widely studied group of donors and a number of motifs have been introduced that improve upon simple dialkylamines (such as dimethyl or diethylamine). Recently, advances in this class of donor have allowed for translation of molecular hyperpolarizabilities to macroscopic susceptibilities[17]. In moving from tert-butyldimethylsily (TBDMS) ethers to tert-butyldiphenylsilyl (TBDPS) ethers, JRD1 was able to realize high macroscopic efficiencies in a neat chromophore system despite having a lower number density than neat YLD124[17]. These structures are shown in Fig. 2.2 to illustrate the subtle changes between AJY1, YLD124 and JRD1, all chromophores with identical bridges and acceptors and slightly different donors. The static hyperpolarizabilities, in vacuum, for the series were calculated to be $444 \times 10^{-30}\,esu$, $460 \times 10^{-30}\,esu$ and $483 \times 10^{-30}\,esu$[17]. This shows the effects of subtle changes to the donor on the properties of chromophores and suggests that the silyloxy groups contribute to the electronic properties, contrary to the the findings of Oudar and Chemla. In their work with para-nitroaniline, they found a negligible effect on β when the amine was replaced by a methylalaninate and concluded that additional σ and non-conjugated π bonds had no effect[18].

In 2004, Spraul and coworkers had presented a number of chromophores based on a bis(4-methoxyphenyl)amine donor with an FTC-type bridge[20] and the following year, the same group presented chromophores with a CLD-type bridge[21]. Their choice was based on work previously performed by Pierre-Bonhote on Ruthenium dyes for solar cell applica-
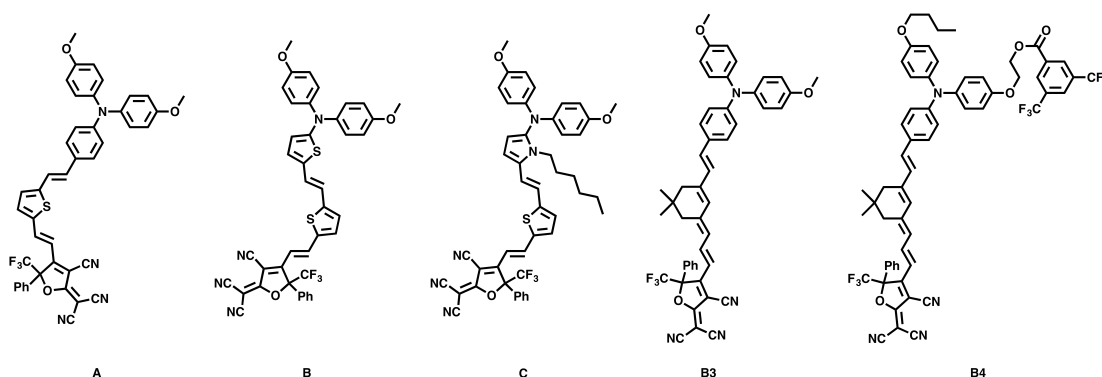
Fig. 2.3 Representative diaryl chromophore based on FTC (A–C)[19] or CLD (B3–4)[9] bridges.

tions[22], who found the donor to possess a long-lived light-induced charge separated state. As previously reported for DAAP chromophore, those of Spraul, Suresh *et al.* had high decomposition temperatures near or above 300°C and exceptional measured hyperpolarizabilities. New DAAP chromophores with both FTC- and CLD-type bridges and the CF3Ph-TCF acceptor where later explored by the Cheng and coworkers and where found to have both large β values and EO coefficients in poled polymer systems(see Fig. 2.3)[9]. A point of interest, the chromophore with 4-methoxyphenyl (B3) aryl units had a higher measured hyperpolarizabilty – as determined by Hyper-Rayleigh Scattering – than than one with a 4-butoxyphenyl and 4-(2-phenoxyethyl 3,5-bis(trifluoromethyl)benzoate) (B4) aryl units, but lower device performance. This may be contributed to enhanced compatibility of B4 with its polymer host by switching from two methoxy groups to a butyloxy group and ethoxy 3,5-bis(trifluoromethyl)benzoate group. This improvement might be compared to that observed when the TBDMS group on YLD124 where replaced by TBDPS. Further improvements were made with these systems by Davies *et al.* in 2008 by replacing the donor phenyl ring with thiophene and pyrrole[19].

The following work will explore the structure-property relationship of EO chromophores to explore how structural changes to the donor affect the predicted hyperpolarizability. All

chromophores contain a simple vinyl bridge coupled to the TCP acceptor, unless otherwise noted (see structure DA-00 in Fig. 2.4). Donor structures falling, roughly, into one of the four groups shown in Fig. 2.1 are evaluated using DFT compared to (DA-00), as a baseline, and YLD124TMS and YLD124M will serve as target goals.
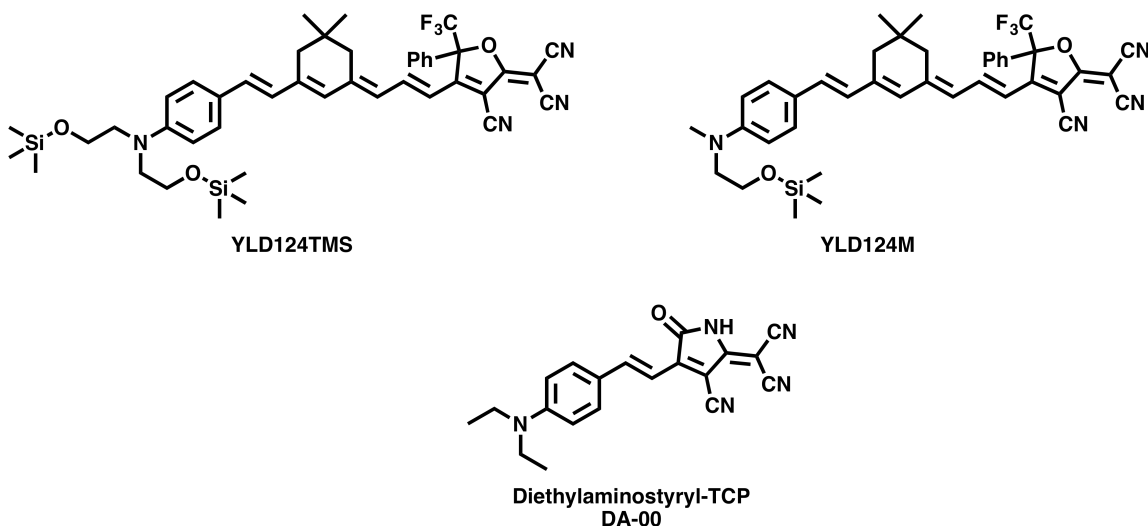
Fig. 2.4 Structures used as guidance in the evaluation of new donors. YLD124TMS contains a bis(2-((trimethylsilyl)oxy)ethyl)amine donor while YLD124M contains a 2-methoxy-*N*-methylethylamine donor. Chromophore DA-00 shows the general structure of all chromophores to be evaluated. This chromophore contains a diethylamine donor and will serve as a basis against which all other donors are compared.

2.2 Computational Methodology

All structure and property calculation for the chromophores found in this study were calculated using the Gaussian 09 program[23]. The CAM-B3LYP hybrid exchange–correlation functional[24] and the 6-31+G* basis set where used for all geometry optimizations in the gas phase. Frequency analysis of the minimized geometries was performed to confirm the absence of imaginary vibration modes. The vertical excitation energies were calculated using time-dependent DFT (TDDFT) formalism with the dispersion-corrected version of the range-separated ωB97X functional[25]. Solvent effects on the excitation energies were sim-

ulated using the polarized continuum model as implemented in Gaussian 09[26,27] and calculated for the first 6 excited states. Population analysis was determined using Mulliken Population Analysis[28] as implemented in the GaussSum package[29].

Molecular hyperpolarizabilities were calculated from the gas phase optimized structures *in vacuo* and in chloroform using the finite-field method[30–33]. Two DFT functionals were used for these calculations to verify the validity of the observed trends. The first was hybrid functional that utilizes the meta generalized-gradient approximation (GGA)[34] from the Minnesota 06 family[35]. Hybrid functionals incorporate some amount of exact exchange from Hartree-Fock(HF) theory that is constant at all points in space. The amount of HF exchange in the M06-2x functional 54% and this family of functionals have been shown to be superior to other hybrid functionals such as B3LYP in calculations where long-range self-interaction error (SIE) is a problem[36]. The other functional was a long-range corrected functional. Functionals from this class have partitioning parameters that allow the amount of HF exchange to be increased as larger inter-electronic distances, thus limiting SIE at large distances where is is known to dominate. The second functional used in this work was the CAM-B3LYP functional with the default partitioning parameters. The 6-31+G* basis set was used for all calculations and static hyperpolarizabilities were deconvoluted from from Gaussian output using MATLAB code originally developed by Bruce Eichinger. It has been updated and converted to Python using numpy and appears in Appendix B. All values are reported according to the Perturbation convention using cgs units. To aid in comparing donor strength, absolute hyperpolarizabilities have been converted to relative changes in hyperpolarizability from structure **DA-00** according to

$$\beta_{rel} = \frac{\beta_{zzz}^{sys} - \beta_{zzz}^{\text{DA-00}}}{\beta_{zzz}^{\text{DA-00}}} \tag{2.1}$$

where β_{zzz}^{sys} bears the donor of interest and $\beta_{zzz}^{\text{DA-00}}$ has a N'N-diethylamine donor.
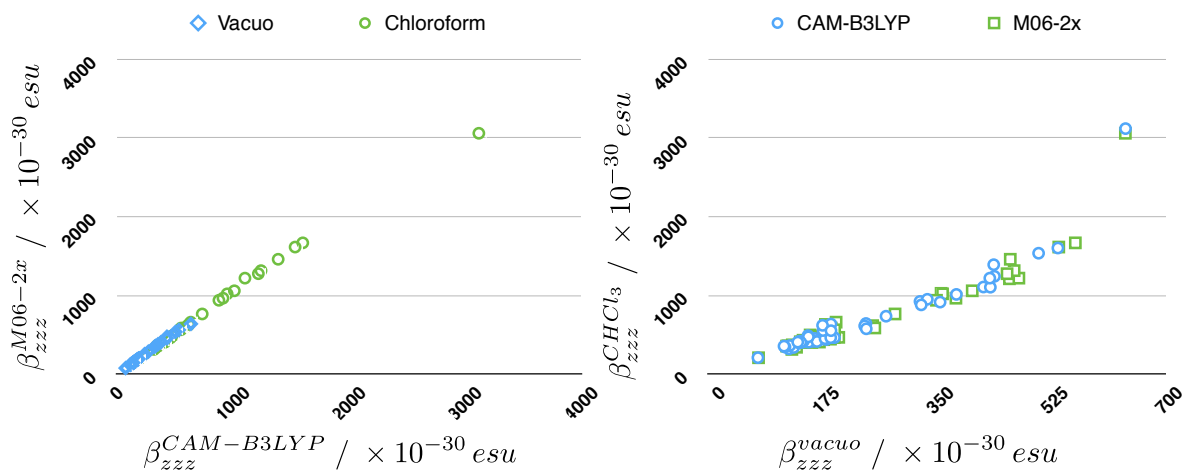
Fig. 2.5 A comparison of $\beta_{zzz}(0)$ calculated at the CAM-B3LYP and M06-2x levels of theory *in vacuo* and in chloroform. On the left is a comparisons of CAM-B3LYP vs M06-2x in vacuum($\diamond$) and chloroform($\circ$). On the right, we compare Vacuum vs chloroform for CAM-B3LYP($\circ$) and M06-2x($\square$)

2.3 Results and Discussion

2.3.1 A brief comparison of methods

In general, DFT is good at predicting the general trends that are observed in experimental measurements, but fails to get the magnitude[37] of the molecular hyperpolarizability. It also fails to capture the gains experimentally observed by moving from an FTC-type bridge to a CLD-type bridge. The structures within this study all contain short bridges of two to four carbon units, but it should be noted that some of the presented predictions may not fully represent the full potential of an actual chromophore. For a given set of conditions, we would expect the property predictions from several methods to yield the same trend. To verify this, the hyperpolarizabilities predicted by CAM-B3LYP and M06-2x, both *in vacuo* and in chloroform were compared. These comparisons are shown in Fig. 2.5. There was a strong correlation found when keeping the solvent system the same, but changing the DFT functional. When comparing the trend of *in vacuo* values to those in chloroform, there was not a strong correlation. It is known that the hyperpolarizability of a molecule will vary

with solvent environment[38], as the ground state structure adopts different conformations based on the dielectric environment. In a study of the effects of the dielectric environment, β_{HRS}^{1907} was observed to increase as the dielectric increased with one odd peculiarity: in dichloromethane, the values decreased for both measured chromophore systems[38]. For this study, the predicted values in chloroform are higher than those *in vacuo*, but the trends do not correlate well with each other as might be expected.

2.3.2 Change in relative static hyperpolarizabilities of donor structures

Due to the similarities between the values predicted by CAM-B3LYP and M06-2x, the focus will on those produced by CAM-B3LYP and the properties predicted with M06-2x will not be presented in Fig. 2.7 but may be found in Appendix **??**. In comparing the predicted values, we find that the improvements from the reference system in chloroform are often worse than in vacuum. In fact, some structures, such as DA-05, DA-06, DA-09, DA-17, DA-19–20 and DA-23, have a negative enhancement in chloroform. Furthermore, many of the structures that had a negative change in vacuum appear to become more negative in chloroform. The structures based on a bis(2-hydroxyethyl)amine donor (DA-05–DA-08) or (2-hydroxyethyl)methylamine were of particular interest due to their common use in chromophores. The asymetric donor, DA-15 has very poor performance based on these calculations. One might expect DA-15 to be closer to DA-07, but there is a 15% difference between the two and latter is predicted to be a weaker donor than the reference diethylamine donor. For other asymmetric donors with longer alkyl chains, the performance is predicted be better than the reference structure and even the base bis(2-hydroxyethyl)amine donor is predicted to be higher than the reference donor. Based on these observations, the decrease in β can reasonably be attributed to the smaller methyl unit on DA-15.

It is important to check theoretical predictions against experimental data, whenever possible, to ensure that the results are valid. The molecular hyperpolarizability is closely tied to the intramolecular charge transfer process. This relationship between the major component of the first-order hyperpolarizability along the dipolar axis and the spectroscopic
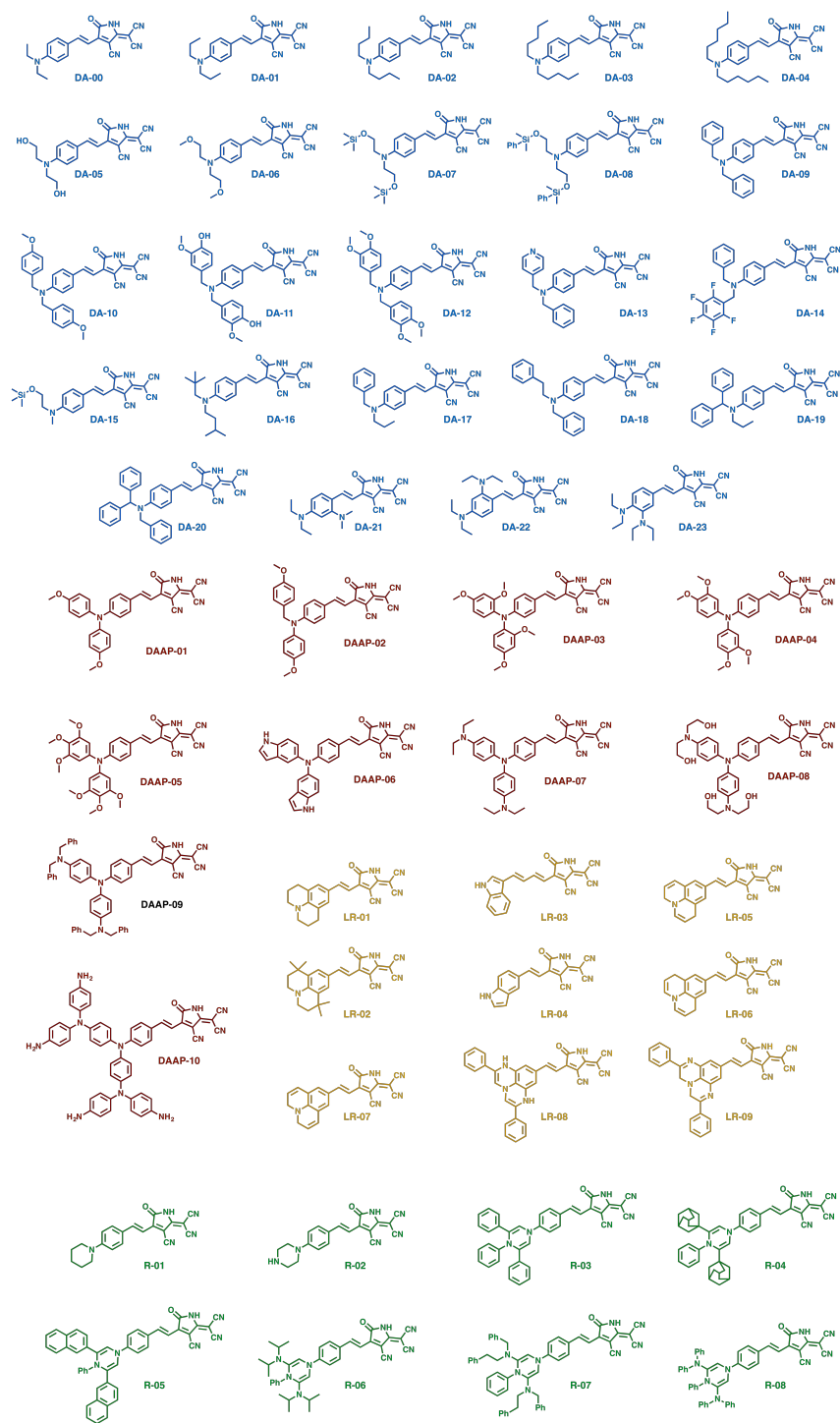
Fig. 2.6 Structures of the chromophores evaluated in this study. They are broken down according to the categories listed in figure Fig. 2.1.
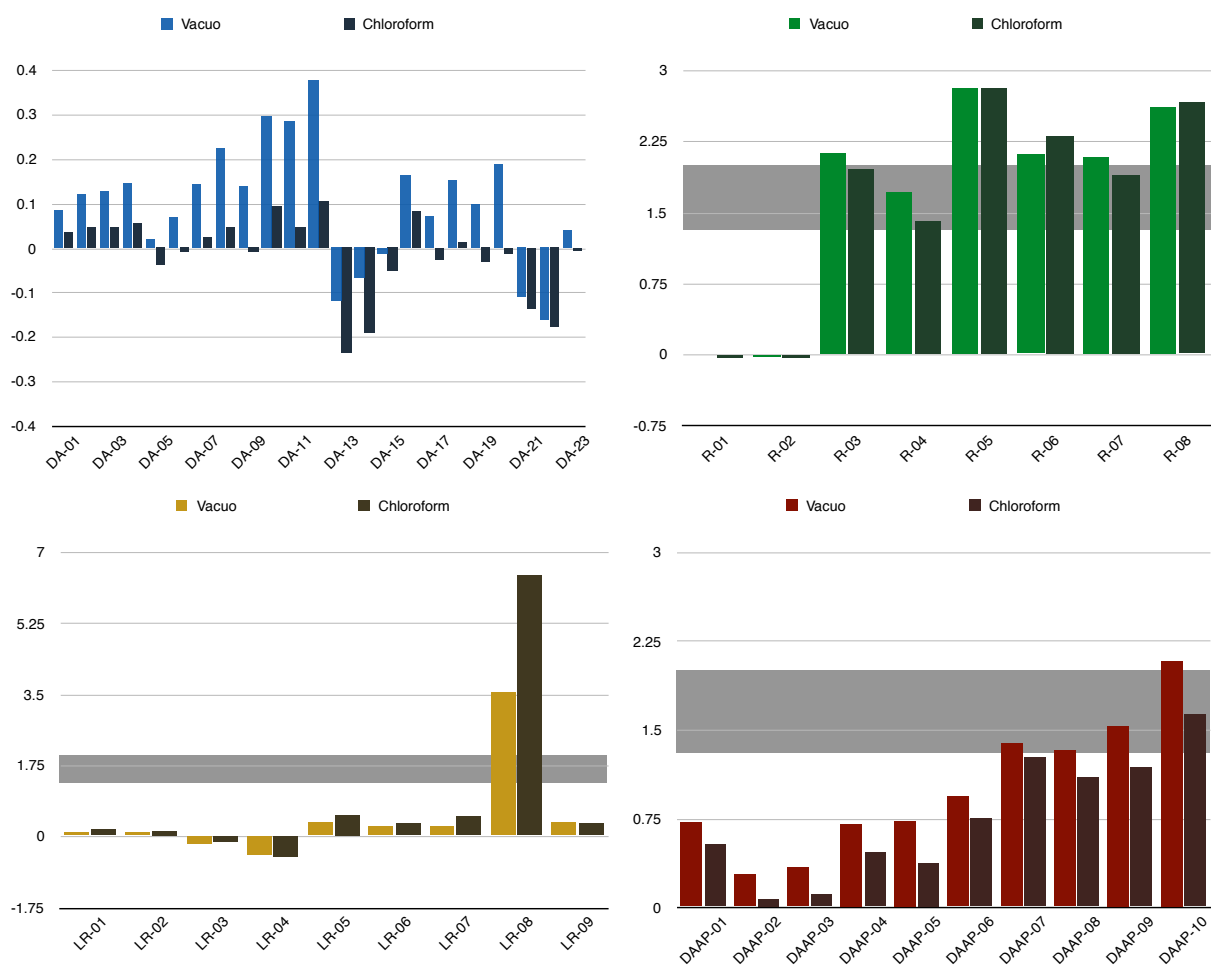
Fig. 2.7 The change in β_{zzz}^{sys} from DA-00 of chromophores *in vacuo* and in chloroform. The shaded area represents the range between YLD124M (bottom) and YLD124TMS (top). Properties were calculated with Gaussian 09d at the CAM-B3LYP/6-31+G*//CAM-B3LYP/6-31+G* level of theory.

properties of a molecule was proposed by Oudar and Chemla[18]. They observed that the ground state was strongly coupled to a single electronic excited (charge transfer) state, allowing a simplification of the sum-over-states approach to just include these two states such that

$$\beta_{zzz} = \frac{\Delta\mu_{ge}\mu_{ge}^2}{E_{ge}^2} \tag{2.2}$$

where $\Delta\mu_{ge}$ is the change in dipole moment, μ_{ge} is the transition state dipole and E_{ge} is the transition energy from the ground to the CT excited state. The term E_{ge} is directly related to the position of the CT band, and if it is assumed that structures DA-02, DA-07 and DA-08 have similar dipole moments and transition dipole moments, then β_{zzz} can be estimated by the position of the CT band with longer wavelengths meaning a higher first-order hyperpolarizability. The optical spectra were calculated using TD-DFT using PCM to simulate the solvent (chloroform) environment and are presented in Fig. 2.8. The CT band for DA-02 is red-shifted from both DA-07 and DA-08. This follows well with the predictions for DA-02 and DA-07, but not for DA-08. In the simulated spectra, there is no change in the position of the CT band for DA-07 and DA-08. Comparing experimental data for three similar chromophores, we find the dibutylamine donor red shifted from either of the bis(silyloxyethyl)amines. The *tert*-butyldimethylsilyloxy have the largest hypsochromic shift, but replacing the methyl groups with phenyl groups decreases this shift and brings the CT band closest to the dibutyl donor. This is in agreement with the predicted trends in β. The same trend is present for chromophores with an extended bridge, such as AJY1(810 nm), YLD124(786 nm)[38] and JRD-1(788 nm)[17], and are shown in **??**.

Overall, comparing the group of alkyl donors, the straight-chain donors merit further study as there was no observed decrease or plateau in β as the chain length was increased. This suggest that there may be some contribution from longer chains that goes beyond two carbons, but the data also suggest that these contributions may be masked by the solvent environment. A solvent whose trends match those in vacuum might be a better solvent for future HRS measurements, but without extensive testing this cannot be concluded with any
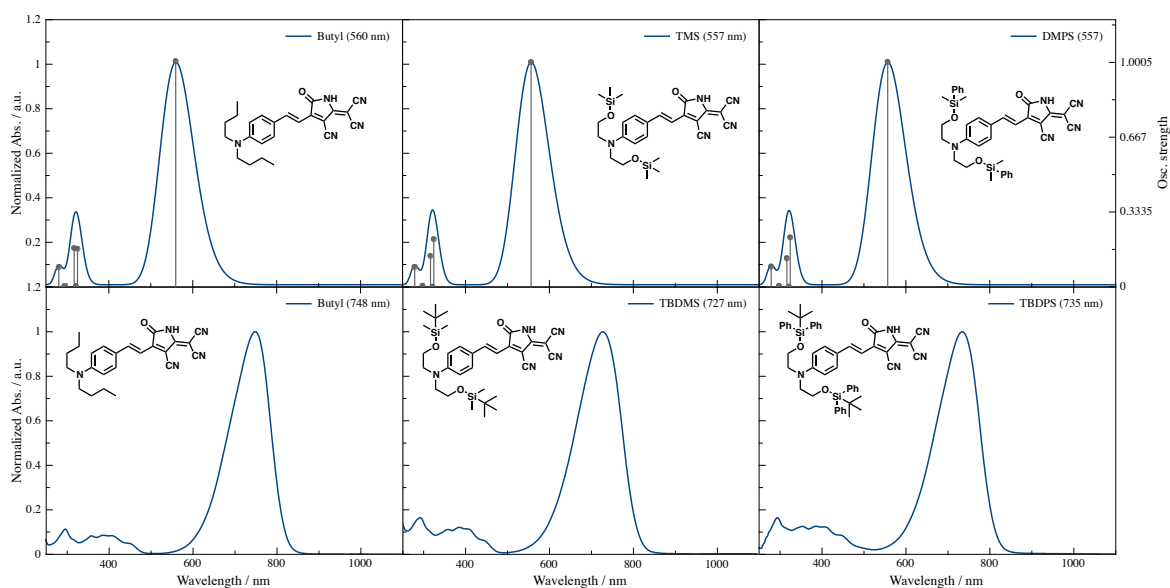
Fig. 2.8 Theoretical (top) and experimental (bottom) optical spectra comparing the effects of silyl ethers on the intramolecular charge transfer band. The vertical lines in the theoretical spectra represent the relative oscillator strength of the transition(s) responsible for the observed peak.

certainty. In designing donors for future chromophores, methyl groups should be avoided as should electron withdrawing groups placed close to the donor. In coupling to hydroxyl groups, ethers are recommended over esters and benzyl or substituted benzyl moieties may be better than the current regime of hydroxyethyl based donors.

The trends observed from locked ring and ring-type donors followed very similar patters. For fused rings, unsaturated six-member rings fused to benzene exhibited better gains than their five member ring analogs. Donors based on indole were among the worst chromophores tested (LR-03–04). Julolidine based donors (LR-01–02) closely matched dipropylamine (DA-01), showing no dirrefence between flexible or rigid propyl groups. There did not appear to be any back-donation from these units into phenyl ring until the saturation was reduced. This improved donor strength, with the increase dependent on the location of the allylic site (LR-05–07). If the carbons in the 3- and 5-positions on the benzene ring are replaced by amines, there is a dramatic increase in the hyperpolarizability resulting in a small chromophore that should be better than a YLD124-class chromophore. Again, the location of the double-bonds matters as the gain seen in LR-08 is reduced considerably in the isomer LR-09.

With ring donors, the same process was followed to realize significant gains in this class of donor. There is no difference from the reference donor and one based on piperazine (R-01). A negative gain was found if the terminal amine is replaced by oxygen or thiophene (R-02), similar to what was observed in going from DA-01 to DA-05. Going back to R-01, if the degree of saturation is decreased and piperazine is converted to a substituted 1,4-dihydropyrazine, there is an improvement comparable to that seen for LR-08. To further investigate this donor, the substituents in the 3- and 5-positions of the pyrazine ring were changed to see how this might affect the donor strength. In structures R-03–08, there is a clear substituent effect on the donating ability of the pyrazine ring. For R-04, replacing the phenyl rings with adamantane reduces the properties to 80% of DA-03, but if those same rings are replaced with naphthyl rings, we see an improvement over DA-03. In fact, we find that the properties can be tuned quite readily by changing these groups, with naphthyl and diphenylamine providing the largest improvements over R-03, and DA-01.

Diaryl donors have already been shown to be better than dialkyl donors in previous studies[7], but these donors were based on anisole. Further explorations to see if additional gains might be realized with this class of donor have been few and only recently have new chromophores been introduced[39]. Placing additional methoxy groups on anisole (DAAP-03–05) yielded little improvement over DAAP-01. This is in contrast to what was observed with DA-10 and DA-12. With the dibenzyl donors, improvements were found with additions of the first and second methoxy groups. Even the asymmetric donor, DAAP-02, failed to perform better than DA-10. The difference between DAAP-03 and DAAP-04 can be explained with sterics. Placing the methoxy groups ortho to the amine inhibits the ring from being able to properly rotate, keeping it from adopting an optimal configuration to allow efficient electron transfer. Why additional methoxy groups on a phenyl ring show a weaker effect on donor strength than those on a benzyl ring is harder to explain and warrants further investigation. Replacing oxygen with an amine has the expected effect as shown in DAAP-06–10. Donors based on indole had the lowest enhancement, but this was still better than the anisole based donor, DAAP-01. Much like what was seen with the dihydropyrazine ring, the substituents off the auxiliary amines affects the overall performance of the donors. Examination of the data suggests that these groups serve as auxiliary donors and that the stronger the auxiliary donor, the stronger the overall donor will be. To test this theory, the molecular hyperpolarizability of the DAAP or R chromophore was plotted as a function of the corresponding DA hyperpolarizability. If donors bearing chalcogens are ignored, there is a linear relationship between the structures shown in Fig. 2.9. This suggest that these are acting as double donor systems and that relative strength of new donors with these basic structures can be predicted by looking at the relative strengths of the auxiliary donors.

As discussed earlier, the first molecular hyperpolarizability can be explained as the change in electron densities of the molecule in going from the HOMO to the LUMO, so it is important to know how these new donors behave in comparison to a more traditional alkyl donor. The visualizations of these orbitals for DA-02, DAAP-09 and R-03 are presented in Fig. 2.10. There are noticeable differences between the three structures. For the bottom two, the
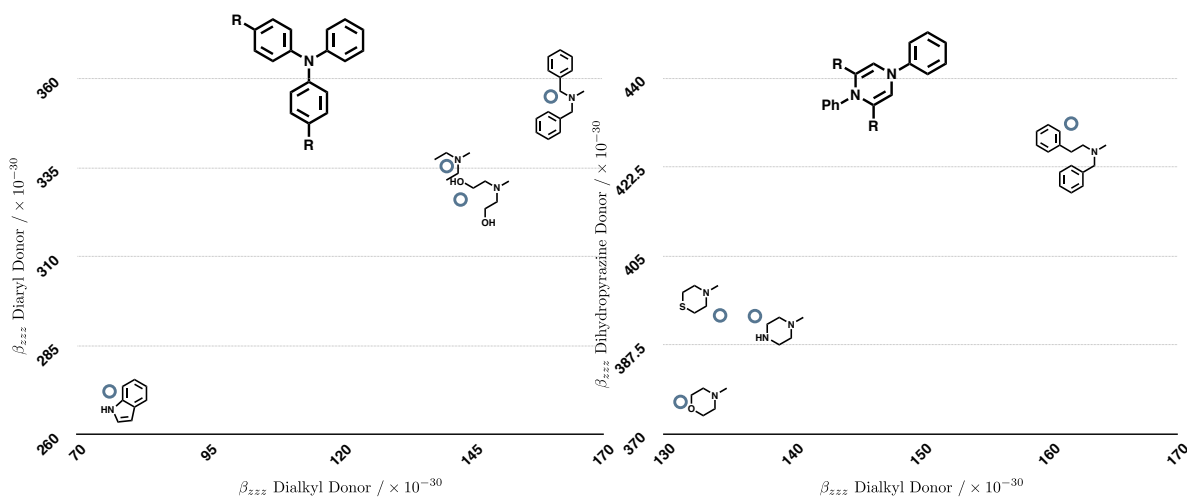
Fig. 2.9 Calculated β_{zzz} of the shown dialkyl donor plotted against β_{zzz} of a diaryl donor (left) or pyrazine donor (right) bearing the same donor.

Table 2.1 Mulliken population analysis of representative chromophores, calculated from Gaussian 09d with the pop=Full keyword and the GaussSum program. $\Delta E = E_{LUMO} + E_{HOMO}$. Values for β_{zzz} where calculated in vacuum.

		Donor	Bridge	Acceptor	ΔE / eV	$\beta_{zzz}(0)$ / $\times 10^{-30}$ esu
DA-02	LUMO	67%	14%	19%	4.15	157.2
	HOMO	12%	14%	74%		
DAAP-09	LUMO	13%	15%	72%	3.66	355.0
	HOMO	86%	6%	8%		
R-03	LUMO	12%	14%	74%	3.51	438.1
	HOMO	88%	5%	7%		
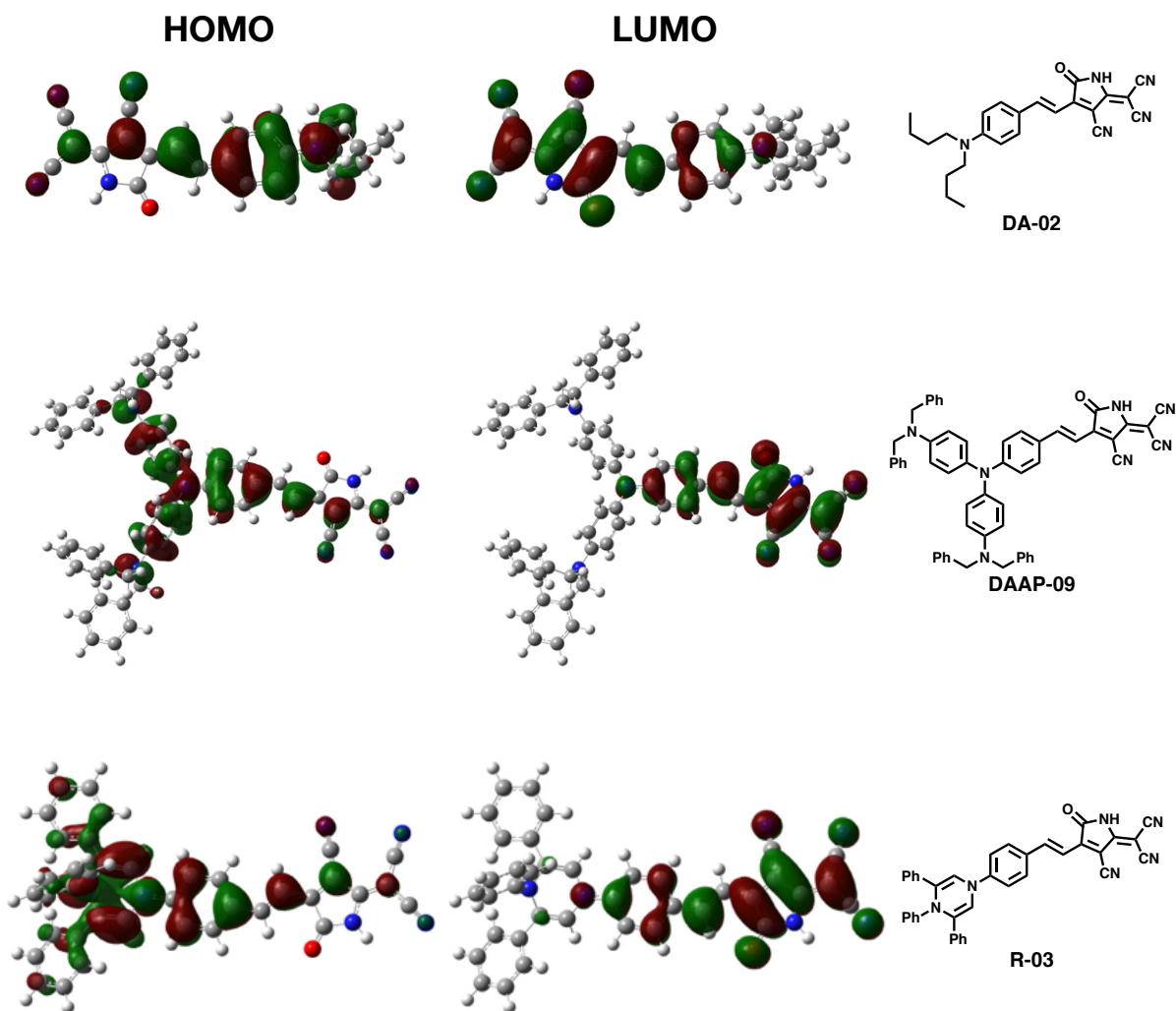
Fig. 2.10 Frontier molecular orbitals of chromophores DA-02, DAAP-09 and R-03. Shown below the orbitals.

HOMO electron density extends further into the expanded structure of the donor, but it is difficult to tell with any clarity if this has had an effect on the electron density of the bridge or acceptor. To answer this, a Mulliken population analysis was performed and the results are presented in table **??**. The chromophores all have the same acceptor and bridge, so there are no expectations for large differences in the LUMO electron density, as this is mostly determined by the acceptor, and we see that there is little to no change across the three molecules. In all cases, for the LUMO, nearly 72% of the electron density is centered around the acceptor. If this were not the case, a simple argument based on improved donor strength would no longer be possible. While the LUMO has not changed across the structures, there is a discernible change in the HOMO. For the new donors, more than 85% of the electron density is centered on the donor. This is a change of nearly 20% from the dibutyl donor. As mentioned above, this density extends into the expanded structure of the donor and corroborates what was seen in Fig. 2.9.

2.4 Conclusion

An extensive study of chromophores with a small vinylic bridge and the TCP acceptor has been conducted to identify motifs that might be employed in designing next-generation donors. The study examined the effects of subtle changes in the donor structure on the overall predicted hyperpolarizability of the chromophore. Systems with chalcogens attached to alkyl chains, whether in a ring formation or not, were found to negatively affect β as compared to an alkyl chain of similar length (ethanol vs propane). Differences between esters, ethers, silyl ethers and silyl ethers bearing arenes was observed and it is recommended that the ethers and aryl-silyl ethers be employed with these types of donors to minimize the impact to β. Several new classes of donors have been identified as potential candidates for use in small chromophore systems with high hyperpolarizability and number density. Chromophores with these new donors had predicted properties that place them close to YLD124 type chromophores. If chromophores can be synthesized with these new donors and the improvements in hyperpolarizability translated from the microscopic to the macroscopic

regimes, this could be an important development in the design of future chromophores.

2.5   Experimental

General information: Chemicals used were purchased from Sigma Aldrich, Alfa Aesar or TCI and used without further purification unless otherwise noted. UV-visible Absorption Spectroscopy was obtained on a Shimadzu 1601. ^{1}H NMR spectra were acquired using a Bruker AVance series instrument running at 300 MHz.
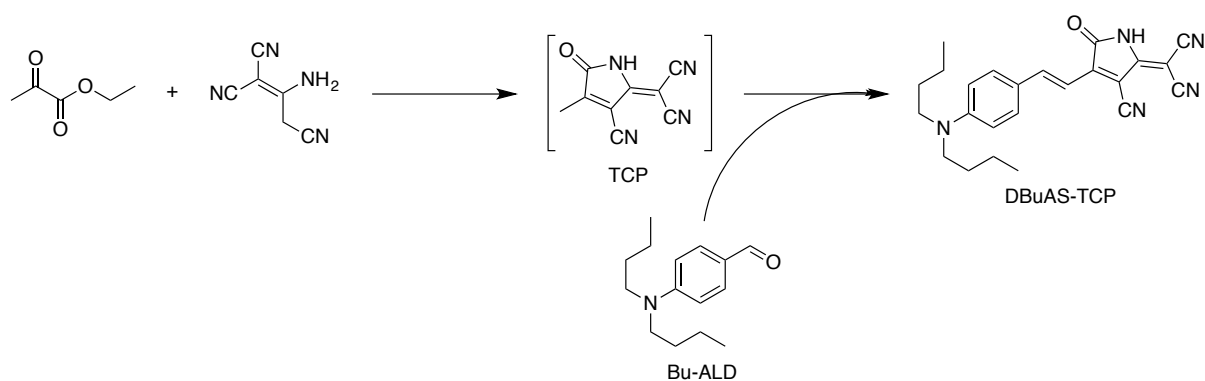
Scheme 2.1   Synthesis of Butyl-TCP.

*Synthesis of (**Butyl-TCP**)*

To a 20 mL vial containing a magnetic stir bar was placed malononitrile dimer (1 eq), ethyl pyruvate (1.1 eq.) and ethanol (2 mL/mmol). The vial was sealed and heated at 85°C for 0.5 hours at which point, **Bu-ALD** (0.9 eq) was added in one portion and heating continued for an additional 6 hours. Once cool, the precipitated product was collected via filtration and washed with isopropanol, ethanol and chloroform until the filtrate ran clear. The solid was dried under vacuum at 60°C overnight to yield 0.56g (54%) Butyl-TCP as a green microcrystals. ^{1}H NMR (300 MHz, DMSO-d6) δ 9.30 (1H, d), 8.76 (1H, d), 7.86 (2H, d), 7.77 (1H, d), 6.97 (2H, d), 4.20 (4H, t), 3.74 (4H, t), 1.97 (6H, s). MS (ESI) 398.4 (M-H).
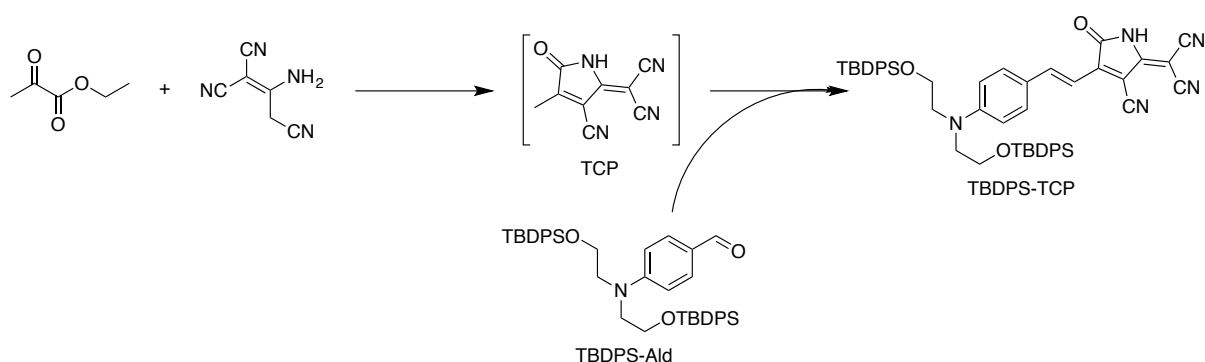
Scheme 2.2 Synthesis of TBDPS-TCP.

*Synthesis of (**TBDPS-TCP**)*

Chromophore **TBDPS-TCP** was synthesized exactly as **Butyl-TCP**, substituting **TBDPS-ALD** for **Bu-ALD**. The solvent was removed from by rotary evaporation and the residue was dissolved in a minimal amount of chloroform and the product precipitated from cold petroleum ether. This process was repeated three times to yield 0.49g (42%) **TBDPS-TCP** as a blue-green solid. ^{1}H NMR (300 MHz, Acetone-d6) δ 8.50 (d, J = 15.3 Hz, 1H), 7.65 (d, J = 6.4 Hz, 8H), 7.42 (dd, J = 15.0, 7.3 Hz, 14H), 7.06 (d, J = 15.3 Hz, 1H), 6.79 (d, J = 9.0 Hz, 2H), 3.89 (dd, J = 21.9, 5.2 Hz, 8H), 1.03 (s, 18H).. MS (ESI) 853.6 (M+H).

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Chapter 3

SYNTHESIS OF DIHYDROPYRAZINE DONOR

3.1 Introduction

Pyrazines and, particularly 1,4-dihydropyrazines, are known compounds[1], but a reliable synthesis for the latter had not been reported until the early 1970s, thanks to the work of Fowler and Chen[2,3]. Their work identified possibly the first confirmed synthesis of 1,4-dihydropyrazine– as opposed to 1,2– dihydropyrazine[4] – through the acetylation of a substituted 5,6-dihydropyrazine[3]. Later, Fourrey reported the synthesis of stable N-aryl dihydropyrazines[5]. Without proper substitution, 1,4-dihydropyrazines are known to undergo a [1,3] alkyl shift[6,7], so by moving from benzyl amine to aniline and avoiding strong Lewis acids, Fourrey reported the successful synthesis of stable ring systems from phenacyl bromide. Following the approaches laid out by Fowler, Chen and Fourrey[2,3,5] and based on the results of theoretical calculations presented in Chapter 2, attempts were made to synthesize a donor based on substituted 1,4-dihydropyrazines for use as electron donors in EO chromophores.

3.2 Results and Discussion

Small molecules hold promise for realizing large EO coeffecients, r_{33} by vitrue of their small size when compared to traditional FTC and CLD based chromophores. One problem with realizing this has been that no donors, when coupled to known acceptors by a small vinylic bridge, have shown performance capable of matching or exceeding current systems. Several donors from the study performed in Chapter 2, when coupled with the TCP acceptor, meet or exceed molecular hyperpolarizabilities of some CLD-class chromophores bearing a CF3Ph-TCF acceptor. Looking at table Table 3.1, a case can be argued for these small chromophores

Table 3.1 Dipole moment (μ_z), hyperpolarizability (β_{zzz}) and number density (ρ_N) of chromophores. [a]The number density was calculated based on an estimated density of $1.00\,\text{g/cc}$. [b]values taken from reference[8]

	$\mu_z(\text{D})$	$\beta_{zzz}(0)$ ($\times10^{30}esu$)	ρ_N ($\times10^{20}molecules/cc)^a$
YLD124[b]	22.0	460	6.83
JRD1[b]	21.4	483	5.33
DAAP-01		242	12.06
R-03	15.0	438	10.37
DAAP-07	18.5	335	10.35
DAAP-09	17.7	355	7.26

as they all have higher than number densities (ρ_N) than the CLD class chromophores with hyperpolarizabilites that range from 51% to 93% of the average β or YLD124 and JRD1.
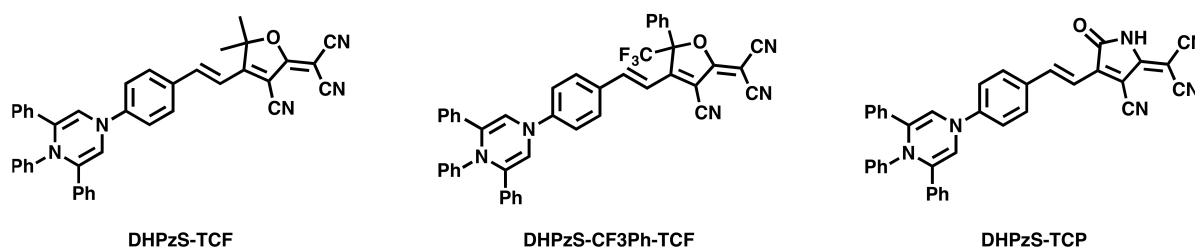
Fig. 3.1 Initial structures proposed for evaluating the dihydropyrazine donor.

3.2.1 Synthesis of 1,4-dihydropyrazine donor

Three chromophores with a dihydropyrazine donor were proposed for initial studies and are shown in figure Fig. 3.1. This class of donor showed the largest improvement in β, a large number density, ρ_N, for a high β chromophore and, had lowest dipole moment of any of the possible donor candidates detailed in table Table 3.1. The synthetic scheme for the formylation of the dihydropyrazine donor is shown in Scheme 3.1, and to the best of the
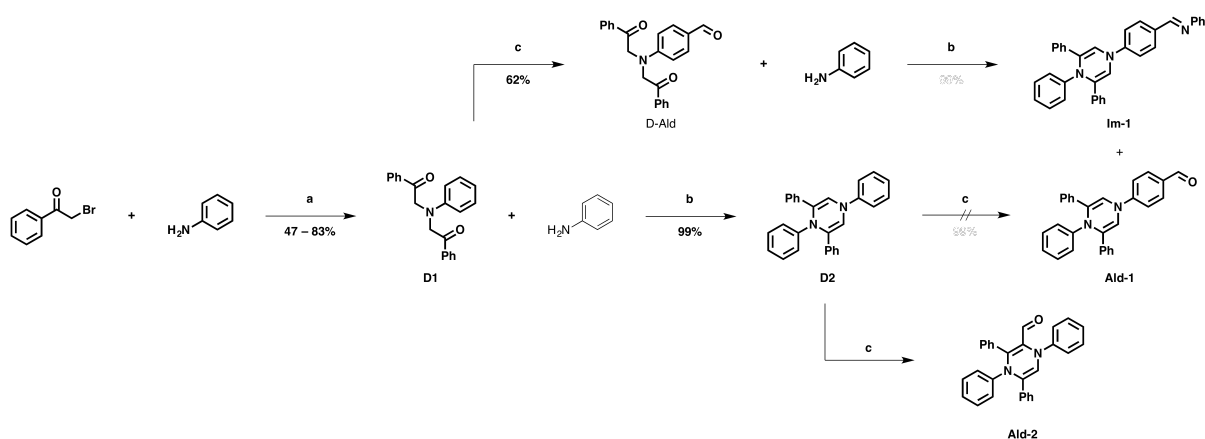
Scheme 3.1 Formylation of dihydropyrazine donor. Reagents and conditions: (a) 1 equiv of aniline, 2.2 equiv halide, 4 equiv base, H_2O, reflux 24 h; (b) 3 equiv aniline, 5% v/v 1:1 trifluoroacetic acid/acetic acid, toluene, reflux, 6h; (c) 1–1.5 equiv $POCl_3$, DMF, rt, 0.5h, 90°C, 0.75h.

author's knowledge, this is the first time such a structure has been synthesized. Phenacyl bromide is commercially available, but may also be prepared by the Friedel-Crafts reaction between bromoacetyl bromide and any appropriate arene using $AlCl_3$ in dichloromethane or carbon sulfide. It may also be prepared from chloroacetyl chloride, but reactions between phenacyl chloride and aniline were found to yield only the monoacylated product. To force di-acetylation, an *in situ* Finkelstein reaction was required to convert the chloride to a bromide or iodide first. The reaction of aniline with phenacyl bromide, to produce D1 was performed in several protic and aprotic solvents. In all cases, sodium or potassium carbonates or bicarbonates gave the best results. Attempts with sodium hydroxide and sodium hydride as the base produced unidentifiable products and required an external cooling bath during addition or the halide to maintain control of an exothermic reaction. Triethylamine also required cooling during the initial stages of the reaction and produced a mixture of mono- and di-alkylated products, even when a large excess of the halide was employed. These were not issues when a milder base was employed. Reactions performed in acetone, propanol, isopropanol, DMF and water all gave the di-alkylated species as the major product. The highest yields were observed when water was used as a solvent and product isolation was

greatly simplified, requiring the precipitated product to be washed with water, dilute acid and aqueous isopropanol for product that was ¿95% pure by NMR.

Ring closure was accomplished by a catalytic system of 1:1 trifluoroacetic acid(TFA) and acetic acid(AcOH) in toluene. Attempts with p-toluenesulfonic acid(PTSA) in toluene had lower yields than the TFA:AcOH system and trace amounts were found to contaminate the final product, even after separation by silica gel and recrystallization from ethanol. It was also found that TFA, on its on, was not a good catalyst for ring closing procedure whereas acetic acid was. Yields were lower than with the 1:1 catalyst, but reactions could be done in toluene or just acetic acid with little to no effect on yield and product isolation from acetic acid could be achieved by inducing crystallization following aqueous dilution.
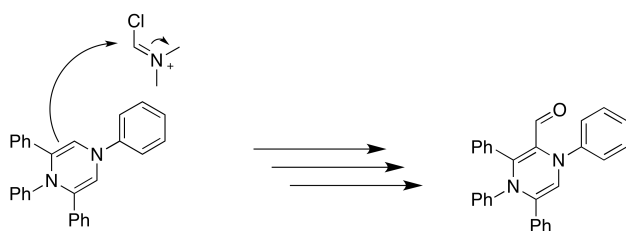
Scheme 3.2 Vilsmeier-Haack formylation of the 1,4-dihydropyrazine system. Instead of formylating the phenyl ring, formylation occurred at the 2 position of the pyrazine ring.

The Villsmeier-Haack formylation of D2 did not yield Ald-1, as expected. Instead, the isolated product was found to be Ald-2. The proposed mechanism is shown in Illustration Scheme 3.2. Instead of the arene reacting with the Villsmeier reagent, the heteroarene at the position ortho to the amine. The Villsmeier-Haack formylation requires an electron rich arene and the fact that the pyrazine ring reacted preferentially to either of the two arenes in the 1 or 4 position suggest that the pyrazine ring is more electron rich than a phenyl ring. Another reaction with tetracyanoethylene (TCNE) produced the same results with the electrophilic substitution occurring ortho at the 2- or 6-position[1]. To get around this, formylation of bis(phenacyl)aniline was done before closing the pyrazine ring. Following this route and the original ring closing procedure, the Schiff base was found to be the major
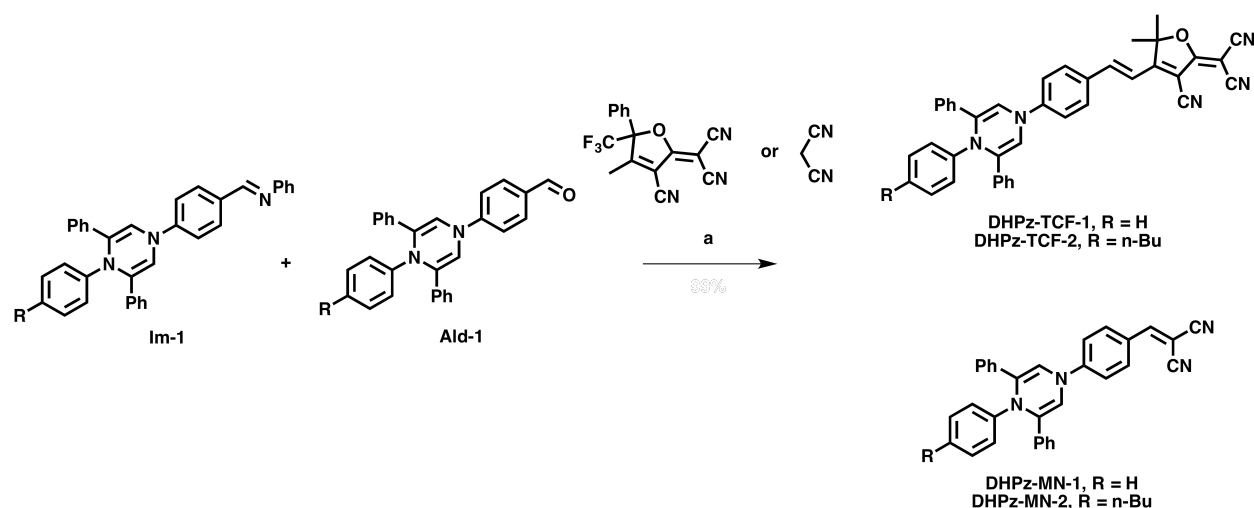
Scheme 3.3 Synthesis of DHPz dyes. a) Ethanol or isopropanol, reflux, 30 minutes.

product. Reducing the amount of aniline present during the ring closing reaction produced both the aldehyde and the Schiff base, which were difficult to separate. An attempt was made to convert the aldehyde to a nitrilre prior to ring-closure, but these reactions were low yielding and ring-closure of the resulting nitrile did not proceed in toluene, but was found to work in chloroform or dichloromethane using 30% acetic acid that contained 5% trifluoroacetic acid. Reversion of the nitrile back to the aldehyde, following ring closure, was accomplished by diisobutylaluminium hydride in dichloromethane at 0°C.
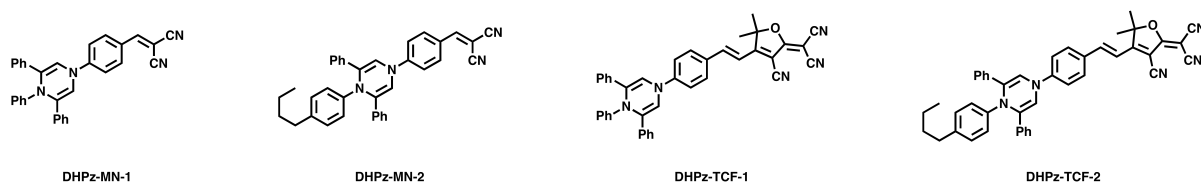
Fig. 3.2 Structures of new chromophores with a dyhydropyrazine donor. Chromophores **DHPz-TCF-1** and **DHPz-TCF-2** were synthesized by Dr. Delwin Elder.

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[1]This was determined qualitatively by comparing the spectrum of the product from this reaction to the spectrum of a chromophore known to have been substituted on the arene para to the the pyrazine ring.

The Knoevenagel condenstation reactions (see scheme Scheme 3.3) of acceptors with either the pure aldehyde or mixed aldehyde/Schiff base appeared to proceed as other acceptor/aldehyde condensations. A color change was noticed within minutes following addition of ethanol to the reaction vessel containing the CF3Ph-TCF acceptor and aldehyde and the reactions were allowed to proceed, under reflex, for 30 minutes at which time TLC showed near complete consumption of the starting material. It was during a typical workup and isolation using silica gel that the dihydropyrazine ring was found to be unstable. For the CF3Ph-TCF chromophore, the ring was removed so that the only isolated product was the chromophore with a free amine. Chromophores with the TCP acceptor were found to decompose even more quickly than those with the CF3Ph-TCF acceptor. Doctor Delwin Elder was able to isolate two chromophores with the TCF acceptor and condensation of the aldehyde with malononitrile in refluxing isopropanol was found to proceed smoothly and without any of the problems experienced with the stronger acceptors. All of the synthesized DHPz dyes are shown in figure Fig. 3.2.

3.2.2   Optical Properties
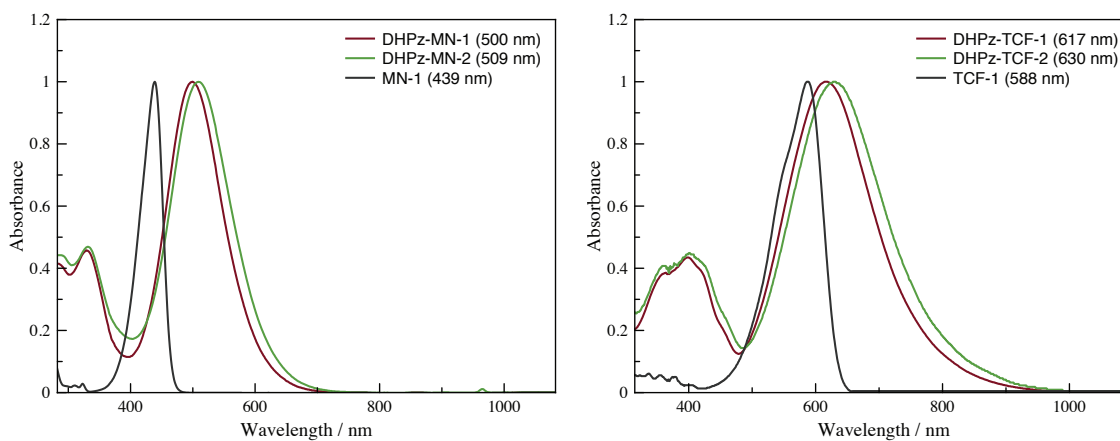
Fig. 3.3   UV-Vis absorption spectra of chromophores **DHPz-MN-1**, **DHPz-MN-2** (left), **DHPz-TCF-1** and **DHPz-TCF-2** (right) in chloroform.

Optical absorption spectra allow us to probe the effects of structural changes on the intramolecular charge transfer band of dipolar chromophores. Per the theoretical calculations performed in Chapter 2, we expect the DHPz structure to be a better donor than diethyl amine. In figure Fig. 3.3 are the UV-Vis spectra of the DHPz chromophores and chromophores Mn-1 and TCF-1 for comparison. All chromophores exhibit a similar low energy transition which accounts for the $\pi \longrightarrow \pi^*$ transition, that is primarily responsible for the NLO response. For the DHPz chromophores, this ICT band is shifted to higher energies and suggest that the DHPz donor is better than the diethyl amine donor. For **DHPz-MN-1** and **DHPz-MN-2**, these shifts are +61 nm and +70 nm, respectively[2]. The addition of the butyl group in **DHPz-MN-2**, along with aiding in solubility, appears to also increase donor strength as evidenced by the +9 nm shift from **DHPz-MN-1**. A similar picture is observed for the TCF chromophores, with **DHPz-TCF-1** having a bathochromic shift of 29 nm from TCF-1 and **DHPz-TCF-2** having a shift of +42 nm. Again, their is a bathochromic shift (of +13 nm) when going from **DHPz-TCF-1** to **DHPz-TCF-2**. Based on theoretical calculations performed for R-03, this high energy transition is primarily attributed to a HOMO-10⟶LUMO transition. Based on the large bathochromic shifts (61–70 nm for the Mn acceptor and 29–42nm for the TCF acceptor), it is concluded that the DHPz donor is better than the diethylamine donor.

3.2.3 Cyclic Voltammetry Measurements

To confirm the results of the UV-Vis study, cyclic voltammetry was performed to ascertain the ionization potential (IP) and electron affinity (EA). These values can be obtained from the oxidation peak and reduction peak onset potentials and are directly related to the HOMO and LUMO levels of the chromophore[9]. With this information, we can determine the energy gap($LUMO - HOMO$) for comparison with our UV-Vis results and directly compare the HOMO levels of each chromophore. The cyclic voltammagrams are shown in figure Fig. 4.2

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[2]The +/- sign convention is used to indicate either a bathochromic (+) or hypsochromic (-) shift. The presence of the sign holds no other significance.
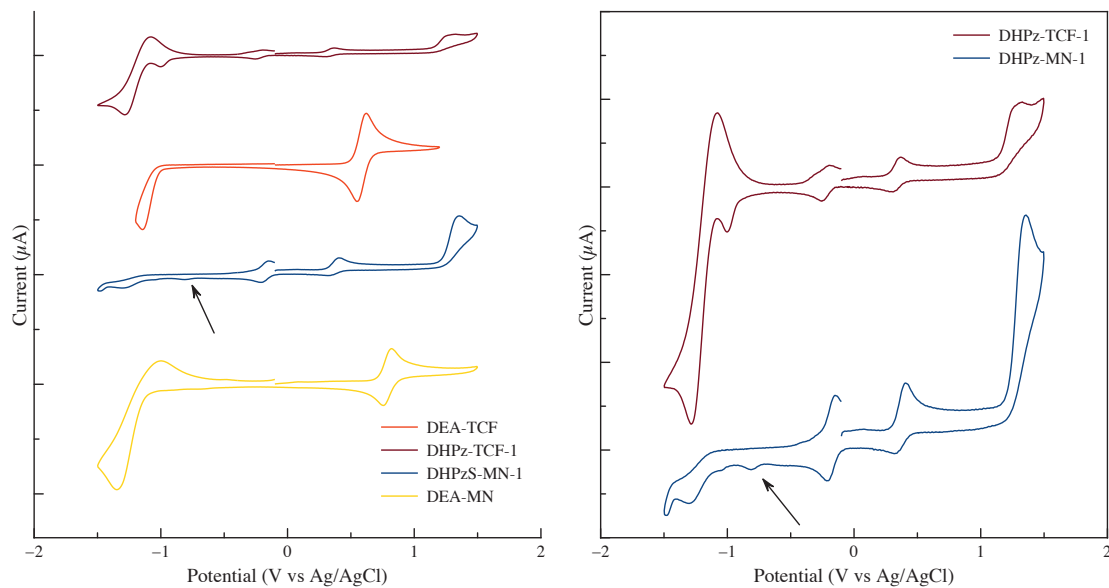
Fig. 3.4 Cyclic voltammograms of chromophores DEA-MN, DEA-TCF, **DHPz-MN-1** and **DHPz-TCF-1** (left) and **DHPz-MN-1** and **DHPz-TCF-1** (right). Voltammograms were recorded in acetonitrile solutions containing a 0.1 M Bu$_4$NPF$_6$ supporting electrolyte at a scan rate of 50 mV s^{-1}.

Table 3.2 Electrochemical and optical properties of chromophores in study.

	$\lambda_{max}^{CHCl_3}$	E_{ox}^{HOMO}	E_{red}^{LUMO}	E_g^{CV}	E_g^{Opt}	$\beta_{zzz}(0)$
	nm	(eV)	(eV)	(eV)	(eV)	($\times10^{-30}$esu)
DEA-MN	439	-5.11	-3.26	1.85	2.66	21.1
DEA-TCF		-4.99	-3.61	1.38		65.7
DHPz-MN-1	500	-4.71	-3.67	1.03	2.04	79.4
DHPz-TCF-1	616	-4.00	-3.49	0.51	1.59	194.2
DHPz-MN-2	509	—	—	—	1.98	—
DHPz-TCF-2	630	—	—	—	1.54	—

and the results tabulated in table Table 4.1. It is clear from the voltammagrams that the HOMO level has shifted to a lower potential in the chromophores **DHPz-MN-1** and **DHPz-TCF-1** compared to MN-1 and TCF-1. The DHPz chromophores have two reversible oxidation peaks, the first one occurring near -0.2 V (vs Ag/AgCl). From this onset potential, the HOMO energy can be found from

$$E_{ox}^{HOMO} = -e[E_{ox}^{onset} + 4.4] \, eV \qquad (3.1)$$

and similarly, the LUMO energy can be determined from

$$E_{red}^{LUMO} = -e[E_{red}^{onset} + 4.4] \, eV \qquad (3.2)$$

where E_{ox}^{onset} and E_{red}^{onset} are in volts and $e = 1\text{eV/v}$[9]. In going from a DEA donor to a DHPz donor, the HOMO energies for **DHPz-MN-1** and **DHPz-TCF-1** change by 0.40eV and 0.99eV, respectively. The effects on the energy gaps where a change from 1.85eV for MN-1 to 1.03eV for **DHPz-MN-1** and 1.03eV for TCF-1 to 0.51eV for **DHPz-TCF-1**. This further suggests that the DHPz donor is better than the DEA donor and that the theoretical predictions where correct.

3.2.4   Thermal Analysis

Thermal properties of **DHPz-TCF-2** were measured by differential scanning calorimetry (DSC)(Fig. 4.3) and thermogravimetric analysis (TGA)(Fig. 4.4). The first scan of the DSC plot shows a small feature near 90°C and a more pronounced, endothermic, feature at 160°C. The feature at 90°C was interpreted as the glass transition temperature based on the temperature at which neat films of the chromophore were poled. Interpretation of the feature at 160°C was not as clear as the feature did not reappear during the repeat scan. The presence of a glass transition temperature (T_g) near 90°C suggests that this material may exist in an amorphous state, but any final conclusions are complicated by the additional endothermic peak. This peak may represent a crystallization event, some unknown solid-

DSC
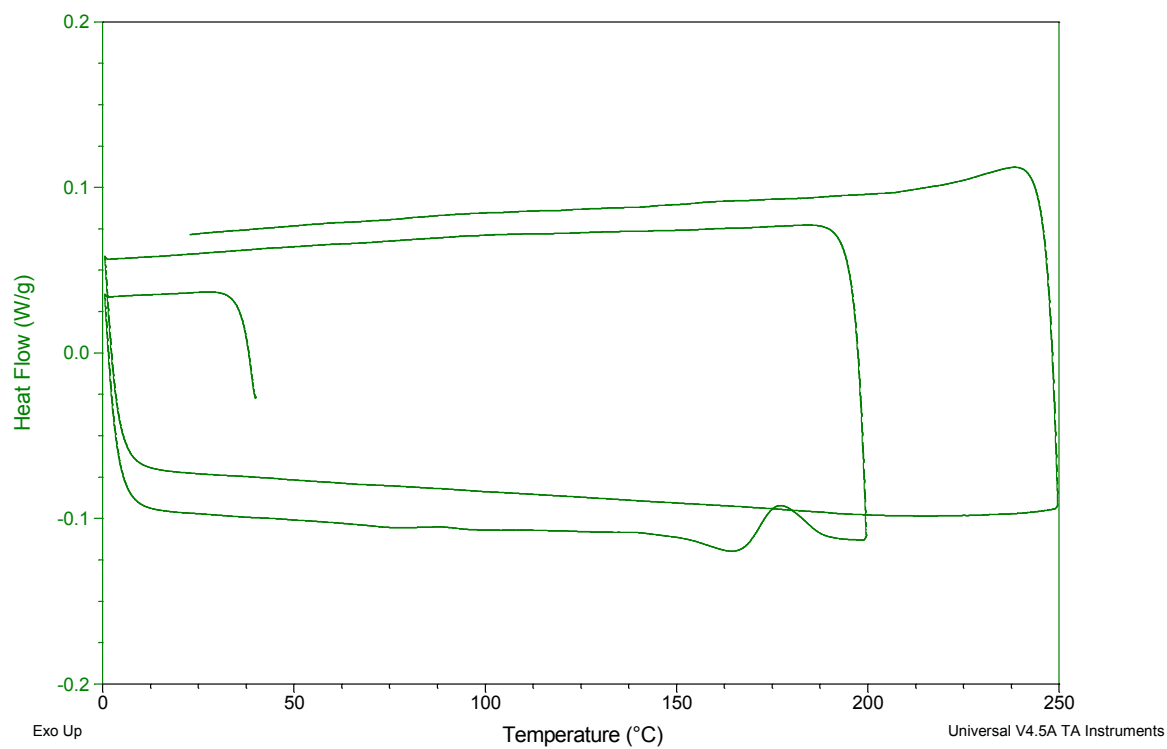
Fig. 3.5 Differential Scanning Calorimetry plot of **DHPz-TCF-2** with a heating rate of 10°C min^{-1} in a nitrogen environment.

265.7°C

Weight (%)

Temperature (°C)

Universal V4.7A TA Instruments
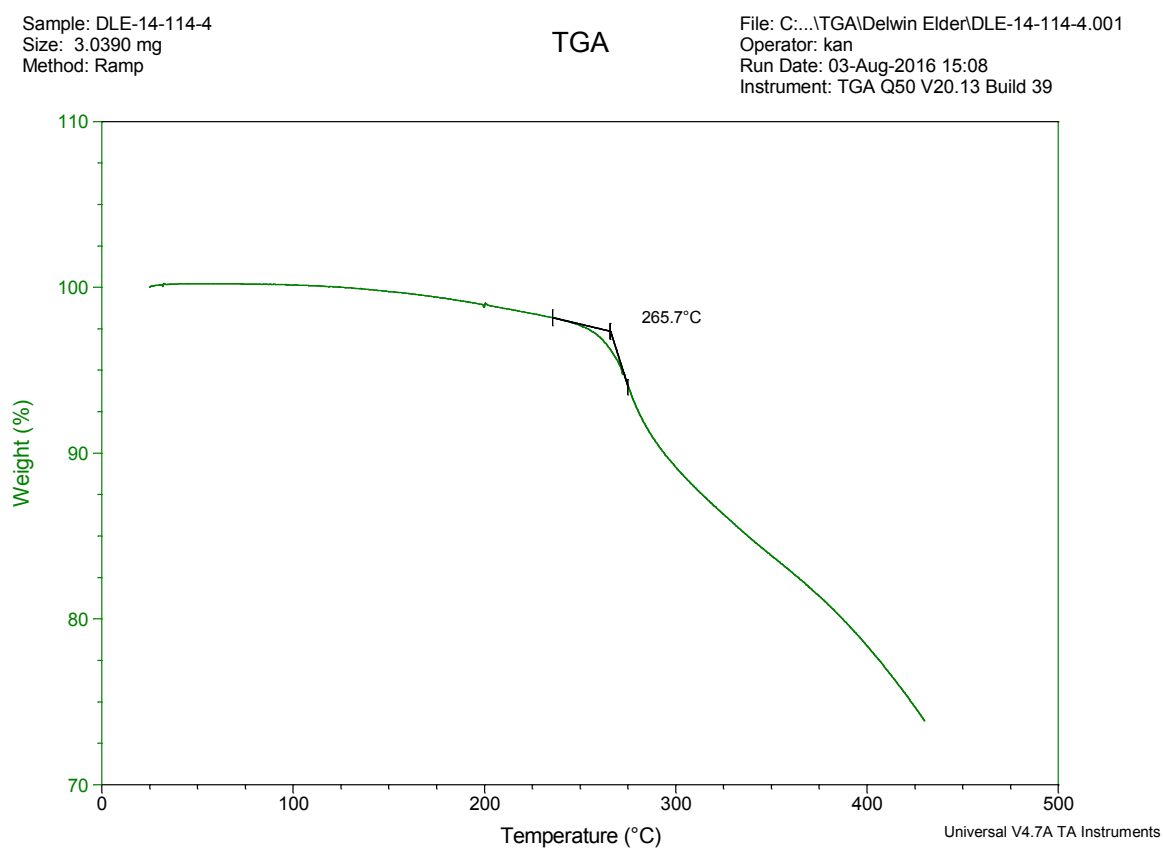
Fig. 3.6 Thermogravimetric analysis curve of **DHPz-TCF-2** with a heating rate of 10°C min^{-1} in a nitrogen environment. $T_d = 265.7$°C.

state transition or decomposition[10,11]. The absence of the peak, or any discernible features in the repeat scan, also indicate this may be a decomposition event, but this is contrary to what was revealed by thermogravimetric analysis.

The decomposition temperature, T_d, was found to be 265.7°C. This is higher than any of the diaryl chromophores reported by Cheng *et al.*[12], and much higher than the endotherm observed by DSC. The aryl substituents on the dihydropyrazine ring would appear to be offering the same enhancement to thermal stability that is observed with the alkyl units are replaced with aryl moieties in more traditional chromophore donors. All of the diaryl chromophores had glass transition temperatures that ranged from 75°C for **B4** on the low end to 114°C for **B4**. With the exception of **A1**, all systems showed only a T_g, but **A1**, which contained a diphenylamine donor, had a T_g at 90°C a crystallization, T_c, at 158°C and a melting point, T_m, at 234°C[12]. No repeat scans over the range of interest were shown, but based on this it would appear that **DHPz-TCF-2** has a similar T_g are 90°C followed by a T_c at 160°C. No melting point was observed, but this may be due to the initial scan ending at 200°C and never reaching the T_m of the material. This may also explain why there are no discernible features in the second scan as the material was locked in a crystalline state following the initial scan. Additional thermal characterization of both **DHPz-TCF-1** and **DHPz-TCF-2** should be more revealing.

3.2.5 Electric Field Poling Experiments

Electric field poling experiments[3] were performed to evaluate the performance of **DHPz-TCF-2** in a simple EO device. The EO activity was measured in a guest-host polymer system using PMMA with 25% chromophore loading and also as a monolithic film. For the guest-host films, the solids were dissolved in 1,1,2-trichloroethane(TCE) to prepare a solution that was 12.5% total solids by weight. This solution was filtered through a $0.2\mu m$ PTFE filter and the filtered solution was spin-coated onto glass slides containing a thin layer of ITO on one half as an electrode. The films were baked in an oven, under vacuum, at 65°C overnight to ensure complete removal of any residual solvent. A gold electrode was sputtered on top
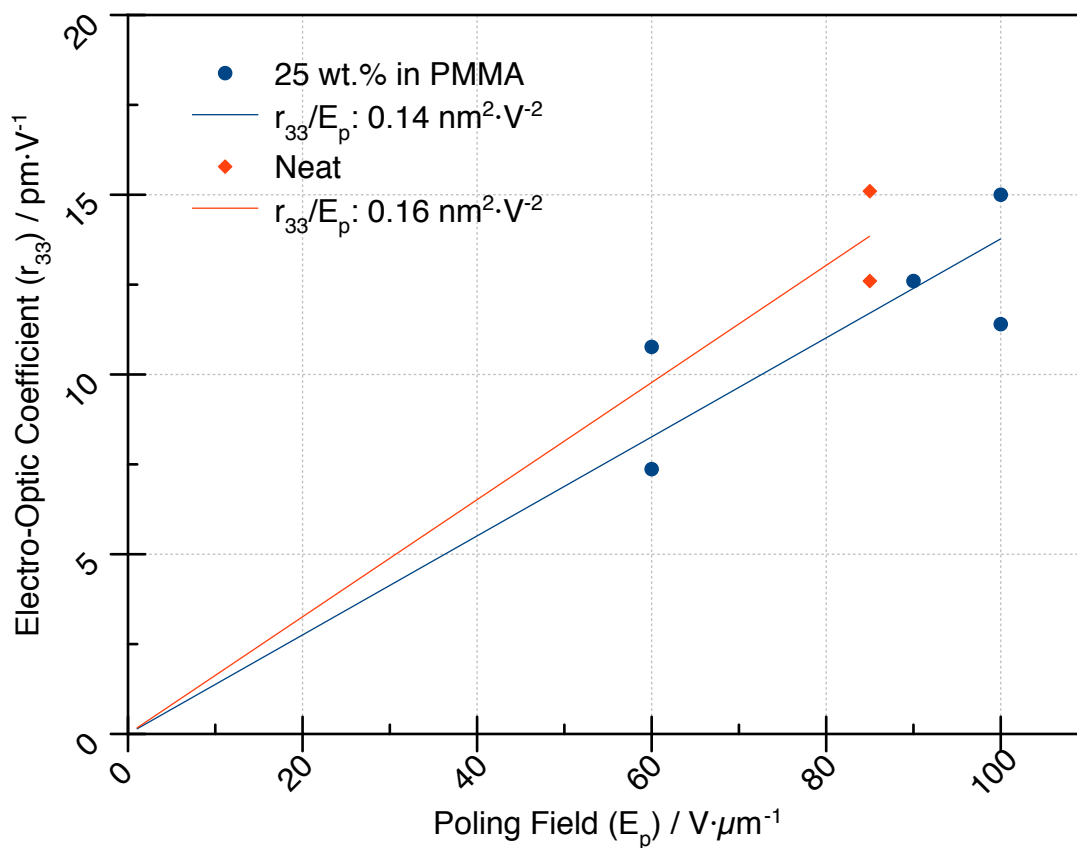
Fig. 3.7 Electro-optic coefficients of **DHPz-TCF-2** films, ○ 25 wt.% in PMMA and ◇ neat film, at different poling voltages. Poling efficiencies, $r_{33}/E_p = 0.14 nm^2 \cdot V^{-2}$ for the guest-host system and $r_{33}/E_p = 0.16 nm^2 \cdot V^{-2}$ for the monolithic film.

of the polymer film to supply a top electrode for contact poling. Monolithic chromophore films were prepared in a similar fashion to the guest-host systems. Initial films prepared from a 7.8 wt.% solution of chromophore in TCE were found to be of very poor quality due to the low solubility of the chromophore in solution. Film quality was improved for films prepared from a 1:1 mixture of **DHPz-TCF-2** with **EZ-FTC**, but the film thickness was much lower and there was still a large amount of solids that did not fully go into solution. All devices prepared from this solution shorted as a result of the very thin films. Changing the solvent from TCE to cyclopentanone yielded much better results. Initial films from a 7.8 wt.% solution produced films that were 550nm and based on previous results, new solutions of a higher concentration were prepared to produce thicker films. The concentration was increased to 12 wt.% to produce films that were 887nm thick.

Electro-optic coefficients, r_{33}, were measured by the Teng-Man simple reflection technique at 1310nm[13]. The results of the poling experiments are shown in figure Fig. 4.5. The films in PMMA had a maximum r_{33} of 15pm/v obtained at a poling field of 100$V/\mu m$. This equates to a maximum poling efficiency (r_{33}/E_p) of 0.15nm^2/v^2 and an average poling efficiency of 0.14nm^2/v^2. The neat chromophore system had a maximum r_{33} of 15.1pm/v obtained at a poling field of 85$V/\mu m$ for a maximum poling efficiency (r_{33}/E_p) of 0.18nm^2/v^2 and an average poling efficiency of 0.16nm^2/v^2. Chromophore **A2**, with a diphenylamine donor, FTC bridge and CF3Ph-TCF acceptor has a reported r_{33} of 19pm/v obtained at a poling field of 100$V/\mu m$, as measured by Teng-Man[12]. **DHPz-TCF-2**, with a shorter bridge and weaker acceptor compares quite favorably and this is attributed to the DHPz donor.

3.3 *Conclusion*

We present, for the first time, several novel chromophores with a 1,4-dihydropyrazine donor for the use in electro-optic applications. Four chromophore were prepared with either the malononitrile or TCF acceptors. This family of chromophores exhibit large bathochromic

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[3]The poling field correction as explained in ref[14] where not applied during this study.

shifts compared to their diethyl amine donor counterparts and were readily soluble in a range of solvents. The HOMO and LUMO levels were determined using Cyclic Voltammetry and were found to be $E_{ox}^{HOMO} = -4.71\,eV$ and $E_{red}^{LUMO} = -3.67\,eV$ for DHPz-MN-A and, $E_{ox}^{HOMO} = -4.00\,eV$ and $E_{red}^{LUMO} = -3.49\,eV$ for **DHPz-TCF-1**. The energy gap for the HOMO⟶LUMO transition $0.82\,eV$ and $0.87\,eV$ lower than their respective diethylamine donor counterparts. Devices were made from the **DHPz-TCF-2** chromophore in PMMA at 25 wt% and as monolithic films. The polymer guest-host system had a poling efficiency of $0.14^{nm^2}/v^2$ and a maximum r_{33} of 15.2 at a field strength of $100^V/_{\mu m}$. The neat chromophore system had a poling efficiency of $0.16^{nm^2}/v^2$ and a maximum r_{33} of 15.1 at a field strength of $85^V/_{\mu m}$. Attempts to attach stronger acceptors such as the CF3Ph-TCF or TCP acceptor failed due to decomposition of the dihydropyrazine ring. If these issues can be addressed, chromophores based on the DHPz donor may prove quite competitive as even with a weaker acceptor, the performance of **DHPz-TCF-2** was on par with an FTC-class chromophore with a CF3Ph-TCF acceptor.

3.4 *Experimental Section*

General information: Chemicals used were purchased from Sigma Aldrich, Alfa Aesar or TCI and used without further purification unless otherwise noted. UV-visible Absorption Spectroscopy was obtained on a Shimadzu 1601 or a Varian Cary 5000 spectrometer. Differential Scanning Calorimetry (DSC) data was acquired on a TA Instruments Q100 with heating and cooling under nitrogen at rates of 10°C per min. Thermogravametric Analysis (TGA) data was acquired on a TA Instruments Q500 with heating under nitrogen at a rate of 10°C per min. ^{1}H NMR spectra were acquired using a Bruker AVance series instrument running at 300 MHz. 1,1,2 trichloroethane (TCE) and cyclopentanone were purified via vacuum distillation prior to use. ITO/glass slides were purchased from Thin FilmDevices, Inc. Optical profilometry measurements were carried out on a WYKO NT-2000 model profilometer. In situ Teng-Man ellipsometry was carried out on a home built device[15]. The compounds IM-1-Bu/Ald-1-Bu, **DHPz-TCF-1** and **DHPz-TCF-2** were prepared by Dr.

Delwin Elder.

*Synthesis of 4-(3,4,5-triphenylpyrazin-1(4H)-yl)benzaldehyde (**D1**)*

A solution of 2,2'-(phenylazanediyl)bis(1-phenylethanone) (1 eq.) in DMF (5 mL/mmol) was cooled to -20°C and to this was added $POCl_3$ (1 eq.) in one portion. The solution was kept at -20°C overnight and heated briefly to 60°C before being poured into ice water containing sodium acetate. The solid was filtered, washed with water, a small amount of isopropanol and diethyl ether. The product was air dried overnight to yield 0.58g (53%) 1,3,4,5-tetraphenyl-1,4-dihydropyrazine-2-carbaldehyde and 4-(3,4,5-triphenylpyrazin-1(4H)-yl)benzaldehyde as an red-orange solid. 1H NMR (300 MHz, Acetone-d6) δ 9.18 (s, 1H), 7.81 (dd, J = 6.6, 3.1 Hz, 2H), 7.63 (dd, J = 8.2, 1.5 Hz, 3H), 7.54 – 7.47 (m, 3H), 7.38 – 7.22 (m, 6H), 7.15 (dd, J = 8.8, 1.2 Hz, 2H), 7.04 – 6.99 (m, 4H), 6.92 (s, 1H).

*Synthesis of 1,2,4,6-tetraphenyl-1,4-dihydropyrazine (**D2**)*

To a 20mL vial containing a stirbar, 2,2'-(phenylazanediyl)bis(1-phenylethanone) (1 eq.) and aniline (1.4 eq.) was added a 5% solution of trifluoacetic acid and acetic acid in toluene (5 mL/mmol). The vial was capped and placed in a bead bath held at 90°C for 6 hours. The vial was removed from the bath, allowed to cool and the contents transfered to a round bottom flask. The solvent was stripped under reduced pressure and the residue was treated with a hot mixture of ethanol or isopropanol and an aqueous solution of saturated sodium bicarbonate. The contents were filtered and washed with alcohol and diethyl ether. The product was air dried overnight to yield 0.89g (99%) 1,2,4,6-tetraphenyl-1,4-dihydropyrazine as a yellow crystalline solid. ^{1}H NMR (300 MHz, DMSO-d6) δ 8.10 (s, 2H), 7.93 – 7.79 (m, 4H), 7.49 (d, J = 8.1 Hz, 2H), 7.39 (q, J = 8.7, 8.3 Hz, 6H), 7.26 (d, J = 7.3 Hz, 2H), 7.15 – 6.95 (m, 3H), 6.71 (dd, J = 17.5, 7.8 Hz, 3H). MS (ESI) 387 (M+H).

*Synthesis of 4-(bis(2-oxo-2-phenylethyl)amino)benzaldehyde (**D-Ald**)*

To a cooled solution of 2,2'-(phenylazanediyl)bis(1-phenylethanone) (1 eq.) in DMF (5 mL/mmol) was added $POCl_3$ (1.5 eq.), dropwise, over 1 minute. The solution was stirred at room temperature for 30 minutes and heated to 90°C for 45 minutes. The cooled solution was neutralized with solid sodium acetate, diluted with ice water and allowed to sit overnight. The solid was filtered, washed with water, a small amount of isopropanol and diethyl ether. The product was air dried overnight to yield 4.15g (62%) 4-(bis(2-oxo-2-phenylethyl)amino)benzaldehyde as dark tan powder. ^{1}H NMR (300 MHz, Acetone-d6) δ 9.72 (s, 1H), 8.11 (d, J = 7.1 Hz, 4H), 7.74 – 7.63 (m, 4H), 7.62 – 7.52 (m, 4H), 6.75 (d, J = 8.9 Hz, 2H), 5.23 (s, 4H).

*Synthesis of N-(4-(3,4,5-triphenylpyrazin-1(4H)-yl)benzylidene)aniline (**IM-1**) and 4-(3,4,5-triphenylpyrazin-1(4H)-yl)benzaldehyde (**Ald-1**)*

To a 20mL vial containing a stirbar, 4-(bis(2-oxo-2-phenylethyl)amino)benzaldehyde (1 eq.) and aniline (3 eq.) was added a 5% solution of trifluoacetic acid and acetic acid in toluene (5 mL/mmol). The vial was capped and placed in a bead bath held at 90°C for 6 hours. The vial was removed from the bath, allowed to cool and the contents transfered to a round bottom flask. The solvent was stripped under reduced pressure and the residue was treated with a hot mixture of ethanol or isopropanol and an aqueous solution of saturated sodium bicarbonate. The contents were filtered and washed with alcohol and diethyl ether. The product was air dried overnight to yield 0.31g (76%) N-(4-(3,4,5-triphenylpyrazin-1(4H)-yl)benzylidene)aniline as a yellow/orange solid. ^{1}H NMR (300 MHz, Acetone-d6) δ 8.53 (s, 1H), 8.03 (s, 2H), 8.01 – 7.90 (m, 7H), 7.60 (d, J = 8.9 Hz, 2H), 7.49 – 7.35 (m, 6H), 7.34 – 7.18 (m, 4H), 7.08 – 6.98 (m, 2H), 6.86 (d, J = 8.2 Hz, 2H), 6.76 (t, J = 7.2 Hz, 1H). MS (ESI) 415, 490 (M+H).

*Synthesis of 2-(4-(3,4,5-triphenylpyrazin-1(4H)-yl)benzylidene)malononitrile (**DHPz-MN-1**)*

To a vial containing a stir bar and IM-1/Ald-1 (1 eq.) in ethanol (1ml/mmol) was added malononitrile (1.1 eq). The vial was capped and placed in a bead bath held at 90°C for 30 minutes. Once cool, the precipitate was filtered and washed with isopropanol and ethanol to yield 0.36g (76%) **DHPz-MN-1** as a maroon solid. ^{1}H NMR (300 MHz, Acetone-d6) δ 8.11–8.04 (m, 3H), 7.94 (d, J = 7.2 Hz, 4H), 7.85 (s, 2H), 7.64 (d, J = 9.1 Hz, 2H), 7.44 (t, J = 7.5 Hz, 4H), 7.33 (t, J = 7.3 Hz, 2H), 7.03 (dd, J = 8.6, 7.3 Hz, 2H), 6.91 (d, J = 7.9 Hz, 2H), 6.80 (t, J = 7.2 Hz, 1H). MS (ESI) 462 (M+).

*Synthesis of 2-(4-(4-(4-butylphenyl)-3,5-diphenylpyrazin-1(4H)-yl)benzylidene)malononitrile (**DHPz-MN-2**)*

DHPz-MN-2 was synthesized exactly the same as **DHPz-MN-1** from Im-1-Bu/Ald-1-Bu. **DHPz-MN-2** as a maroon solid. ^{1}H NMR (300 MHz, Acetone-d6) δ 8.07 (d, J = 7.4 Hz, 3H), 7.93 (d, J = 7.4 Hz, 4H), 7.75 (s, 2H), 7.61 (d, J = 9.1 Hz, 2H), 7.43 (t, J = 7.5 Hz, 4H), 7.33 (t, J = 6.8 Hz, 2H), 6.87 (s, 4H), 2.47–2.32 (m, 2H), 1.43 (p, J = 7.8, 7.4 Hz, 2H), 1.24 (dt, J = 14.9, 7.2 Hz, 2H), 1.15 (s, 1H), 0.83 (t, J = 7.3 Hz, 2H). MS (ESI) 519 (M+H).

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Chapter 4

SYNTHESIS OF DIAMINOTRIPHENYLAMINE(DATPA) DONOR

4.1 Introduction

One of the difficulties in designing new donors is developing a feasible synthetic scheme to give the desired product in the fewest steps possible with an adequate yield. With diaryl donors, one of these synthetic steps invariably involves the coupling of a functionalized aryl ring to an aryl amine[1–4]. This reaction is nontrivial as typical nucleophilic substitutions tend to fail except for in a few select cases[5]. Aryl amines are an important feedstock as they can be found in a number of natural products and pharmaceuticals, so to address these needs, a number of synthetic methods have been developed.

The Buchwald-Hartwig amination (BHA) is one of the more popular methods owing to its mild conditions and moderate–to–high yields[5]. This is a palladium catalyzed synthesis of aryl amines from aryl halides and primary or secondary amines. The efficacy of this reaction can depend upon the type of ligand used and a whole field of chemistry has emerged around the optimization of these ligands. To date, the most effective systems have involved palladium with bulky phosphine ligands[6–10]. This system has allowed the breadth and scope of C-N coupling reactions to expand to include a wider variety of substrates such that virtual any transformation may now be achieved with the proper ligand. Disadvantages of this class of reaction is that not all ligands perform equally, potentially requiring an assortment of ligands for work with several substrates, and these reactions tend to perform better with electron-poor aryl halides.

The Goldberg reaction[11], or Ullmann condensation[12], is a another type of C-N coupling reaction. This reaction relies on copper or copper salts and aryl halides. Traditionally, this

method required stoichiometric amounts of copper and harsh reaction conditions, but recent advances have been made that allow catalytic amounts of copper(I) chloride or copper(I) iodide to be used in conjunction with diamine ligands[13–16]. This reaction works well for both electron-rich and electron-poor aryl halides, but can require large amounts of base and is used almost exclusively with aryl iodides.

Other reactions include the Chan-Lam coupling which allows boronic acids, stannanes or siloxanes to be oxidatively coupled to amines at room temperature in air. The reaction can be performed with stoichiometric or catalytic amounts of copper, but the requirement of boronic acids introduces an additional step not required in the previous methods. Reductive aminations, such as the Eschweiler-Clarke reaction, are a facile method for converting carbonyls to amines, but the reactions are typically not employed in the synthesis of triaryl amines[17–22].

4.2   Results and Discussion

The triaryl amines in this work were synthesized from deactivated aryl fluorides in the presence of a mild base. This method offered the advantage of not requiring any specialized ligands, handling or transition metal catalyst. The conditions for these reactions are similar to nucleophilic substitution reactions between amines and alkyl halides and are known to proceed with excellent yields. This method also allows the possibility to investigate many systems from one common starting point using commercially available starting reagents.

4.2.1   Synthesis of 4',4-Diaminotriphenylamine Donor

Synthesis of 4',4-diaminotriphenylamine (DATPA) was performed in two steps from 4-fluoronitrobenzene and aniline and the overall synthesis is shown in scheme Scheme 4.1. In the first step, 4-fluoronitrobenzene was reacted with aniline in the presence of potassium carbonate in dimethylformamide. The aniline/potassium carbonate slurry was activated by sonication for 5 minutes before addition of 4-fluoronitrobenzene. The reaction proceeded smoothly and 4',4-dinitrotriphenylamine (DNTPA) converted to DATPA by reduction with tin(II) chloride
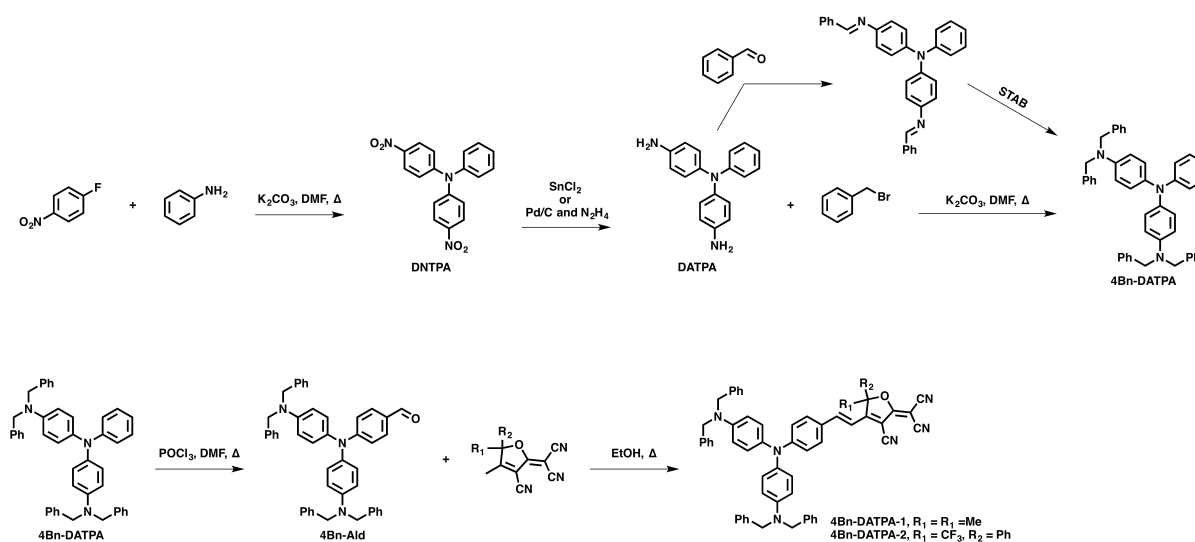
Scheme 4.1 Synthesis of DATPA chromophores.

dihydrate in ethanol or 10% Pd/C and hydrazine hydrate in ethanol. Both reactions gave the desired product in excellent yields, but tin salts were a constant problem with the tin(II) chloride reductions. No such problems were encountered during reductions with hydrazine. **4Bn-DATPA** was achieved via two methods. The first method was a direct nucleophilic substitution of DATPA with benzyl bromide. The second method was a reductive amination with benzyl bromide and sodium triacetoxyborohydride (STAB). Product isolation from the reductive amination was not as clean as the nucleophilic substitution due to difficulty in isolating the fully substituted product from the partially substituted products. **4Bn-Ald** was prepared by a Vilsmeier-Haack reaction using phosphorous ocxychloride in dimethyformamide. Chromophores **4B-DATPA-TCF-1** and **4B-DATPA-TCF-2** were obtained *via* Knoevenagel condensation reactions with the TCF or CF3Ph-TCF acceptors in refluxing ethanol.
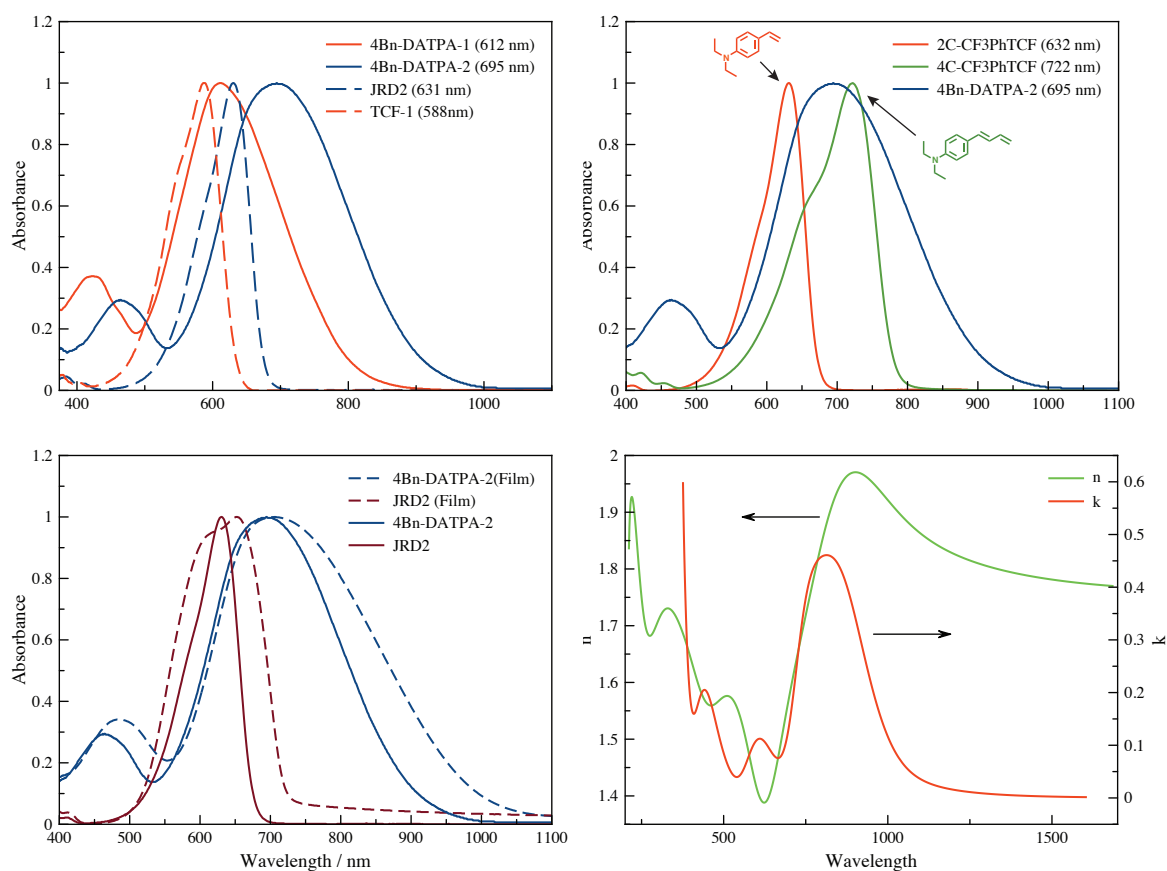
Fig. 4.1 Top left, optical spectra of chromophores in chloroform. Top right, comparison with chromophores with a 2 carbon and 4 carbon bridge. Bottom left, comparison with **JRD2** in chloroform and as a film. Bottom right, optical constants, n and k, obtained from VASE measurements.

4.2.2   Optical Properties

The optical absorption spectra of chromophores **4Bn-DATPA-1** and **4Bn-DATPA-2** where measured in chloroform and compared to chromophores **JRD2**[23], TCF-1 (labeled GIM2), **2C-CF3PhTCF** and **4C-CF3PhTCF**(see figure **??**). The λ_{max} of these chromophores are 612nm, 695nm, 631nm, 588nm, 632nm and 722nm, respectively. The DATPA donor caused the ICT band to shift to lower energies for both chromophores. For **4Bn-DATPA-1**, this shift is +24nm[1], and places it very close to **JRD2** and **2C-CF3PhTCF**, both with the stronger CF3PhTCF acceptor. **4Bn-DATPA-2** is red-shifted 64nm from JRD2 and 63nm from **2C-CF3PhTCF**. The bathochromic shifts in the DATPA chromophores can be attributed to the new diary system contributing more to the donating strength of the conjugated system. To gauge how large this effect is, **4Bn-DATPA-2** was compared to chromophores have a 2 carbon bridge and a 4 carbon bridge. Extension of the bridge increases β due to greater charge separation and **4Bn-DATPA-2** is blue-shifted from **4C-CF3PhTCF** by 27nm. This suggests that **4Bn-DATPA-2** and **4C-CF3PhTCF** should have similar values of β and illustrates the enhanced donating ability of the DATPA donor. Neat films cast from 1,1,2-trichloroethane solutions were prepared from both **JRD2** and **4Bn-DATPA-2**. Chromophores capable of forming glassy materials are of great interest as they allow for higher number densities than is typically possible in guest-host polymer systems. One issue that becomes more apparent in these glassy materials is aggregation, as seen by the appearance of a shoulder on the ICT transition. This can be seen clearly in the neat film prepared from **JRD2** as a low energy shoulder. There is no apparent shoulder in the neat film of **4Bn-DATPA-2**, but it is not clear if one is present due to line broadening of the peak transition. Optical constants, n and k, were obtained from the thin film of **4Bn-DATPA-2** using a VASE®ellipsometer.

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[1]The +/- sign convention is used to indicate either a bathochromic (+) or hypsochromic (-) shift. The presence of the sign holds no other significance.

4.2.3 Cyclic Voltammetry Measurements
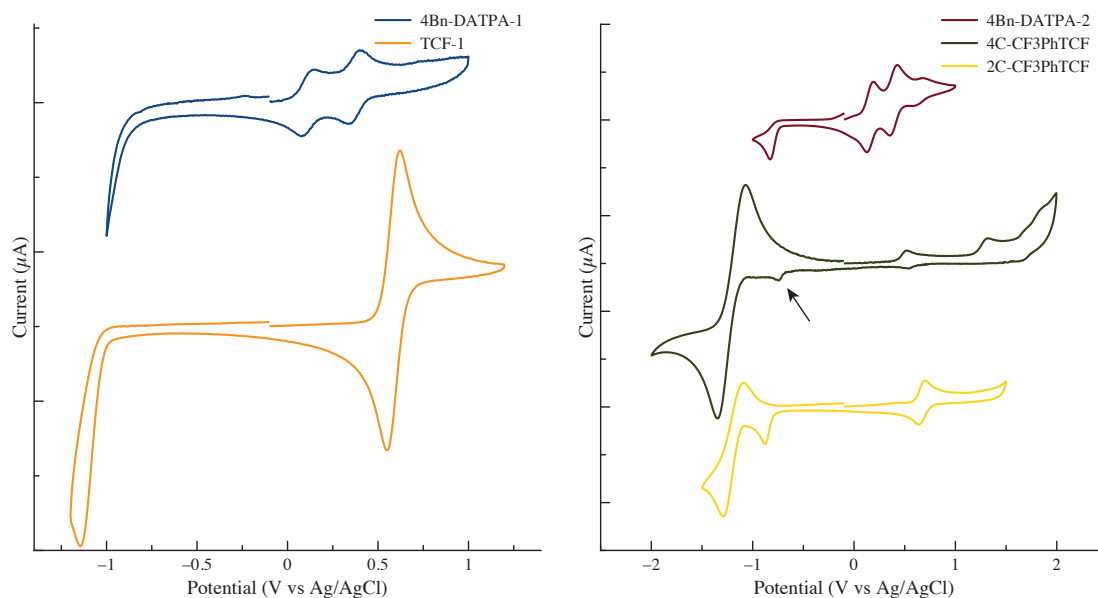
Fig. 4.2 Cyclic voltammetry of CF3Ph-TCF chromophores. The bottom has a 2-carbon bridge with a diethylamine donor, the middle has a 4-carbon bridge with a diethylamine donor and the top has the DATPA donor.

The redox properties of chromophores **4Bn-DATPA-1** and **4Bn-DATPA-2** were determined by cyclic voltammetry in degassed acetonitrile solutions containing a 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte at a scan rate of 50 mV s^{-1}. The voltammograms are shown in figure Fig. 4.2 and the relevant data is tabulated in table Table 4.1. **4Bn-DATPA-1** had two reversible oxidation peaks and one irreversible reduction peak. Both oxidation peaks occurred at much lower potentials than **TCF-1**, suggesting an increase in the HOMO energies. The energy gap was determined to be 1.51eV for **TCF-1** with an E_{ox}^{HOMO} at about -4.90eV and an E_{red}^{LUMO} at -3.39eV. **4Bn-DATPA-1** had an energy gap of 0.90eV with an E_{ox}^{HOMO} at -4.43eV and an E_{red}^{LUMO} at -3.52eV. For **4Bn-DATPA-2**, a third reversible oxidation peak appeared and E_{ox}^{HOMO} was found to be -4.48eV and E_{red}^{LUMO} was -3.66eV for an energy gap of 0.82eV. This was smaller than both

Table 4.1 Electrochemical and optical properties of chromophores in study.

	$\lambda_{max}^{CHCl_3}$	E_{ox}	E_{red}	E_g^{CV}	E_g^{Opt}	$\beta_{zzz}(0)$
	nm	(eV)	(eV)	(eV)	(eV)	($\times 10^{-30}$esu)
TCF-1		-4.90	-3.39	1.51		65.7
4Bn-DATPA-1	612	-4.43	-3.52	0.90	1.37	164.1[a]
2C-CF3PhTCF	632	-4.99	-3.62	1.37	1.85	
4C-CF3PhTCF	722	-4.82	-3.73	1.09	1.58	
4Bn-DATPA-2	695	-4.48	-3.66	0.82	1.56	193.6[a]

2C-CF3PhTCF (1.37eV) and **4C-CF3PhTCF** (1.09eV). This trend followed what was observed with the optical energy gap. The data confirms the theoretical results that the DATPA donors are improvements over dialkyl donors as in all cases, the HOMO energies for the DATPA chromophores are higher than their dialkyl counterparts. Further more, **4Bn-DATPA-2** has a HOMO that is higher than **4C-CF3PhTCF** which has had its bridge extended by two carbons.

4.2.4 Thermal Analysis

Thermal properties of **4Bn-DATPA-2** were measure by differential scanning calorimetry (DSC)(figure Fig. 4.3) thermogravimetric analysis (TGA)(figure Fig. 4.4). This chromophore only exhibits a glass transition temperature (T_g) 76.7°C, suggesting that it is an amorphous glassy material. We see this transition on both the first and second scans suggesting that the amorphous state is thermodynamically stable. The combination of benzyl groups and the diaryl structure of the donor are most likely responsible for this. The non-planar nature of the triphenyl donor and the benzyl groups likely prevent close packing of the molecules, thus inhibiting crystallization**??**. The extended aryl system may also interact favorably with each other through dipole-quadrupole or quadrapole-quadrapole interactions leading to an
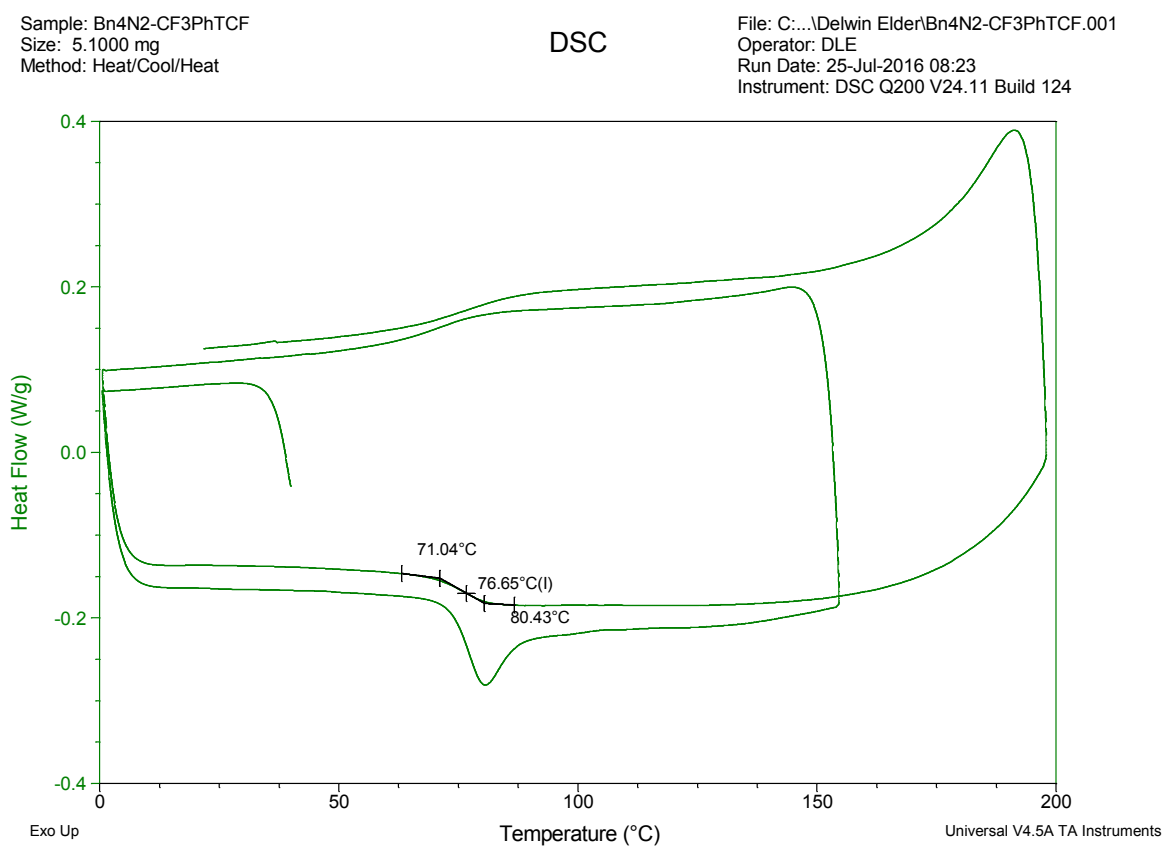
Fig. 4.3 Differential Scanning Calorimetry plot of **4Bn-DATPA-2** with a heating rate of $10°C$ min^{-1} in a nitrogen environment. $T_g = 76.7°C$.
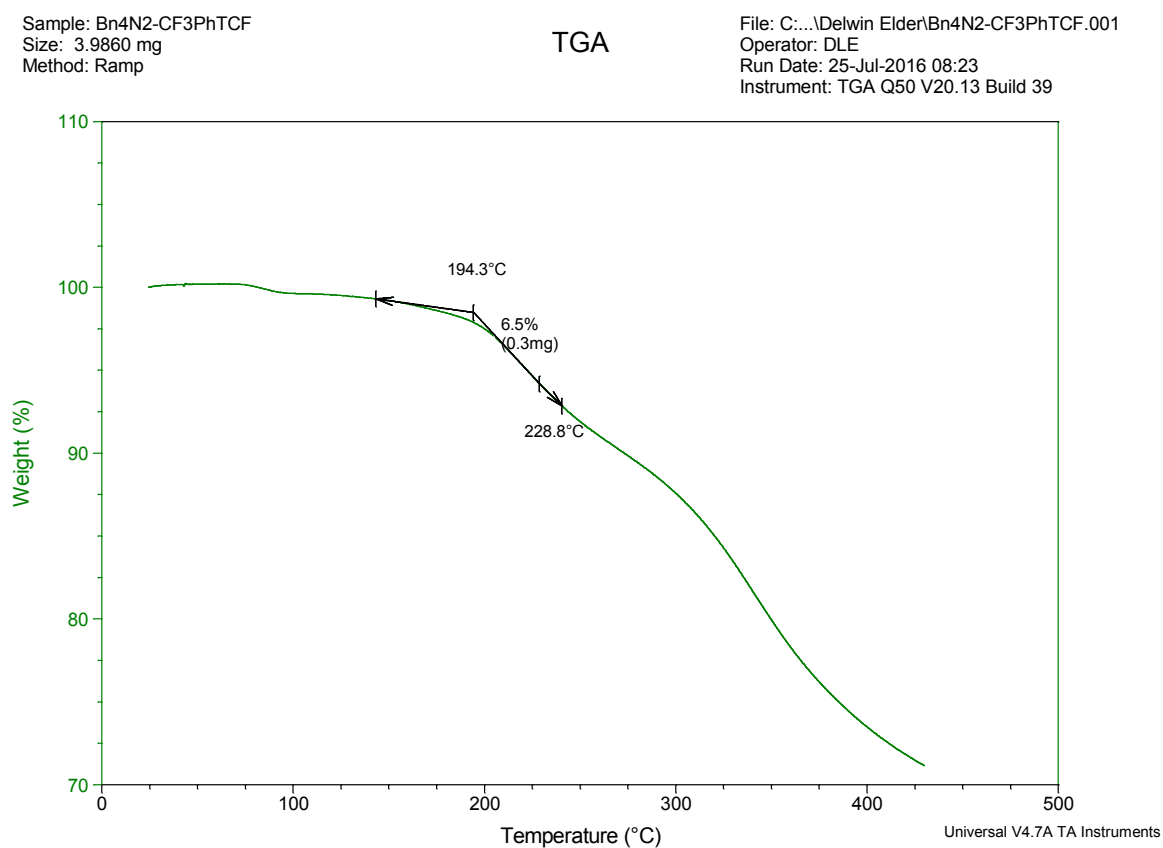
Fig. 4.4 Thermogravimetric analysis curve of **4Bn-DATPA-2** with a heating rate of 10°C min^{-1} in a nitrogen environment.$T_d = 194.3$°C.

extended network that behaves as a much large system. A more systematic study of these systems are likely to reveal both the role of the diaryl and benzyl moieties and offer incite as to what role they play in the organization of this chromophore. It should also be noted that this T_g is higher than **JRD2**[23] which exhibits similar behavior.

The decomposition temperature, T_d, is 194°C. This is lower than what has been reported for other diaryl chromophores[1], but is similar to what is seen for dialkylamino donors. This reduction in T_d is likely caused by the 4 benzyl groups. By reducing their number or replacing them altogether, it should be possible to raise the T_d but the effects on the other, aforementioned, properties are not yet known and it may be more beneficial to leave the benzyl rings as the T_d is still on par with typical chromophores such as **YLD124**[1,23].

4.2.5 Electric Field Poling Experiments

Electric field poling experiments were performed to evaluate the performance of **4Bn-DATPA-2** in a simple EO device. The EO activity was measured from a monolithic organic glass(neat film). The chromophore was dissolved in 1,1,2-trichloroethane to prepare a solution that was 8.5 wt% and filtered through a $0.2\mu m$ PTFE filter. The filtered solution was spin-coated onto glass slides containing a thin layer of ITO on one half as an electrode. The films were baked in an oven, under vacuum, at 65°C overnight to ensure complete removal of any residual solvent. A gold electrode was sputtered on top of the polymer film to supply a top electrode for contact poling. The r_{33} values were measured by the Teng-Man simple reflection technique at 1310nm[24]. The results of the poling experiments are shown in figure Fig. 4.5.

4Bn-DATPA-2 performed well as a neat system with a maximum r_{33} of 49pm/v at a poling field of 72V/μm. Poled films of **JRD2**, another small chromophore monolithic glassy material, had a maximum r_{33} of 22pm/v at a poling field of 54V/μm[23,25]. The r_{33} of the DATPA chromophore was more than twice **JRD2** and the poling efficiency, r_{33}/E_p, nearly doubled. This, along with a T_g that is 22°C higher than **JRD2** suggest that the 4Bn-DATPA donor may be a good replacement for the shaped-modified dialkyl donor present on
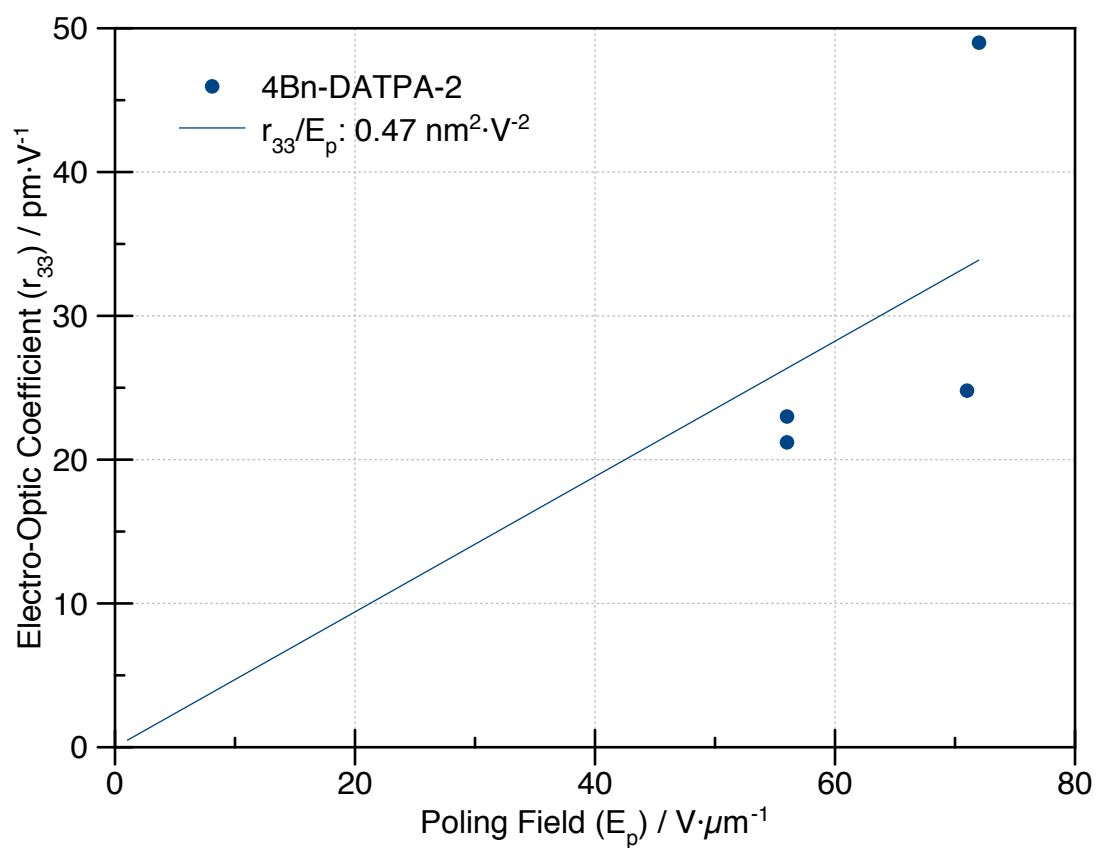
Fig. 4.5 Electro-optic coefficients of **4Bn-DATPA-2** monolithic films at different poling voltages. Poling efficiency, $r_{33}/E_p = 0.47 nm^2 \cdot V^{-2}$.

JRD2. These results demonstrate that the 4Bn-DATPA donor appears to be offering the same benefits as the shape-modified donor while also improving β and T_g. More data and testing are required before any conclusive determinations can be made, but what is presented here is very promising and indicates that this functional donor motif may be superior.

4.3 Conclusion

Two new chromophores containing benzylated DATPA donors have been synthesized. The CF3Ph-TCF chromophore forms an amorphous solid with excellent film forming qualities on par with those bearing TBDPS groups[23]. Use of benzyl groups has lowered the thermal decomposition temperature, compared to that reported for other diaryl chromophores, to 194°C, but the glass transition temperature is improved over a similar chromophore to TBDPS groups from 60°C to 77°C. Poled films of **4Bn-DATPA-2** had a maximum r_{33} of 49.0pm/v, measured for a monolithic film poled under a field of 72V/$_{\mu m}$ for a poling efficiency of 0.68nm²/v². These results are higher than what has previously been reported for the small chromophore-neat film system, **JRD2**. As both chromophores have similar number densities, and assuming around the same order, this improvement can be explained as an increase in the first molecular hyperpolarizability. Increasing the bridge length should allow for even higher performing chromophores, ones that have the benefits of the TBDPS groups introduced to **JRD2**, but with a stronger donor that can be easily modified to include crosslinking or other moieties without decreasing donor strength.

4.4 Experimental

General information: Chemicals used were purchased from Sigma Aldrich, Alfa Aesar or TCI and used without further purification unless otherwise noted. UV-visible Absorption Spectroscopy was obtained on a Shimadzu 1601 or a Varian Cary 5000 spectrometer. Differential Scanning Calorimetry (DSC) data was acquired on a TA Instruments Q100 with heating and cooling under nitrogen at rates of 10°C per min. Thermogravametric Analysis (TGA) data was acquired on a TA Instruments Q500 with heating under nitrogen at a rate of

10°C per min. ^{1}H NMR spectra were acquired using a Bruker AVance series instrument running at 300 MHz. 1,1,2 trichloroethane (TCE) and cyclopentanone were purified via vacuum distillation prior to use. ITO/glass slides were purchased from Thin FilmDevices, Inc. Optical profilometry measurements were carried out on a WYKO NT-2000 model profilometer. In situ Teng-Man ellipsometry was carried out on a home built device[26].

Synthesis of 4-nitro-N-(4-nitrophenyl)-N-phenylaniline (DNTPA)

A solution of aniline (1 eq.) and potassium carbonate (4 eq.) in DMF (5 ml/mmol) were sonicated for five minutes. To this solution was added 4-fluorobenzaldehyde (2.2 eq.) and the solution was heated to 100°C for 24 hours. Once cool, the solution was diluted with ice water and allowed to settle overnight. The solid was collected on a filter and washed with excess warm water, isopropyl alcohol and hexanes. The solid was dried under vacuum at 60°C overnight to yield 8.84g (87%) 4-nitro-N-(4-nitrophenyl)-N-phenylaniline. MS (ESI) 335.7 (M+). ^{1}H NMR (300 MHz, Acetone-d6) δ 10.00 (d, J = 19.7 Hz, 1H), 8.34 − 8.22 (m, 2H), 8.20 − 8.13 (m, 1H), 8.02 − 7.95 (m, 1H), 7.93 − 7.86 (m, 2H), 7.47 (dd, J = 14.1, 8.1 Hz, 1H), 7.42 − 7.37 (m, 3H), 7.31 (dd, J = 8.3, 6.4 Hz, 2H), 7.22 − 7.13 (m, 1H).

Synthesis of N^1-(4-aminophenyl)-N^1-phenylbenzene-1,4-diamine (DATPA) (Method 1)

To a stirred solution of **DNTPA** (1 eq.) in ethanol (100 mL) was added $SnCl_2 \cdot 2\,H_2O$ (5 eq). The flask was attached to a condenser and heated under reflux for 8 hours and allowed to cool to room temperature. The cooled solution was poured onto ice and neutralized with a saturated solution of $NaHCO_3$ to a pH of 7–8. The mixture was immediately filtered and washed with excess water and a 50% aqueous isopropanol solution. The product was air dried to yield 0.81g (73–99%) N^1-(4-aminophenyl)-N^1-phenylbenzene-1,4-diamine which was used directly in the next step. ^{1}H NMR (300 MHz, Acetone-d6) δ 7.07 (dd, J = 8.8, 7.2 Hz, 2H), 6.85 (d, J = 8.6 Hz, 4H), 6.78–6.67 (m, 3H), 6.64 (d, J = 8.7 Hz, 4H), 4.51 (s, 4H). MS (ESI) 275.2 (M+).

Synthesis of N¹-(4-aminophenyl)-N¹-phenylbenzene-1,4-diamine (DATPA) (Method 2)

To a solution of **DNTPA** (1 eq.) in ethanol (100 mL) was added 10%Pd/C (10mg/mmol). The solution was heated to reflux under a nitrogen and hydrazine monohydrate was slowly added (16 eq.). The addition took approximately 10 minutes to ensure the gas evolution did not get out of control. Reflux was continued for 8 hours and the contents were filtered through celite to remove the catalyst while still hot. The celite was washed with additional ethanol followed by a small amount of THF. This solution was left to cool overnight and the resulting crystals were collected by filtration and washed by a small amount of 85% cold ethanol. The product was air dried to yield 0.81g (96%) N^1-(4-aminophenyl)-N^1-phenylbenzene-1,4-diamine which was used directly in the next step. ^{1}H NMR (300 MHz, Acetone-d6) δ 7.07 (dd, J = 8.8, 7.2 Hz, 2H), 6.85 (d, J = 8.6 Hz, 4H), 6.78–6.67 (m, 3H), 6.64 (d, J = 8.7 Hz, 4H), 4.51 (s, 4H). MS (ESI) 276.3 (M+H).

Synthesis of N¹,N¹-dibenzyl-N⁴-(4-(dibenzylamino)phenyl)-N⁴-phenylbenzene-1,4-diamine (4Bn-DATPA)

A stirred solution of **DATPA** (1 eq.) and potassium carbonate(4 eq.) in DMF (5 ml/mmol) was placed in a ice bath (0–5°C) and benzyl bromide (2.2 eq.) was added over the course of five minutes. The ice bath was removed and the solution was heated to 100°C for 24 hours. Once cool, the solution was diluted with ice water and allowed to settle overnight. The solid was collected on a filter and washed with excess warm water, cold hexanes and air dried over night. The crude material was purified via a short column of silica with a gradient elution of 4:1 to 1:4 hexanes/toluene. The solvent was stripped under reduced pressure and the solid dried under vacuum at 60°C overnight to yield 0.67g (83%) N^1-(4-(dibenzylamino)phenyl)-N^4,N^4-dimethyl-N^1-phenylbenzene-1,4-diamine as an off-white solid. ^{1}H NMR (300 MHz, Acetone-d6) δ 7.30 (s, 16H), 7.27–7.19 (m, 3H), 7.06 (dd, J = 8.4, 6.9 Hz, 2H), 6.89 (d, J = 8.9 Hz, 4H), 6.77–6.64 (m, 8H), 4.67 (s, 8H). MS (ESI) 636.5 (M+H).

*Synthesis of 4-(bis(4-(dibenzylamino)phenyl)amino)benzaldehyde (**4Bn-Ald**)*

To a cooled solution of **4Bn-DATPA** (1 eq.) in DMF (5 mL/mmol) was added $POCl_3$ (1.5 eq.), dropwise, over 1 minute. The solution was stirred at room temperature for 30 minutes and heated to 80°C for 8 hours. The cooled solution was neutralized with solid sodium acetate, diluted with water and extracted with chloroform. The organic extract was dried over sodium sulphate and the solvent removed under reduced pressure. The residue was dissolved in a minimal amount of 1:1 hexane/toluene and purified by a short column of silica gel eluting with toluene. (46%) 4-(bis(4-(dibenzylamino)phenyl)amino)benzaldehyde as a semi-solid. ^{1}H NMR (300 MHz, Acetone-d6) δ 9.69 (s, 1H), 7.57 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 2.8 Hz, 16H), 7.29–7.19 (m, 2H), 7.03 (s, 4H), 6.81–6.74 (m, 4H), 6.72 (t, J = 4.6 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 4.74 (s, 8H). MS (ESI) 664.8 (M+H).

*Synthesis of (E)-2-(4-(4-(bis(4-(dibenzylamino)phenyl)amino)styryl)-3-cyano-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (**4Bn-DATPA-1**)*

To a vial containing a stir bar and **4Bn-Ald** (1 eq.) in ethanol (1ml/mmol) was added TCF acceptor (1.1 eq). The vial was capped and placed in a bead bath held at 90°C for 45 minutes to 1 hour. Once cool, the solvent was stripped by rotary evaporation and the residue loaded onto a column of silica gel with a toluene followed by a gradient elution with 1:1 toluene in chloroform to 100% chloroform. (53%) **4Bn-DATPA-1** as a dark blue solid. ^{1}H NMR (300 MHz, Acetone-d6) δ 8.39 (d, J = 8.7 Hz, 2H), 8.06 (d, J = 15.4 Hz, 1H), 7.74 (d, J = 5.2 Hz, 2H), 7.58–7.50 (m, 16H), 7.29 (d, J = 8.9 Hz, 2H), 7.03 (d, J = 3.5 Hz, 2H), 7.00 (d, J = 9.1 Hz, 4H), 6.61 (d, J = 9.1 Hz, 4H), 6.15 (d, J = 15.4 Hz, 1H), 4.75 (s, 8H), 2.80 (s, 6H). MS (ESI) 846.3 (M+H).

*Synthesis of (E)-2-(4-(4-(bis(4-(dibenzylamino)phenyl)amino)styryl)-3-cyano-5-phenyl-5-(trifluoromethyl)f 2(5H)-ylidene)malononitrile (**4Bn-DATPA-2**)*

4Bn-DATPA-2 was synthesized in a manner similar to **4Bn-DATPA-1** from CF3Ph-TCF acceptor and **4Bn-Ald**. **4Bn-DATPA-2** as a dark green solid. ^{1}H NMR (300 MHz, Acetone-d6) δ 7.73 (dd, J = 9.2, 5.7 Hz, 4H), 7.59 (dd, J = 5.1, 1.6 Hz, 4H), 7.49 (d, J = 8.9 Hz, 2H), 7.29 (dt, J = 11.4, 7.6 Hz, 16H), 7.03 (d, J = 8.9 Hz, 4H), 6.90 (d, J = 15.6 Hz, 1H), 6.78 (d, J = 9.0 Hz, 4H), 6.70 (d, J = 8.9 Hz, 2H), 6.64 (d, J = 8.9 Hz, 2H), 4.75 (s, 8H). MS (ESI) 961.3 (M+).

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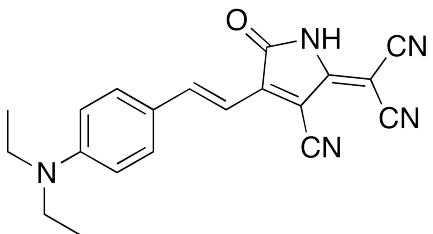
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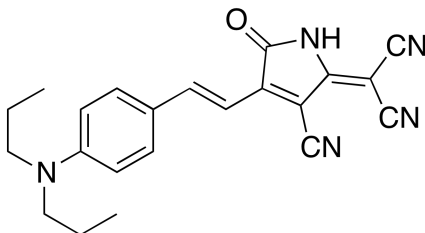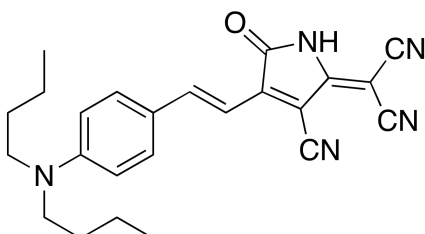
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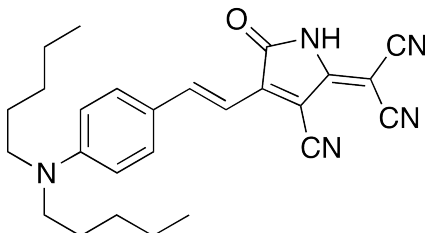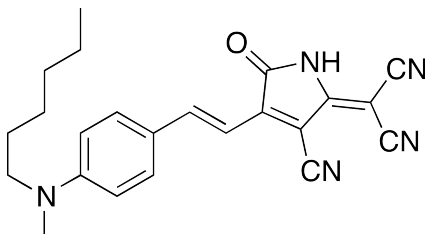
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Appendix A
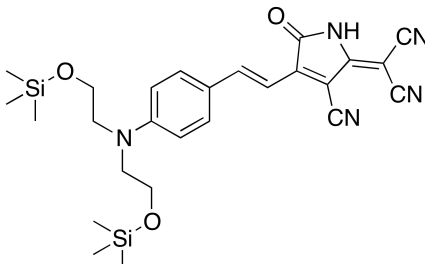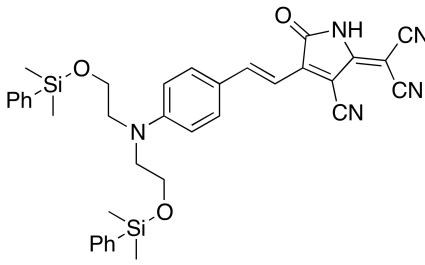
COMPLETE STRUCTURES AND CALCULATED PROPERTIES

DA-00

cam-b3lyp vacuo	Dipole	14.9618	Debye
	$\mu\beta$	1328.8084	$\times 10^{-48}$ esu
	β_{HRS}	64.3414	$\times 10^{-30}$ esu
	β_{zzz}	140.2909	$\times 10^{-30}$ esu
	β_{avg}	153.4608	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	Dipole	14.9620	Debye
	$\mu\beta$	3997.0782	$\times 10^{-48}$ esu
	β_{HRS}	193.2914	$\times 10^{-30}$ esu
	β_{zzz}	420.2842	$\times 10^{-30}$ esu
	β_{avg}	461.7995	$\times 10^{-30}$ esu
m062x vacuo	Dipole	14.9621	Debye
	$\mu\beta$	1374.4307	$\times 10^{-48}$ esu
	β_{HRS}	66.2848	$\times 10^{-30}$ esu
	β_{zzz}	145.2381	$\times 10^{-30}$ esu
	β_{avg}	158.3922	$\times 10^{-30}$ esu
m062x (chloroform)	Dipole	18.8429	Debye
	$\mu\beta$	5203.2717	$\times 10^{-48}$ esu
	β_{HRS}	199.7291	$\times 10^{-30}$ esu
	β_{zzz}	430.9754	$\times 10^{-30}$ esu
	β_{avg}	478.2471	$\times 10^{-30}$ esu

DA-01

		Dipole	14.5917	Debye
cam-b3lyp vacuo		$\mu\beta$	1414.2082	$\times10^{-48}$ esu
		β_{HRS}	70.0630	$\times10^{-30}$ esu
		β_{zzz}	151.9172	$\times10^{-30}$ esu
		β_{avg}	167.6915	$\times10^{-30}$ esu
		Dipole	14.5915	Debye
cam-b3lyp (chloroform)		$\mu\beta$	4062.1252	$\times10^{-48}$ esu
		β_{HRS}	201.1771	$\times10^{-30}$ esu
		β_{zzz}	435.6815	$\times10^{-30}$ esu
		β_{avg}	481.6923	$\times10^{-30}$ esu
		Dipole	14.5913	Debye
m062x vacuo		$\mu\beta$	1465.2289	$\times10^{-48}$ esu
		β_{HRS}	72.3444	$\times10^{-30}$ esu
		β_{zzz}	157.5793	$\times10^{-30}$ esu
		β_{avg}	173.4139	$\times10^{-30}$ esu
		Dipole	18.1961	Debye
m062x (chloroform)		$\mu\beta$	5238.8422	$\times10^{-48}$ esu
		β_{HRS}	208.2926	$\times10^{-30}$ esu
		β_{zzz}	446.1836	$\times10^{-30}$ esu
		β_{avg}	499.6909	$\times10^{-30}$ esu

DA-02

		Dipole	14.5174	Debye
cam-b3lyp vacuo		$\mu\beta$	1456.1930	$\times10^{-48}$ esu
		β_{HRS}	72.5007	$\times10^{-30}$ esu
		β_{zzz}	157.1621	$\times10^{-30}$ esu
		β_{avg}	173.5521	$\times10^{-30}$ esu
		Dipole	14.5193	Debye
cam-b3lyp (chloroform)		$\mu\beta$	4082.2911	$\times10^{-48}$ esu
		β_{HRS}	203.1949	$\times10^{-30}$ esu
		β_{zzz}	439.8402	$\times10^{-30}$ esu
		β_{avg}	486.5401	$\times10^{-30}$ esu
		Dipole	14.5190	Debye
m062x vacuo		$\mu\beta$	1511.2841	$\times10^{-48}$ esu
		β_{HRS}	74.9813	$\times10^{-30}$ esu
		β_{zzz}	163.2701	$\times10^{-30}$ esu
		β_{avg}	179.7580	$\times10^{-30}$ esu
		Dipole	18.0462	Debye
m062x (chloroform)		$\mu\beta$	5248.5596	$\times10^{-48}$ esu
		β_{HRS}	210.4882	$\times10^{-30}$ esu
		β_{zzz}	450.2607	$\times10^{-30}$ esu
		β_{avg}	504.9729	$\times10^{-30}$ esu

DA-03

cam-b3lyp vacuo	$Dipole$	14.7030	Debye
	$\mu\beta$	1482.3481	$\times 10^{-48}$ esu
	β_{HRS}	72.7728	$\times 10^{-30}$ esu
	β_{zzz}	158.0760	$\times 10^{-30}$ esu
	β_{avg}	174.3112	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	14.7022	Debye
	$\mu\beta$	4123.8707	$\times 10^{-48}$ esu
	β_{HRS}	202.5141	$\times 10^{-30}$ esu
	β_{zzz}	439.2655	$\times 10^{-30}$ esu
	β_{avg}	485.0499	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	14.7027	Debye
	$\mu\beta$	1537.2109	$\times 10^{-48}$ esu
	β_{HRS}	75.2194	$\times 10^{-30}$ esu
	β_{zzz}	164.1225	$\times 10^{-30}$ esu
	β_{avg}	180.4299	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	18.2476	Debye
	$\mu\beta$	5289.7988	$\times 10^{-48}$ esu
	β_{HRS}	209.6290	$\times 10^{-30}$ esu
	β_{zzz}	449.2077	$\times 10^{-30}$ esu
	β_{avg}	503.0404	$\times 10^{-30}$ esu

DA-04

cam-b3lyp vacuo	$Dipole$	14.6320	Debye
	$\mu\beta$	1501.5863	$\times 10^{-48}$ esu
	β_{HRS}	74.0991	$\times 10^{-30}$ esu
	β_{zzz}	160.8698	$\times 10^{-30}$ esu
	β_{avg}	177.4562	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	14.6316	Debye
	$\mu\beta$	4148.3623	$\times 10^{-48}$ esu
	β_{HRS}	204.7623	$\times 10^{-30}$ esu
	β_{zzz}	443.9036	$\times 10^{-30}$ esu
	β_{avg}	490.3604	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	14.6324	Debye
	$\mu\beta$	1557.7532	$\times 10^{-48}$ esu
	β_{HRS}	76.6116	$\times 10^{-30}$ esu
	β_{zzz}	167.0676	$\times 10^{-30}$ esu
	β_{avg}	183.7436	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	18.1505	Debye
	$\mu\beta$	5317.6641	$\times 10^{-48}$ esu
	β_{HRS}	211.9352	$\times 10^{-30}$ esu
	β_{zzz}	453.7644	$\times 10^{-30}$ esu
	β_{avg}	508.5156	$\times 10^{-30}$ esu

		Value	Units
cam-b3lyp vacuo (DA-05)	$Dipole$	16.8706	Debye
	$\mu\beta$	1527.7508	$\times 10^{-48}$ esu
	β_{HRS}	65.5450	$\times 10^{-30}$ esu
	β_{zzz}	142.9243	$\times 10^{-30}$ esu
	β_{avg}	156.5167	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	16.8696	Debye
	$\mu\beta$	4313.0492	$\times 10^{-48}$ esu
	β_{HRS}	184.5809	$\times 10^{-30}$ esu
	β_{zzz}	403.5118	$\times 10^{-30}$ esu
	β_{avg}	441.2544	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	16.8695	Debye
	$\mu\beta$	1578.3231	$\times 10^{-48}$ esu
	β_{HRS}	67.4855	$\times 10^{-30}$ esu
	β_{zzz}	147.7004	$\times 10^{-30}$ esu
	β_{avg}	161.4280	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	20.3227	Debye
	$\mu\beta$	5341.4210	$\times 10^{-48}$ esu
	β_{HRS}	190.5864	$\times 10^{-30}$ esu
	β_{zzz}	407.6723	$\times 10^{-30}$ esu
	β_{avg}	456.5705	$\times 10^{-30}$ esu

DA-05

		Value	Units
cam-b3lyp vacuo (DA-06)	$Dipole$	16.4625	Debye
	$\mu\beta$	1553.2910	$\times 10^{-48}$ esu
	β_{HRS}	68.1739	$\times 10^{-30}$ esu
	β_{zzz}	150.0398	$\times 10^{-30}$ esu
	β_{avg}	162.6032	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	16.4632	Debye
	$\mu\beta$	4299.7875	$\times 10^{-48}$ esu
	β_{HRS}	188.0393	$\times 10^{-30}$ esu
	β_{zzz}	415.6387	$\times 10^{-30}$ esu
	β_{avg}	449.1930	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	16.4637	Debye
	$\mu\beta$	1601.0763	$\times 10^{-48}$ esu
	β_{HRS}	70.0171	$\times 10^{-30}$ esu
	β_{zzz}	154.6459	$\times 10^{-30}$ esu
	β_{avg}	167.3032	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	19.8448	Debye
	$\mu\beta$	5303.4050	$\times 10^{-48}$ esu
	β_{HRS}	193.3596	$\times 10^{-30}$ esu
	β_{zzz}	417.3568	$\times 10^{-30}$ esu
	β_{avg}	462.8983	$\times 10^{-30}$ esu

DA-06

cam-b3lyp vacuo	*Dipole*	16.9389	Debye
	$\mu\beta$	1713.1778	$\times 10^{-48}$ esu
	β_{HRS}	73.1501	$\times 10^{-30}$ esu
	β_{zzz}	160.2791	$\times 10^{-30}$ esu
	β_{avg}	174.5148	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	*Dipole*	16.9398	Debye
	$\mu\beta$	4584.5610	$\times 10^{-48}$ esu
	β_{HRS}	194.8771	$\times 10^{-30}$ esu
	β_{zzz}	430.1845	$\times 10^{-30}$ esu
	β_{avg}	465.6230	$\times 10^{-30}$ esu
m062x vacuo	*Dipole*	16.9394	Debye
	$\mu\beta$	1765.9128	$\times 10^{-48}$ esu
	β_{HRS}	75.1286	$\times 10^{-30}$ esu
	β_{zzz}	165.2705	$\times 10^{-30}$ esu
	β_{avg}	179.5514	$\times 10^{-30}$ esu
m062x (chloroform)	*Dipole*	20.3548	Debye
	$\mu\beta$	5631.7314	$\times 10^{-48}$ esu
	β_{HRS}	200.2823	$\times 10^{-30}$ esu
	β_{zzz}	431.2397	$\times 10^{-30}$ esu
	β_{avg}	479.5746	$\times 10^{-30}$ esu

DA-07

cam-b3lyp vacuo	*Dipole*	17.2598	Debye
	$\mu\beta$	1870.9165	$\times 10^{-48}$ esu
	β_{HRS}	78.1912	$\times 10^{-30}$ esu
	β_{zzz}	171.5972	$\times 10^{-30}$ esu
	β_{avg}	186.8726	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	*Dipole*	17.2606	Debye
	$\mu\beta$	4765.8374	$\times 10^{-48}$ esu
	β_{HRS}	198.5617	$\times 10^{-30}$ esu
	β_{zzz}	438.9478	$\times 10^{-30}$ esu
	β_{avg}	474.7319	$\times 10^{-30}$ esu
m062x vacuo	*Dipole*	17.2605	Debye
	$\mu\beta$	1926.0903	$\times 10^{-48}$ esu
	β_{HRS}	80.2582	$\times 10^{-30}$ esu
	β_{zzz}	176.7565	$\times 10^{-30}$ esu
	β_{avg}	192.1021	$\times 10^{-30}$ esu
m062x (chloroform)	*Dipole*	20.4437	Debye
	$\mu\beta$	5752.6617	$\times 10^{-48}$ esu
	β_{HRS}	203.6109	$\times 10^{-30}$ esu
	β_{zzz}	438.2575	$\times 10^{-30}$ esu
	β_{avg}	487.7877	$\times 10^{-30}$ esu

DA-08

DA-09

	Dipole	14.7789	Debye
cam-b3lyp vacuo	$\mu\beta$	1515.1215	$\times 10^{-48}$ esu
	β_{HRS}	74.5805	$\times 10^{-30}$ esu
	β_{zzz}	160.0986	$\times 10^{-30}$ esu
	β_{avg}	178.0743	$\times 10^{-30}$ esu
	Dipole	14.7793	Debye
cam-b3lyp (chloroform)	$\mu\beta$	3913.0292	$\times 10^{-48}$ esu
	β_{HRS}	191.6849	$\times 10^{-30}$ esu
	β_{zzz}	416.0459	$\times 10^{-30}$ esu
	β_{avg}	457.9881	$\times 10^{-30}$ esu
	Dipole	14.7796	Debye
m062x vacuo	$\mu\beta$	1564.7854	$\times 10^{-48}$ esu
	β_{HRS}	76.7509	$\times 10^{-30}$ esu
	β_{zzz}	165.3658	$\times 10^{-30}$ esu
	β_{avg}	183.5942	$\times 10^{-30}$ esu
	Dipole	17.8511	Debye
m062x (chloroform)	$\mu\beta$	4818.2132	$\times 10^{-48}$ esu
	β_{HRS}	197.0283	$\times 10^{-30}$ esu
	β_{zzz}	413.3774	$\times 10^{-30}$ esu
	β_{avg}	471.8021	$\times 10^{-30}$ esu
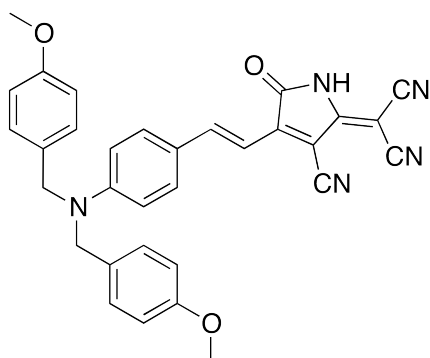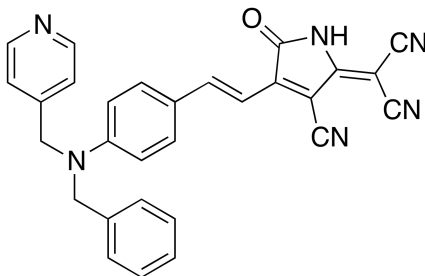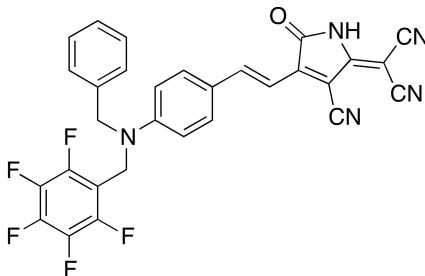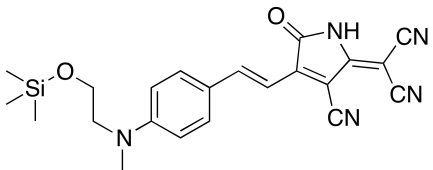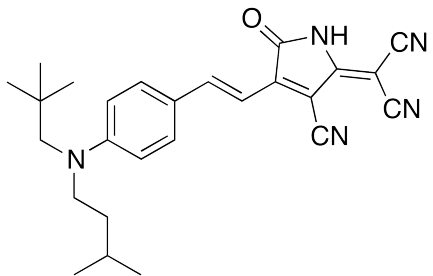
DA-10

	Dipole	16.5376	Debye
cam-b3lyp vacuo	$\mu\beta$	1874.2067	$\times 10^{-48}$ esu
	β_{HRS}	81.3779	$\times 10^{-30}$ esu
	β_{zzz}	181.7489	$\times 10^{-30}$ esu
	β_{avg}	194.7211	$\times 10^{-30}$ esu
	Dipole	16.5369	Debye
cam-b3lyp (chloroform)	$\mu\beta$	4701.3902	$\times 10^{-48}$ esu
	β_{HRS}	203.0983	$\times 10^{-30}$ esu
	β_{zzz}	460.0917	$\times 10^{-30}$ esu
	β_{avg}	485.6811	$\times 10^{-30}$ esu
	Dipole	16.5360	Debye
m062x vacuo	$\mu\beta$	1930.0207	$\times 10^{-48}$ esu
	β_{HRS}	83.5674	$\times 10^{-30}$ esu
	β_{zzz}	187.0380	$\times 10^{-30}$ esu
	β_{avg}	200.2760	$\times 10^{-30}$ esu
	Dipole	19.6513	Debye
m062x (chloroform)	$\mu\beta$	5683.8388	$\times 10^{-48}$ esu
	β_{HRS}	208.4333	$\times 10^{-30}$ esu
	β_{zzz}	456.2199	$\times 10^{-30}$ esu
	β_{avg}	499.4972	$\times 10^{-30}$ esu

DA-11

Method	Quantity	Value	Unit
cam-b3lyp vacuo	$Dipole$	16.2879	Debye
	$\mu\beta$	1969.4105	$\times 10^{-48}$ esu
	β_{HRS}	88.8068	$\times 10^{-30}$ esu
	β_{zzz}	180.5505	$\times 10^{-30}$ esu
	β_{avg}	214.0023	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	16.2871	Debye
	$\mu\beta$	4760.3430	$\times 10^{-48}$ esu
	β_{HRS}	214.1472	$\times 10^{-30}$ esu
	β_{zzz}	440.0002	$\times 10^{-30}$ esu
	β_{avg}	515.0611	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	16.2874	Debye
	$\mu\beta$	2041.4619	$\times 10^{-48}$ esu
	β_{HRS}	91.8912	$\times 10^{-30}$ esu
	β_{zzz}	187.0830	$\times 10^{-30}$ esu
	β_{avg}	221.6647	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	19.2386	Debye
	$\mu\beta$	5780.4880	$\times 10^{-48}$ esu
	β_{HRS}	221.3332	$\times 10^{-30}$ esu
	β_{zzz}	444.7866	$\times 10^{-30}$ esu
	β_{avg}	533.1746	$\times 10^{-30}$ esu

DA-12

Method	Quantity	Value	Unit
cam-b3lyp vacuo	$Dipole$	15.8689	Debye
	$\mu\beta$	1988.4582	$\times 10^{-48}$ esu
	β_{HRS}	90.6030	$\times 10^{-30}$ esu
	β_{zzz}	193.2379	$\times 10^{-30}$ esu
	β_{avg}	218.0783	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	15.8704	Debye
	$\mu\beta$	4731.8102	$\times 10^{-48}$ esu
	β_{HRS}	215.1258	$\times 10^{-30}$ esu
	β_{zzz}	463.5461	$\times 10^{-30}$ esu
	β_{avg}	517.0113	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	15.8710	Debye
	$\mu\beta$	2059.0105	$\times 10^{-48}$ esu
	β_{HRS}	93.6474	$\times 10^{-30}$ esu
	β_{zzz}	199.8795	$\times 10^{-30}$ esu
	β_{avg}	225.6413	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	18.4968	Debye
	$\mu\beta$	5662.3652	$\times 10^{-48}$ esu
	β_{HRS}	222.1085	$\times 10^{-30}$ esu
	β_{zzz}	467.6866	$\times 10^{-30}$ esu
	β_{avg}	534.6357	$\times 10^{-30}$ esu

DA-13

		Dipole	14.4870	Debye
cam-b3lyp vacuo		$\mu\beta$	1311.6766	$\times 10^{-48}$ esu
		β_{HRS}	70.2581	$\times 10^{-30}$ esu
		β_{zzz}	123.4936	$\times 10^{-30}$ esu
		β_{avg}	167.7809	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)		Dipole	14.4851	Debye
		$\mu\beta$	3369.6848	$\times 10^{-48}$ esu
		β_{HRS}	178.9696	$\times 10^{-30}$ esu
		β_{zzz}	321.3591	$\times 10^{-30}$ esu
		β_{avg}	427.6870	$\times 10^{-30}$ esu
m062x vacuo		Dipole	14.4840	Debye
		$\mu\beta$	1356.8902	$\times 10^{-48}$ esu
		β_{HRS}	72.3827	$\times 10^{-30}$ esu
		β_{zzz}	128.1106	$\times 10^{-30}$ esu
		β_{avg}	173.1664	$\times 10^{-30}$ esu
m062x (chloroform)		Dipole	17.7065	Debye
		$\mu\beta$	4178.4737	$\times 10^{-48}$ esu
		β_{HRS}	184.0426	$\times 10^{-30}$ esu
		β_{zzz}	314.4412	$\times 10^{-30}$ esu
		β_{avg}	440.7609	$\times 10^{-30}$ esu

DA-14

		Dipole	14.0479	Debye
cam-b3lyp vacuo		$\mu\beta$	1255.0671	$\times 10^{-48}$ esu
		β_{HRS}	66.8228	$\times 10^{-30}$ esu
		β_{zzz}	130.8993	$\times 10^{-30}$ esu
		β_{avg}	159.9242	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)		Dipole	14.0490	Debye
		$\mu\beta$	3222.2927	$\times 10^{-48}$ esu
		β_{HRS}	170.5644	$\times 10^{-30}$ esu
		β_{zzz}	339.1578	$\times 10^{-30}$ esu
		β_{avg}	408.1701	$\times 10^{-30}$ esu
m062x vacuo		Dipole	14.0493	Debye
		$\mu\beta$	1294.7953	$\times 10^{-48}$ esu
		β_{HRS}	68.6697	$\times 10^{-30}$ esu
		β_{zzz}	135.2333	$\times 10^{-30}$ esu
		β_{avg}	164.5961	$\times 10^{-30}$ esu
m062x (chloroform)		Dipole	17.1330	Debye
		$\mu\beta$	4014.1631	$\times 10^{-48}$ esu
		β_{HRS}	174.7832	$\times 10^{-30}$ esu
		β_{zzz}	341.5018	$\times 10^{-30}$ esu
		β_{avg}	419.0955	$\times 10^{-30}$ esu

cam-b3lyp vacuo	$Dipole$	15.4556	Debye
	$\mu\beta$	1406.2311	$\times 10^{-48}$ esu
	β_{HRS}	67.0141	$\times 10^{-30}$ esu
	β_{zzz}	138.6888	$\times 10^{-30}$ esu
	β_{avg}	159.9679	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	15.4557	Debye
	$\mu\beta$	4067.7864	$\times 10^{-48}$ esu
	β_{HRS}	194.0138	$\times 10^{-30}$ esu
	β_{zzz}	398.1825	$\times 10^{-30}$ esu
	β_{avg}	463.6440	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	15.4562	Debye
	$\mu\beta$	1449.8994	$\times 10^{-48}$ esu
	β_{HRS}	68.7950	$\times 10^{-30}$ esu
	β_{zzz}	143.3699	$\times 10^{-30}$ esu
	β_{avg}	164.4888	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	19.1020	Debye
	$\mu\beta$	5168.1171	$\times 10^{-48}$ esu
	β_{HRS}	199.5796	$\times 10^{-30}$ esu
	β_{zzz}	405.4728	$\times 10^{-30}$ esu
	β_{avg}	477.9506	$\times 10^{-30}$ esu

DA-15

cam-b3lyp vacuo	$Dipole$	15.3365	Debye
	$\mu\beta$	1577.5544	$\times 10^{-48}$ esu
	β_{HRS}	74.0875	$\times 10^{-30}$ esu
	β_{zzz}	163.0700	$\times 10^{-30}$ esu
	β_{avg}	177.1593	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	15.3382	Debye
	$\mu\beta$	4396.9005	$\times 10^{-48}$ esu
	β_{HRS}	206.2888	$\times 10^{-30}$ esu
	β_{zzz}	454.0170	$\times 10^{-30}$ esu
	β_{avg}	493.5632	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	15.3387	Debye
	$\mu\beta$	1632.7767	$\times 10^{-48}$ esu
	β_{HRS}	76.4177	$\times 10^{-30}$ esu
	β_{zzz}	168.8913	$\times 10^{-30}$ esu
	β_{avg}	183.0115	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	19.1051	Debye
	$\mu\beta$	5643.3849	$\times 10^{-48}$ esu
	β_{HRS}	212.9616	$\times 10^{-30}$ esu
	β_{zzz}	462.3110	$\times 10^{-30}$ esu
	β_{avg}	510.5826	$\times 10^{-30}$ esu

DA-16

DA-17

cam-b3lyp vacuo	$Dipole$	14.6320	Debye
	$\mu\beta$	1412.2094	$\times 10^{-48}$ esu
	β_{HRS}	70.1039	$\times 10^{-30}$ esu
	β_{zzz}	150.2747	$\times 10^{-30}$ esu
	β_{avg}	167.6031	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	14.6325	Debye
	$\mu\beta$	3833.9712	$\times 10^{-48}$ esu
	β_{HRS}	189.8317	$\times 10^{-30}$ esu
	β_{zzz}	409.3118	$\times 10^{-30}$ esu
	β_{avg}	454.0291	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	14.6321	Debye
	$\mu\beta$	1458.7988	$\times 10^{-48}$ esu
	β_{HRS}	72.1636	$\times 10^{-30}$ esu
	β_{zzz}	155.3631	$\times 10^{-30}$ esu
	β_{avg}	172.8196	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	18.0060	Debye
	$\mu\beta$	4834.3929	$\times 10^{-48}$ esu
	β_{HRS}	195.2835	$\times 10^{-30}$ esu
	β_{zzz}	412.6556	$\times 10^{-30}$ esu
	β_{avg}	468.0561	$\times 10^{-30}$ esu
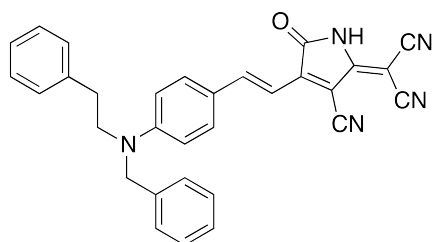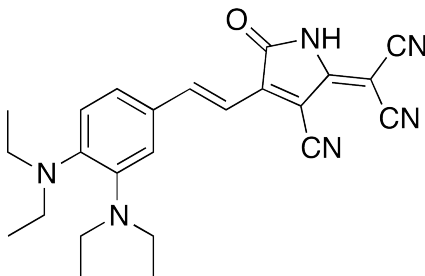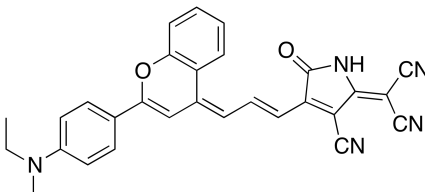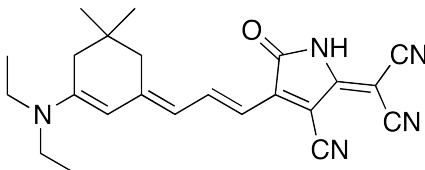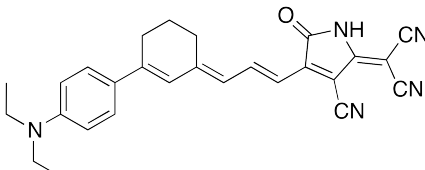
DA-18
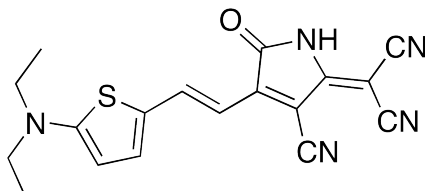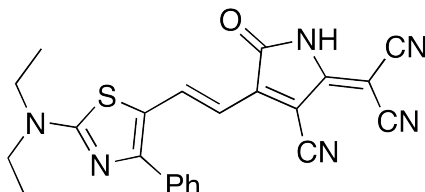
cam-b3lyp vacuo	$Dipole$	14.5505	Debye
	$\mu\beta$	1493.3353	$\times 10^{-48}$ esu
	β_{HRS}	74.3248	$\times 10^{-30}$ esu
	β_{zzz}	161.7415	$\times 10^{-30}$ esu
	β_{avg}	177.3623	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	14.5514	Debye
	$\mu\beta$	3928.2494	$\times 10^{-48}$ esu
	β_{HRS}	195.0271	$\times 10^{-30}$ esu
	β_{zzz}	425.4445	$\times 10^{-30}$ esu
	β_{avg}	466.0347	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	14.5517	Debye
	$\mu\beta$	1548.2303	$\times 10^{-48}$ esu
	β_{HRS}	76.7882	$\times 10^{-30}$ esu
	β_{zzz}	167.6708	$\times 10^{-30}$ esu
	β_{avg}	183.5781	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	17.8270	Debye
	$\mu\beta$	4945.5100	$\times 10^{-48}$ esu
	β_{HRS}	201.3345	$\times 10^{-30}$ esu
	β_{zzz}	429.3140	$\times 10^{-30}$ esu
	β_{avg}	482.1793	$\times 10^{-30}$ esu

	Dipole	14.7700	Debye
cam-b3lyp vacuo	$\mu\beta$	1466.1214	$\times 10^{-48}$ esu
	β_{HRS}	72.4306	$\times 10^{-30}$ esu
	β_{zzz}	153.8601	$\times 10^{-30}$ esu
	β_{avg}	172.9231	$\times 10^{-30}$ esu
	Dipole	14.7696	Debye
cam-b3lyp (chloroform)	$\mu\beta$	3838.6384	$\times 10^{-48}$ esu
	β_{HRS}	188.5387	$\times 10^{-30}$ esu
	β_{zzz}	406.4311	$\times 10^{-30}$ esu
	β_{avg}	450.4722	$\times 10^{-30}$ esu
	Dipole	14.7696	Debye
m062x vacuo	$\mu\beta$	1510.6620	$\times 10^{-48}$ esu
	β_{HRS}	74.3782	$\times 10^{-30}$ esu
	β_{zzz}	158.5867	$\times 10^{-30}$ esu
	β_{avg}	177.9000	$\times 10^{-30}$ esu
	Dipole	18.0712	Debye
m062x (chloroform)	$\mu\beta$	4776.7247	$\times 10^{-48}$ esu
	β_{HRS}	193.4070	$\times 10^{-30}$ esu
	β_{zzz}	402.5404	$\times 10^{-30}$ esu
	β_{avg}	463.1409	$\times 10^{-30}$ esu

DA-19

	Dipole	15.1932	Debye
cam-b3lyp vacuo	$\mu\beta$	1609.0046	$\times 10^{-48}$ esu
	β_{HRS}	76.7105	$\times 10^{-30}$ esu
	β_{zzz}	166.5638	$\times 10^{-30}$ esu
	β_{avg}	183.2432	$\times 10^{-30}$ esu
	Dipole	14.6028	Debye
cam-b3lyp (chloroform)	$\mu\beta$	3842.3321	$\times 10^{-48}$ esu
	β_{HRS}	190.1035	$\times 10^{-30}$ esu
	β_{zzz}	414.7047	$\times 10^{-30}$ esu
	β_{avg}	454.3519	$\times 10^{-30}$ esu
	Dipole	14.6027	Debye
m062x vacuo	$\mu\beta$	1590.5472	$\times 10^{-48}$ esu
	β_{HRS}	78.8343	$\times 10^{-30}$ esu
	β_{zzz}	170.2475	$\times 10^{-30}$ esu
	β_{avg}	188.6832	$\times 10^{-30}$ esu
	Dipole	17.5423	Debye
m062x (chloroform)	$\mu\beta$	4681.7654	$\times 10^{-48}$ esu
	β_{HRS}	194.8463	$\times 10^{-30}$ esu
	β_{zzz}	407.8910	$\times 10^{-30}$ esu
	β_{avg}	466.7664	$\times 10^{-30}$ esu

DA-20

DA-21

		Dipole	15.8301	Debye
cam-b3lyp vacuo		$\mu\beta$	1216.9027	$\times 10^{-48}$ esu
		β_{HRS}	55.1080	$\times 10^{-30}$ esu
		β_{zzz}	124.8018	$\times 10^{-30}$ esu
		β_{avg}	131.4031	$\times 10^{-30}$ esu
		Dipole	15.8307	Debye
cam-b3lyp (chloroform)		$\mu\beta$	3560.9770	$\times 10^{-48}$ esu
		β_{HRS}	161.1272	$\times 10^{-30}$ esu
		β_{zzz}	363.0158	$\times 10^{-30}$ esu
		β_{avg}	384.8403	$\times 10^{-30}$ esu
		Dipole	15.8311	Debye
m062x vacuo		$\mu\beta$	1254.5323	$\times 10^{-48}$ esu
		β_{HRS}	56.5257	$\times 10^{-30}$ esu
		β_{zzz}	128.7675	$\times 10^{-30}$ esu
		β_{avg}	135.0903	$\times 10^{-30}$ esu
		Dipole	20.2190	Debye
m062x (chloroform)		$\mu\beta$	4700.2964	$\times 10^{-48}$ esu
		β_{HRS}	166.1792	$\times 10^{-30}$ esu
		β_{zzz}	372.4896	$\times 10^{-30}$ esu
		β_{avg}	398.0388	$\times 10^{-30}$ esu

DA-22

		Dipole	16.0032	Debye
cam-b3lyp vacuo		$\mu\beta$	1240.5364	$\times 10^{-48}$ esu
		β_{HRS}	56.9910	$\times 10^{-30}$ esu
		β_{zzz}	117.5910	$\times 10^{-30}$ esu
		β_{avg}	135.8666	$\times 10^{-30}$ esu
		Dipole	16.0040	Debye
cam-b3lyp (chloroform)		$\mu\beta$	3696.2493	$\times 10^{-48}$ esu
		β_{HRS}	170.5489	$\times 10^{-30}$ esu
		β_{zzz}	344.6027	$\times 10^{-30}$ esu
		β_{avg}	407.3617	$\times 10^{-30}$ esu
		Dipole	16.0038	Debye
m062x vacuo		$\mu\beta$	1284.7343	$\times 10^{-48}$ esu
		β_{HRS}	58.7092	$\times 10^{-30}$ esu
		β_{zzz}	122.0356	$\times 10^{-30}$ esu
		β_{avg}	140.3051	$\times 10^{-30}$ esu
		Dipole	20.4389	Debye
m062x (chloroform)		$\mu\beta$	4925.0752	$\times 10^{-48}$ esu
		β_{HRS}	176.9913	$\times 10^{-30}$ esu
		β_{zzz}	360.0533	$\times 10^{-30}$ esu
		β_{avg}	423.9278	$\times 10^{-30}$ esu

cam-b3lyp vacuo	Dipole	12.7793	Debye
	$\mu\beta$	1190.6438	$\times 10^{-48}$ esu
	β_{HRS}	67.9149	$\times 10^{-30}$ esu
	β_{zzz}	145.5862	$\times 10^{-30}$ esu
	β_{avg}	162.0317	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	Dipole	12.7791	Debye
	$\mu\beta$	3395.7418	$\times 10^{-48}$ esu
	β_{HRS}	192.4842	$\times 10^{-30}$ esu
	β_{zzz}	417.0472	$\times 10^{-30}$ esu
	β_{avg}	460.0718	$\times 10^{-30}$ esu
m062x vacuo	Dipole	12.7787	Debye
	$\mu\beta$	1226.2707	$\times 10^{-48}$ esu
	β_{HRS}	69.6865	$\times 10^{-30}$ esu
	β_{zzz}	150.0542	$\times 10^{-30}$ esu
	β_{avg}	166.5386	$\times 10^{-30}$ esu
m062x (chloroform)	Dipole	15.8947	Debye
	$\mu\beta$	4319.4549	$\times 10^{-48}$ esu
	β_{HRS}	197.9204	$\times 10^{-30}$ esu
	β_{zzz}	418.4359	$\times 10^{-30}$ esu
	β_{avg}	474.0051	$\times 10^{-30}$ esu

DA-23

cam-b3lyp vacuo	Dipole	20.6622	Debye
	$\mu\beta$	3075.1664	$\times 10^{-48}$ esu
	β_{HRS}	112.8118	$\times 10^{-30}$ esu
	β_{zzz}	214.6521	$\times 10^{-30}$ esu
	β_{avg}	268.0687	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	Dipole	20.6611	Debye
	$\mu\beta$	7509.5192	$\times 10^{-48}$ esu
	β_{HRS}	296.4501	$\times 10^{-30}$ esu
	β_{zzz}	504.8690	$\times 10^{-30}$ esu
	β_{avg}	683.4432	$\times 10^{-30}$ esu
m062x vacuo	Dipole	20.6612	Debye
	$\mu\beta$	3320.5914	$\times 10^{-48}$ esu
	β_{HRS}	119.7325	$\times 10^{-30}$ esu
	β_{zzz}	233.0507	$\times 10^{-30}$ esu
	β_{avg}	286.7732	$\times 10^{-30}$ esu
m062x (chloroform)	Dipole	26.8849	Debye
	$\mu\beta$	11308.7372	$\times 10^{-48}$ esu
	β_{HRS}	329.1760	$\times 10^{-30}$ esu
	β_{zzz}	586.8748	$\times 10^{-30}$ esu
	β_{avg}	774.5636	$\times 10^{-30}$ esu

DA-25

  DA-24	cam-b3lyp vacuo	*Dipole*	21.5320	Debye
		$\mu\beta$	1388.9019	$\times 10^{-48}$ esu
		β_{HRS}	50.4625	$\times 10^{-30}$ esu
		β_{zzz}	95.3157	$\times 10^{-30}$ esu
		β_{avg}	117.5122	$\times 10^{-30}$ esu
	cam-b3lyp (chloroform)	*Dipole*	21.5318	Debye
		$\mu\beta$	1745.1302	$\times 10^{-48}$ esu
		β_{HRS}	94.0341	$\times 10^{-30}$ esu
		β_{zzz}	91.3983	$\times 10^{-30}$ esu
		β_{avg}	192.5457	$\times 10^{-30}$ esu
	m062x vacuo	*Dipole*	21.5323	Debye
		$\mu\beta$	1514.6575	$\times 10^{-48}$ esu
		β_{HRS}	53.4684	$\times 10^{-30}$ esu
		β_{zzz}	105.5676	$\times 10^{-30}$ esu
		β_{avg}	125.9054	$\times 10^{-30}$ esu
	m062x (chloroform)	*Dipole*	29.5587	Debye
		$\mu\beta$	3119.1572	$\times 10^{-48}$ esu
		β_{HRS}	101.5433	$\times 10^{-30}$ esu
		β_{zzz}	134.8966	$\times 10^{-30}$ esu
		β_{avg}	220.2002	$\times 10^{-30}$ esu
  DA-26	cam-b3lyp vacuo	*Dipole*	18.2114	Debye
		$\mu\beta$	4400.4608	$\times 10^{-48}$ esu
		β_{HRS}	174.8114	$\times 10^{-30}$ esu
		β_{zzz}	372.5279	$\times 10^{-30}$ esu
		β_{avg}	420.0797	$\times 10^{-30}$ esu
	cam-b3lyp (chloroform)	*Dipole*	18.2122	Debye
		$\mu\beta$	14034.8958	$\times 10^{-48}$ esu
		β_{HRS}	556.8620	$\times 10^{-30}$ esu
		β_{zzz}	1193.3208	$\times 10^{-30}$ esu
		β_{avg}	1337.5658	$\times 10^{-30}$ esu
	m062x vacuo	*Dipole*	18.2120	Debye
		$\mu\beta$	4707.4358	$\times 10^{-48}$ esu
		β_{HRS}	186.3468	$\times 10^{-30}$ esu
		β_{zzz}	398.5585	$\times 10^{-30}$ esu
		β_{avg}	448.6461	$\times 10^{-30}$ esu
	m062x (chloroform)	*Dipole*	23.1126	Debye
		$\mu\beta$	19155.4907	$\times 10^{-48}$ esu
		β_{HRS}	599.4357	$\times 10^{-30}$ esu
		β_{zzz}	1269.4755	$\times 10^{-30}$ esu
		β_{avg}	1443.2913	$\times 10^{-30}$ esu

DA-27

cam-b3lyp vacuo	$Dipole$	16.6385	Debye
	$\mu\beta$	1041.9628	$\times 10^{-48}$ esu
	β_{HRS}	46.5866	$\times 10^{-30}$ esu
	β_{zzz}	98.1978	$\times 10^{-30}$ esu
	β_{avg}	109.7311	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	16.6380	Debye
	$\mu\beta$	2780.2837	$\times 10^{-48}$ esu
	β_{HRS}	127.8902	$\times 10^{-30}$ esu
	β_{zzz}	258.1782	$\times 10^{-30}$ esu
	β_{avg}	297.9029	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	16.6377	Debye
	$\mu\beta$	1074.3517	$\times 10^{-48}$ esu
	β_{HRS}	47.5727	$\times 10^{-30}$ esu
	β_{zzz}	101.3833	$\times 10^{-30}$ esu
	β_{avg}	112.5717	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	21.9488	Debye
	$\mu\beta$	3818.2902	$\times 10^{-48}$ esu
	β_{HRS}	131.5545	$\times 10^{-30}$ esu
	β_{zzz}	266.0206	$\times 10^{-30}$ esu
	β_{avg}	309.0472	$\times 10^{-30}$ esu

DA-28

cam-b3lyp vacuo	$Dipole$	14.2601	Debye
	$\mu\beta$	779.1824	$\times 10^{-48}$ esu
	β_{HRS}	38.8388	$\times 10^{-30}$ esu
	β_{zzz}	83.7025	$\times 10^{-30}$ esu
	β_{avg}	93.6006	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	14.2581	Debye
	$\mu\beta$	2098.4420	$\times 10^{-48}$ esu
	β_{HRS}	106.5923	$\times 10^{-30}$ esu
	β_{zzz}	224.1342	$\times 10^{-30}$ esu
	β_{avg}	254.6760	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	14.2580	Debye
	$\mu\beta$	819.1819	$\times 10^{-48}$ esu
	β_{HRS}	40.5290	$\times 10^{-30}$ esu
	β_{zzz}	88.2012	$\times 10^{-30}$ esu
	β_{avg}	98.0884	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	17.8717	Debye
	$\mu\beta$	2817.0153	$\times 10^{-48}$ esu
	β_{HRS}	113.0123	$\times 10^{-30}$ esu
	β_{zzz}	239.1405	$\times 10^{-30}$ esu
	β_{avg}	271.9372	$\times 10^{-30}$ esu

	Dipole	15.4062	Debye
cam-b3lyp vacuo	$\mu\beta$	2417.5513	$\times 10^{-48}$ esu
	β_{HRS}	113.2183	$\times 10^{-30}$ esu
	β_{zzz}	241.5123	$\times 10^{-30}$ esu
	β_{avg}	272.7453	$\times 10^{-30}$ esu
	Dipole	15.4066	Debye
cam-b3lyp (chloroform)	$\mu\beta$	6435.3764	$\times 10^{-48}$ esu
	β_{HRS}	301.1697	$\times 10^{-30}$ esu
	β_{zzz}	643.5371	$\times 10^{-30}$ esu
	β_{avg}	725.4265	$\times 10^{-30}$ esu
	Dipole	15.4066	Debye
m062x vacuo	$\mu\beta$	2532.8203	$\times 10^{-48}$ esu
	β_{HRS}	118.3129	$\times 10^{-30}$ esu
	β_{zzz}	252.9634	$\times 10^{-30}$ esu
	β_{avg}	285.4191	$\times 10^{-30}$ esu

DAAP-01

	Dipole	16.6355	Debye
cam-b3lyp vacuo	$\mu\beta$	1880.5110	$\times 10^{-48}$ esu
	β_{HRS}	80.9450	$\times 10^{-30}$ esu
	β_{zzz}	178.8342	$\times 10^{-30}$ esu
	β_{avg}	194.5018	$\times 10^{-30}$ esu
	Dipole	16.6367	Debye
cam-b3lyp (chloroform)	$\mu\beta$	4714.7168	$\times 10^{-48}$ esu
	β_{HRS}	202.7056	$\times 10^{-30}$ esu
	β_{zzz}	451.1963	$\times 10^{-30}$ esu
	β_{avg}	486.2405	$\times 10^{-30}$ esu
	Dipole	16.6366	Debye
m062x vacuo	$\mu\beta$	1942.5771	$\times 10^{-48}$ esu
	β_{HRS}	83.3606	$\times 10^{-30}$ esu
	β_{zzz}	184.7553	$\times 10^{-30}$ esu
	β_{avg}	200.5987	$\times 10^{-30}$ esu
	Dipole	19.8950	Debye
m062x (chloroform)	$\mu\beta$	5768.7860	$\times 10^{-48}$ esu
	β_{HRS}	208.7582	$\times 10^{-30}$ esu
	β_{zzz}	451.9857	$\times 10^{-30}$ esu
	β_{avg}	501.7989	$\times 10^{-30}$ esu

DAAP-02

DAAP-03

cam-b3lyp vacuo	$Dipole$	17.6034	Debye
	$\mu\beta$	2098.3640	$\times 10^{-48}$ esu
	β_{HRS}	85.8297	$\times 10^{-30}$ esu
	β_{zzz}	187.5952	$\times 10^{-30}$ esu
	β_{avg}	205.7903	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	17.6040	Debye
	$\mu\beta$	5179.3354	$\times 10^{-48}$ esu
	β_{HRS}	212.0979	$\times 10^{-30}$ esu
	β_{zzz}	463.2474	$\times 10^{-30}$ esu
	β_{avg}	507.9686	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	17.6036	Debye
	$\mu\beta$	2159.0590	$\times 10^{-48}$ esu
	β_{HRS}	88.0147	$\times 10^{-30}$ esu
	β_{zzz}	193.1015	$\times 10^{-30}$ esu
	β_{avg}	211.3697	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	20.4995	Debye
	$\mu\beta$	6164.3086	$\times 10^{-48}$ esu
	β_{HRS}	217.6168	$\times 10^{-30}$ esu
	β_{zzz}	465.6092	$\times 10^{-30}$ esu
	β_{avg}	522.3746	$\times 10^{-30}$ esu
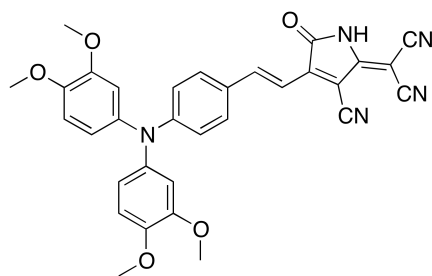
DAAP-04

cam-b3lyp vacuo	$Dipole$	14.9575	Debye
	$\mu\beta$	2452.1610	$\times 10^{-48}$ esu
	β_{HRS}	121.2624	$\times 10^{-30}$ esu
	β_{zzz}	239.5183	$\times 10^{-30}$ esu
	β_{avg}	292.4477	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	14.9605	Debye
	$\mu\beta$	6269.2005	$\times 10^{-48}$ esu
	β_{HRS}	309.4806	$\times 10^{-30}$ esu
	β_{zzz}	613.2646	$\times 10^{-30}$ esu
	β_{avg}	746.1884	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	14.9606	Debye
	$\mu\beta$	2574.5651	$\times 10^{-48}$ esu
	β_{HRS}	126.9242	$\times 10^{-30}$ esu
	β_{zzz}	251.7031	$\times 10^{-30}$ esu
	β_{avg}	306.4990	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	17.5182	Debye
	$\mu\beta$	7617.8833	$\times 10^{-48}$ esu
	β_{HRS}	325.4603	$\times 10^{-30}$ esu
	β_{zzz}	616.1204	$\times 10^{-30}$ esu
	β_{avg}	786.0139	$\times 10^{-30}$ esu
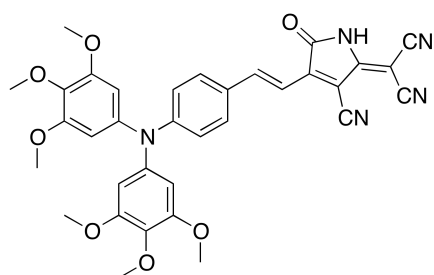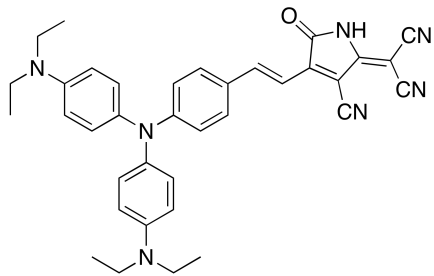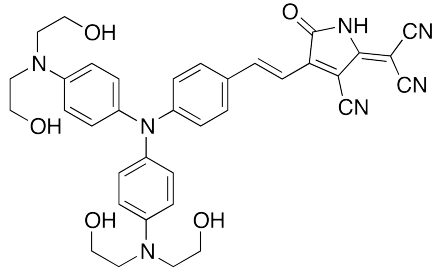
DAAP-05

cam-b3lyp vacuo	$Dipole$	13.6566	Debye
	$\mu\beta$	2113.0355	$\times 10^{-48}$ esu
	β_{HRS}	111.3874	$\times 10^{-30}$ esu
	β_{zzz}	241.9286	$\times 10^{-30}$ esu
	β_{avg}	267.2147	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	13.6582	Debye
	$\mu\beta$	5024.4275	$\times 10^{-48}$ esu
	β_{HRS}	264.3027	$\times 10^{-30}$ esu
	β_{zzz}	576.2219	$\times 10^{-30}$ esu
	β_{avg}	634.5148	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	13.6577	Debye
	$\mu\beta$	2228.3711	$\times 10^{-48}$ esu
	β_{HRS}	117.1893	$\times 10^{-30}$ esu
	β_{zzz}	255.0378	$\times 10^{-30}$ esu
	β_{avg}	281.5175	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	15.8315	Debye
	$\mu\beta$	6078.5522	$\times 10^{-48}$ esu
	β_{HRS}	278.3052	$\times 10^{-30}$ esu
	β_{zzz}	586.7992	$\times 10^{-30}$ esu
	β_{avg}	669.2565	$\times 10^{-30}$ esu
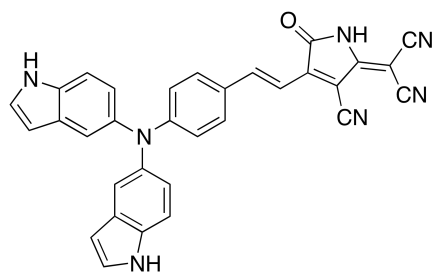
DAAP-06

cam-b3lyp vacuo	$Dipole$	17.6455	Debye
	$\mu\beta$	2999.1703	$\times 10^{-48}$ esu
	β_{HRS}	120.7077	$\times 10^{-30}$ esu
	β_{zzz}	272.2086	$\times 10^{-30}$ esu
	β_{avg}	290.1538	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	17.6444	Debye
	$\mu\beta$	8118.0918	$\times 10^{-48}$ esu
	β_{HRS}	326.1223	$\times 10^{-30}$ esu
	β_{zzz}	736.0851	$\times 10^{-30}$ esu
	β_{avg}	784.8853	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	17.6447	Debye
	$\mu\beta$	3154.6331	$\times 10^{-48}$ esu
	β_{HRS}	126.6093	$\times 10^{-30}$ esu
	β_{zzz}	286.0199	$\times 10^{-30}$ esu
	β_{avg}	304.8918	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	20.9009	Debye
	$\mu\beta$	10125.5341	$\times 10^{-48}$ esu
	β_{HRS}	344.4271	$\times 10^{-30}$ esu
	β_{zzz}	764.5700	$\times 10^{-30}$ esu
	β_{avg}	830.6158	$\times 10^{-30}$ esu

DAAP-07

cam-b3lyp vacuo	$Dipole$	18.5080	Debye
	$\mu\beta$	3871.9436	$\times 10^{-48}$ esu
	β_{HRS}	145.7741	$\times 10^{-30}$ esu
	β_{zzz}	335.4266	$\times 10^{-30}$ esu
	β_{avg}	353.9823	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	18.5060	Debye
	$\mu\beta$	10964.6713	$\times 10^{-48}$ esu
	β_{HRS}	412.8680	$\times 10^{-30}$ esu
	β_{zzz}	950.7737	$\times 10^{-30}$ esu
	β_{avg}	1002.2392	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	18.5059	Debye
	$\mu\beta$	4155.0557	$\times 10^{-48}$ esu
	β_{HRS}	155.9598	$\times 10^{-30}$ esu
	β_{zzz}	358.7063	$\times 10^{-30}$ esu
	β_{avg}	379.7002	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	22.0305	Debye
	$\mu\beta$	14173.0866	$\times 10^{-48}$ esu
	β_{HRS}	448.6621	$\times 10^{-30}$ esu
	β_{zzz}	1020.1341	$\times 10^{-30}$ esu
	β_{avg}	1092.2233	$\times 10^{-30}$ esu

DAAP-08

cam-b3lyp vacuo	$Dipole$	19.4875	Debye
	$\mu\beta$	4002.2614	$\times 10^{-48}$ esu
	β_{HRS}	143.3468	$\times 10^{-30}$ esu
	β_{zzz}	326.0516	$\times 10^{-30}$ esu
	β_{avg}	348.5788	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	19.4946	Debye
	$\mu\beta$	10755.3166	$\times 10^{-48}$ esu
	β_{HRS}	385.6278	$\times 10^{-30}$ esu
	β_{zzz}	879.9269	$\times 10^{-30}$ esu
	β_{avg}	935.8859	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	19.4956	Debye
	$\mu\beta$	4298.7056	$\times 10^{-48}$ esu
	β_{HRS}	153.4178	$\times 10^{-30}$ esu
	β_{zzz}	349.3994	$\times 10^{-30}$ esu
	β_{avg}	373.8817	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	22.8115	Debye
	$\mu\beta$	13601.7744	$\times 10^{-48}$ esu
	β_{HRS}	417.6789	$\times 10^{-30}$ esu
	β_{zzz}	938.4234	$\times 10^{-30}$ esu
	β_{avg}	1016.2056	$\times 10^{-30}$ esu

cam-b3lyp vacuo	$Dipole$	17.7129	Debye
	$\mu\beta$	3959.5700	$\times 10^{-48}$ esu
	β_{HRS}	156.1920	$\times 10^{-30}$ esu
	β_{zzz}	354.9586	$\times 10^{-30}$ esu
	β_{avg}	379.6719	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	17.7134	Debye
	$\mu\beta$	10164.9910	$\times 10^{-48}$ esu
	β_{HRS}	401.4566	$\times 10^{-30}$ esu
	β_{zzz}	915.0796	$\times 10^{-30}$ esu
	β_{avg}	974.0340	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	17.7138	Debye
	$\mu\beta$	4240.4246	$\times 10^{-48}$ esu
	β_{HRS}	166.7184	$\times 10^{-30}$ esu
	β_{zzz}	379.1700	$\times 10^{-30}$ esu
	β_{avg}	406.2001	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	20.6194	Debye
	$\mu\beta$	12681.3130	$\times 10^{-48}$ esu
	β_{HRS}	431.8442	$\times 10^{-30}$ esu
	β_{zzz}	964.7365	$\times 10^{-30}$ esu
	β_{avg}	1050.3921	$\times 10^{-30}$ esu

DAAP-09
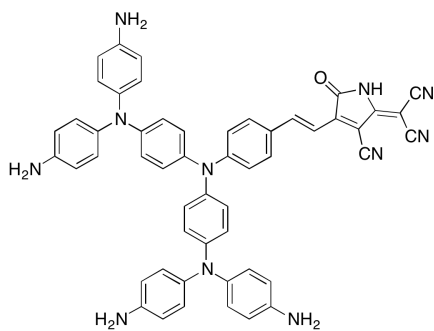
cam-b3lyp vacuo	$Dipole$	20.8387	Debye
	$\mu\beta$	5764.4938	$\times 10^{-48}$ esu
	β_{HRS}	190.3601	$\times 10^{-30}$ esu
	β_{zzz}	431.8559	$\times 10^{-30}$ esu
	β_{avg}	468.7162	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	20.8388	Debye
	$\mu\beta$	14607.0371	$\times 10^{-48}$ esu
	β_{HRS}	483.9030	$\times 10^{-30}$ esu
	β_{zzz}	1104.1311	$\times 10^{-30}$ esu
	β_{avg}	1186.5383	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	20.8382	Debye
	$\mu\beta$	6396.0038	$\times 10^{-48}$ esu
	β_{HRS}	210.3250	$\times 10^{-30}$ esu
	β_{zzz}	475.5164	$\times 10^{-30}$ esu
	β_{avg}	520.0035	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	24.0745	Debye
	$\mu\beta$	18972.4635	$\times 10^{-48}$ esu
	β_{HRS}	544.6266	$\times 10^{-30}$ esu
	β_{zzz}	1219.4868	$\times 10^{-30}$ esu
	β_{avg}	1341.3550	$\times 10^{-30}$ esu

DAAP-10

DAAP-11

		Value	Units
cam-b3lyp vacuo	$Dipole$	20.1747	Debye
	$\mu\beta$	2550.1272	$\times 10^{-48}$ esu
	β_{HRS}	89.3927	$\times 10^{-30}$ esu
	β_{zzz}	205.3166	$\times 10^{-30}$ esu
	β_{avg}	215.2461	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	20.1759	Debye
	$\mu\beta$	6739.8232	$\times 10^{-48}$ esu
	β_{HRS}	239.0543	$\times 10^{-30}$ esu
	β_{zzz}	542.3055	$\times 10^{-30}$ esu
	β_{avg}	572.2944	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	20.1764	Debye
	$\mu\beta$	2693.7362	$\times 10^{-48}$ esu
	β_{HRS}	93.7961	$\times 10^{-30}$ esu
	β_{zzz}	215.8621	$\times 10^{-30}$ esu
	β_{avg}	226.8685	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	25.1198	Debye
	$\mu\beta$	9029.9530	$\times 10^{-48}$ esu
	β_{HRS}	256.6280	$\times 10^{-30}$ esu
	β_{zzz}	570.9052	$\times 10^{-30}$ esu
	β_{avg}	618.8139	$\times 10^{-30}$ esu

DAAP-12

		Value	Units
cam-b3lyp vacuo	$Dipole$	12.3824	Debye
	$\mu\beta$	1534.2193	$\times 10^{-48}$ esu
	β_{HRS}	90.7157	$\times 10^{-30}$ esu
	β_{zzz}	188.9442	$\times 10^{-30}$ esu
	β_{avg}	217.1249	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	12.3826	Debye
	$\mu\beta$	4143.6176	$\times 10^{-48}$ esu
	β_{HRS}	244.1091	$\times 10^{-30}$ esu
	β_{zzz}	510.1343	$\times 10^{-30}$ esu
	β_{avg}	585.4650	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	12.3826	Debye
	$\mu\beta$	1630.8200	$\times 10^{-48}$ esu
	β_{HRS}	96.1105	$\times 10^{-30}$ esu
	β_{zzz}	200.8072	$\times 10^{-30}$ esu
	β_{avg}	230.4787	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	15.0166	Debye
	$\mu\beta$	5335.6445	$\times 10^{-48}$ esu
	β_{HRS}	260.9882	$\times 10^{-30}$ esu
	β_{zzz}	530.1470	$\times 10^{-30}$ esu
	β_{avg}	627.2227	$\times 10^{-30}$ esu

DAAP-13

cam-b3lyp vacuo	*Dipole*	17.1330	Debye
	$\mu\beta$	2055.2544	$\times 10^{-48}$ esu
	β_{HRS}	84.8537	$\times 10^{-30}$ esu
	β_{zzz}	192.2284	$\times 10^{-30}$ esu
	β_{avg}	204.4704	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	*Dipole*	17.1335	Debye
	$\mu\beta$	4632.3581	$\times 10^{-48}$ esu
	β_{HRS}	191.2559	$\times 10^{-30}$ esu
	β_{zzz}	434.7164	$\times 10^{-30}$ esu
	β_{avg}	460.2936	$\times 10^{-30}$ esu
m062x vacuo	*Dipole*	17.1335	Debye
	$\mu\beta$	2122.4471	$\times 10^{-48}$ esu
	β_{HRS}	87.3974	$\times 10^{-30}$ esu
	β_{zzz}	198.4930	$\times 10^{-30}$ esu
	β_{avg}	210.8879	$\times 10^{-30}$ esu
m062x (chloroform)	*Dipole*	19.7305	Debye
	$\mu\beta$	5438.1195	$\times 10^{-48}$ esu
	β_{HRS}	195.6930	$\times 10^{-30}$ esu
	β_{zzz}	436.5979	$\times 10^{-30}$ esu
	β_{avg}	471.9197	$\times 10^{-30}$ esu
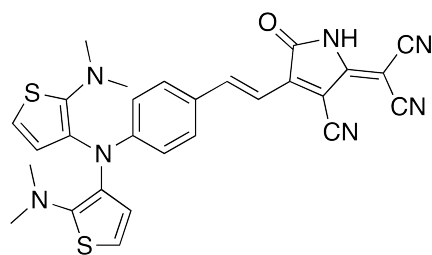
DAAP-14

cam-b3lyp vacuo	*Dipole*	14.4767	Debye
	$\mu\beta$	1931.1531	$\times 10^{-48}$ esu
	β_{HRS}	96.3549	$\times 10^{-30}$ esu
	β_{zzz}	209.3504	$\times 10^{-30}$ esu
	β_{avg}	230.7007	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	*Dipole*	14.4765	Debye
	$\mu\beta$	5024.8872	$\times 10^{-48}$ esu
	β_{HRS}	249.9975	$\times 10^{-30}$ esu
	β_{zzz}	544.3053	$\times 10^{-30}$ esu
	β_{avg}	599.4816	$\times 10^{-30}$ esu
m062x vacuo	*Dipole*	14.4762	Debye
	$\mu\beta$	2035.3655	$\times 10^{-48}$ esu
	β_{HRS}	101.2549	$\times 10^{-30}$ esu
	β_{zzz}	220.7073	$\times 10^{-30}$ esu
	β_{avg}	242.7919	$\times 10^{-30}$ esu
m062x (chloroform)	*Dipole*	17.3042	Debye
	$\mu\beta$	6311.8849	$\times 10^{-48}$ esu
	β_{HRS}	264.0967	$\times 10^{-30}$ esu
	β_{zzz}	561.9620	$\times 10^{-30}$ esu
	β_{avg}	634.4182	$\times 10^{-30}$ esu

DAAP-15
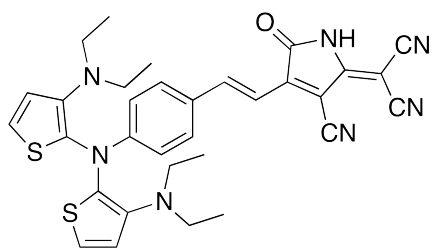
Method	Property	Value	Unit
cam-b3lyp vacuo	$Dipole$	14.3918	Debye
	$\mu\beta$	1449.2904	$\times 10^{-48}$ esu
	β_{HRS}	72.7516	$\times 10^{-30}$ esu
	β_{zzz}	158.9150	$\times 10^{-30}$ esu
	β_{avg}	173.8525	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	14.3920	Debye
	$\mu\beta$	3418.5834	$\times 10^{-48}$ esu
	β_{HRS}	171.2849	$\times 10^{-30}$ esu
	β_{zzz}	374.7650	$\times 10^{-30}$ esu
	β_{avg}	409.6318	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	14.3920	Debye
	$\mu\beta$	1502.2880	$\times 10^{-48}$ esu
	β_{HRS}	75.1572	$\times 10^{-30}$ esu
	β_{zzz}	164.8325	$\times 10^{-30}$ esu
	β_{avg}	179.8910	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	17.0166	Debye
	$\mu\beta$	4134.4112	$\times 10^{-48}$ esu
	β_{HRS}	176.0151	$\times 10^{-30}$ esu
	β_{zzz}	376.6038	$\times 10^{-30}$ esu
	β_{avg}	421.8110	$\times 10^{-30}$ esu

DAAP-16
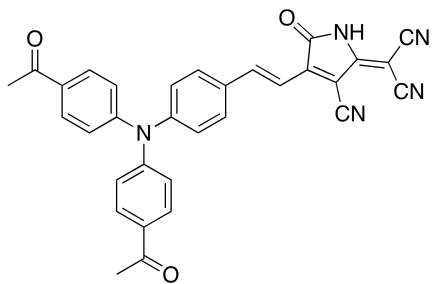
Method	Property	Value	Unit
cam-b3lyp vacuo	$Dipole$	6.3993	Debye
	$\mu\beta$	594.6805	$\times 10^{-48}$ esu
	β_{HRS}	88.6992	$\times 10^{-30}$ esu
	β_{zzz}	82.8691	$\times 10^{-30}$ esu
	β_{avg}	206.0548	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	6.3990	Debye
	$\mu\beta$	1379.6011	$\times 10^{-48}$ esu
	β_{HRS}	202.7902	$\times 10^{-30}$ esu
	β_{zzz}	195.9884	$\times 10^{-30}$ esu
	β_{avg}	474.4171	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	6.3985	Debye
	$\mu\beta$	629.7725	$\times 10^{-48}$ esu
	β_{HRS}	93.3986	$\times 10^{-30}$ esu
	β_{zzz}	88.5443	$\times 10^{-30}$ esu
	β_{avg}	217.7229	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	7.7385	Debye
	$\mu\beta$	1621.5101	$\times 10^{-48}$ esu
	β_{HRS}	213.1686	$\times 10^{-30}$ esu
	β_{zzz}	156.4230	$\times 10^{-30}$ esu
	β_{avg}	500.3883	$\times 10^{-30}$ esu
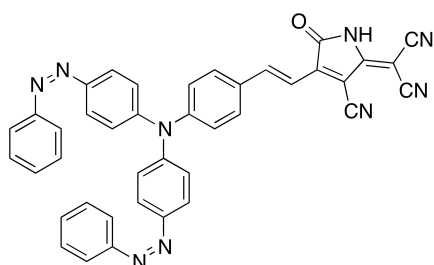
DAAP-17

cam-b3lyp vacuo	$Dipole$	12.2682	Debye
	$\mu\beta$	1708.1137	$\times 10^{-48}$ esu
	β_{HRS}	113.6209	$\times 10^{-30}$ esu
	β_{zzz}	176.0623	$\times 10^{-30}$ esu
	β_{avg}	268.4177	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	12.2685	Debye
	$\mu\beta$	3874.9187	$\times 10^{-48}$ esu
	β_{HRS}	257.5898	$\times 10^{-30}$ esu
	β_{zzz}	395.1736	$\times 10^{-30}$ esu
	β_{avg}	610.0556	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	12.2686	Debye
	$\mu\beta$	1816.3179	$\times 10^{-48}$ esu
	β_{HRS}	120.2555	$\times 10^{-30}$ esu
	β_{zzz}	187.4335	$\times 10^{-30}$ esu
	β_{avg}	284.8971	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	14.6603	Debye
	$\mu\beta$	4785.6034	$\times 10^{-48}$ esu
	β_{HRS}	272.5889	$\times 10^{-30}$ esu
	β_{zzz}	384.2930	$\times 10^{-30}$ esu
	β_{avg}	647.5315	$\times 10^{-30}$ esu
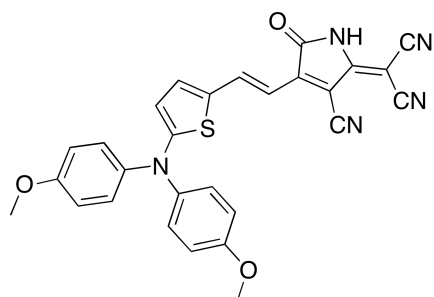
DAAP-18

cam-b3lyp vacuo	$Dipole$	17.3353	Debye
	$\mu\beta$	1841.1483	$\times 10^{-48}$ esu
	β_{HRS}	77.5457	$\times 10^{-30}$ esu
	β_{zzz}	165.2170	$\times 10^{-30}$ esu
	β_{avg}	185.3916	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	17.3350	Debye
	$\mu\beta$	4892.9465	$\times 10^{-48}$ esu
	β_{HRS}	207.8904	$\times 10^{-30}$ esu
	β_{zzz}	439.8066	$\times 10^{-30}$ esu
	β_{avg}	494.3204	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	17.3346	Debye
	$\mu\beta$	1904.7971	$\times 10^{-48}$ esu
	β_{HRS}	79.7469	$\times 10^{-30}$ esu
	β_{zzz}	170.8305	$\times 10^{-30}$ esu
	β_{avg}	191.2433	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	21.6035	Debye
	$\mu\beta$	6331.4862	$\times 10^{-48}$ esu
	β_{HRS}	216.3953	$\times 10^{-30}$ esu
	β_{zzz}	445.0195	$\times 10^{-30}$ esu
	β_{avg}	517.2187	$\times 10^{-30}$ esu

DAAP-19
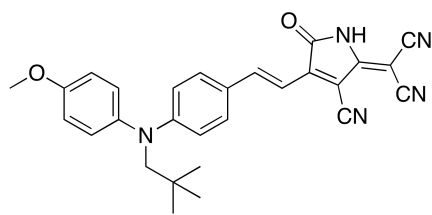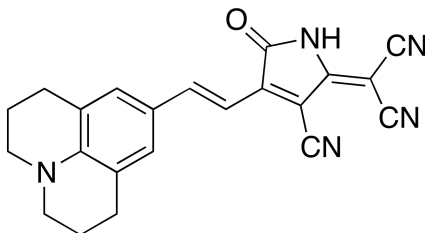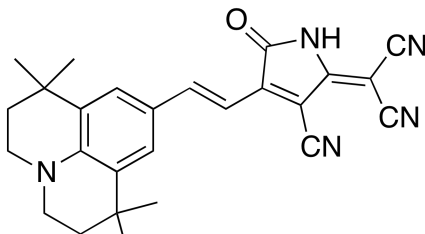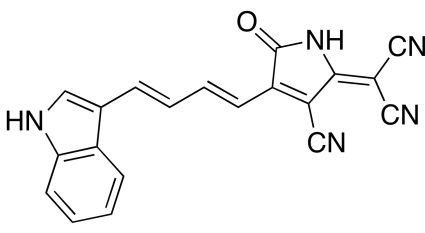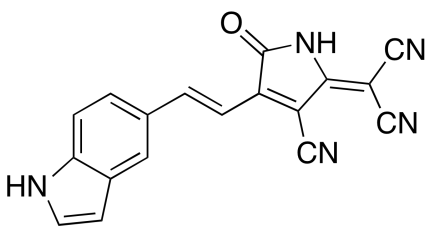
Method	Property	Value	Units
cam-b3lyp vacuo	$Dipole$	15.2894	Debye
	$\mu\beta$	1712.1933	$\times 10^{-48}$ esu
	β_{HRS}	80.4379	$\times 10^{-30}$ esu
	β_{zzz}	177.8932	$\times 10^{-30}$ esu
	β_{avg}	192.7885	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	15.2897	Debye
	$\mu\beta$	4527.6441	$\times 10^{-48}$ esu
	β_{HRS}	212.1476	$\times 10^{-30}$ esu
	β_{zzz}	472.1855	$\times 10^{-30}$ esu
	β_{avg}	508.3347	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	15.2895	Debye
	$\mu\beta$	1774.2588	$\times 10^{-48}$ esu
	β_{HRS}	83.1021	$\times 10^{-30}$ esu
	β_{zzz}	184.3164	$\times 10^{-30}$ esu
	β_{avg}	199.4754	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	18.5338	Debye
	$\mu\beta$	5632.2318	$\times 10^{-48}$ esu
	β_{HRS}	219.5058	$\times 10^{-30}$ esu
	β_{zzz}	472.7315	$\times 10^{-30}$ esu
	β_{avg}	527.0693	$\times 10^{-30}$ esu

DAAP-20
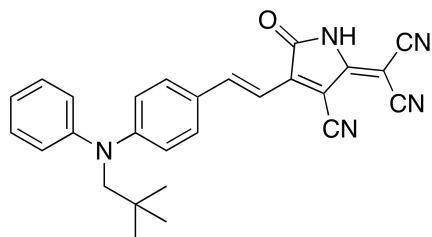
Method	Property	Value	Units
cam-b3lyp vacuo	$Dipole$	14.4808	Debye
	$\mu\beta$	1536.4316	$\times 10^{-48}$ esu
	β_{HRS}	76.6893	$\times 10^{-30}$ esu
	β_{zzz}	167.1680	$\times 10^{-30}$ esu
	β_{avg}	183.2060	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	14.4801	Debye
	$\mu\beta$	4123.5105	$\times 10^{-48}$ esu
	β_{HRS}	205.5788	$\times 10^{-30}$ esu
	β_{zzz}	448.1616	$\times 10^{-30}$ esu
	β_{avg}	491.6144	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	14.4796	Debye
	$\mu\beta$	1594.3001	$\times 10^{-48}$ esu
	β_{HRS}	79.3398	$\times 10^{-30}$ esu
	β_{zzz}	173.5756	$\times 10^{-30}$ esu
	β_{avg}	189.8363	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	17.6764	Debye
	$\mu\beta$	5181.7754	$\times 10^{-48}$ esu
	β_{HRS}	212.9061	$\times 10^{-30}$ esu
	β_{zzz}	452.0313	$\times 10^{-30}$ esu
	β_{avg}	510.1808	$\times 10^{-30}$ esu

cam-b3lyp vacuo	$Dipole$	16.1399	Debye
	$\mu\beta$	1554.2843	$\times10^{-48}$ esu
	β_{HRS}	69.5775	$\times10^{-30}$ esu
	β_{zzz}	152.7118	$\times10^{-30}$ esu
	β_{avg}	166.0732	$\times10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	16.1409	Debye
	$\mu\beta$	5020.7171	$\times10^{-48}$ esu
	β_{HRS}	225.0691	$\times10^{-30}$ esu
	β_{zzz}	490.0760	$\times10^{-30}$ esu
	β_{avg}	537.6387	$\times10^{-30}$ esu
m062x vacuo	$Dipole$	16.1407	Debye
	$\mu\beta$	1586.1938	$\times10^{-48}$ esu
	β_{HRS}	70.7473	$\times10^{-30}$ esu
	β_{zzz}	156.0854	$\times10^{-30}$ esu
	β_{avg}	169.1142	$\times10^{-30}$ esu
m062x (chloroform)	$Dipole$	20.8826	Debye
	$\mu\beta$	6619.5939	$\times10^{-48}$ esu
	β_{HRS}	228.8400	$\times10^{-30}$ esu
	β_{zzz}	497.8532	$\times10^{-30}$ esu
	β_{avg}	547.7498	$\times10^{-30}$ esu

LR-01

cam-b3lyp vacuo	$Dipole$	16.1087	Debye
	$\mu\beta$	1552.2912	$\times10^{-48}$ esu
	β_{HRS}	69.8795	$\times10^{-30}$ esu
	β_{zzz}	153.3524	$\times10^{-30}$ esu
	β_{avg}	166.2830	$\times10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	16.1080	Debye
	$\mu\beta$	4846.3455	$\times10^{-48}$ esu
	β_{HRS}	218.3898	$\times10^{-30}$ esu
	β_{zzz}	474.3558	$\times10^{-30}$ esu
	β_{avg}	520.6235	$\times10^{-30}$ esu
m062x vacuo	$Dipole$	16.1077	Debye
	$\mu\beta$	1581.9742	$\times10^{-48}$ esu
	β_{HRS}	70.9438	$\times10^{-30}$ esu
	β_{zzz}	156.5532	$\times10^{-30}$ esu
	β_{avg}	169.0855	$\times10^{-30}$ esu
m062x (chloroform)	$Dipole$	20.8447	Debye
	$\mu\beta$	6392.0283	$\times10^{-48}$ esu
	β_{HRS}	221.9730	$\times10^{-30}$ esu
	β_{zzz}	482.1291	$\times10^{-30}$ esu
	β_{avg}	530.3138	$\times10^{-30}$ esu

LR-02

	Dipole	15.0645	Debye
cam-b3lyp vacuo	$\mu\beta$	1237.8168	$\times 10^{-48}$ esu
	β_{HRS}	62.5466	$\times 10^{-30}$ esu
	β_{zzz}	116.0599	$\times 10^{-30}$ esu
	β_{avg}	149.5425	$\times 10^{-30}$ esu
	Dipole	15.0652	Debye
cam-b3lyp (chloroform)	$\mu\beta$	3775.3123	$\times 10^{-48}$ esu
	β_{HRS}	189.8873	$\times 10^{-30}$ esu
	β_{zzz}	356.2560	$\times 10^{-30}$ esu
	β_{avg}	454.2037	$\times 10^{-30}$ esu
	Dipole	15.0652	Debye
m062x vacuo	$\mu\beta$	1273.9506	$\times 10^{-48}$ esu
	β_{HRS}	63.9697	$\times 10^{-30}$ esu
	β_{zzz}	119.9632	$\times 10^{-30}$ esu
	β_{avg}	153.3065	$\times 10^{-30}$ esu
	Dipole	19.3199	Debye
m062x (chloroform)	$\mu\beta$	4929.6591	$\times 10^{-48}$ esu
	β_{HRS}	193.9857	$\times 10^{-30}$ esu
	β_{zzz}	356.5283	$\times 10^{-30}$ esu
	β_{avg}	465.3445	$\times 10^{-30}$ esu

LR-03

	Dipole	12.4413	Debye
cam-b3lyp vacuo	$\mu\beta$	589.5190	$\times 10^{-48}$ esu
	β_{HRS}	33.8658	$\times 10^{-30}$ esu
	β_{zzz}	76.1266	$\times 10^{-30}$ esu
	β_{avg}	81.0644	$\times 10^{-30}$ esu
	Dipole	12.4426	Debye
cam-b3lyp (chloroform)	$\mu\beta$	1626.7391	$\times 10^{-48}$ esu
	β_{HRS}	93.0392	$\times 10^{-30}$ esu
	β_{zzz}	209.8092	$\times 10^{-30}$ esu
	β_{avg}	223.1544	$\times 10^{-30}$ esu
	Dipole	12.4426	Debye
m062x vacuo	$\mu\beta$	596.7852	$\times 10^{-48}$ esu
	β_{HRS}	34.0952	$\times 10^{-30}$ esu
	β_{zzz}	77.0940	$\times 10^{-30}$ esu
	β_{avg}	81.8228	$\times 10^{-30}$ esu
	Dipole	15.1979	Debye
m062x (chloroform)	$\mu\beta$	1993.2717	$\times 10^{-48}$ esu
	β_{HRS}	93.2331	$\times 10^{-30}$ esu
	β_{zzz}	208.6528	$\times 10^{-30}$ esu
	β_{avg}	224.2296	$\times 10^{-30}$ esu

LR-04

	Dipole	13.1782	Debye
cam-b3lyp vacuo	$\mu\beta$	1531.9707	$\times 10^{-48}$ esu
	β_{HRS}	83.1091	$\times 10^{-30}$ esu
	β_{zzz}	187.9063	$\times 10^{-30}$ esu
	β_{avg}	198.5351	$\times 10^{-30}$ esu
	Dipole	13.1792	Debye
cam-b3lyp (chloroform)	$\mu\beta$	5207.6085	$\times 10^{-48}$ esu
	β_{HRS}	281.1318	$\times 10^{-30}$ esu
	β_{zzz}	636.9900	$\times 10^{-30}$ esu
	β_{avg}	673.8147	$\times 10^{-30}$ esu
	Dipole	13.1793	Debye
m062x vacuo	$\mu\beta$	1597.2578	$\times 10^{-48}$ esu
	β_{HRS}	86.3812	$\times 10^{-30}$ esu
	β_{zzz}	195.7979	$\times 10^{-30}$ esu
	β_{avg}	206.7190	$\times 10^{-30}$ esu
	Dipole	16.6326	Debye
m062x (chloroform)	$\mu\beta$	6875.8481	$\times 10^{-48}$ esu
	β_{HRS}	294.5544	$\times 10^{-30}$ esu
	β_{zzz}	660.3976	$\times 10^{-30}$ esu
	β_{avg}	707.1208	$\times 10^{-30}$ esu

LR-05
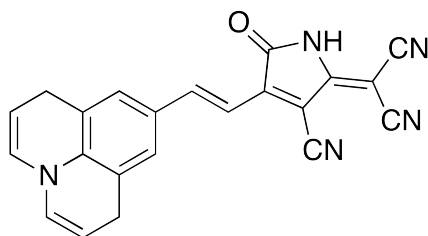
	Dipole	11.6234	Debye
cam-b3lyp vacuo	$\mu\beta$	1337.8230	$\times 10^{-48}$ esu
	β_{HRS}	84.9348	$\times 10^{-30}$ esu
	β_{zzz}	175.8631	$\times 10^{-30}$ esu
	β_{avg}	202.2286	$\times 10^{-30}$ esu
	Dipole	11.6239	Debye
cam-b3lyp (chloroform)	$\mu\beta$	4217.3147	$\times 10^{-48}$ esu
	β_{HRS}	266.0068	$\times 10^{-30}$ esu
	β_{zzz}	553.8394	$\times 10^{-30}$ esu
	β_{avg}	635.8876	$\times 10^{-30}$ esu
	Dipole	11.6243	Debye
m062x vacuo	$\mu\beta$	1433.9503	$\times 10^{-48}$ esu
	β_{HRS}	90.7031	$\times 10^{-30}$ esu
	β_{zzz}	188.2898	$\times 10^{-30}$ esu
	β_{avg}	216.4785	$\times 10^{-30}$ esu
	Dipole	14.3271	Debye
m062x (chloroform)	$\mu\beta$	5606.4999	$\times 10^{-48}$ esu
	β_{HRS}	288.5568	$\times 10^{-30}$ esu
	β_{zzz}	585.8299	$\times 10^{-30}$ esu
	β_{avg}	691.2497	$\times 10^{-30}$ esu

LR-06
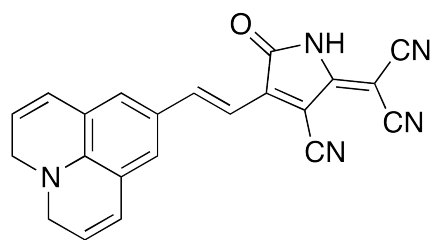
LR-07 | cam-b3lyp vacuo | *Dipole* | 15.1206 | Debye |
		$\mu\beta$	1667.4338	$\times 10^{-48}$ esu
		β_{HRS}	79.8937	$\times 10^{-30}$ esu
		β_{zzz}	175.0508	$\times 10^{-30}$ esu
		β_{avg}	190.3961	$\times 10^{-30}$ esu
	cam-b3lyp (chloroform)	*Dipole*	15.1205	Debye
		$\mu\beta$	5943.9407	$\times 10^{-48}$ esu
		β_{HRS}	283.8586	$\times 10^{-30}$ esu
		β_{zzz}	620.0568	$\times 10^{-30}$ esu
		β_{avg}	678.7642	$\times 10^{-30}$ esu
	m062x vacuo	*Dipole*	15.1207	Debye
		$\mu\beta$	1708.0722	$\times 10^{-48}$ esu
		β_{HRS}	81.5550	$\times 10^{-30}$ esu
		β_{zzz}	179.3808	$\times 10^{-30}$ esu
		β_{avg}	194.6941	$\times 10^{-30}$ esu
	m062x (chloroform)	*Dipole*	19.6705	Debye
		$\mu\beta$	7900.8032	$\times 10^{-48}$ esu
		β_{HRS}	289.5773	$\times 10^{-30}$ esu
		β_{zzz}	631.3961	$\times 10^{-30}$ esu
		β_{avg}	693.6357	$\times 10^{-30}$ esu
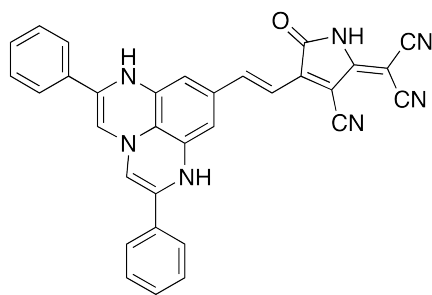
LR-08 | cam-b3lyp vacuo | *Dipole* | 13.8592 | Debye |
		$\mu\beta$	5617.8224	$\times 10^{-48}$ esu
		β_{HRS}	297.6600	$\times 10^{-30}$ esu
		β_{zzz}	638.7527	$\times 10^{-30}$ esu
		β_{avg}	704.6707	$\times 10^{-30}$ esu
	cam-b3lyp (chloroform)	*Dipole*	13.8577	Debye
		$\mu\beta$	27712.9212	$\times 10^{-48}$ esu
		β_{HRS}	1446.6454	$\times 10^{-30}$ esu
		β_{zzz}	3118.2126	$\times 10^{-30}$ esu
		β_{avg}	3465.9939	$\times 10^{-30}$ esu
	m062x vacuo	*Dipole*	13.8576	Debye
		$\mu\beta$	5618.7443	$\times 10^{-48}$ esu
		β_{HRS}	297.7946	$\times 10^{-30}$ esu
		β_{zzz}	638.4755	$\times 10^{-30}$ esu
		β_{avg}	704.9660	$\times 10^{-30}$ esu
	m062x (chloroform)	*Dipole*	18.2409	Debye
		$\mu\beta$	36023.3961	$\times 10^{-48}$ esu
		β_{HRS}	1431.9490	$\times 10^{-30}$ esu
		β_{zzz}	3058.8916	$\times 10^{-30}$ esu
		β_{avg}	3432.3455	$\times 10^{-30}$ esu

LR-09
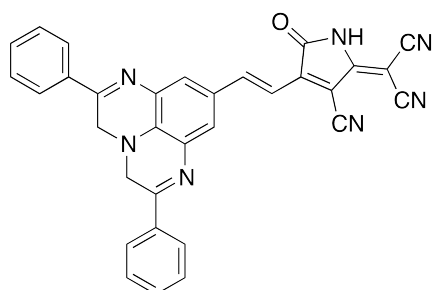
Method	Property	Value	Unit
cam-b3lyp vacuo	$Dipole$	16.2792	Debye
	$\mu\beta$	1852.9134	$\times10^{-48}$ esu
	β_{HRS}	82.4258	$\times10^{-30}$ esu
	β_{zzz}	187.9678	$\times10^{-30}$ esu
	β_{avg}	194.4810	$\times10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	16.2797	Debye
	$\mu\beta$	5494.5607	$\times10^{-48}$ esu
	β_{HRS}	242.2101	$\times10^{-30}$ esu
	β_{zzz}	552.3976	$\times10^{-30}$ esu
	β_{avg}	575.5966	$\times10^{-30}$ esu
m062x vacuo	$Dipole$	16.2798	Debye
	$\mu\beta$	1910.2359	$\times10^{-48}$ esu
	β_{HRS}	84.6683	$\times10^{-30}$ esu
	β_{zzz}	193.5631	$\times10^{-30}$ esu
	β_{avg}	200.2021	$\times10^{-30}$ esu
m062x (chloroform)	$Dipole$	20.5852	Debye
	$\mu\beta$	7135.5624	$\times10^{-48}$ esu
	β_{HRS}	248.5354	$\times10^{-30}$ esu
	β_{zzz}	563.7089	$\times10^{-30}$ esu
	β_{avg}	591.8813	$\times10^{-30}$ esu

LR-10
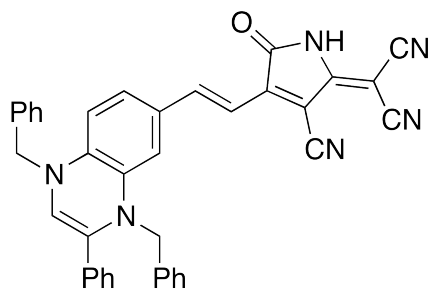
Method	Property	Value	Unit
cam-b3lyp vacuo	$Dipole$	14.3242	Debye
	$\mu\beta$	2319.4867	$\times10^{-48}$ esu
	β_{HRS}	122.2438	$\times10^{-30}$ esu
	β_{zzz}	231.8893	$\times10^{-30}$ esu
	β_{avg}	291.7918	$\times10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	14.3234	Debye
	$\mu\beta$	6905.8687	$\times10^{-48}$ esu
	β_{HRS}	363.0641	$\times10^{-30}$ esu
	β_{zzz}	689.6809	$\times10^{-30}$ esu
	β_{avg}	869.2152	$\times10^{-30}$ esu
m062x vacuo	$Dipole$	14.3229	Debye
	$\mu\beta$	2438.8903	$\times10^{-48}$ esu
	β_{HRS}	128.3618	$\times10^{-30}$ esu
	β_{zzz}	243.1217	$\times10^{-30}$ esu
	β_{avg}	306.9209	$\times10^{-30}$ esu
m062x (chloroform)	$Dipole$	17.6227	Debye
	$\mu\beta$	8863.1915	$\times10^{-48}$ esu
	β_{HRS}	383.3836	$\times10^{-30}$ esu
	β_{zzz}	696.7219	$\times10^{-30}$ esu
	β_{avg}	919.5729	$\times10^{-30}$ esu
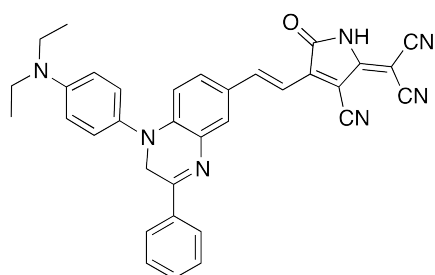
cam-b3lyp vacuo	*Dipole*	19.1843	Debye
	$\mu\beta$	2320.6592	$\times10^{-48}$ esu
	β_{HRS}	89.5857	$\times10^{-30}$ esu
	β_{zzz}	179.4981	$\times10^{-30}$ esu
	β_{avg}	214.3232	$\times10^{-30}$ esu
cam-b3lyp (chloroform)	*Dipole*	19.1847	Debye
	$\mu\beta$	6143.3178	$\times10^{-48}$ esu
	β_{HRS}	238.3956	$\times10^{-30}$ esu
	β_{zzz}	471.1685	$\times10^{-30}$ esu
	β_{avg}	570.2608	$\times10^{-30}$ esu
m062x vacuo	*Dipole*	19.1846	Debye
	$\mu\beta$	2390.9604	$\times10^{-48}$ esu
	β_{HRS}	91.8782	$\times10^{-30}$ esu
	β_{zzz}	185.3308	$\times10^{-30}$ esu
	β_{avg}	220.2140	$\times10^{-30}$ esu
m062x (chloroform)	*Dipole*	23.1720	Debye
	$\mu\beta$	7604.4631	$\times10^{-48}$ esu
	β_{HRS}	244.0743	$\times10^{-30}$ esu
	β_{zzz}	479.8148	$\times10^{-30}$ esu
	β_{avg}	585.1387	$\times10^{-30}$ esu

LR-11
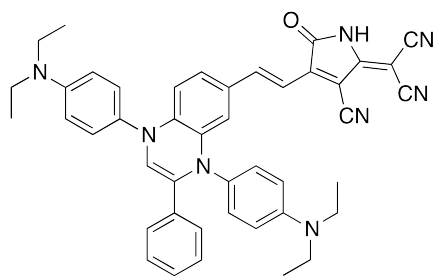
cam-b3lyp vacuo	*Dipole*	16.9394	Debye
	$\mu\beta$	3651.4400	$\times10^{-48}$ esu
	β_{HRS}	161.4224	$\times10^{-30}$ esu
	β_{zzz}	312.4962	$\times10^{-30}$ esu
	β_{avg}	386.4935	$\times10^{-30}$ esu
cam-b3lyp (chloroform)	*Dipole*	16.9406	Debye
	$\mu\beta$	12833.3728	$\times10^{-48}$ esu
	β_{HRS}	568.0321	$\times10^{-30}$ esu
	β_{zzz}	1095.7036	$\times10^{-30}$ esu
	β_{avg}	1361.5245	$\times10^{-30}$ esu
m062x vacuo	*Dipole*	16.9402	Debye
	$\mu\beta$	3708.6612	$\times10^{-48}$ esu
	β_{HRS}	163.6915	$\times10^{-30}$ esu
	β_{zzz}	316.1961	$\times10^{-30}$ esu
	β_{avg}	392.6989	$\times10^{-30}$ esu
m062x (chloroform)	*Dipole*	21.1011	Debye
	$\mu\beta$	16113.3661	$\times10^{-48}$ esu
	β_{HRS}	574.9623	$\times10^{-30}$ esu
	β_{zzz}	1087.6069	$\times10^{-30}$ esu
	β_{avg}	1380.8533	$\times10^{-30}$ esu

LR-12
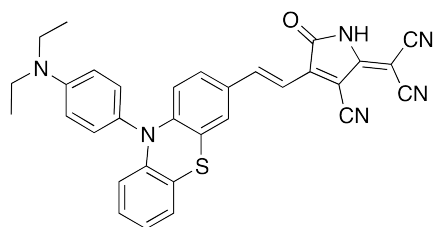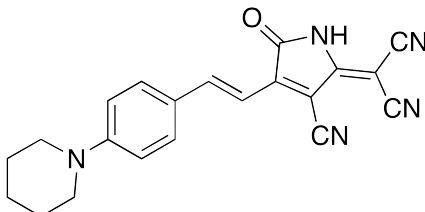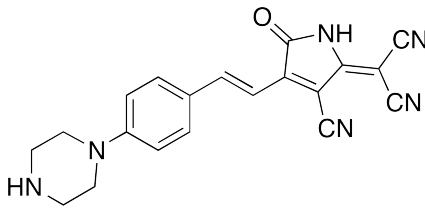
LR-13
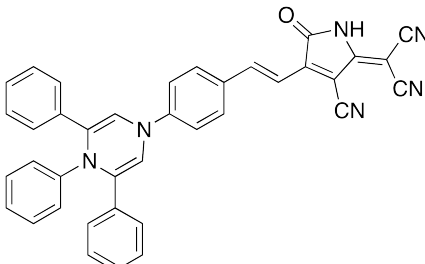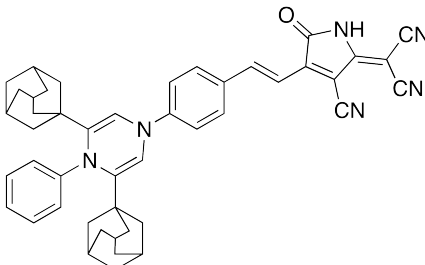
	Dipole	16.8671	Debye
cam-b3lyp vacuo	$\mu\beta$	2170.4782	$\times 10^{-48}$ esu
	β_{HRS}	101.9228	$\times 10^{-30}$ esu
	β_{zzz}	162.9032	$\times 10^{-30}$ esu
	β_{avg}	244.9335	$\times 10^{-30}$ esu
	Dipole	16.8677	Debye
cam-b3lyp (chloroform)	$\mu\beta$	5206.3120	$\times 10^{-48}$ esu
	β_{HRS}	247.1752	$\times 10^{-30}$ esu
	β_{zzz}	382.5686	$\times 10^{-30}$ esu
	β_{avg}	593.7504	$\times 10^{-30}$ esu
	Dipole	16.8680	Debye
m062x vacuo	$\mu\beta$	2299.2387	$\times 10^{-48}$ esu
	β_{HRS}	107.7084	$\times 10^{-30}$ esu
	β_{zzz}	172.6527	$\times 10^{-30}$ esu
	β_{avg}	259.2583	$\times 10^{-30}$ esu
	Dipole	19.7840	Debye
m062x (chloroform)	$\mu\beta$	6401.2681	$\times 10^{-48}$ esu
	β_{HRS}	262.4467	$\times 10^{-30}$ esu
	β_{zzz}	388.6430	$\times 10^{-30}$ esu
	β_{avg}	631.6556	$\times 10^{-30}$ esu
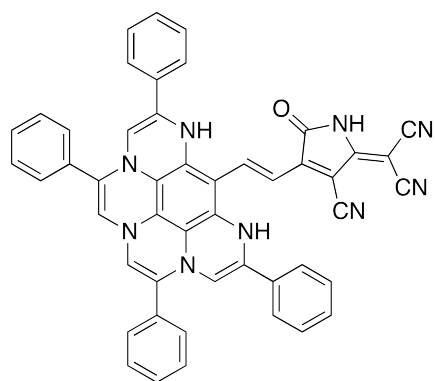
LR-14

	Dipole	13.5019	Debye
cam-b3lyp vacuo	$\mu\beta$	4488.7698	$\times 10^{-48}$ esu
	β_{HRS}	251.9161	$\times 10^{-30}$ esu
	β_{zzz}	509.3259	$\times 10^{-30}$ esu
	β_{avg}	592.2387	$\times 10^{-30}$ esu
	Dipole	13.4999	Debye
cam-b3lyp (chloroform)	$\mu\beta$	21507.7608	$\times 10^{-48}$ esu
	β_{HRS}	1182.2579	$\times 10^{-30}$ esu
	β_{zzz}	2402.4049	$\times 10^{-30}$ esu
	β_{avg}	2820.6460	$\times 10^{-30}$ esu
	Dipole	13.4996	Debye
m062x vacuo	$\mu\beta$	4740.5377	$\times 10^{-48}$ esu
	β_{HRS}	266.6150	$\times 10^{-30}$ esu
	β_{zzz}	534.1728	$\times 10^{-30}$ esu
	β_{avg}	627.5289	$\times 10^{-30}$ esu
	Dipole	17.4783	Debye
m062x (chloroform)	$\mu\beta$	30919.2916	$\times 10^{-48}$ esu
	β_{HRS}	1318.8222	$\times 10^{-30}$ esu
	β_{zzz}	2626.8099	$\times 10^{-30}$ esu
	β_{avg}	3151.9458	$\times 10^{-30}$ esu

R-01			
cam-b3lyp vacuo	$Dipole$	13.8247	Debye
	$\mu\beta$	1250.1201	$\times 10^{-48}$ esu
	β_{HRS}	65.5773	$\times 10^{-30}$ esu
	β_{zzz}	141.6945	$\times 10^{-30}$ esu
	β_{avg}	156.6432	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	13.8247	Debye
	$\mu\beta$	3570.9921	$\times 10^{-48}$ esu
	β_{HRS}	187.0017	$\times 10^{-30}$ esu
	β_{zzz}	404.3007	$\times 10^{-30}$ esu
	β_{avg}	447.1777	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	13.8248	Debye
	$\mu\beta$	1283.2896	$\times 10^{-48}$ esu
	β_{HRS}	67.1058	$\times 10^{-30}$ esu
	β_{zzz}	145.4426	$\times 10^{-30}$ esu
	β_{avg}	160.5535	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	16.9732	Debye
	$\mu\beta$	4467.7846	$\times 10^{-48}$ esu
	β_{HRS}	191.0692	$\times 10^{-30}$ esu
	β_{zzz}	406.6638	$\times 10^{-30}$ esu
	β_{avg}	457.7621	$\times 10^{-30}$ esu
R-02			
cam-b3lyp vacuo	$Dipole$	14.9058	Debye
	$\mu\beta$	1349.3100	$\times 10^{-48}$ esu
	β_{HRS}	66.6225	$\times 10^{-30}$ esu
	β_{zzz}	137.1054	$\times 10^{-30}$ esu
	β_{avg}	159.3151	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	14.9071	Debye
	$\mu\beta$	4014.6329	$\times 10^{-48}$ esu
	β_{HRS}	198.1882	$\times 10^{-30}$ esu
	β_{zzz}	407.4014	$\times 10^{-30}$ esu
	β_{avg}	473.9805	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	14.9070	Debye
	$\mu\beta$	1385.9261	$\times 10^{-48}$ esu
	β_{HRS}	68.1757	$\times 10^{-30}$ esu
	β_{zzz}	140.9501	$\times 10^{-30}$ esu
	β_{avg}	163.2952	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	18.6424	Debye
	$\mu\beta$	5128.1217	$\times 10^{-48}$ esu
	β_{HRS}	202.7293	$\times 10^{-30}$ esu
	β_{zzz}	411.5850	$\times 10^{-30}$ esu
	β_{avg}	485.8157	$\times 10^{-30}$ esu

cam-b3lyp vacuo	*Dipole*	15.0331	Debye
	$\mu\beta$	4231.8482	$\times 10^{-48}$ esu
	β_{HRS}	202.8892	$\times 10^{-30}$ esu
	β_{zzz}	438.1202	$\times 10^{-30}$ esu
	β_{avg}	487.4065	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	*Dipole*	15.0347	Debye
	$\mu\beta$	12004.1417	$\times 10^{-48}$ esu
	β_{HRS}	573.9803	$\times 10^{-30}$ esu
	β_{zzz}	1242.4450	$\times 10^{-30}$ esu
	β_{avg}	1380.8563	$\times 10^{-30}$ esu
m062x vacuo	*Dipole*	15.0347	Debye
	$\mu\beta$	4526.8338	$\times 10^{-48}$ esu
	β_{HRS}	216.6612	$\times 10^{-30}$ esu
	β_{zzz}	468.2684	$\times 10^{-30}$ esu
	β_{avg}	521.0551	$\times 10^{-30}$ esu
m062x (chloroform)	*Dipole*	17.9851	Debye
	$\mu\beta$	15478.0871	$\times 10^{-48}$ esu
	β_{HRS}	623.0272	$\times 10^{-30}$ esu
	β_{zzz}	1314.7031	$\times 10^{-30}$ esu
	β_{avg}	1500.5998	$\times 10^{-30}$ esu

R-03

cam-b3lyp vacuo	*Dipole*	14.8809	Debye
	$\mu\beta$	3614.8843	$\times 10^{-48}$ esu
	β_{HRS}	174.1973	$\times 10^{-30}$ esu
	β_{zzz}	379.8400	$\times 10^{-30}$ esu
	β_{avg}	419.1649	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	*Dipole*	14.8804	Debye
	$\mu\beta$	9626.6846	$\times 10^{-48}$ esu
	β_{HRS}	463.4038	$\times 10^{-30}$ esu
	β_{zzz}	1012.7588	$\times 10^{-30}$ esu
	β_{avg}	1115.2733	$\times 10^{-30}$ esu
m062x vacuo	*Dipole*	14.8803	Debye
	$\mu\beta$	3846.2666	$\times 10^{-48}$ esu
	β_{HRS}	185.0877	$\times 10^{-30}$ esu
	β_{zzz}	404.1248	$\times 10^{-30}$ esu
	β_{avg}	445.7370	$\times 10^{-30}$ esu
m062x (chloroform)	*Dipole*	17.9192	Debye
	$\mu\beta$	12325.8525	$\times 10^{-48}$ esu
	β_{HRS}	495.9254	$\times 10^{-30}$ esu
	β_{zzz}	1058.8303	$\times 10^{-30}$ esu
	β_{avg}	1194.7391	$\times 10^{-30}$ esu

R-04

	Dipole	17.6370	Debye
cam-b3lyp vacuo	$\mu\beta$	5978.9423	$\times 10^{-48}$ esu
	β_{HRS}	241.9967	$\times 10^{-30}$ esu
	β_{zzz}	535.2172	$\times 10^{-30}$ esu
	β_{avg}	582.2997	$\times 10^{-30}$ esu
	Dipole	17.6373	Debye
cam-b3lyp (chloroform)	$\mu\beta$	17902.0007	$\times 10^{-48}$ esu
	β_{HRS}	723.7570	$\times 10^{-30}$ esu
	β_{zzz}	1602.0442	$\times 10^{-30}$ esu
	β_{avg}	1742.6122	$\times 10^{-30}$ esu
	Dipole	17.6376	Debye
m062x vacuo	$\mu\beta$	6280.4734	$\times 10^{-48}$ esu
	β_{HRS}	253.9204	$\times 10^{-30}$ esu
	β_{zzz}	561.9125	$\times 10^{-30}$ esu
	β_{avg}	611.3990	$\times 10^{-30}$ esu
	Dipole	21.2723	Debye
m062x (chloroform)	$\mu\beta$	22756.9219	$\times 10^{-48}$ esu
	β_{HRS}	766.4004	$\times 10^{-30}$ esu
	β_{zzz}	1667.5167	$\times 10^{-30}$ esu
	β_{avg}	1846.7610	$\times 10^{-30}$ esu

R-05
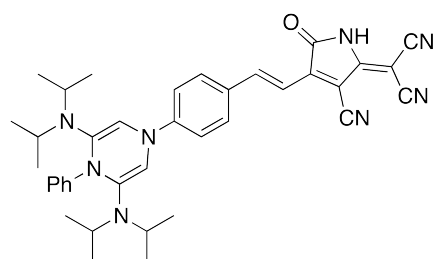
	Dipole	17.9994	Debye
cam-b3lyp vacuo	$\mu\beta$	4929.5485	$\times 10^{-48}$ esu
	β_{HRS}	194.1644	$\times 10^{-30}$ esu
	β_{zzz}	437.0060	$\times 10^{-30}$ esu
	β_{avg}	467.6857	$\times 10^{-30}$ esu
	Dipole	17.9995	Debye
cam-b3lyp (chloroform)	$\mu\beta$	15692.6728	$\times 10^{-48}$ esu
	β_{HRS}	617.6241	$\times 10^{-30}$ esu
	β_{zzz}	1390.1843	$\times 10^{-30}$ esu
	β_{avg}	1488.3651	$\times 10^{-30}$ esu
	Dipole	17.9992	Debye
m062x vacuo	$\mu\beta$	5214.3137	$\times 10^{-48}$ esu
	β_{HRS}	205.0423	$\times 10^{-30}$ esu
	β_{zzz}	462.3333	$\times 10^{-30}$ esu
	β_{avg}	494.2998	$\times 10^{-30}$ esu
	Dipole	22.2805	Debye
m062x (chloroform)	$\mu\beta$	20580.4856	$\times 10^{-48}$ esu
	β_{HRS}	656.2575	$\times 10^{-30}$ esu
	β_{zzz}	1459.0319	$\times 10^{-30}$ esu
	β_{avg}	1583.0175	$\times 10^{-30}$ esu

R-06

R-07
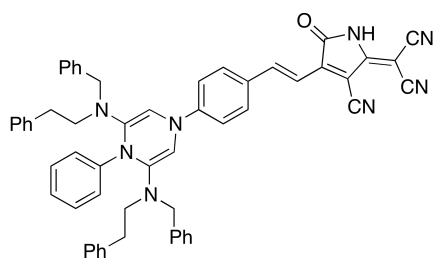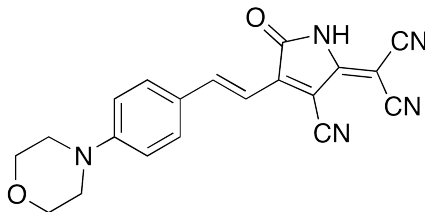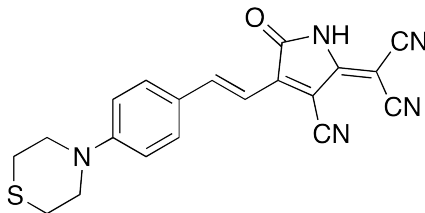
		Dipole	16.7839	Debye
cam-b3lyp vacuo		$\mu\beta$	4541.3585	$\times 10^{-48}$ esu
		β_{HRS}	192.0209	$\times 10^{-30}$ esu
		β_{zzz}	431.0212	$\times 10^{-30}$ esu
		β_{avg}	462.5451	$\times 10^{-30}$ esu
		Dipole	16.7898	Debye
cam-b3lyp (chloroform)		$\mu\beta$	12857.2029	$\times 10^{-48}$ esu
		β_{HRS}	543.4477	$\times 10^{-30}$ esu
		β_{zzz}	1219.4213	$\times 10^{-30}$ esu
		β_{avg}	1308.9277	$\times 10^{-30}$ esu
		Dipole	16.7901	Debye
m062x vacuo		$\mu\beta$	4823.1327	$\times 10^{-48}$ esu
		β_{HRS}	203.5098	$\times 10^{-30}$ esu
		β_{zzz}	457.4616	$\times 10^{-30}$ esu
		β_{avg}	490.6831	$\times 10^{-30}$ esu
		Dipole	20.2224	Debye
m062x (chloroform)		$\mu\beta$	16408.4817	$\times 10^{-48}$ esu
		β_{HRS}	578.2939	$\times 10^{-30}$ esu
		β_{zzz}	1275.8686	$\times 10^{-30}$ esu
		β_{avg}	1394.3696	$\times 10^{-30}$ esu

R-08
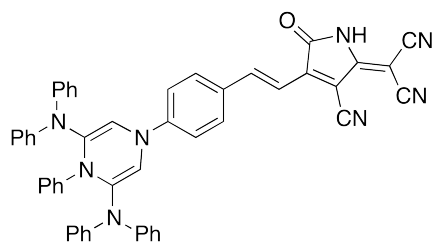
		Dipole	17.6049	Debye
cam-b3lyp vacuo		$\mu\beta$	5614.7279	$\times 10^{-48}$ esu
		β_{HRS}	226.1320	$\times 10^{-30}$ esu
		β_{zzz}	505.6874	$\times 10^{-30}$ esu
		β_{avg}	545.7172	$\times 10^{-30}$ esu
		Dipole	17.6079	Debye
cam-b3lyp (chloroform)		$\mu\beta$	17071.8348	$\times 10^{-48}$ esu
		β_{HRS}	687.2275	$\times 10^{-30}$ esu
		β_{zzz}	1535.9450	$\times 10^{-30}$ esu
		β_{avg}	1658.7923	$\times 10^{-30}$ esu
		Dipole	17.6089	Debye
m062x vacuo		$\mu\beta$	5962.5082	$\times 10^{-48}$ esu
		β_{HRS}	239.6949	$\times 10^{-30}$ esu
		β_{zzz}	536.5857	$\times 10^{-30}$ esu
		β_{avg}	579.0374	$\times 10^{-30}$ esu
		Dipole	21.2615	Debye
m062x (chloroform)		$\mu\beta$	21947.3392	$\times 10^{-48}$ esu
		β_{HRS}	735.0094	$\times 10^{-30}$ esu
		β_{zzz}	1614.1386	$\times 10^{-30}$ esu
		β_{avg}	1776.0866	$\times 10^{-30}$ esu

R-09

cam-b3lyp vacuo	$Dipole$	12.7036	Debye
	$\mu\beta$	1097.8441	$\times 10^{-48}$ esu
	β_{HRS}	63.4671	$\times 10^{-30}$ esu
	β_{zzz}	131.3071	$\times 10^{-30}$ esu
	β_{avg}	151.8161	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	12.7031	Debye
	$\mu\beta$	3235.8466	$\times 10^{-48}$ esu
	β_{HRS}	187.0028	$\times 10^{-30}$ esu
	β_{zzz}	386.7788	$\times 10^{-30}$ esu
	β_{avg}	447.3735	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	12.7031	Debye
	$\mu\beta$	1128.1124	$\times 10^{-48}$ esu
	β_{HRS}	64.9895	$\times 10^{-30}$ esu
	β_{zzz}	135.0687	$\times 10^{-30}$ esu
	β_{avg}	155.6974	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	16.0711	Debye
	$\mu\beta$	4185.4102	$\times 10^{-48}$ esu
	β_{HRS}	191.4758	$\times 10^{-30}$ esu
	β_{zzz}	391.1874	$\times 10^{-30}$ esu
	β_{avg}	458.9644	$\times 10^{-30}$ esu

R-10

cam-b3lyp vacuo	$Dipole$	12.3868	Debye
	$\mu\beta$	1100.0321	$\times 10^{-48}$ esu
	β_{HRS}	65.4712	$\times 10^{-30}$ esu
	β_{zzz}	134.3893	$\times 10^{-30}$ esu
	β_{avg}	156.4036	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	12.3874	Debye
	$\mu\beta$	3189.7923	$\times 10^{-48}$ esu
	β_{HRS}	189.6275	$\times 10^{-30}$ esu
	β_{zzz}	389.2179	$\times 10^{-30}$ esu
	β_{avg}	453.3399	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	12.3873	Debye
	$\mu\beta$	1133.1658	$\times 10^{-48}$ esu
	β_{HRS}	67.1893	$\times 10^{-30}$ esu
	β_{zzz}	138.5588	$\times 10^{-30}$ esu
	β_{avg}	160.7741	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	15.5632	Debye
	$\mu\beta$	4095.9052	$\times 10^{-48}$ esu
	β_{HRS}	194.3602	$\times 10^{-30}$ esu
	β_{zzz}	392.3326	$\times 10^{-30}$ esu
	β_{avg}	465.5648	$\times 10^{-30}$ esu

R-11

cam-b3lyp vacuo	$Dipole$	15.4985	Debye
	$\mu\beta$	4522.4932	$\times 10^{-48}$ esu
	β_{HRS}	209.7742	$\times 10^{-30}$ esu
	β_{zzz}	455.9916	$\times 10^{-30}$ esu
	β_{avg}	504.1204	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	15.4986	Debye
	$\mu\beta$	12808.5774	$\times 10^{-48}$ esu
	β_{HRS}	592.9647	$\times 10^{-30}$ esu
	β_{zzz}	1290.5905	$\times 10^{-30}$ esu
	β_{avg}	1426.7398	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	15.4986	Debye
	$\mu\beta$	4827.0833	$\times 10^{-48}$ esu
	β_{HRS}	223.5663	$\times 10^{-30}$ esu
	β_{zzz}	486.4064	$\times 10^{-30}$ esu
	β_{avg}	537.8048	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	18.4958	Debye
	$\mu\beta$	16437.5213	$\times 10^{-48}$ esu
	β_{HRS}	641.6877	$\times 10^{-30}$ esu
	β_{zzz}	1364.7111	$\times 10^{-30}$ esu
	β_{avg}	1545.6923	$\times 10^{-30}$ esu
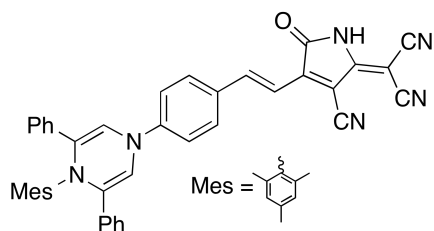
R-12

cam-b3lyp vacuo	$Dipole$	18.3053	Debye
	$\mu\beta$	6119.1748	$\times 10^{-48}$ esu
	β_{HRS}	236.2610	$\times 10^{-30}$ esu
	β_{zzz}	537.7179	$\times 10^{-30}$ esu
	β_{avg}	568.7266	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	18.3080	Debye
	$\mu\beta$	19748.9742	$\times 10^{-48}$ esu
	β_{HRS}	761.6093	$\times 10^{-30}$ esu
	β_{zzz}	1733.4704	$\times 10^{-30}$ esu
	β_{avg}	1834.7562	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	18.3085	Debye
	$\mu\beta$	6443.2749	$\times 10^{-48}$ esu
	β_{HRS}	248.4683	$\times 10^{-30}$ esu
	β_{zzz}	565.9227	$\times 10^{-30}$ esu
	β_{avg}	598.4885	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	22.4662	Debye
	$\mu\beta$	25677.0217	$\times 10^{-48}$ esu
	β_{HRS}	809.8543	$\times 10^{-30}$ esu
	β_{zzz}	1818.1091	$\times 10^{-30}$ esu
	β_{avg}	1952.4805	$\times 10^{-30}$ esu

R-13

cam-b3lyp vacuo	$Dipole$	17.9403	Debye
	$\mu\beta$	5691.2394	$\times 10^{-48}$ esu
	β_{HRS}	224.8610	$\times 10^{-30}$ esu
	β_{zzz}	504.5859	$\times 10^{-30}$ esu
	β_{avg}	542.1023	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	17.9407	Debye
	$\mu\beta$	16880.9637	$\times 10^{-48}$ esu
	β_{HRS}	667.0342	$\times 10^{-30}$ esu
	β_{zzz}	1497.3281	$\times 10^{-30}$ esu
	β_{avg}	1607.6660	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	17.9412	Debye
	$\mu\beta$	6017.2695	$\times 10^{-48}$ esu
	β_{HRS}	237.4706	$\times 10^{-30}$ esu
	β_{zzz}	533.3869	$\times 10^{-30}$ esu
	β_{avg}	572.8573	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	21.7567	Debye
	$\mu\beta$	21734.7238	$\times 10^{-48}$ esu
	β_{HRS}	711.4121	$\times 10^{-30}$ esu
	β_{zzz}	1570.6955	$\times 10^{-30}$ esu
	β_{avg}	1715.9790	$\times 10^{-30}$ esu

R-14

cam-b3lyp vacuo	$Dipole$	16.6550	Debye
	$\mu\beta$	4422.0558	$\times 10^{-48}$ esu
	β_{HRS}	190.8316	$\times 10^{-30}$ esu
	β_{zzz}	412.7220	$\times 10^{-30}$ esu
	β_{avg}	459.3242	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	16.6536	Debye
	$\mu\beta$	13233.7085	$\times 10^{-48}$ esu
	β_{HRS}	570.3421	$\times 10^{-30}$ esu
	β_{zzz}	1236.6253	$\times 10^{-30}$ esu
	β_{avg}	1373.4585	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	16.6535	Debye
	$\mu\beta$	4704.8398	$\times 10^{-48}$ esu
	β_{HRS}	202.7666	$\times 10^{-30}$ esu
	β_{zzz}	438.6376	$\times 10^{-30}$ esu
	β_{avg}	488.6022	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	20.2917	Debye
	$\mu\beta$	17176.1783	$\times 10^{-48}$ esu
	β_{HRS}	612.2175	$\times 10^{-30}$ esu
	β_{zzz}	1291.4032	$\times 10^{-30}$ esu
	β_{avg}	1476.1326	$\times 10^{-30}$ esu

R-15

	Property	Value	Units
cam-b3lyp vacuo	$Dipole$	16.9839	Debye
	$\mu\beta$	4518.6342	$\times 10^{-48}$ esu
	β_{HRS}	189.5959	$\times 10^{-30}$ esu
	β_{zzz}	422.2746	$\times 10^{-30}$ esu
	β_{avg}	455.9520	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	16.9828	Debye
	$\mu\beta$	14811.2568	$\times 10^{-48}$ esu
	β_{HRS}	621.0373	$\times 10^{-30}$ esu
	β_{zzz}	1382.1417	$\times 10^{-30}$ esu
	β_{avg}	1494.6633	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	16.9822	Debye
	$\mu\beta$	4755.4282	$\times 10^{-48}$ esu
	β_{HRS}	199.2776	$\times 10^{-30}$ esu
	β_{zzz}	444.3471	$\times 10^{-30}$ esu
	β_{avg}	479.6146	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	21.0825	Debye
	$\mu\beta$	19449.5241	$\times 10^{-48}$ esu
	β_{HRS}	658.6764	$\times 10^{-30}$ esu
	β_{zzz}	1449.4565	$\times 10^{-30}$ esu
	β_{avg}	1586.6356	$\times 10^{-30}$ esu

R-16
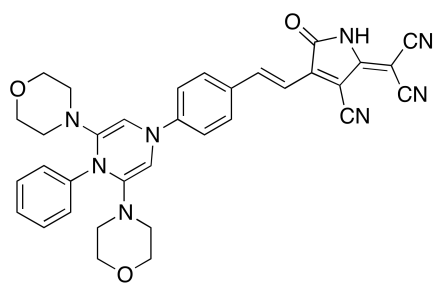
	Property	Value	Units
cam-b3lyp vacuo	$Dipole$	15.5362	Debye
	$\mu\beta$	3741.0775	$\times 10^{-48}$ esu
	β_{HRS}	172.8472	$\times 10^{-30}$ esu
	β_{zzz}	376.3596	$\times 10^{-30}$ esu
	β_{avg}	415.8540	$\times 10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	15.5362	Debye
	$\mu\beta$	11517.1302	$\times 10^{-48}$ esu
	β_{HRS}	532.0296	$\times 10^{-30}$ esu
	β_{zzz}	1156.0334	$\times 10^{-30}$ esu
	β_{avg}	1280.7352	$\times 10^{-30}$ esu
m062x vacuo	$Dipole$	15.5374	Debye
	$\mu\beta$	3973.2572	$\times 10^{-48}$ esu
	β_{HRS}	183.2433	$\times 10^{-30}$ esu
	β_{zzz}	399.4510	$\times 10^{-30}$ esu
	β_{avg}	441.3502	$\times 10^{-30}$ esu
m062x (chloroform)	$Dipole$	19.2078	Debye
	$\mu\beta$	15194.3503	$\times 10^{-48}$ esu
	β_{HRS}	569.3597	$\times 10^{-30}$ esu
	β_{zzz}	1221.3020	$\times 10^{-30}$ esu
	β_{avg}	1372.2099	$\times 10^{-30}$ esu
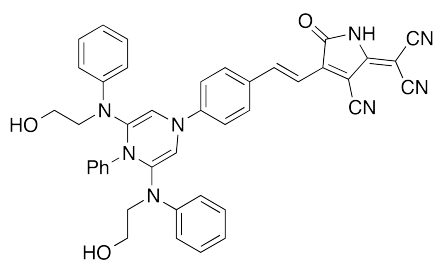
cam-b3lyp vacuo	*Dipole*	17.7093	Debye
	$\mu\beta$	4806.5000	$\times10^{-48}$ esu
	β_{HRS}	194.1344	$\times10^{-30}$ esu
	β_{zzz}	422.4721	$\times10^{-30}$ esu
	β_{avg}	468.5523	$\times10^{-30}$ esu
cam-b3lyp (chloroform)	*Dipole*	17.7078	Debye
	$\mu\beta$	14673.8659	$\times10^{-48}$ esu
	β_{HRS}	593.4954	$\times10^{-30}$ esu
	β_{zzz}	1285.7295	$\times10^{-30}$ esu
	β_{avg}	1432.3838	$\times10^{-30}$ esu
m062x vacuo	*Dipole*	17.7071	Debye
	$\mu\beta$	5088.6294	$\times10^{-48}$ esu
	β_{HRS}	205.1621	$\times10^{-30}$ esu
	β_{zzz}	447.1513	$\times10^{-30}$ esu
	β_{avg}	495.7220	$\times10^{-30}$ esu
m062x (chloroform)	*Dipole*	21.4581	Debye
	$\mu\beta$	18956.2836	$\times10^{-48}$ esu
	β_{HRS}	633.6284	$\times10^{-30}$ esu
	β_{zzz}	1360.6898	$\times10^{-30}$ esu
	β_{avg}	1531.1295	$\times10^{-30}$ esu
cam-b3lyp vacuo	*Dipole*	15.3338	Debye
	$\mu\beta$	4212.9127	$\times10^{-48}$ esu
	β_{HRS}	197.4243	$\times10^{-30}$ esu
	β_{zzz}	431.2675	$\times10^{-30}$ esu
	β_{avg}	473.9754	$\times10^{-30}$ esu
cam-b3lyp (chloroform)	*Dipole*	15.3310	Debye
	$\mu\beta$	12053.2215	$\times10^{-48}$ esu
	β_{HRS}	563.8237	$\times10^{-30}$ esu
	β_{zzz}	1229.9070	$\times10^{-30}$ esu
	β_{avg}	1356.2622	$\times10^{-30}$ esu
m062x vacuo	*Dipole*	15.3309	Debye
	$\mu\beta$	4519.9938	$\times10^{-48}$ esu
	β_{HRS}	211.4419	$\times10^{-30}$ esu
	β_{zzz}	462.6491	$\times10^{-30}$ esu
	β_{avg}	508.2247	$\times10^{-30}$ esu
m062x (chloroform)	*Dipole*	18.5368	Debye
	$\mu\beta$	15866.2023	$\times10^{-48}$ esu
	β_{HRS}	616.0084	$\times10^{-30}$ esu
	β_{zzz}	1323.7231	$\times10^{-30}$ esu
	β_{avg}	1483.5525	$\times10^{-30}$ esu
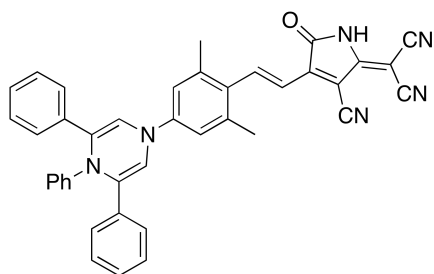
R-19
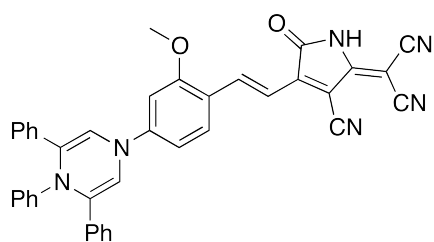
		Dipole	16.3890	Debye
cam-b3lyp vacuo		$\mu\beta$	3914.6742	$\times 10^{-48}$ esu
		β_{HRS}	167.9590	$\times 10^{-30}$ esu
		β_{zzz}	393.3211	$\times 10^{-30}$ esu
		β_{avg}	402.8927	$\times 10^{-30}$ esu
		Dipole	16.3874	Debye
cam-b3lyp (chloroform)		$\mu\beta$	11304.6430	$\times 10^{-48}$ esu
		β_{HRS}	483.8743	$\times 10^{-30}$ esu
		β_{zzz}	1131.9711	$\times 10^{-30}$ esu
		β_{avg}	1163.2573	$\times 10^{-30}$ esu
		Dipole	16.3873	Debye
m062x vacuo		$\mu\beta$	4208.9016	$\times 10^{-48}$ esu
		β_{HRS}	180.2682	$\times 10^{-30}$ esu
		β_{zzz}	422.5640	$\times 10^{-30}$ esu
		β_{avg}	432.9368	$\times 10^{-30}$ esu
		Dipole	19.8225	Debye
m062x (chloroform)		$\mu\beta$	14862.0752	$\times 10^{-48}$ esu
		β_{HRS}	527.0806	$\times 10^{-30}$ esu
		β_{zzz}	1218.8429	$\times 10^{-30}$ esu
		β_{avg}	1268.7257	$\times 10^{-30}$ esu

R-20
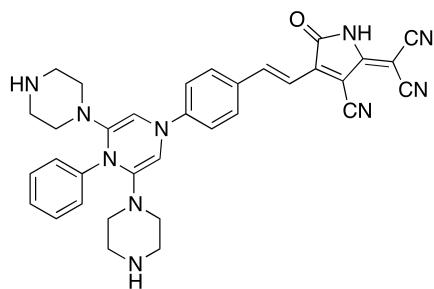
		Dipole	16.2689	Debye
cam-b3lyp vacuo		$\mu\beta$	4092.6929	$\times 10^{-48}$ esu
		β_{HRS}	180.7721	$\times 10^{-30}$ esu
		β_{zzz}	393.2095	$\times 10^{-30}$ esu
		β_{avg}	434.7689	$\times 10^{-30}$ esu
		Dipole	16.2694	Debye
cam-b3lyp (chloroform)		$\mu\beta$	12875.6615	$\times 10^{-48}$ esu
		β_{HRS}	567.0848	$\times 10^{-30}$ esu
		β_{zzz}	1238.2843	$\times 10^{-30}$ esu
		β_{avg}	1365.1840	$\times 10^{-30}$ esu
		Dipole	16.2690	Debye
m062x vacuo		$\mu\beta$	4344.2126	$\times 10^{-48}$ esu
		β_{HRS}	191.5066	$\times 10^{-30}$ esu
		β_{zzz}	417.1465	$\times 10^{-30}$ esu
		β_{avg}	461.1198	$\times 10^{-30}$ esu
		Dipole	20.1121	Debye
m062x (chloroform)		$\mu\beta$	16908.4780	$\times 10^{-48}$ esu
		β_{HRS}	605.9457	$\times 10^{-30}$ esu
		β_{zzz}	1294.5693	$\times 10^{-30}$ esu
		β_{avg}	1460.4300	$\times 10^{-30}$ esu

R-21
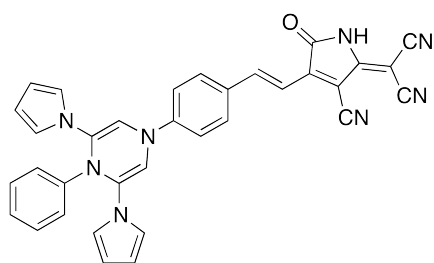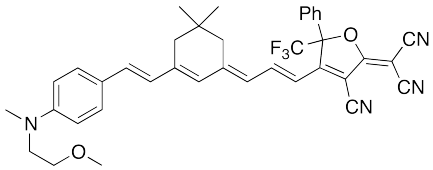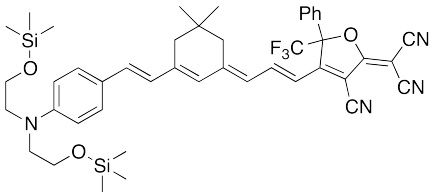
		Dipole	12.3824	Debye
cam-b3lyp vacuo		$\mu\beta$	2584.4197	$\times 10^{-48}$ esu
		β_{HRS}	151.5305	$\times 10^{-30}$ esu
		β_{zzz}	317.4414	$\times 10^{-30}$ esu
		β_{avg}	364.9301	$\times 10^{-30}$ esu
		Dipole	12.3843	Debye
cam-b3lyp (chloroform)		$\mu\beta$	6771.1235	$\times 10^{-48}$ esu
		β_{HRS}	396.7647	$\times 10^{-30}$ esu
		β_{zzz}	832.1122	$\times 10^{-30}$ esu
		β_{avg}	955.4404	$\times 10^{-30}$ esu
		Dipole	12.3845	Debye
m062x vacuo		$\mu\beta$	2792.0050	$\times 10^{-48}$ esu
		β_{HRS}	163.3239	$\times 10^{-30}$ esu
		β_{zzz}	342.8712	$\times 10^{-30}$ esu
		β_{avg}	393.8115	$\times 10^{-30}$ esu
		Dipole	14.8193	Debye
m062x (chloroform)		$\mu\beta$	8727.5787	$\times 10^{-48}$ esu
		β_{HRS}	432.5306	$\times 10^{-30}$ esu
		β_{zzz}	870.8392	$\times 10^{-30}$ esu
		β_{avg}	1042.9469	$\times 10^{-30}$ esu

R-22
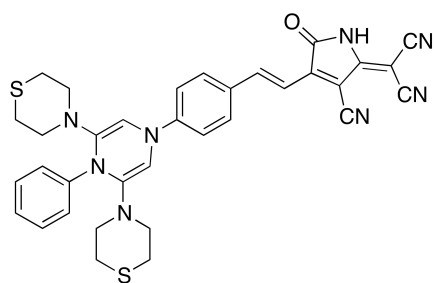
		Dipole	15.5066	Debye
cam-b3lyp vacuo		$\mu\beta$	3922.4599	$\times 10^{-48}$ esu
		β_{HRS}	181.9540	$\times 10^{-30}$ esu
		β_{zzz}	393.3464	$\times 10^{-30}$ esu
		β_{avg}	437.7091	$\times 10^{-30}$ esu
		Dipole	15.5076	Debye
cam-b3lyp (chloroform)		$\mu\beta$	12219.1790	$\times 10^{-48}$ esu
		β_{HRS}	566.7147	$\times 10^{-30}$ esu
		β_{zzz}	1221.5666	$\times 10^{-30}$ esu
		β_{avg}	1364.5342	$\times 10^{-30}$ esu
		Dipole	15.5080	Debye
m062x vacuo		$\mu\beta$	4155.8226	$\times 10^{-48}$ esu
		β_{HRS}	192.3978	$\times 10^{-30}$ esu
		β_{zzz}	416.6126	$\times 10^{-30}$ esu
		β_{avg}	463.3609	$\times 10^{-30}$ esu
		Dipole	19.2766	Debye
m062x (chloroform)		$\mu\beta$	16127.6917	$\times 10^{-48}$ esu
		β_{HRS}	603.2186	$\times 10^{-30}$ esu
		β_{zzz}	1285.6409	$\times 10^{-30}$ esu
		β_{avg}	1454.0761	$\times 10^{-30}$ esu

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cam-b3lyp vacuo	$Dipole$	20.7774	Debye
	$\mu\beta$	4843.7888	$\times10^{-48}$ esu
	β_{HRS}	177.2178	$\times10^{-30}$ esu
	β_{zzz}	324.1447	$\times10^{-30}$ esu
	β_{avg}	426.3199	$\times10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	20.7763	Debye
	$\mu\beta$	13552.7647	$\times10^{-48}$ esu
	β_{HRS}	490.9072	$\times10^{-30}$ esu
	β_{zzz}	924.0015	$\times10^{-30}$ esu
	β_{avg}	1181.2377	$\times10^{-30}$ esu
m062x vacuo	$Dipole$	20.7759	Debye
	$\mu\beta$	5319.0401	$\times10^{-48}$ esu
	β_{HRS}	193.8792	$\times10^{-30}$ esu
	β_{zzz}	356.4684	$\times10^{-30}$ esu
	β_{avg}	467.2286	$\times10^{-30}$ esu
m062x (chloroform)	$Dipole$	25.9908	Debye
	$\mu\beta$	18897.8854	$\times10^{-48}$ esu
	β_{HRS}	546.2065	$\times10^{-30}$ esu
	β_{zzz}	1026.4985	$\times10^{-30}$ esu
	β_{avg}	1316.8991	$\times10^{-30}$ esu

YLD-124TMS

cam-b3lyp vacuo	$Dipole$	21.5677	Debye
	$\mu\beta$	6136.0044	$\times10^{-48}$ esu
	β_{HRS}	209.7172	$\times10^{-30}$ esu
	β_{zzz}	421.2932	$\times10^{-30}$ esu
	β_{avg}	504.3321	$\times10^{-30}$ esu
cam-b3lyp (chloroform)	$Dipole$	21.5678	Debye
	$\mu\beta$	15858.0574	$\times10^{-48}$ esu
	β_{HRS}	537.2482	$\times10^{-30}$ esu
	β_{zzz}	1106.7487	$\times10^{-30}$ esu
	β_{avg}	1292.4591	$\times10^{-30}$ esu
m062x vacuo	$Dipole$	21.5684	Debye
	$\mu\beta$	6715.2422	$\times10^{-48}$ esu
	β_{HRS}	228.8289	$\times10^{-30}$ esu
	β_{zzz}	461.0190	$\times10^{-30}$ esu
	β_{avg}	551.2016	$\times10^{-30}$ esu
m062x (chloroform)	$Dipole$	26.3806	Debye
	$\mu\beta$	21439.0137	$\times10^{-48}$ esu
	β_{HRS}	594.5852	$\times10^{-30}$ esu
	β_{zzz}	1211.3032	$\times10^{-30}$ esu
	β_{avg}	1433.1786	$\times10^{-30}$ esu

Appendix B

PYTHON CODE FOR GDR.PY

```python
#gdr.py rev. 1.0.3
#Nathaniel Phillips-Sylvain, 2014
#The below code was originally written for MATLAB by Dr. Bruce Eichinger.  It
#has been converted to Python using the numpy library.  The only requirements
#to use it are Python and numpy.  Type the following to use it in your code:
#from gdr import GDR
#
#and then to call it, use
#GDR([x,y,z],[xxx,xxy,xyy,yyy,xxz,xyz,yyz,xzz,yzz,zzz])
#The function returns the dipole moment(D), muBeta, BetaHRS, BetaVec
#and BetaTot
#BetaVec is the same as BetaZZZ
#
#This function converts Gaussian data into beta hrs and beta zzz so as to
#be compatible with DMol method.  The Gaussian dipole data is in x,y,z
#components, and the beta data is
# bxxx  bxxy  bxyy  byyy  bxxz  bxyz  byyz  bxzz  byzz  bzzz
#The straightforward way to handle this is to convert to ijk notation and
#apply the algorithm used with DMol calculations.

from __future__ import division
import numpy as np

def GDR(mu,b):

    b = np.asarray(b)
    mutemp = np.asarray(mu)
    M = np.linalg.norm(mutemp)

# This takes a 1x3 vector and finds the matrix that rotates
# the vector to the z axis.  The function returns the rotation matrix
# and the new vector (as a check).  Note that the vector is represented
# as a row, and the way that the matrix is constructed one needs to take the
# transpose to get the new vector.  To construct the rotation, note that mu
# = |mu|xunit vector, so that one row of the rotation matrix is the unit
# vector.  The other two rows are constructed using Gram-Schmidt
# orthogonalization, making certain that the rows are unit vectors.

    u = mutemp / M
    t = np.sqrt(1 - u[0] ** 2)
```

```python
     Rt = np.matrix([[ 0,       u[2]/t,              -u[1]/t ],
                     [ t,       -u[0]*u[1]/t,        -u[0]*u[2]/t ],
                     [ u[0],    u[1],                u[2]]
                    ])
     R = Rt.getT()
     munu = mutemp * R
     b = -b / 2

# The preceeding line was modified 9/7/05 to change from Taylor's series
    convention to
# perturbation series convention.  This also changes the sign to correct for
# the wrong sign convention used by Gaussian.
#
# b1=b111, b2 =b112=b211=b121, b3=b122=b212=b221, b4=b222,
# b5=b113=b131=b311, b6=b123=b321=b132=b312=b213=b231, b7=b223=b232=b322,
# b8=b133=b313=b331, b9 = b233=b323=b332, b10 = b333

     Beta=np.zeros((3,3,3))

     Beta[0,0,0]=b[0]

     Beta[1,0,0]=b[1]
     Beta[0,0,1]=Beta[1,0,0]
     Beta[0,1,0]=Beta[1,0,0]

     Beta[0,1,1]=b[2]
     Beta[1,1,0]=Beta[0,1,1]
     Beta[1,0,1]=Beta[0,1,1]

     Beta[1,1,1]=b[3]

     Beta[2,0,0]=b[4]
     Beta[0,0,2]=Beta[2,0,0]
     Beta[0,2,0]=Beta[2,0,0]

     Beta[1,0,2]=b[5]
     Beta[0,1,2]=Beta[1,0,2]
     Beta[0,2,1]=Beta[1,0,2]
     Beta[1,2,0]=Beta[1,0,2]
     Beta[2,0,1]=Beta[1,0,2]
     Beta[2,1,0]=Beta[1,0,2]

     Beta[2,1,1]=b[6]
     Beta[1,1,2]=Beta[2,1,1]
     Beta[1,2,1]=Beta[2,1,1]

     Beta[0,2,2]=b[7]
     Beta[2,2,0]=Beta[0,2,2]
     Beta[2,0,2]=Beta[0,2,2]
```

```python
91      Beta[1,2,2]=b[8]
92      Beta[2,2,1]=Beta[1,2,2]
93      Beta[2,1,2]=Beta[1,2,2]

95      Beta[2,2,2]=b[9]

97      beta1=R.T * Beta[:,:,0] * R
98      beta2=R.T * Beta[:,:,1] * R
99      beta3=R.T * Beta[:,:,2] * R
100     Betat=np.zeros((3,3,3))
101     Betat[:,:,0]=beta1
102     Betat[:,:,1]=beta2
103     Betat[:,:,2]=beta3
104     BetaT=np.transpose(Betat,(2,0,1))
105     B=np.zeros((3,3,3))
106     t=np.zeros((3,3,3))
107     for n in range(3):
108         t[:,:,n]=R.T * BetaT[:,:,n]
109     B=np.transpose(t,(1,2,0))
110     Bpp=0.6 * np.trace(B[:,:,2])
111     muBeta=M * 2.5418 * Bpp * 0.863916 * 10 ** -50
112     diag=0
113     sum_=0
114     for k in range(3):
115         diag=diag + B[k,k,k] ** 2
116     for k in range(3):
117         for m in range(3):
118             sum_=sum_ + (16 * B[k,k,k] * B[k,m,m] + 38 * B[k,k,m] ** 2) / 105
119     b2=- 12 * diag / 35 + sum_ + 16 * (B[0,0,1] * B[1,2,2] + B[1,1,2] * B
        [2,0,0] + B[2,2,0] * B[0,1,1]) / 105 + (20 / 35) * B[0,1,2] ** 2
120     bx=B[0,0,0] + B[0,1,1] + B[0,2,2]
121     by=B[1,1,1] + B[1,0,0] + B[1,2,2]
122     bz=B[2,2,2] + B[2,0,0] + B[2,1,1]
123     b1=np.sqrt(b2)
124     mu = munu
125     mu_Debyes = munu * 2.5418
126     Beta_HRS=b1 * 0.863916 * 10**-32
127     Beta_zzz=B[2,2,2] * 0.863916 * 10**-32
128     Beta_avg=np.sqrt(bx ** 2 + by ** 2 + bz ** 2) * 0.863916 * 10**-32

130     return dict("dipole" = mu_Debyes[0,2], "mubeta" = muBeta, "betaHRS" =
        Beta_HRS, "betaZZZ" = Beta_zzz, "betaAVG" = Beta_avg)
```

VITA

Anything that's human is mentionable, and anything that is mentionable can be more manageable. When we can talk about our feelings, they become less overwhelming, less upsetting, and less scary. The people we trust with that important talk can help us know that we are not alone.

– Fred Rogers