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Donor–Acceptor 1,4-Fluorenylene Chromophores: Photophysics, Electrochemistry, and Synthesis through a Route for Asymmetric Chromophore Preparation

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Fourteen chromophores of the form 1-(4-X-styryl)-4-(4-nitrostyryl)benzene or 1-(4-X-styryl)-4-(4-nitrostyryl)fluorene have been synthesized with X = CF_3, Cl, I, H, CH_3, OCH_3, or $OCH(CH_3)_3$. An innovative synthetic route was developed in the course of this work wherein phosphonium-phosphonate ester bifunctional precursors were employed. By exploiting steric considerations and the difference in acidity of protons in the position alpha to the phosphonium and phosphonate ester, target asymmetric chromophores were assembled in a straightforward fashion with high selectivity. The photophysical characteristics of the chromophores are described, including notable solvatochromism revealed by measuring photophysical properties in acetonitrile, dichloromethane, tetrahydrofuran, and toluene. Electrochemical analysis by cyclic voltammetry, along with DFT calculations (B3LYP-6-31G*) were employed to reveal the HOMO and LUMO distributions and energies, thus providing further understanding of the properties of these materials and the similarities/differences between phenylene-centered and fluorenylene-centered chromophores.

Introduction

There has been a recent surge in interest in π-conjugated molecules and polymers that feature both electron-releasing and electron-withdrawing subunits: so-called donor–acceptor (D–A) chromophores. This trend stems, in part, from the advantages that such materials hold for certain organic photonic and electronic applications such as nonlinear optics (NLO)[2–8] and organic photovoltaics.[9–12] One type of conjugated backbone system that is of interest in this field of research are poly(*p*-phenylenevinylene) and oligo(*p*-phenylenevinylene) (OPV) derivatives.[13] These materials are also useful in applications including laser dyes, field-effect transistors (FETs),[14,15] memory storage devices and electrochemical supercapacitors,[16] and as dyes for biological sensing. Polymeric systems such as PPV can, however, be difficult to characterize because of high molecular weights, poor solubility, polydispersity, and structural defects, among other problems. To develop a deeper understanding of how properties change as the effective conjugation length of a π-system increases, many insightful studies have focused on analogous oligomers that can be fully characterized.[13] The simplest examples of small segments of D–A OPVs include asymmetrically substituted stilbene and 1,4-distyrylbenzene (DSB) derivatives, which have been extensively studied for several decades.[17] In the case of NLO applications, it is ultimately the manner in which dipoles derived from asymmetric substitution of the chromophore are aligned that eventually dictates the utility of the material.[18] In photovoltaics, the asymmetric substitution of the chromophore not only provides a means for tuning the absorption wavelength, but can also influence the electron affinity and ionization potential of the material, which are key considerations for leveraging charge transport through the active layer of organic bulk heterojunction solar cells. Both NLO and photovoltaic applications also rely on the molecular-level orientation and film morphology for proper alignment of materials.

As part of an effort to improve structure/morphology control in PPV and OPV systems, we previously reported several polymers[19,20] and small-molecule models[21] wherein the commonly employed 1,4-phenylene π-systems are replaced by 1,4-fluorenylene[22–26] moieties (Figure 1).

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This substitution leads to greatly improved solubility of the chromophores in many cases, without significantly altering the absorption, photoluminescence, solvatochromic, or electrochemical properties of their composite chromophores. We were therefore interested in preparing asymmetrically substituted chromophores, including D–A systems, incorporating the 1,4-fluorenylene unit for comparison to known 1,4-phenylene-containing analogues.

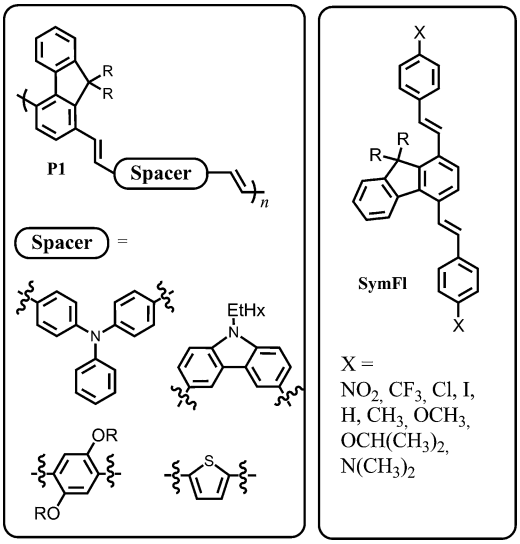
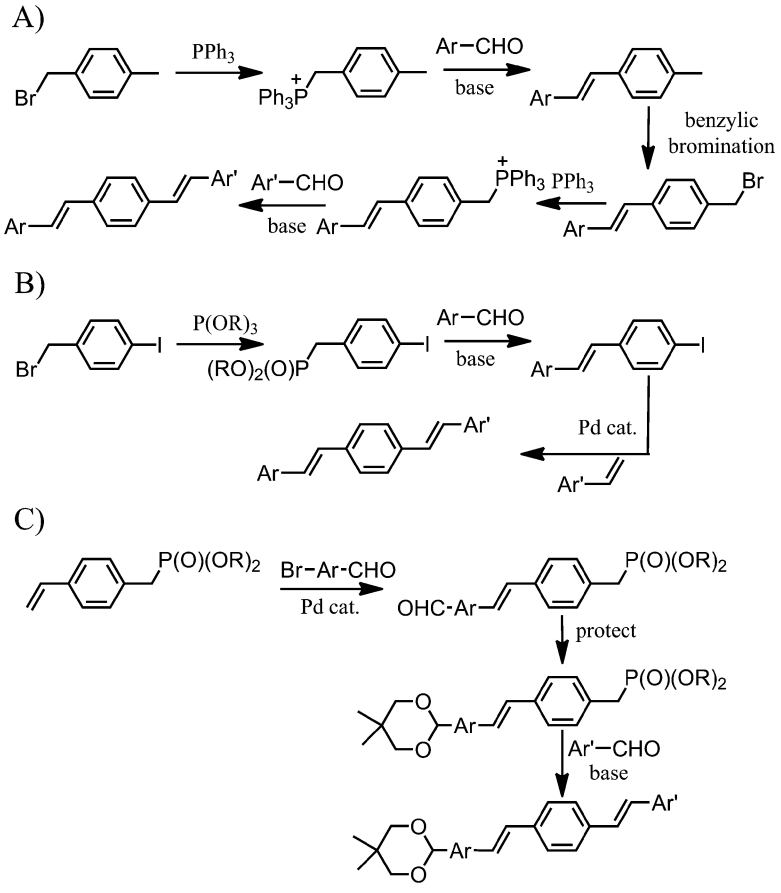


Figure 1. Selected polymers (left) and small-molecule models (right) containing the 1,4-fluorenylene unit (R = *n*-hexyl, EtHx = 2-ethylhexyl).

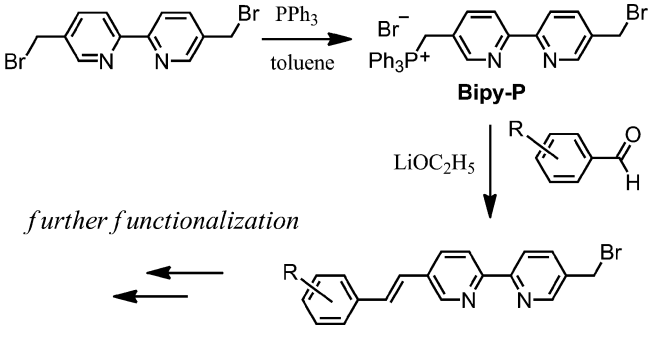
One challenge facing researchers interested in exploring asymmetrically substituted chromophores is that the sequential placement of two or more differently substituted chromophore subunits on a central core is often required for their synthesis. Taking DSBs as an example, this problem has led to the development of several routes to achieve the asymmetric substitution. It is possible to substitute a styryl units for one of two substituents of a 1,4-X_2-benzene precursor, but this approach generally requires tedious separation of starting materials, monosubstituted and disubstituted materials and consequently produces poor overall yields.[27] One of the common site-selective procedures to synthesize asymmetrically substituted DSB derivatives (Scheme 1, A) involves synthesis of a phosphonium salt, Wittig reaction of the salt with an aldehyde, radical bromination of a benzylic methyl *para* to the substituted position, a second substitution of a phosphonium group on the benzylic bromomethyl, followed by a second Wittig reaction. Alternatively, a Wittig reaction can be carried out to yield a stilbene moiety having a halogen substituent that can be



Scheme 1. Representative generalized routes to asymmetrically substituted 1,4-distyrylbenzene chromophores based on current literature precedent.

subsequently converted into either an aldehyde for the second Wittig-type coupling or used for Heck coupling to yield the second olefin linkage (Scheme 1, B).[28] Other multistep and consequently low-yielding syntheses have been devizsed involving iterative Pd-catalyzed C–C bond formation/Wittig-type coupling, sometimes requiring additional protection/deprotection sequences (Scheme 1, C)[29] or tethering precursors to a support such as a perfluorous alkyl unit[30] or silica-immobilized linker[31] to allow for separation of reaction mixtures followed by removal of the molecule from the support. These routes are often low-yielding after so many steps and are sometimes not viable due to the sensitivity of alkene units to halogenation under the radical bromination conditions.

One interesting report[32] describing the preparation of asymmetrically derivatized 2,2′-bipyridyl chromophores made use of the low solubility of phosphonium salt Bipy-P (Scheme 2) to isolate the monophosphonium/monobromomethyl bipyridyl derivative, which was then employed in a Wittig reaction to append the first stilbenyl unit. This allowed the remaining benzylic bromide position to be modified with different chromophoric subunits (Scheme 2). Although this strategy worked well on the bipyridine derivative, it is not directly as useful for preparing 1,4-distyrylbenzene derivatives because the electronic communication between the two benzylic sites leads to side reactions such as polymerization through Gilch-like pathways[33] upon exposure to the base required for the Wittig reaction stage. The overall strategy of exploiting the ready isolation of a monophosphonium salt from a bis(benzylic bromide), however, could be an excellent step to improving asymmetric substitution. Despite the attractiveness of this approach, however, there do not appear to be additional applications of it to the synthesis of other asymmetrically substituted chromophores. In the current work, we report a general strategy for the preparation of asymmetrically substituted 1,4-phenylene and 1,4-fluorenylene chromophores wherein we exploit differences in solubility, pK_a values of deprotonation sites, and reaction rates, to attain high selectivity. By using these routes, fourteen chromophores were prepared and then studied by photophysical and electrochemical methods as well as by DFT calculations.



Scheme 2. Synthetic route to asymmetrically substituted 2,2′-bipyridyl chromophores.

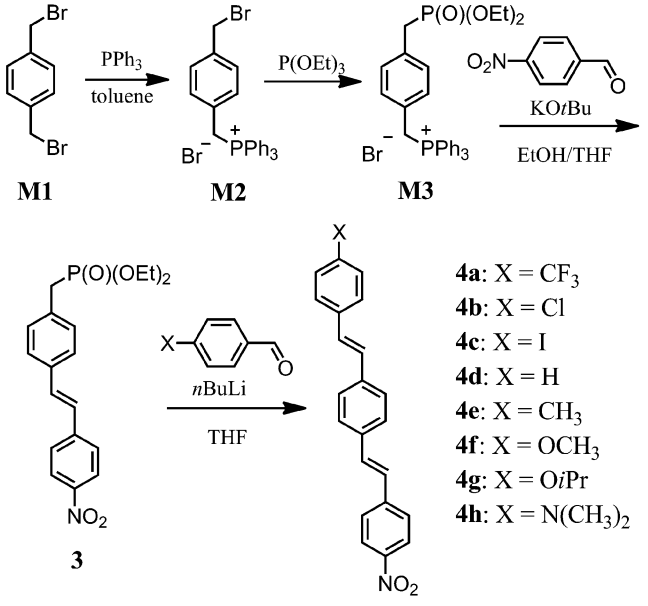
Results and Discussion

Design Rationale and Synthesis of Asymmetric Molecules

The target molecules for this study were chosen to feature a strongly electron-withdrawing nitro substituent at one end of the chromophore and a substituent X at the other end of the chromophore. Substituents X were chosen to sample a range of electron-donating or -releasing abilities, as quantified by their Hammett substituent constants (Table 1).[1] To efficiently place the two differently substituted styryl moieties onto the 1,4-phenylene or 1,4-fluorenylene core, a difunctional core structure from which all targets could be easily derived was desired to avoid an unnecessarily long, low-yielding route. The synthetic route shown in Scheme 3 was thus devised as a potentially convenient and general route to asymmetric chromophores bearing phenylenevinylene subunits.

Table 1. Hammett substituent constants for relevant functional groups.[1]

Substituent	σ_{para}
NO_2	0.78
CF_3	0.54
Cl	0.23
I	0.18
H	0.00
CH_3	–0.17
OCH_3	–0.27
$OCH(CH_3)_2$	–0.45
$N(CH_3)_2$	–0.83



Scheme 3. Route to asymmetrically substituted distyrylbenzene derivatives.

To our surprise, key intermediate α-phosphonium-α′-(phosphonate ester)-*p*-xylene **M3** does not appear to have been reported previously, even though its immediate precursor, **M2**, is commercially available. For our study, **M2** was synthesized by reaction of triphenylphosphine with **M1** in

toluene. Isolation of **M2** was straightforward because the target product precipitates upon monosubstitution. Compound **M2** was thus collected by simple filtration in > 95% purity and was used without further purification.

The next step was a Michaelis–Arbuzov reaction between **M2** and triethylphosphite, which afforded **M3** in good yield (> 75%). Precursor **M3** provided the difunctional scaffold necessary for sequential placement of the two different styryl groups desired to access the asymmetric chromophore. On the basis of the difference in acidity of benzylic protons adjacent to a phosphonium (pK_a ca. 17.6) vs. those in a phosphonate ester α-position (pK_a ca. 27.6, Figure 2), we hypothesized that the phosphonium site could be selectively deprotonated to afford the phosphonium ylide under Wittig conditions in tetrahydrofuran (THF) en route to the requisite olefin, leaving the phosphonate ester in place for subsequent reaction. Indeed, when **M3** and 4-nitrobenzaldehyde react in the presence of KO*t*Bu, the major product was target **3**. Solubility is also an important factor in this step, with improved yields obtained when ethanol was employed as solvent in place of THF, owing to the better solubility of **M3** in ethanol.

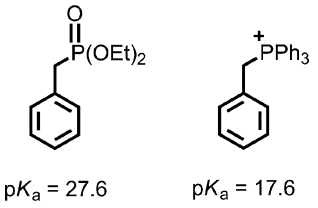


Figure 2. The pK_a values[20] for a benzyl phosphonate ester (left) and benzyl phosphonium salt that model the possible potential deprotonation sites of **M3**.

To assess the selectivity for reaction at the phosphonium site over the phosphonate ester site, the crude reaction mixture of **3** was analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of product **3** showed that the integration ratio of the proton signals corresponding to –CH_2P(O)-(OEt)$_2$ and –CH_2P$^+$Ph$_3$ was 13:1, corresponding to 93% of the desired product **3** and only 7% of the product resulting from olefination at the phosphonate ester site.

The purification of **3** requires removal of the side product triphenylphosphine oxide, which proved to require a multistep process. By using column chromatography with an eluent of CH_2Cl_2 with 2% methanol, a majority of product was isolated. Unfortunately, **3** and triphenylphosphine oxide have similar retention factors (R_f), which lead to co-elution of the two compounds in several fractions. These fractions were thus collected and repurified by preparative TLC (CH_2Cl_2 with 2% methanol) to collect the rest of the desired product **3**. It was observed that **3** was isolable as a mixture of *E* and *Z* isomers, which rapidly interconvert on exposure to light; this is a common issue for these types of stilbene derivatives.[34]

The target reference molecules **4a**–**h** were then conveniently synthesized by reaction of common precursor **3** with the requisite *para*-substituted benzaldehydes. In almost every case, **4** precipitated out of solution after quenching the base with water, allowing facile collection by filtration. For each molecule, the olefin units were observed by ^{1}H NMR spectroscopic analysis to exist in both *E* and *Z* isomeric forms. The *E*,*E* isomers were readily obtained by isomerization mediated by heating the crude solids to reflux in toluene with a catalytic amount of iodine. The compounds were then either collected by filtration or were extracted from the cooled reaction mixture. Compounds **4** were obtained in modest to good yields, ranging from 39–82%, and included previously unreported DSB derivatives **4a**–**c** and **4g**. It is noteworthy that the route outlined in Scheme 3 allows easy access to a wide array of asymmetrically substituted DSBs in only three-steps from commercially available **M2** and any commercial aldehydes that are stable to Wittig condensation. Preparation of symmetrically substituted 1,4-di(4-nitrostyryl)benzene (**5b**; Figure 3) did not require use of the new synthetic protocol, but it was prepared as previously reported[21] for comparison of its properties to asymmetrically substituted molecules **4** (see below).

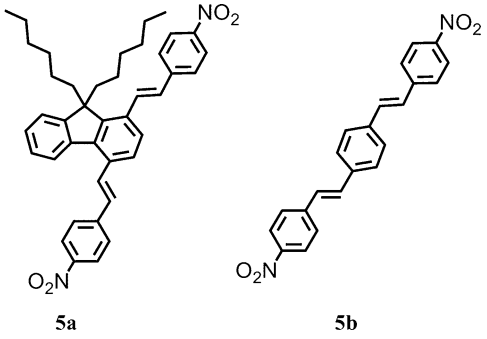
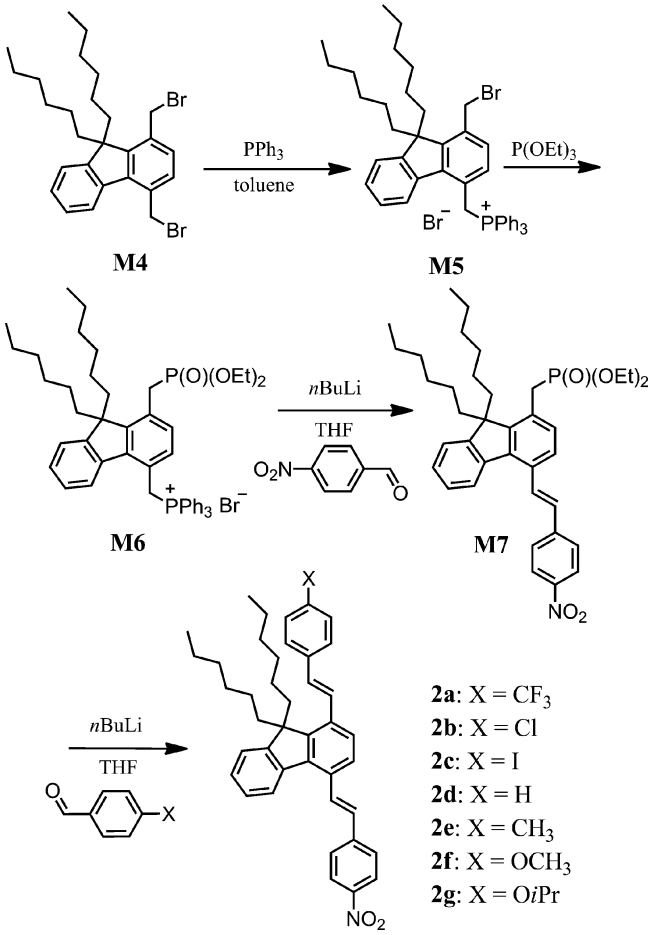


Figure 3. Symmetrically substituted fluorenylene and phenylene compounds with nitro groups.

The synthetic route required to access asymmetrically derivatized 1,4-fluorenylene chromophores (Scheme 4) is more complex than the route shown in Scheme 3 because, unlike the phenylene core, the 1- and 4-positions of the fluorenylene core are inequivalent. Scheme 4 thus illustrates the synthetic route devised to access the target asymmetrically substituted fluorene derivatives **2**.

The starting material **M4** was first prepared as previously reported.[35] After heating **M4** to reflux in toluene with triphenylphosphine for 2 h, the reaction mixture was cooled and product **M5** precipitated out of solution as a white powder, which was collected by filtration. As with the 1,4-phenylene system, this route exploits the selective precipitation of the mono-phosphonium salt as a convenient isolation of target **M5** without any of the bis(phosphonium) observable by NMR spectroscopic analysis. Unlike the 1,4-phenylene system, the two benzylic sites in **M4** are inequivalent. The inequivalency of the two benzylic sites means that two products are possible, but, on the basis of steric considerations, chemical intuition would suggest that placing a bulky triphenylphosphine moiety at the 1-position of the fluorene ring, adjacent to the quaternary 9-position carbon, would face a significant kinetic barrier compared with sub-



Scheme 4. Route to asymmetrically substituted fluoreneylene derivatives **2**.

stitution at the benzylic site at the 4-position of the fluorene ring. Indeed, when **M4** was treated with triphenylphosphine in a 1:0.9 molar equivalence ratio, the ^{1}H NMR spectrum of the crude reaction mixture showed only one phosphonium product, indicating ≥ 95% selectivity for one monosubstituted product over the other. To confirm the anticipated regiochemistry of the product, NMR experiments using the Nuclear Overhauser Effect (NOE) were employed. These experiments confirmed the hypothesis that the C-4 benzylic site was the site that underwent selective substitution to form the phosphonium salt, giving the regioisomer of **M5** depicted in Scheme 4.

The Michaelis–Arbuzov reaction of **M5** with excess triethylphosphite was a facile reaction requiring heating for 3 h, followed by vacuum distillation to remove remaining excess triethylphosphite. The reaction of **M5** with triethylphosphite afforded **M6**, a crystalline solid, in high yield (ca. 94%).

The synthesis of **M7** was carried out by reaction of **M6** with *p*-nitrobenzaldehyde in THF. Phosphonium-phosphonate ester **M6**, unlike phenylene analogue **M3**, was soluble in THF, presumably due to the presence of two hexyl groups on **M6**. The synthesis of **M7** was thus first attempted by reacting **M6** and *p*-nitrobenzaldehyde in THF by using $KOC(CH_3)_3$ as base. Under these conditions, however, most of the starting materials remained unreacted even after heating the mixture for over 12 h. When *n*-butyllithium was used as base in place of $KOC(CH_3)_3$, **M7** was obtained in 36% yield.

It is well-known that metal ions can influence the *E*/*Z* isomer ratio and product yield in the Horner–Wadsworth–Emmons variation of the Wittig reaction,[21,22] and that Li^+ in particular has a significant beneficial influence on yield. This aspect of the reaction was therefore explored in more detail. In one experiment, 5 mol equiv. of LiCl per mol of $KOC(CH_3)_3$ was added to the reaction mixture, keeping all other conditions the same as the first failed attempt that had employed $KOC(CH_3)_3$ as base. In the second experiment, 5 mol equiv. of LiCl was used as an additive and a significantly weaker base, 1 equiv. of $N(CH_3)_3$, was employed. In both cases where LiCl was present as an additive, the reaction went to at least 50% completion, similar to the reaction with *n*-butyllithium, after the same period of time. This data suggests that this particular Horner–Wadsworth–Emmons variation of the Wittig reaction is significantly dependent on cation effects to drive the reaction to completion, more so than the base strength or reaction temperature.

As observed in the preparation of **3** (Scheme 3), it was found that the deprotonation is selective for the phosphonium α-carbon over the phosphonate α-carbon, with no other products observable in a ^{1}H NMR spectrum of the crude reaction mixture. The pure product was isolated by column chromatography. Even after purification, however, the proton NMR spectrum showed evidence for the presence of both *E* and *Z* isomers, which interconvert rapidly upon exposure to light or thermally upon standing in the dark at room temperature. Once purified by column chromatography, **M7** was used, with the unavoidable contamination of some *Z* isomer, for synthesis of the target asymmetrically substituted fluorenylene molecules **2a**–**g**.

Compounds **2a**–**g** were successfully synthesized by combining **M7** with the requisite *para*-substituted benzaldehyde in anhydrous THF. The desired Horner–Wittig reaction was carried out by addition of *n*-butyllithium to the reaction mixture, just as with the phenylene derivatives **4**. Once again, when the reaction was attempted with potassium *tert*-butoxide as the base, most of the starting material was recovered unreacted. Thus, *n*BuLi was employed and the reactions proceeded well upon stirring at room temperature for 18 h or more. Workup involved quenching the excess base with water, followed by extraction with CH_2Cl_2. Purification involved either column chromatography on silica or preparative thin-layer chromatography on silica, giving yields of 22–36%. As previously reported,[34] compounds **2** isomerize readily upon exposure to light as well as thermally at room temperature, so although the molecules were isolated predominantly as all-*E* isomers, it was not possible to isolate them without small amounts of *Z* isomer at room temperature.

Symmetrically substituted 9,9-dihexyl-1,4-bis(4-nitrostyryl)fluorene (**5a**; Figure 3) was also prepared as pre-

viously reported for comparison to asymmetrically substituted molecules **2**.[21]

Photophysical Properties

Table 2 and Table 3 provide data from the photophysical characterization of series **2** and **4**. For comparison, the photophysical properties of **5a** and **5b**[23] (Table 3) are included in the tables. One of the main purposes of evaluating the photophysical properties of these molecules was to evaluate the effect not only of the additional steric encumbrance resulting from fluorenylene attachment but also the effect of varying the donor or acceptor strength of the group at the opposite end of the chromophore from the nitro group. There was also interest in evaluating any solvatochromic effects, so the photophysical characteristics of each molecule were evaluated in four solvents sampling differing polarities (CH_3CN, CH_2Cl_2, THF, and toluene).

Table 2. Selected photophysical properties of asymmetrically substituted fluorenylene-bearing molecules **2a**–**g** and **5a**.

	Solvent	λ_{max} [nm]	λ_{em} [nm]	Φ (±0.02)	Stokes' shift [nm]
5a	CH_3CN	391	591	0.06[a]	200
	CH_2Cl_2	393	564	0.24	171
	THF	391	500	0.22	109
	CH_3Ph	380	465	0.06[a]	85
2a X = CF_3	CH_3CN	370	607	0.11	237
	CH_2Cl_2	376	577	0.27	201
	THF	374	515	0.35	141
	CH_3Ph	388	487	0.11	99
2b X = Cl	CH_3CN	369	610	0.04	241
	CH_2Cl_2	373	590	0.20	217
	THF	377	532	0.38	155
	CH_3Ph	388	491	0.16	103
2c X = I	CH_3CN	381	615	0.03	234
	CH_2Cl_2	381	598	0.21	217
	THF	379	533	0.25	154
	CH_3Ph	376	489	0.12	113
2d X = H	CH_3CN	376	606	0.02	230
	CH_2Cl_2	385	594	0.16	209
	THF	376	526	0.21	145
	CH_3Ph	373	486	0.12	113
2e X = CH_3	CH_3CN	378	470	0.05	92
	CH_2Cl_2	385	469	0.15	84
	THF	382	543	0.43	161
	CH_3Ph	390	499	0.54	109
2f X = OCH_3	CH_3CN	373	459	0.04	86
	CH_2Cl_2	381	466	0.05	85
	THF	379	568	0.18	189
	CH_3Ph[a]	394	530	0.47	136
2g X = O*i*Pr	CH_3CN	388	474	0.01	86
	CH_2Cl_2	392	586	0.01	194
	THF	388	574	0.21	186
	CH_3Ph	391	517	0.41	126

[a] Poor solubility of the molecule in solvent.

For **2a**–**g**, regardless of solvent, no observable trend was seen in λ_{max} when the X group was varied between donor and acceptors; the change in λ_{max} from **2d** (X = H), varied by only about 5–12 nm regardless of substituent X. The most strongly electron-donating group [X = $OCH(CH_3)_2$] caused the largest shift in λ_{max} [e.g., in THF, λ_{max} undergoes a progressive shift from 376 to 388 nm when X changes from H to $OCH(CH_3)_2$]. In contrast, for **4a**–**h**, a stronger trend emerged in the λ_{max} values. Regardless of solvent, when electron-donor strength increased, the λ_{max} values were redshifted compared with **4d**, in which X = H. Specifically, in CH_2Cl_2, λ_{max} = 394, 394, 402, and 460 nm for X = CH_3, OCH_3, $OCH(CH_3)_2$, and $N(CH_3)_2$, respectively. This would be the expected trend based on the contributions of the electron-rich donor groups.

Table 3. Photophysical characterization of asymmetrically substituted distyrylbenzene derivatives **4a**–**h** and **5b**.

	Solvent	λ_{max} [nm]	λ_{em} [nm]	Φ (±0.02)	Stokes' shift [nm]
5b	CH_3CN	397	577	0.32	180
	CH_2Cl_2	402	540	0.43	138
	THF	400	488	0.13	88
	CH_3Ph	397	478	0.03	81
4a X = CF_3	CH_3CN	380	584	0.08	204
	CH_2Cl_2	386	559	0.32	173
	THF	383	508	0.08	125
	CH_3Ph	385	460	0.01	75
4b X = Cl	CH_3CN	383	620	0.02	237
	CH_2Cl_2	388	587	0.04	199
	THF	387	520	0.29	133
	CH_3Ph	392	483	0.02	91
4c X = I	CH_3CN	386	620	0.02	234
	CH_2Cl_2	392	583	0.17	191
	THF	390	524	0.23	134
	CH_3Ph	393	480	0.03	87
4d X = H	CH_3CN	382	622	0.01	240
	CH_2Cl_2	390	588	0.14	198
	THF	388	634	0.29	246
	CH_3Ph	390	479	0.04	89
4e X = CH_3	CH_3CN	388	638	0.01	250
	CH_2Cl_2	394	611	0.05	217
	THF	392	541	0.34	149
	CH_3Ph	396	491	0.35	95
4f X = OCH_3	CH_3CN	388	467	0.03	79
	CH_2Cl_2	394	454	0.03	60
	THF	392	467/564	0.25	
	CH_3Ph[a]	388	500	0.18	112
4g X = O*i*Pr	CH_3CN	396	450	0.00	54
	CH_2Cl_2	402	604	0.00	202
	THF	400	582	0.12	182
	CH_3Ph	404	515	0.53	111
4h X = $N(CH_3)_2$	CH_3CN	392	438	0.03	46
	CH_2Cl_2	460	588	0.01	128
	THF	426	541	0.02	115
	CH_3Ph	430	594	0.20	164

[a] Poor solubility of the molecule in solvent.

When comparing chromophores in series **2** to the analogously substituted members of series **4**, it was found that the λ_{max} for molecules **2a**–**g** were blueshifted compared with those of **4a**–**g**, which is attributable to twisting of adjacent π-conjugated segments of the chromophore in the fluoren-

ylene derivatives out of coplanarity due to the steric encumbrance of dihexyl substitution at C-9.

Based on previous work[23] in which it was observed that the photoluminescence maxima (λ_{em}) of symmetrically substituted fluorenylene and phenylene chromophores varied in response to changes in solvent polarity, it was of interest to examine whether similar solvatochromic effects were exhibited by series **2** and **4**. Indeed, a significant solvatochromic effect is evident visually when cuvettes of the compounds in different solvents are observed under illumination from a handheld UV light (λ_{excit} = 365 nm; Figure 4).

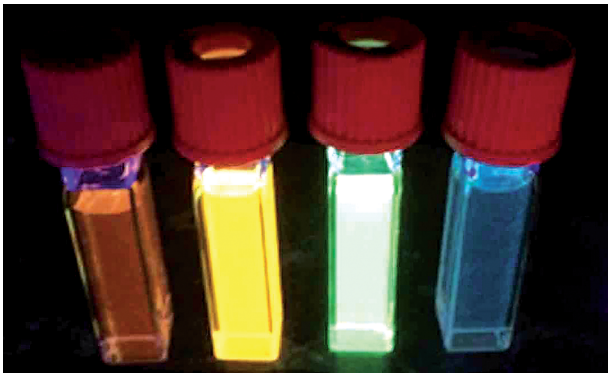


Figure 4. A significant solvatochromic effect in the photoluminescence of **4b** in CH_3CN, CH_2Cl_2, THF, and CH_3Ph (left to right) under a handheld UV lamp (λ_{excit} = 365 nm).

For molecules **2a**–**d**, the consistent trend was that as the solvent polarity increased, the λ_{em} became progressively more redshifted (e.g., for **2a**, λ_{em} = 487 nm in toluene and 607 nm in CH_3CN). This is due to the fact that in the excited state the dipole moment of the molecule increases, therefore a solvent with a larger dipole better stabilizes the excited state, leading to a lower energy emission (redshift).[36,37]

Interestingly, with the molecules substituted with donor groups (i.e., **2e**–**g**), the λ_{em} blueshifted as the solvent polarity increased from toluene to acetonitrile (e.g., for **2f**, λ_{em} = 530 and 474 nm in toluene and CH_3CN, respectively). This is a phenomenon that is commonly termed "negative solvatochromism".[38] Negative solvatochromism occurs when charge is transferred back to the donor on the molecule in the excited state, diminishing the dipole moment, in contrast to the more typical case described above.[4,38]

Molecules **4a**–**h** exhibit similar behavior in λ_{em} to the trend observed in series **2**. For **4a**–**e**, the molecules with X = acceptor groups, or inductive donating groups, the λ_{em} increases as the solvent polarity increases; this again can be explained by stabilization of the increased dipole moment of the molecule in the excited state by the more polar solvents. As with **2g** and **2f** [X = OCH_3, $OCH(CH_3)_2$], **4g**–**h** [for **4h**, X = $N(CH_3)_2$], exhibit behavior this is opposite to the trend observed when X = acceptor groups. As solvent polarity increases, the λ_{em} for these molecules shows a hypsochromic shift (e.g., for **4f**, λ_{em} = 500 and 467 nm for toluene and acetonitrile, respectively), which is again attributable to charge in the molecule being transferred back to the donor in the excited state.

DFT Calculations and Electrochemistry

The ground state HOMO and LUMO distributions are shown in Figure 5 and Figure 6, respectively, for **2/4a**–**g** calculated by density functional theory at the B3LYP-6-31G* level. It can be seen that, generally, the localization for both series is on the DSB unit, although for series **2**, the HOMO is spread out onto the fluorenylene unit. As the X group increases in donor strength, the localization of the HOMO shifts more to the side of the DSB backbone to which the X group is attached and away from the second aryl ring of the fluorenylene unit. On the other hand, the LUMO is localized on the side of the chromophore with the nitro

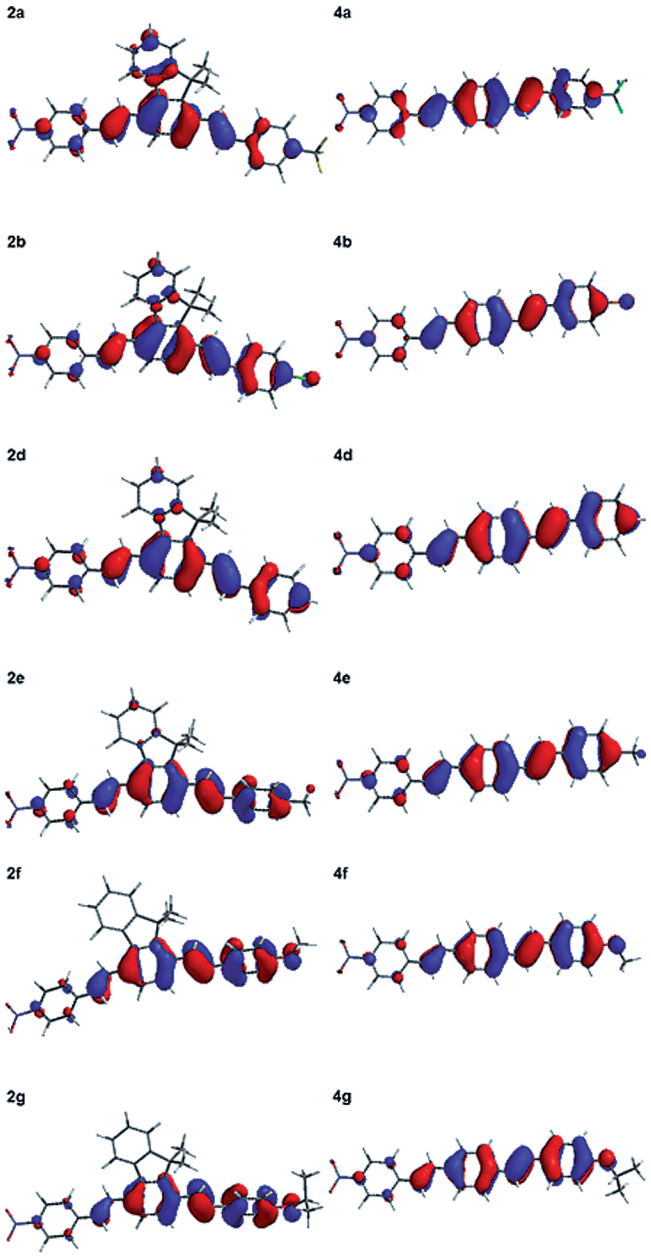


Figure 5. HOMO plots obtained by DFT calculations (B3LYP-6-31G*) for compounds **2a**–**g** (left) and **4a**–**g** (right). Hexyl groups for series **2** were truncated to methyl groups to simplify calculations.

group, which is explained by the fact that the areas of occupation by the LUMO should have a greater ability to gain electrons. As the nitro group is the most electron-withdrawing unit, these calculations are consistent.

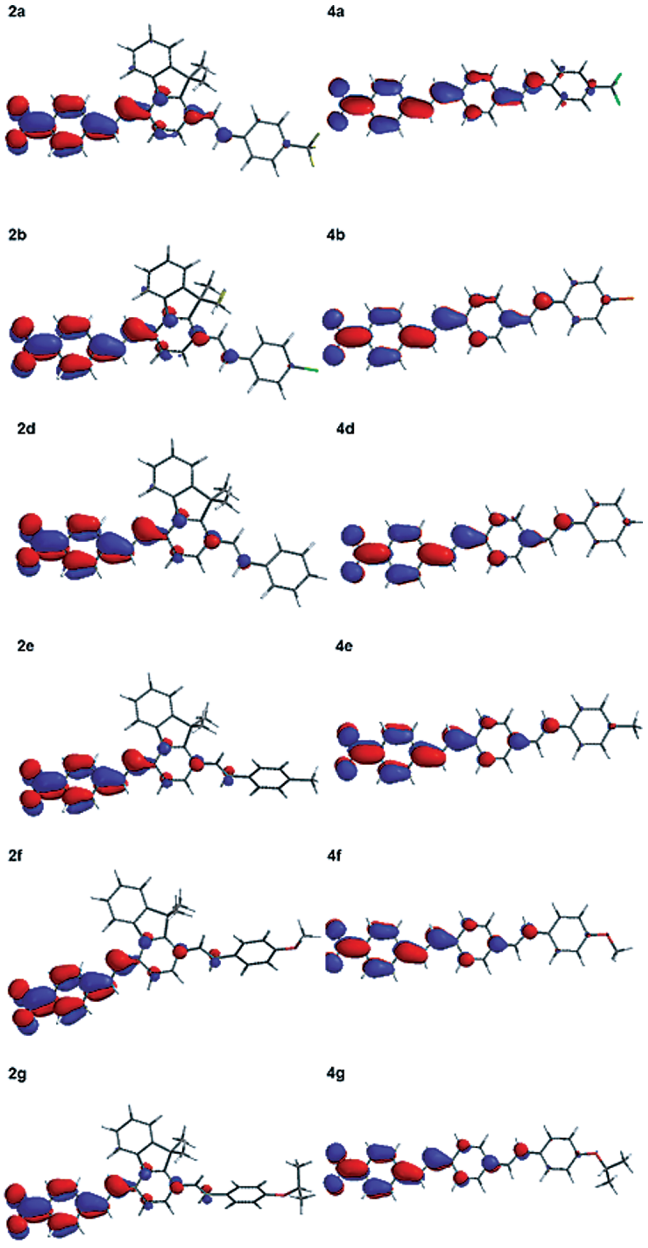


Figure 6. LUMO plots obtained by DFT calculations (B3LYP-6-31G*) for compounds **2a**–**g** (left) and **4a**–**g** (right). Hexyl groups for series **2** were truncated to methyl groups to simplify calculations.

The calculations are supported by electrochemical analyses (Table 4). Cyclic voltammetry of **2** and **4** revealed highly conserved redox processes among all functional groups for both scaffolds. All variants of **2** and **4** exhibited quasireversible first reduction peaks that fell within a narrow range (–1.63 to –1.68 V), and all but **2a**, **2c** and **4c** had quasireversible second reduction peaks ranging from –2.10 to –2.23 V. The reduction onset potentials for **2** and **4** show similar behavior, where the first onset spans 70 mV (–1.54 to –1.61 V) and the second 80 mV (–1.98 to –2.16 V). The similar reduction potentials for both reduction processes are consistent with a LUMO that is essentially equivalent to a 4-nitrostyrylbenzene unit for all members of a series.

Table 4. Electrochemical properties of **2**, **4**, and **5**.

	$E_{1/2}$ [V]	E_{onset} [V]		$E_{1/2}$ [V]	E_{onset} [V]
2a X = CF_3	–1.65, irrev.	–1.58, –2.11	**4a**	–1.61, –2.10	–1.54, –1.98
2b X = Cl	–1.66, –2.15	–1.57, –2.10	**4b**	–1.61, –2.17	–1.54, –2.09
2c X = I	–1.65, irrev.	–1.58, –2.10	**4c**	–1.67, irrev.	–1.60, –2.16
2d X = H	–1.68, –2.20	–1.61, –2.03	**4d**	–1.64, –2.23	–1.57, –2.07
2e X = Me	–1.63, –2.20	–1.59, –2.15	**4e**	–1.63, –2.18	–1.54, –2.08
2f X = OMe	–1.63, –2.14	–1.54, –2.03	**4f**	–	–
2g X = O*i*Pr	–1.66, –2.21	–1.58, –2.09	**4g**	–	–

Conclusions

We have synthesized a new series of molecules incorporating a 1,4-fluorenylene scaffold with varying D–A character. Additionally, new DSBs were synthesized that were analogous to the fluorenylene molecules to study the effect on synthesis and properties resulting from the larger π-conjugated system and asymmetry of the 9,9-dihexyl-1,4-fluorenylene unit in series **2** compared with the 1,4-phenylene unit in **4**. It was found that both the DSB derivatives and analogous fluorenylene molecules exhibit solvatochromic behavior in the excited state. Further investigation of these molecules including electrochemical characterization and experiments to examine NLO behavior could show other interesting features of the 1,4-fluorenelyne scaffold molecules, making them useful for further applications.

Experimental Section

Reagents and General Methods: Reagents were obtained from Aldrich Chemical Co., TCI America, Acros or Alfa Aesar and used without further purification. Air-sensitive reactions were carried out in solvents purified by passage through alumina columns under a dry N_2 atmosphere employing an MBraun solvent purification system. Air-sensitive operations were done in an MBraun dry box or by using standard Schlenk line techniques under N_2. NMR spectra were obtained with a Jeol 300 spectrometer operating at 300 MHz for protons, 75 MHz for carbon, and 121.47 MHz for phosphorus. All spectra were collected at 25 °C and referenced to residual solvent signals. Coupling constants are reported in Hz.

Electrochemistry: All electrochemical experiments were performed with a CH Instruments Electrochemical Workstation 660D using an airtight three-electrode cell under a nitrogen atmosphere. A gold working electrode and tungsten wire counter electrode were used, along with a silver wire quasi-reference electrode. Measurements

were made using anhydrous CH_2Cl_2 with 0.1 M $[nBu_4N][PF_6]$ as supporting electrolyte. Ferrocene (Fc) was chosen as the internal standard. All reported potentials were collected with a 100 mV s^{-1} scan rate and were referenced to Fc by shifting $[Fc]^{+/0}$ to 0 V.

General Spectroscopic Methods: Photoluminescence (PL) spectra were acquired with a Varian Cary Eclipse fluorescence spectrophotometer. Absorption spectra were recorded with a Varian Cary 50 Bio absorption spectrophotometer. Samples for all absorbance and PL spectra were prepared in Spectrosil quartz cuvettes having a path length of 1 cm. The solvents for all optical measurements were purified and made anhydrous/anaerobic by passage through alumina columns under a N_2 atmosphere employing an MBraun solvent purification system. Photoluminescence quantum yields were measured relative to quinine bisulfate (Φ = 0.564) in 1 N aqueous sulfuric acid.[39]

Synthesis of M2: To a stirring solution of **M1** (10.0 g, 37.9 mmol) in toluene (100 mL), triphenylphosphine (8.95 g, 34.1 mmol) was added. The reaction mixture was heated to reflux under nitrogen for 1 h and then cooled to room temperature. A precipitate formed during the reaction, which was collected by vacuum filtration. The solid was then washed with toluene (50 mL), followed by diethyl ether (100 mL). The resulting white solid was used without any further purification. Spectroscopic properties match those previously reported.

Synthesis of M3: To triphenyl(4-bromomethylbenzyl)phosphonium bromide (**M2**; 1.00 g, 2.24 mmol), triethylphosphite (1.86 g, 11.2 mmol) was added. The reaction mixture was heated to reflux at 110 °C under N_2 for 3 h. The excess triethylphosphite was then removed by vacuum distillation at 115 °C for 5 h. A white crystalline powder (1.03 g, 78.6%) was collected; m.p. 201–204 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.21 (t, J = 7.2 Hz, 6 H), 3.05 (d, J = 20.2 Hz, 2 H), 3.93–4.03 (m, 4 H), 7.06 (s, 4 H), 7.58–7.78 (m, 15 H) ppm. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ = 23.61, 26.36 ppm. $C_{30}H_{33}BrO_3P_2$ (583.44): calcd. C 61.76, H 5.70, N 0.00; found C 61.68, H 5.87, N 0.00.

Synthesis of M4: To a solution of **M3** (0.100 g, 0.171 mmol) in ethanol (15 mL), a solution of 4-nitrobenzaldehyde (0.0300 g, 0.198 mmol) in THF (2 mL) was added. The reaction mixture was placed under N_2 and stirred for 10 min. To this solution, potassium *tert*-butoxide (0.0192 g, 0.171 mmol) in ethanol (2 mL) was added. The colorless solution turned bright-yellow once the base was added. The reaction was stirred under N_2 at room temperature for 2.5 h, then H_2O (5 mL) was added to quench the base. The solvents were then removed by rotary evaporation. The crude product was further purified by preparative TLC using CH_2Cl_2 with 2% methanol as the eluent (R_f = 0.46). This afforded a yellow oil (0.0525 g, 81.6%) that was isolable as a mixture of *E* and *Z* isomers, which was observed to rapidly interconvert on exposure to light or heat. Due to the low stability of the product to isomerization, it was employed as a mixture for the preparation of compounds **4** without additional purification; m.p. 99–111 °C. HRMS: *m*/*z* calcd. for $C_{19}H_{22}NO_5P$ $[M]^+$ 375.1236; found 375.1232.

Synthesis of M5: Triphenylphosphine (0.475 g, 1.81 mmol) was added to **M4** (1.05 g, 2.01 mmol) in toluene (11 mL). The reaction mixture was stirred under nitrogen for 1 h and then heated to reflux for 1 h. After allowing the reaction mixture to cool, the solution was filtered through a fritted funnel. The collected solid was washed with toluene (30 mL), followed by Et_2O (75 mL). The solid was collected and dried, yielding a white powder (1.15 g, 73.0%); m.p. 202.8–205.8 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.18–0.47 (m, 4 H), 0.77 (t, J = 7 Hz, 6 H), 1.05–1.15 (m, 12 H), 1.93 (td, J = 4, 13 Hz, 2 H), 2.19 (td, J = 4, 13 Hz, 2 H), 4.66 (s, 2 H), 6.02 (d, J = 14.4 Hz, 2 H), 6.90 (t, J = 6.5 Hz, 1 H), 7.06–7.34 (m, signal overlaps solvent signal; spectrum indicates 5 H), 7.53–7.86 (m, 15 H) ppm. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ = 20.97 ppm. HRMS: *m*/*z* calcd. for $C_{45}H_{51}BrP$ $[M]^+$ 701.2912; found 701.2912.

Synthesis of M6: To **M5** (0.300 g, 0.383 mmol), triethylphosphite (0.284 g, 1.71 mmol) was added. The reaction was heated to reflux under nitrogen for 3 h at 110 °C, then the excess triethylphosphite was removed by vacuum distillation to give an off-white crystalline solid (0.304 g, 94.4%); m.p. 58–69 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.19–0.51 (m, 3 H), 0.71–0.80 (m, 6 H), 1.05 (br. s, 14 H), 1.24–1.39 (m, 5 H), 1.87–2.20 (m, 4 H), 3.34 (d, J = 22 Hz, 2 H), 4.02–4.13 (m, 4 H), 5.92 (d, J = 15 Hz, 2 H), 6.86–6.91 (m, 1 H), 7.08–7.20 (m, 2 H), 7.28–7.34 (m, partially overlaps solvent signal; spectrum indicates 3 H), 7.52–7.71 (m, 9 H), 7.77–7.84 (m, 6 H) ppm. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ = 20.82, 27.18 ppm. HRMS: *m*/*z* calcd. for $C_{49}H_{61}O_3P_2$ $[M]^+$ 759.4096; found 759.4084.

Synthesis of M7: In a dry box, **M6** (0.810, 0.964 mmol) and 4-nitrobenzaldehyde (0.0541 g, 0.964 mmol) were dissolved in THF (125 mL) in a pressure flask. A solution of potassium *tert*-butoxide (0.180 g, 0.964 mmol) in THF (20 mL) was added dropwise to the reaction mixture. The reaction mixture turned a turbid gold-green upon complete addition of base. The reaction mixture was sealed with a Teflon® screw cap and removed from the dry box. The solution was stirred at room temperature for 2 h, then heated in an oil bath at 65 °C for 17 h. The reaction mixture was then cooled to room temperature and methanol (50 mL) was added to the mixture. The solvents were removed under reduced pressure, yielding a yellow oil. The crude product was further purified by column chromatography on silica, eluting with CH_2Cl_2 with 1% methanol (R_f = 0.46). It was found that to get full separation from other impurities, a column with a diameter of 2 inches and 8 inches of silica were needed. Other columns tried did not provide sufficient separation of impurities from target compound. After column chromatography, the compound was collected as a bright-yellow oil (0.412 g, 67.7%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.37–0.58 (m, 4 H), 0.71–0.79 (m, 6 H), 1.01–1.14 (m, 12 H), 1.25–1.32 (m, 6 H), 1.99–2.28 (m, 4 H), 3.39–3.48 (m, 2 H), 4.00–4.19 (m, 4 H), 6.84 (d, J = 12 Hz, 1 H), 6.94 (d, J = 7.9 Hz, 1 H), 7.11 (d, J = 16 Hz, 1 H), 7.18 (d, J = 8.9 Hz, 2 H), 7.29–7.36 (m, 5 H), 7.43–7.48 (m, 2 H), 7.60–7.64 (m, 1 H),7.70–7.77 (m, 2 H), 7.87–7.92 (m, 2 H), 8.04 (d, J = 18 Hz, 1 H), 8.28 (d, J = 8.9 Hz, 2 H) ppm. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ = 27.72 ppm. HRMS: *m*/*z* calcd. for $C_{38}H_{50}NO_5P$ $[M]^+$ 631.3426; found 631.3421.

General Method for Synthesis of Asymmetric Fluorenylene Molecules: For each molecule, **1** and the corresponding aldehyde were combined in anhydrous THF in a dry box. To this reaction mixture, *n*-butyllithium was added and the reaction was stirred under nitrogen for several hours. Purification techniques involved preparative TLC or passing through silica. Due to the light-sensitivity of the series **2** molecules that leads to rapid interconversion between *E* and *Z* isomers, ^{13}C NMR spectroscopic data is not reported; for ^{1}H NMR analysis, integrations in the aromatic region are not always reported as whole integers, because it was difficult to differentiate peaks resulting from either *E* or *Z* isomers.

Synthesis of 2a (X = CF_3): In a dry box, to a solution of **1** (0.100 g, 0.158 mmol) in THF (10 mL), 4-(trifluoromethyl)benzaldehyde (0.0300 g, 0.174 mmol) was added in a pressure tube. The reaction mixture was stirred for 5 min, then *n*-butyllithium (2.5 M in hexanes, 0.070 mL, 0.174 mmol) was added. The solution became dark-red when the *n*-butyllithium was added dropwise. The reaction mixture was capped with a Teflon® screw cap and stirred in the dry box for 23 h. H_2O (15 mL) was added, the compound was

extracted with CH_2Cl_2 (30 mL), and the organic layer was washed with H_2O (3 × 50 mL). The solvents were removed by rotary evaporation and the compound was further purified by passage through a silica plug (hexanes/CH_2Cl_2, 1:1). This afforded **2a** (0.023 g, 22%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.41–0.76 (m, 9 H), 0.89–1.06 (m, 13 H), 2.08 (td, J = 4.4, 12 Hz, 2 H), 2.32 (td, J = 4.5, 12 Hz, 2 H), 7.06–7.19 (m, 1.75 H), 7.33–7.48 (m, 4.5 H), 7.54–7.75 (m, 10.75 H), 7.80–7.83 (m, 1.25 H), 7.94 (d, J = 8.6 Hz, 1.38 H), 8.10 (d, J = 16.1 Hz, 0.8 H), 8.30 (d, J = 8.6 Hz, 1.75 H) ppm. HRMS: m/z calcd. for $C_{42}H_{44}NO_2F_3$ $[M]^+$ 651.3324; found 651.3316.

Synthesis of 2b (X = Cl): In a pressure tube in a dry box, **1** (0.100 g, 0.158 mmol) and 4-chlorobenzaldehyde (0.0240 g, 0.174 mmol) were combined in THF (20 mL), and *n*-butyllithium (2.5 M in hexanes, 0.070 mL, 0.174 mmol) was added. The solution turned from yellow to dark-brown/black when the base was added. The reaction mixture was sealed with a Teflon® screw cap and stirred under nitrogen for 72 h. H_2O (15 mL) was then added to the solution, which appeared to turn cloudy, but no precipitate formed, so the compound was extracted with CH_2Cl_2 (50 mL) and washed with H_2O (3 × 50 mL). The organic layer was collected and all solvents were removed by rotary evaporation. The compound was further purified by dissolving in a solution of CH_2Cl_2/hexanes (1:1) and passing through silica. The silica was washed several times with this eluent, which was then collected. After removing the solvents by rotary evaporation, **2b** (0.021 g, 22%) was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.40–0.76 (m, 9 H), 0.98–1.08 (m, 13 H), 2.07 (td, J = 4.4, 12 Hz, 2 H), 2.32 (td, J = 4.4, 12 Hz, 2 H), 6.84–6.93 (m, 0.15 H), 6.98–7.03 (m, 0.90 H), 7.15 (d, J = 16.1 Hz, 0.60 H), 7.23–7.49 (m, 11.8 H), 7.54–7.66 (m, 1.9 H), 7.73 (d, J = 8.6 Hz, 1.1 H), 7.79–7.82 (m, 0.54 H), 7.91–7.95 (m, 0.41 H), 8.09 (d, J = 16.1 Hz, 0.63 H), 8.29 (d, J = 8.6 Hz, 1.3 H) ppm. HRMS: m/z calcd. for $C_{41}H_{44}NO_2Cl$ $[M]^+$ 617.3061; found 617.3057.

Synthesis of 2c (X = I): In a dry box, **1** (0.100 g, 0.158 mmol) and 4-iodobenzaldehyde (0.0400 g, 0.174 mmol) were combined in THF (20 mL) in a pressure tube, and *n*-butyllithium (2.5 M in hexanes, 0.070 mL, 0.174 mmol) was added. The solution turned from yellow to golden-brown when the base was added. The reaction mixture was sealed with a Teflon® screw cap and stirred under nitrogen for 72 h. H_2O (15 mL) was added and the compound was extracted with CH_2Cl_2 (60 mL) and washed with H_2O (3 × 50 mL). The organic layer was collected and all solvents were removed by rotary evaporation. The compound was further purified by dissolving in a solution of CH_2Cl_2/hexanes (1:1) and passing through silica. The silica was washed several times with this solution mixture. After removing the solvents by rotary evaporation, **2c** (0.027 g, 24%) was obtained as a viscous oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.39–0.59 (m, 3 H), 0.67–0.74 (m, 6 H), 0.89–1.08 (m, 13 H), 2.06 (td, J = 4.4, 12 Hz, 2 H), 2.31 (td, J = 4.4, 12 Hz, 2 H), 6.60 (d, J = 11.6 Hz, 0.06 H), 6.84–6.91 (m, 0.15 H), 6.95–7.00 (m, 0.1 H), 7.15 (d, J = 16.1 Hz, 0.63 H), 7.23–7.42 (m, 9.6 H), 7.48–7.62 (m, 1.5 H), 7.66 (d, J = 16.1 Hz, 0.75 H), 7.72–7.81 (m, 3.8 H), 7.91–7.95 (m, 0.25 H), 8.09 (d, J = 16.1 Hz, 0.75 H), 8.29 (d, J = 8.9 Hz, 1.5 H) ppm. HRMS: m/z calcd. for $C_{41}H_{44}NO_2I$ $[M]^+$ 709.2417; found 709.2409.

Synthesis of 2d (X = H): In a pressure tube, **1** (0.100 g, 0.158 mmol) and benzaldehyde (0.0185 g, 0.174 mmol) were combined in THF (15 mL) in a dry box, and *n*-butyllithium (2.5 M in hexanes, 0.070 mL, 0.174 mmol) was added (the reaction mixture turned dark-brown). The pressure tube was sealed with a Teflon® screw cap and stirred for 24 h. H_2O (5 mL) was added to the reaction mixture and all solvents were removed by rotary evaporation. The resulting oil was reddish-brown. The compound was further purified by preparative TLC, using CH_2Cl_2 as eluent (R_f = 0.92), affording **2d** (0.033 g, 35%) as a reddish-brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.39–0.74 (m, 9 H), 0.80–1.08 (m, 13 H), 2.07 (td, J = 4.4, 12 Hz, 2 H), 2.28–2.41 (m, 2 H), 6.54 (d, J = 12 Hz, 0.3 H), 6.62 (d, J = 12 Hz, 0.3 H), 6.78–6.82 (m, 0.2 H), 6.86 (d, J = 12 Hz, 0.1 H), 6.95–7.21 (m, 1.9 H), 7.24–7.96 (m, 13.7 H), 8.00–8.03 (m, 0.2 H), 8.11 (d, J = 16.1 Hz, 0.3 H), 8.22 (d, J = 8.9 Hz, 0.1 H), 8.29 (d, J = 8.9 Hz, 0.8 H), 8.34–8.43 (m, 0.2) ppm. HRMS: m/z calcd. for $C_{41}H_{45}NO_2$ $[M]^+$ 583.3450; found 583.3443.

Synthesis of 2e (X = CH_3): In a dry box, **1** (0.100 g, 0.158 mmol) and *p*-tolualdehyde (0.0210 g, 0.174 mmol) were combined in THF (20 mL) in a pressure tube, and *n*-butyllithium (2.5 M in hexanes, 0.070 mL, 0.174 mmol) was added (the solution became black). The reaction mixture was sealed with a Teflon® screw cap and stirred under N_2 for 71 h. H_2O (10 mL) was added to the solution and the compound was extracted with CH_2Cl_2 (2 × 50 mL). The organic layer was washed with H_2O (2 × 100 mL), the organic layer was collected, and all solvents were removed by rotary evaporation. The compound was further purified by dissolving in a solution of CH_2Cl_2/hexanes (1:1) and passing through silica. The solution was collected and solvents were removed by rotary evaporation to yield **2e** (0.034 g, 36%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.40–0.75 (m, 10 H), 0.89–1.09 (m, 12 H), 2.07 (td, J = 3.8, 12 Hz, 2 H), 2.28–2.40 (m, 5 H), 6.85 (d, J = 12 Hz, 0.15 H), 6.98–7.10 (m, 0.6 H), 7.15 (d, J = 16.1 Hz, 0.6 H), 7.22–7.68 (m, 9.8 H), 7.73 (d, J = 8.9 Hz, 1.2 H), 7.78–7.82 (m, 0.6 H), 7.91–7.95 (m, 0.5 H), 8.11 (d, J = 15.8 Hz, 0.6 H), 8.29 (d, J = 8.6 Hz, 1.4 H) ppm. HRMS: m/z calcd. for $C_{42}H_{47}NO_2$ $[M]^+$ 597.3607; found 597.3600.

Synthesis of 2f (X = OCH_3): In a dry box, **1** (0.132 g, 0.210 mmol) was dissolved in anhydrous THF (25 mL) and 4-methoxybenzaldehyde (0.0314 g, 0.231 mmol) was added. The reaction mixture was stirred for several minutes, then *n*-butyllithium (2.5 M in hexanes, 0.092 mL) was slowly added dropwise. The golden-yellow solution slowly became dark-brown/black as the base was added. The reaction mixture was stirred at room temperature for 5 days, then removed from the dry box. H_2O (30 mL) was added and the mixture became orange and cloudy. The organic products were extracted with CH_2Cl_2 (75 mL) and the organic layer was washed with H_2O (3 × 100 mL). The organic layers were collected and solvent was removed by rotary evaporation. The resulting reddish-brown oil was washed with methanol (ca. 5 mL), which helped to remove some of the excess aldehyde. The oil was then dissolved in minimal CH_2Cl_2 and added dropwise to methanol. The product stuck to the sides of the glass of an Erlenmeyer flask, so the methanol was decanted away. The oil was dissolved in CH_2Cl_2 and recollected. The methanol wash was also collected and the solvent was removed by rotary evaporation. The resulting oil was then washed again with methanol (3 × 10 mL) and was then recollected. It was determined by NMR spectroscopy that both collected oils were the desired product. All product was collected to yield **2f** (0.0548 g, 42.6%) as a reddish brown sticky oil; the compound was isolated as a mixture of *E* and *Z* isomers that interconvert rapidly upon exposure to light. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.95–7.00 (m, 4 H), 7.09 (d, J = 18.8 Hz, 1 H), 7.29–7.58 (m, 13.25 H), 7.72 (d, J = 8.9 Hz, 2.50 H), 7.80–7.83 (m, 0.5 H), 8.11 (d, J = 16.1 Hz, 0.5 H), 8.29 (d, J = 8.6 Hz, 2.75 H) ppm. Due to the presence of both *E* and Z isomers, NMR integrations in the aromatic region are not reported as whole integers relative to the alkyl-region peaks. HRMS: m/z calcd. for $C_{42}H_{47}NO_3$ $[M]^+$ 613.3556; found 613.3563.

Synthesis of 2g [Y = $OCH(CH_3)_2$]: In a pressure tube, **1** (0.100 g, 0.158 mmol) and 4-isopropoxybenzaldehyde (0.0286 g, 0.174 mmol)

were combined in THF (15 mL) in a dry box. To this solution, *n*-butyllithium (2.5 M in hexanes, 0.070 mL, 0.174 mmol) was added and the reaction mixture turned turbid green-brown. The pressure tube was sealed with a Teflon® screw cap and stirred for 24 h. H_2O (15 mL) was then added to the reaction mixture and all solvents were removed by rotary evaporation. The compound was further purified by preparative TLC, using CH_2Cl_2 as the eluent (R_f = 0.92), affording **2g** (0.035 g, 35%) as a yellow-brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.39–0.77 (m, 9 H), 0.85–1.08 (m, 13 H), 1.37 (d, J = 5.9 Hz, 6 H), 2.06 (td, J = 4.4, 12 Hz, 2 H), 2.37 (td, J = 4.4, 12 Hz, 2 H), 4.57–4.65 (m. 1 H), 6.92–7.04 (m, 3.5 H), 7.14 (d, J = 15.8 Hz, 1 H), 7.35–7.42 (m, 3.5 H), 7.47–7.58 (m, 6 H), 7.79–7.82 (m, 1 H), 8.11 (d, J = 16.1 Hz, 1 H), 8.29 (d, J = 8.9 Hz, 2 H) ppm. HRMS: *m*/*z* calcd. for $C_{44}H_{51}NO_3$ $[M]^+$ 641.3869; found 641.3860.

General Method for Synthesis of Asymmetric Phenylene Molecules: For each molecule, **3** was dissolved in ethanol and stirred under nitrogen. To this solution, the corresponding benzaldehyde was added, then KO*t*Bu was added and the reaction mixture was stirred over a period of several hours. The reaction was quenched with H_2O. Workup involved collection by filtration or extraction with $CHCl_3$. The *E*,*E*-isomers of the molecules were obtained by heating to reflux in toluene with a catalytic amount of iodine, then collecting by filtration or extraction. Compounds **4d**,[35] **4e**,[40] **4f**,[41] and **4h**[41] have been reported previously and their preparative procedures are not repeated here.

Synthesis of 4a (X = CF_3): To a solution of **3** (0.100 g, 0.172 mmol) in ethanol (15 mL), 4-(trifluoromethyl)benzaldehyde (0.0330 g, 0.190 mmol) in THF (3 mL) was added. The mixture was stirred for 5 min under N_2, then KO*t*Bu (0.039 g, 0.345 mmol) was added. When the base was added, the bright-yellow solution became amber-brown. The reaction mixture was then stirred under N_2 for 21.5 h, then H_2O (20 mL) was added. Extraction with CH_2Cl_2 (2× 50 mL) followed by vacuum evaporation of solvents afforded the crude product, which was a mixture of *E* and *Z* isomers, as indicated by NMR spectroscopy. The crude material was dissolved in toluene (20 mL) and a catalytic amount of iodine was added. The reaction was heated to reflux under N_2 for 4 h. After cooling to room temperature, aq. Na_2SO_3 (10 mL) was added to reduce the iodine. The product was extracted with $CHCl_3$ and the organic layers were washed with H_2O (3× 50 mL). The organic layer was collected and solvents were removed by rotary evaporation, yielding **4a** (0.056 g, 82%) as a yellow solid; m.p. 196–199 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.15–7.20 (m, 2 H), 7.23–7.31 (m, includes overlap from solvent signal, structure implies 3 H), 7.43–7.49 (m, 2 H), 7.52–7.57 (m, 3 H), 7.62–7.70 (m, 5 H), 8.23 (d, J = 8.6 Hz, 1 H) ppm. ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 124.13, 125.65, 125.78, 126.52, 126.75, 126.98, 127.31, 127.52, 128.50, 128.66, 130.51, 131.94, 132.07, 132.60, 136.29, 137.19, 143.86 ppm. HRMS: *m*/*z* calcd. for $C_{23}H_{16}NO_2F_3$ $[M]^+$ 395.1133; found 395.1126.

Synthesis of 4b (Y = Cl): To a solution of **3** (0.150 g, 0.258 mmol) in ethanol (20 mL), 4-chlorobenzaldehyde (0.0406 g, 0.289 mmol) in THF (4 mL) was added, followed by potassium *tert*-butoxide (0.0580 g, 0.517 mmol). The solution turned green-brown when addition of the base was complete. The reaction mixture was stirred under N_2 for 17.5 h, then the solution was removed from the dry box and H_2O (20 mL) was added. The mixture appeared to be a fine suspension, so it was centrifuged, then the solvents were decanted away from the fine solid. The solid was then dissolved in toluene (10 mL) and a catalytic amount of iodine was added. The reaction was heated to reflux under nitrogen for 16.5 h. After cooling to room temperature, aq. Na_2SO_3 (50 mL) was added to the mixture. After shaking vigorously, the red-brown solution turned pale-yellow. The compound was extracted with $CHCl_3$ and washed with H_2O (3× 50 mL). The organic layers were collected and the solvent was removed under reduced pressure to yield **4b** (0.066 g, 70%) as a yellow solid; m.p. 241–244 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.09–7.26 (m, includes overlap from solvent signal, structure implies 4 H), 7.30–7.47 (m, 4 H), 7.54 (s, 4 H), 7.64 (d, J = 8.9 Hz, 2 H), 8.23 (d, J = 8.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 124.30, 126.30, 126.94, 127.13, 127.55, 127.83, 128.14, 128.62, 129.03, 132.86, 133.55, 135.70, 135.77, 137.66, 143.91, 146.83 ppm. HRMS: *m*/*z* calcd. for $C_{22}H_{17}NO_2Cl$ $[M + 1]^+$ 362.0948; found 362.0952.

Synthesis of 4c (Y = I): To a solution of **3** (0.100 g, 0.172 mmol) in ethanol (15 mL), 4-iodobenzaldehyde (0.0440 g, 0.190 mmol) in THF (3 mL) was added. The mixture was stirred for 5 min under N_2 and then KO*t*Bu (0.039 g, 0.345 mmol) was added. After adding the base, the reaction mixture turned a murky brown. This reaction mixture was then stirred under N_2 for 21.5 h, then H_2O (20 mL) was added and a precipitate formed. The precipitate was collected by vacuum filtration and washed with additional H_2O (20 mL). The crude material was dissolved in toluene (20 mL) and a catalytic amount of iodine was added. The reaction was heated to reflux under N_2 for 4 h. After cooling to room temperature, a precipitate formed that was collected by vacuum filtration. This afforded the pure compound (0.051 g, 65%) as a yellow solid; m.p. 314–317 °C. ^{1}H NMR ([D_8]THF, 300 MHz): δ = 7.13–7.21 (m, 2 H), 7.26–7.34 (m, 3 H), 7.42 (d, J = 16.5 Hz, 1 H), 7.55–7.62 (m, 4 H), 7.68 (d, J = 8.6 Hz, 2 H), 7.76 (d, J = 8.9 Hz, 2 H), 8.20 (d, J = 8.6 Hz, 2 H) ppm. Due to poor solubility, reasonable ^{13}C NMR could not be obtained. HRMS: *m*/*z* calcd. for $C_{22}H_{16}NO_2I$ $[M]^+$ 453.0226; found 453.0220.

Synthesis of 4g [Y = $OCH(CH_3)_2$]: To a solution of **3** (0.100 g, 0.172 mmol) in ethanol (15 mL), 4-isopropoxybenzaldehyde (0.0312 g, 0.190 mmol) in THF (2 mL) was added. This reaction mixture was stirred and then KO*t*Bu (0.0390 g, 0.345 mmol) was added. When the base was added, the solution turned a cloudy brown-green. The reaction was stirred under N_2 for 6 h, then H_2O (15 mL) was added and a yellow precipitate formed in the flask. The solid was collected by vacuum filtration. To obtain all *E* isomer, the compound was then added to toluene with a catalytic amount of iodine. This reaction mixture was heated to reflux under N_2 for 15.5 h, and then it was cooled to room temperature. Once cool, the compound precipitated out of the toluene. The solid was again collected by vacuum filtration, yielding **4g** (0.026 g, 39%) as a yellow solid; m.p. 263–265 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.35 (d, J = 5.8 Hz, 6 H), 4.56–4.63 (m, 1 H), 6.89 (d, J = 8.6 Hz, 2 H), 6.97 (d, J = 16.1 Hz, 1 H), 7.09–7.17 (m, 2 H), 7.21–7.30 (m, includes overlap from solvent signal, structure implies 2 H), 7.45 (d, J = 8.6 Hz, 2 H), 7.49–7.56 (m, 3 H), 7.64 (d, J = 8.9 Hz, 2 H), 8.22 (d, J = 8.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 22.15, 70.03, 116.10, 124.29, 125.76, 125.82, 126.78, 126.88, 127.51, 127.97, 129.16, 129.71, 133.07, 135.04, 138.49, 144.06, 146.72, 157.96 ppm. HRMS: *m*/*z* calcd. for $C_{25}H_{23}NO_3$ $[M]^+$ 385.1678; found 385.162.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H, ^{31}P, and ^{13}C NMR spectra, NOE experiments, UV/Vis absorption spectra and photoluminescence spectra in all four solvents..

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