

# Synthesis, Morphology, and Optical Properties of Tetrahedral Oligo(phenylenevinylene) Materials

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**Abstract:** A novel topological strategy is described for designing amorphous molecular solids suitable for optoelectronic applications. In this approach, chromophores are attached to a tetrahedral point of convergence. Stilbenoid units were covalently linked to tetraphenylmethane, tetraphenyladamantane, or tetraphenylsilane cores using palladium catalyzed coupling methodology. Thus, reaction of  $E(C_6H_5X)_4$  ( $E = C$  and adamantane,  $X = I$ ;  $E = Si$ ,  $X = Br$ ) with styrene or 4,4'-*tert*-butylvinylstilbene under Heck coupling conditions yields the corresponding tetrakis(stilbenyl) ( $E(STB)_4$ ) and tetrakis(4-*tert*-butylstyrylstilbenyl) ( $E(BuSSB)_4$ ) compounds. Similarly, reaction of 1,1-diphenyl-2-(4-dihydroxyboronphenyl)ethene or 2-(4-pinacoloboronphenyl)-3,3-diphenylacrylonitrile with tetrakis(4-bromophenyl)methane using Suzuki coupling methodology gives tetrakis(4,4'-(2,2-diphenyl-vinyl)-1,1'-biphenyl)methane ( $C(DPVBi)_4$ ) or tetrakis(4,4'-(3,3-diphenylacrylonitrile)-1,1'-biphenyl)methane ( $C(DPAB)_4$ ), respectively, in good yields. Compounds with more extended conjugation can also be prepared. Thus, reaction of excess 1-(4'-*tert*-butylstyryl)-4-(4'-vinylstyryl)benzene with  $C(C_6H_4I)_4$  provides tetrakis(4-(4'-(4''-*tert*-butylstyryl)styryl)stilbenyl)methane ( $C(4R-^1Bu)_4$ ) in low yield (~20%). The more soluble analogue, tetrakis(4-(4'-(3'',5''-di-*tert*-butylstyryl)styryl)stilbenyl)methane ( $C(4R-2^1Bu)_4$ ) is prepared similarly using 1-(3',5'-di-*tert*-butylstyryl)-4-(4'-vinylstyryl)benzene and in better yield (~80%). Alkoxy substituents can also be used to increase solubility. Tetrakis(4-(2',5'-dioctyloxy-4'-styryl)styryl)stilbenyl)methane,  $C(4R-(OC_8H_{17})_2)_4$ , was prepared by treatment of  $C(C_6H_4I)_4$  with excess 2,5-dioctyloxy-1-styryl-4-(4'-vinylstyryl)benzene (yield ~ 73%). The simple stilbenyl-derivatives were found by DSC measurements and powder diffraction experiments to be crystalline compounds. Comparison of single-crystal X-ray diffraction data shows that  $C(STB)_4$  and  $Si(STB)_4$  form isomorphous crystals. The larger  $E(BuSSB)_4$ ,  $C(DPVBi)_4$ , and  $C(DPAB)_4$  compounds readily form amorphous glasses with elevated glass transition temperatures ( $T_g = 142$ – $190$  °C) in the absence of solvent. Extending the conjugation length of the arm leads to more stable glasses. For example, the glass transition temperature of  $C(4R-^1Bu)_4$  was measured at 230 °C. Solution phase optical spectroscopic data of  $E(BuSSB)_4$  ( $E = C$ , adamantane, and Si) are characteristic of the parent distyrylbenzene chromophore. Films, however, show broad and significantly red-shifted emission spectra. In contrast,  $C(DPVBi)_4$  gives absorption and emission spectra which are nearly identical between dilute solution phase samples and neat solid films. The emission of  $C(DPAB)_4$  is broad and structureless, reminiscent of exciplex or excimer emission. Films of the tetramers with longer arms ( $C(4R-^1Bu)_4$ ,  $C(4R-2^1Bu)_4$ , and  $C(4R-(OC_8H_{17})_2)_4$ ) show emission properties which are dependent on sample history. Annealing the sample at elevated temperature leads to red-shifted emission as a result of better interdigitation between the optically active fragments.

## Introduction

The notion that  $\pi$ -conjugated organic materials should possess interesting and useful electronic properties analogous to conventional inorganic semiconductors such as silicon or gallium arsenide is now well established in the scientific literature.<sup>1,2</sup> Many of these expectations have been realized with the practical demonstration of electronic devices in which conjugated organic materials are responsible for charge transport and/or light generation. Examples include polymer or small molecule light-emitting diodes (LEDs),<sup>3,4,5</sup> photovoltaic devices,<sup>6</sup> and field-effect transistors.<sup>7,8</sup> The prospect of realizing electrically driven organic lasers is also under intense investigation.<sup>9</sup> Much of the motivation for studying organic materials stems from the

potential to tailor desirable optoelectronic properties and processing characteristics by manipulation of the primary

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chemical structure. Strategies for raising or lowering the HOMO and LUMO levels include conjugation length control, as well as the introduction of electron donating or withdrawing groups to the parent chromophore.<sup>10</sup> Regulating the HOMO and LUMO energy levels permits fine-tuning of charge injection properties. In emissive devices, the HOMO/LUMO energy difference directly controls emission frequency. Organic materials also offer the opportunity to adjust optical properties by taking advantage of processes unique to the excited state, i.e., excimer and exciplex formation.<sup>11</sup>

It is generally appreciated that the morphology of organic films plays a fundamental role in defining the functional characteristics of the material. However, studies that clearly relate electroluminescence and charge transport properties with molecular morphology remain scarce. The tendency of many small molecules to spontaneously crystallize<sup>12</sup> presents a limitation for LED applications because crystal formation destroys film homogeneity and crystal boundaries raise the resistance of the sample, eventually leading to electric shorting.<sup>13</sup> The thermal stability of amorphous molecular solids as measured by the glass transition temperature has been shown to directly correlate with electroluminescence stability.<sup>14</sup> It has been argued that in some cases thermal cycling of an organic LED heterostructure device

above the glass transition temperature causes degradation resulting from disruption of the organic–organic interface rather than crystallization.<sup>15</sup> It is proposed on the basis of X-ray specular reflectivity data that large thermal expansion of one of the components associated with its glass transition causes catastrophic strain release at the hetero-interface between materials. For transistor applications, proper alignment of chromophores is desired because it enhances charge transport.<sup>16</sup> On the other hand, in the case of polymer LEDs, ordered regions result in strong interchain coupling and lower emission quantum yields.<sup>17</sup> Despite the obvious need to control the final arrangement of individual molecules in the bulk a priori, a detailed understanding of the relationship between chemical structure of a given organic material with the resulting morphology is still lacking.

Strategies to minimize interchain contacts in conjugated polymers have generally implemented the use of bulky side groups on the polymer backbone. These attachments improve solubility by limiting interchain contacts but are typically aliphatic in nature and therefore limit charge injection and migration across the solid sample.<sup>18</sup> In response to these limitations, considerable efforts have been dedicated to developing molecules of intermediate molecular weight that minimize the aliphatic content and at the same time resist crystallization. Molecular *shape* is an important parameter in these efforts. Some of the recent strategies rely on creating molecular shapes that, from an intuitive perspective, can be considered “awkward” to packing. Examples include “starburst”, dendritic, tetrahedral, and spiro shaped molecules, as shown below.<sup>19</sup>

Solution processing methods can be employed with these materials to yield kinetically trapped, amorphous solids that resist crystallization. Furthermore, these materials show elevated

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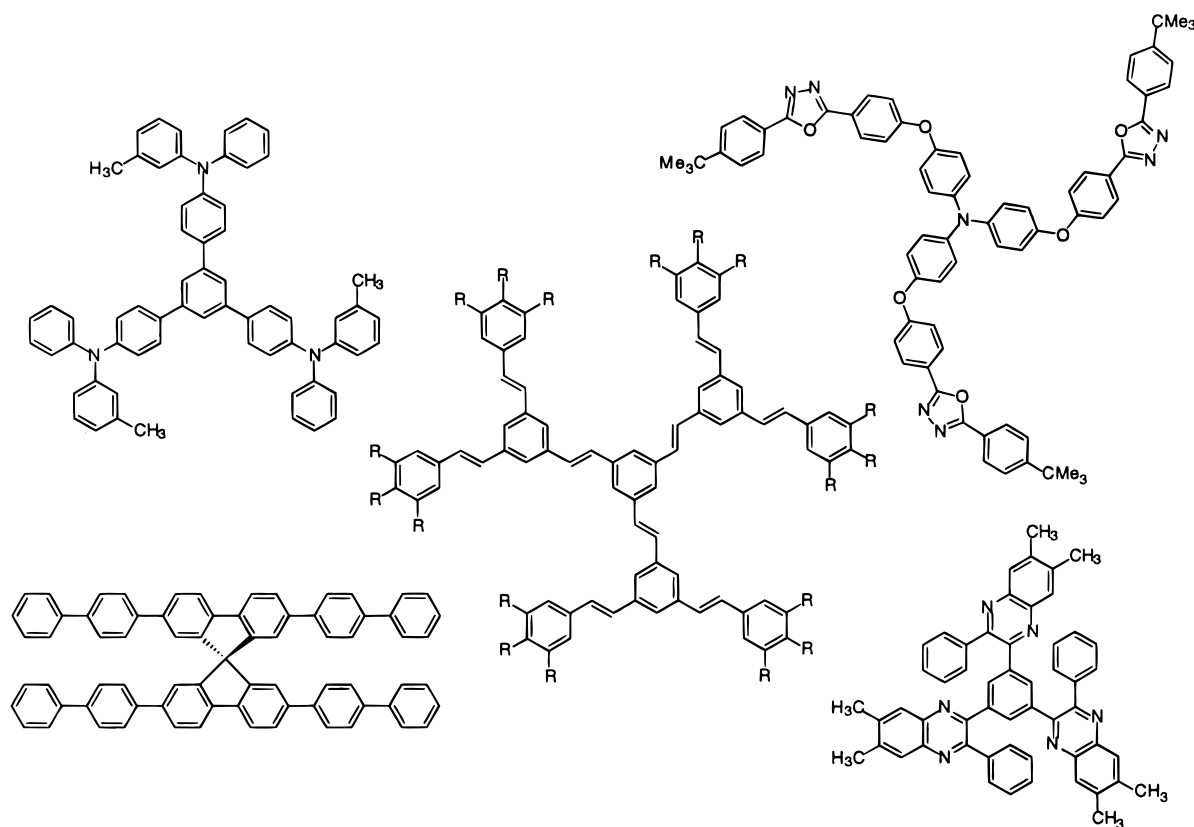
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Chart 1



glass transition temperatures despite their modest molecular dimensions. Molecules such as the ones above embody all of the beneficial properties of small molecules, namely, purity and well-defined structure, combined with the ability to cast thermally robust films directly from solution, a property characteristic of polymeric materials.

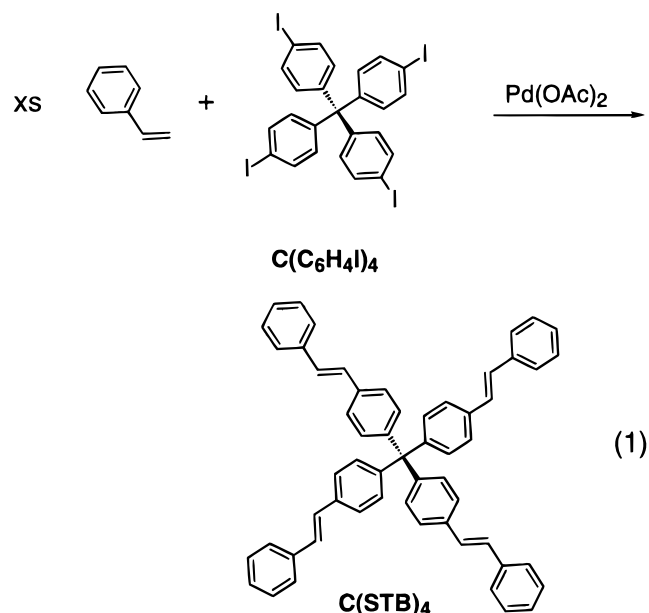
In this contribution we explore the generality of the tetrahedral approach for designing amorphous optoelectronic organic materials.<sup>20</sup> Complete synthetic details are presented for a range of tetrahedral junction sites and chromophore “arms” of different structure and conjugation length. We then compare the optical properties observed in fluid solution with those of the amorphous thin films. These data give insight into the extent of chromophore/chromophore interactions in the solid state and the potential utility of these materials in optoelectronic devices.

## Results and Discussion

**Synthesis of Carbon-Centered Tetramers.** The synthesis of the parent compound in this series, tetrastilbenylmethane ( $C(STB)_4$ ), is readily obtained by reaction of tetrakis(4-iodophenyl)methane ( $C(C_6H_4I)_4$ ) with excess styrene under palladium-mediated Heck coupling conditions in 86% yield (eq 1). Tetrakis(4-bromophenyl)methane consistently gave lower yields under analogous conditions.  $C(STB)_4$  has also recently been prepared in comparable yield via the corresponding tetrakis-diazonium salt using a modified Heck coupling procedure.<sup>21</sup>

A high yielding synthesis of tetrakis(4-*tert*-butylstyrylstilbenyl)methane ( $C(tBuSSB)_4$ ) from  $C(C_6H_4I)_4$  and 4,4'-*tert*-butylvinylstilbene proved slightly more difficult. Because four independent coupling reactions must be accomplished using

the less active 4,4'-*tert*-butylvinylstilbene, an efficient coupling methodology is important. Two procedures were identified as



suitable. We initially reported the use of Jeffery's phosphine-free phase transfer catalyst system<sup>22</sup> to obtain  $C(tBuSSB)_4$  in approximately 30% yield (eq 2).

Although the isolated product is obtained in good purity, the low yield prompted us to consider other protocols. In part, we attribute the low yield in the previous reaction to the low solubility of partially coupled intermediates and to gradual

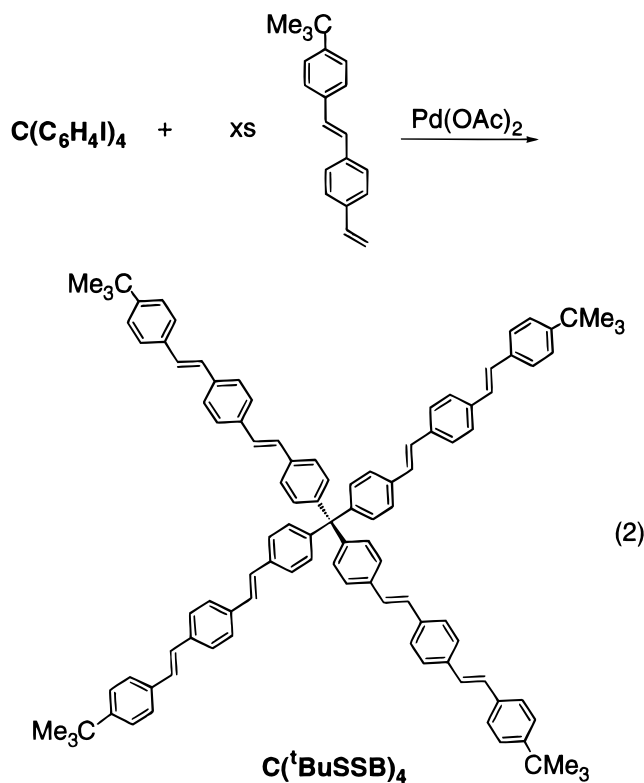
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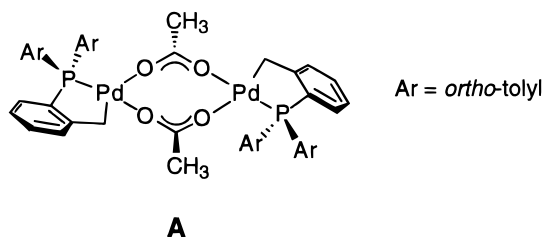
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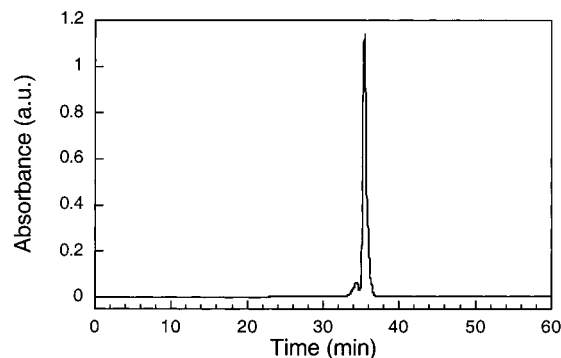
catalyst deactivation over the 3 days of reaction. To address this problem, the thermally robust catalyst **A**<sup>23</sup> was utilized at elevated temperatures (140 °C); conditions presumed to favor a more homogeneous reaction mixture.



Although reactions catalyzed by **A** seem to progress more slowly compared to Jeffery conditions, they may be carried out for up to 3–4 days without significant degradation of the catalyst. The improved longevity of catalyst **A** ultimately results in a modest improvement in yield to about 50%.

Isolated **C(<sup>t</sup>BuSSB)<sub>4</sub>** is obtained as an off-white powder that has been characterized using NMR spectroscopy, fast atom bombardment mass spectroscopy (FABMS), size exclusion chromatography (SEC), and elemental analysis. As detailed in the Experimental Section, the <sup>1</sup>H NMR spectrum (aromatic region) reveals three different AA'BB' patterns assigned to the 1,4-substituted phenylene rings, as well as two different AB patterns resulting from the *trans*-vinylic linking groups. The parent ion pattern expected for **C(<sup>t</sup>BuSSB)<sub>4</sub>** (C<sub>105</sub>H<sub>100</sub>) is centered at 1362 amu when analyzed by FABMS. Prominent daughter peaks at 1101 and 1024 amu correspond to loss of 4,4'-vinyl-*tert*-butylstilbene and 4-*tert*-butyldistyrylbenzene, respectively. The most abundant molecular ion is observed at 763 amu and results from loss of both of 4,4'-vinyl-*tert*-butylstilbene and 4-*tert*-butyldistyrylbenzene from the parent ion. Routine measure of purity can be established by SEC

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**Figure 1.** SEC trace of **C(<sup>t</sup>BuSSB)<sub>4</sub>**.

analysis because of the significant difference in hydrodynamic volume between the desired tetramer and partially coupled products. SEC analysis of **C(<sup>t</sup>BuSSB)<sub>4</sub>**, eluting with chloroform, reveals two peaks near 35 min elution time in a 5:95 ratio (Figure 1). The two peaks give identical absorption spectra by use of an in-line photodiode array detector. We assign the minor fraction to the tetramer containing one *cis*-vinylic linkage. The *cis*-vinylic stereoisomer is expected to increase the hydrodynamic by forcing the three other distyrylbenzene arms to spread out due to increased steric crowding. We can rule out incompletely coupled products because these should occupy less molar volume than **C(<sup>t</sup>BuSSB)<sub>4</sub>** and should therefore elute at longer retention times. Furthermore, elemental analysis for the combined fractions is consistent with the C<sub>105</sub>H<sub>100</sub> formulation. The small part of the product containing a *cis*-vinyl linkage affects the morphology of the sample, as will be described below.

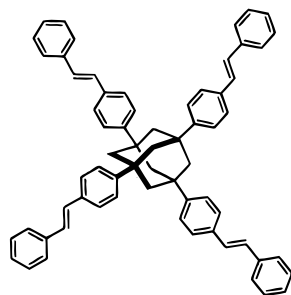
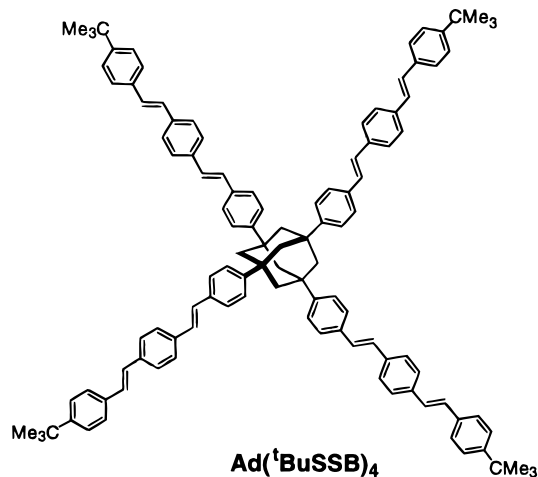
**Adamantane and Silane Cores.** In addition to the tetraphenylmethane core, we chose to study tetrahedral shaped complexes linked by tetraphenyladamantane and tetraphenylsilane cores. These specific fragments were chosen because they are readily available using literature procedures, they are easily functionalized, and they maintain a rigid tetrahedral relationship between the radiating groups. Furthermore, comparison of the adamantane, methane, and silane cores allows one to probe the effect of core volume on the morphological properties.

Reaction of tetrakis(4-iodophenyl)adamantane (**Ad(C<sub>6</sub>H<sub>4</sub>I)<sub>4</sub>**)<sup>24</sup> with excess styrene under Heck conditions similar to eq 1 affords tetra<sup>t</sup>stilbenyladamantane (**Ad(STB)<sub>4</sub>**) in approximately 25% yield. The optimized reaction conditions described for the tetraphenylmethane core are transferable to the other cores so that discussion of the experimental procedures will be kept to a minimum for the new cores. Purification by precipitation of a hot benzene solution into methanol provides **Ad(STB)<sub>4</sub>** as a white powder. Palladium catalyzed coupling of **Ad(C<sub>6</sub>H<sub>4</sub>I)<sub>4</sub>** with excess 4,4'-*tert*-butylvinylstilbene gives tetrakis(4-*tert*-butylstyrylstilbenyl)adamantane (**Ad(<sup>t</sup>BuSSB)<sub>4</sub>**). In this case we find little difference in final yield between the phase transfer conditions (28%) and the use of Hermann's catalyst, **A** (31%).

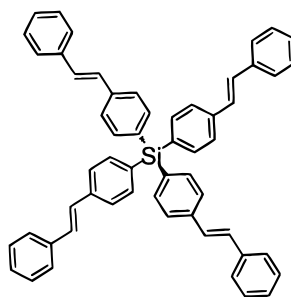
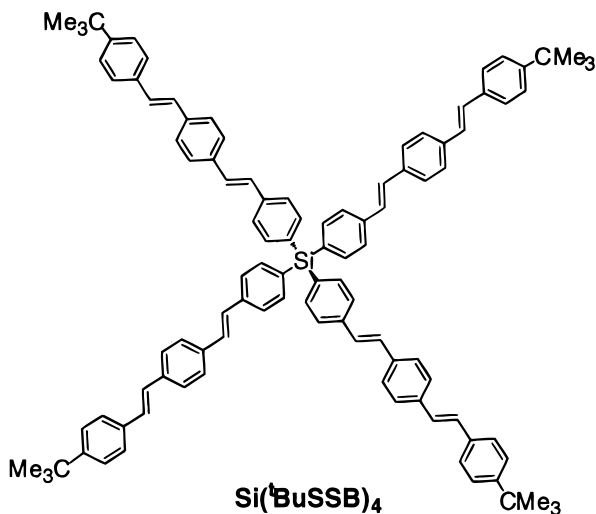
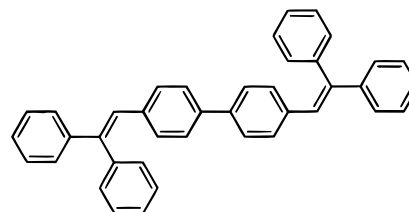
Use of tetrakis(4-bromophenyl)silane (**Si(C<sub>6</sub>H<sub>4</sub>Br)<sub>4</sub>**) gives access to structural analogues containing a silicon atom at the tetrahedral junction. Thus, reaction of **Si(C<sub>6</sub>H<sub>4</sub>Br)<sub>4</sub>** with excess styrene gives tetra<sup>t</sup>stilbenylsilane (**Si(STB)<sub>4</sub>**) in 52% yield using Pd(OAc)<sub>2</sub> under phase transfer conditions. Similarly, (**Si(C<sub>6</sub>H<sub>4</sub>Br)<sub>4</sub>**) and 4,4'-*tert*-butylvinylstilbene yields tetrakis(4-*tert*-butylstyrylstilbenyl)silane (**Si(<sup>t</sup>BuSSB)<sub>4</sub>**) in 40% yield.

**Triphenylethene Derivatives.** Efficient blue organic LEDs have recently been constructed using the active material, 4,4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl (**DPVBi**) to function

(24) Mathias, L. J.; Reichert, V. R.; Muir, A. V. G. *Chem. Mater.* **1993**, *5*, 4–5.

Ad(STB)<sub>4</sub>Ad('BuSSB)<sub>4</sub>

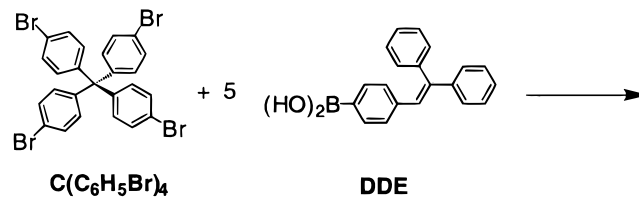
as both the electron transport and electroluminescence layer.<sup>25</sup> The active emitting material in these devices is characterized by high solid-state photoluminescence efficiency and is based on the triphenylethene chromophore.

Si(STB)<sub>4</sub>Si('BuSSB)<sub>4</sub>

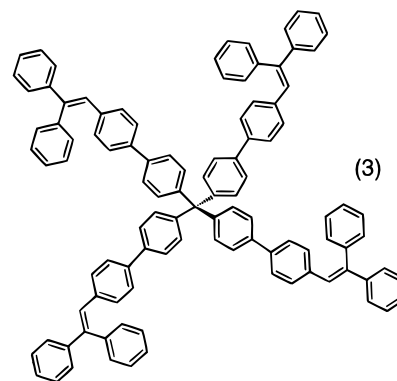
DPVBi

difference in fluorescence efficiency between solution and solid phase experiments to conformationally controlled radiationless transitions that are typical of *trans*-stilbenes.<sup>26</sup> Amorphous films of DPVBi fabricated by vacuum evaporation have a tendency to crystallize. For example, when investigated by differential scanning calorimetry, we have found that frozen glasses formed by rapidly quenching a melted sample of DPVBi with liquid nitrogen, undergo a glass transition at 64 °C, then crystallize at 106 °C ( $\Delta T = 10$  °C/min).<sup>27</sup> The promising electroluminescent properties of DPVBi make it an ideal candidate to integrate within a tetrahedral structure to change its bulk morphology. A specific goal would be to attain a material that is identical to DPVBi in electroluminescent and charge transport properties, but with a significantly higher glass transition temperature and reduced tendency toward crystallization.

A suitably functionalized triphenylethene unit was prepared in two steps. A Horner–Wadsworth–Emmons reaction between 4-bromobenzyl(diethylphosphonate) and benzophenone gives bromine substituted triphenylethene.<sup>28</sup> Treatment of this compound with *n*-BuLi and then reaction with B(O*i*-Pr)<sub>3</sub>, followed by aqueous workup, provides 1,1-diphenyl-2-(4-dihydroxyboronphenyl)ethene (DDE).<sup>29</sup> Suzuki coupling<sup>30</sup> of the aromatic boron reagent and tetrakis(4-bromophenyl)methane (C(C<sub>6</sub>H<sub>4</sub>-Br)<sub>4</sub>) gives the desired target, tetrakis(4,4'-(2,2-diphenyl-vinyl)-1,1'-biphenyl)methane (C(DPVBi)<sub>4</sub>) (eq 3).

C(C<sub>6</sub>H<sub>5</sub>Br)<sub>4</sub>

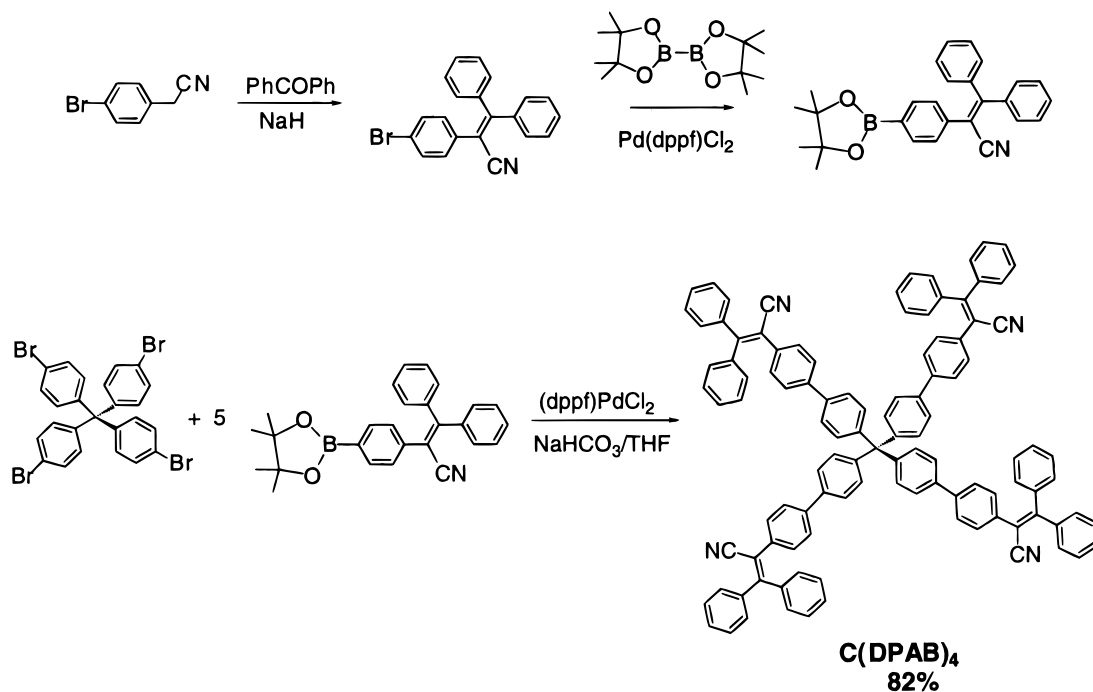
DDE

C(DPVBi)<sub>4</sub>

(25) Shaheen, S. E.; Jabbour, G. E.; Morrell, M. M.; Kawabe, Y.; Kippelen, B.; Peyghambarian, N.; Nabor, M. -F.; Schlaf, R.; Mash, E. A.; Armstrong, N. R. *J. Appl. Phys.* **1998**, *84*, 2324–2327.

(26) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991; pp 170–172.

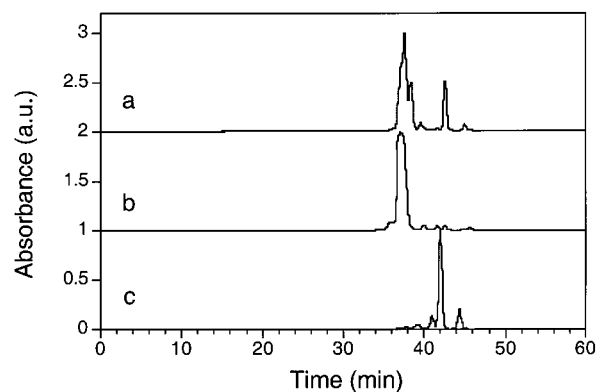
## Scheme 1



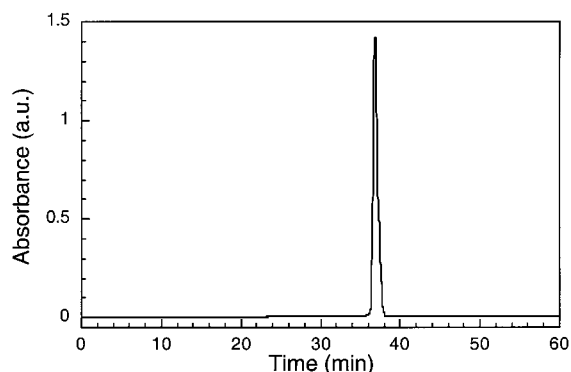
Three different Suzuki coupling protocols were evaluated to optimize reaction yields.<sup>31</sup> A direct comparison of the reaction between **DDE** and **C(C<sub>6</sub>H<sub>4</sub>Br)<sub>4</sub>** using either Pd(PPh<sub>3</sub>)<sub>4</sub> (4%) or Pd(dppf)Cl<sub>2</sub> (4%) as catalyst precursor was carried out. Both reactions were performed at the same reactant concentrations in THF at 75 °C using excess 2 M NaHCO<sub>3</sub> as the base. The third protocol evaluated in eq 3 employed the cyclometalated palladium catalyst, **A** (2%), under the previously published<sup>32</sup> optimized coupling conditions with K<sub>2</sub>CO<sub>3</sub> as base and *ortho*-xylene as solvent at 130 °C. In each case a small aliquot of the crude product mixture was diluted with chloroform and the resulting homogeneous solution was then analyzed by size exclusion chromatography. As shown in Figure 2b, the reaction catalyzed by Pd(dppf)Cl<sub>2</sub> results in complete conversion to the desired **C(DPVBi)<sub>4</sub>**. SEC analysis of the reaction catalyzed with Pd(PPh<sub>3</sub>)<sub>4</sub> shows a mixture of **C(DPVBi)<sub>4</sub>** and partially coupled products (Figure 2a). Finally, the cyclometalated palladium catalyst, **A**, was found to be completely inactive for these substrates (Figure 2c).

Optimized conditions using Pd(dppf)Cl<sub>2</sub> gives **C(DPVBi)<sub>4</sub>** in 82–86% yield following purification by flash chromatography (silica gel, hexanes/chloroform). The white powder can be recrystallized upon diffusion of methanol into a chloroform solution. The fine crystalline needles thus obtained were too small for X-ray analysis. The SEC trace of the product demonstrates excellent purity (Figure 3).

A related material was prepared in which the vinylic hydrogen of **C(DPVBi)<sub>4</sub>** is substituted with a cyano group. The stabilized



**Figure 2.** SEC analysis of crude product mixture of **C(DPVBi)<sub>4</sub>** obtained using (a) Pd(PPh<sub>3</sub>)<sub>4</sub>, (b) Pd(dppf)Cl<sub>2</sub>, and (c) Herrmann's catalyst, **A**, as Suzuki coupling catalysts, respectively.



**Figure 3.** SEC analysis of **C(DPVBi)<sub>4</sub>**.

LUMO of the cyano-substituted triphenylethene fragment (2,3,3-triphenylacrylonitrile) is expected to enhance electron injection and transport as is observed for CN-PPV.<sup>33</sup> Knoevenagel condensation between 4-bromobenzonitrile and benzophenone gives 2-(4-bromophenyl)-3,3-diphenylacrylonitrile (Scheme 1).

(27) Oldham, W. J., Jr.; Bazan, G. C. Unpublished results.

(28) Lawrence, N. J. In *Preparation of Alkenes: A Practical Approach*; Williams, J. M. J., Ed.; Oxford University Press: New York, 1996; pp 37–38.

(29) On the basis of the procedures found in: (a) Brown, H. C.; Cole, T. E. *Organometallics* **1983**, *2*, 1316–1319. (b) Komiyama, S., Ed. *Synthesis of Organometallic Compounds*; John Wiley and Sons: New York, 1997; p 354.

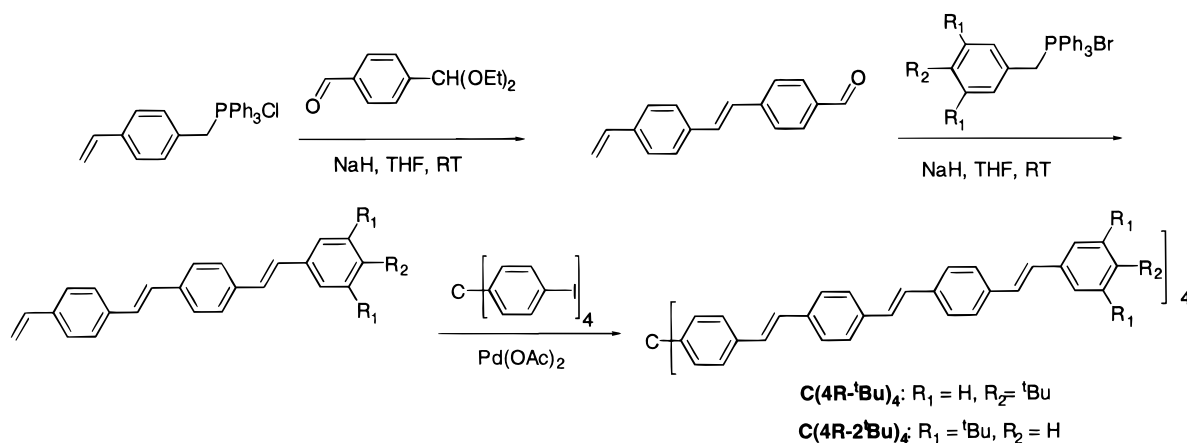
(30) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.

(31) For a similar evaluation of Suzuki coupling protocols, see: Kowitz, C.; Wegner, G. *Tetrahedron* **1997**, *53*, 15553–15574.

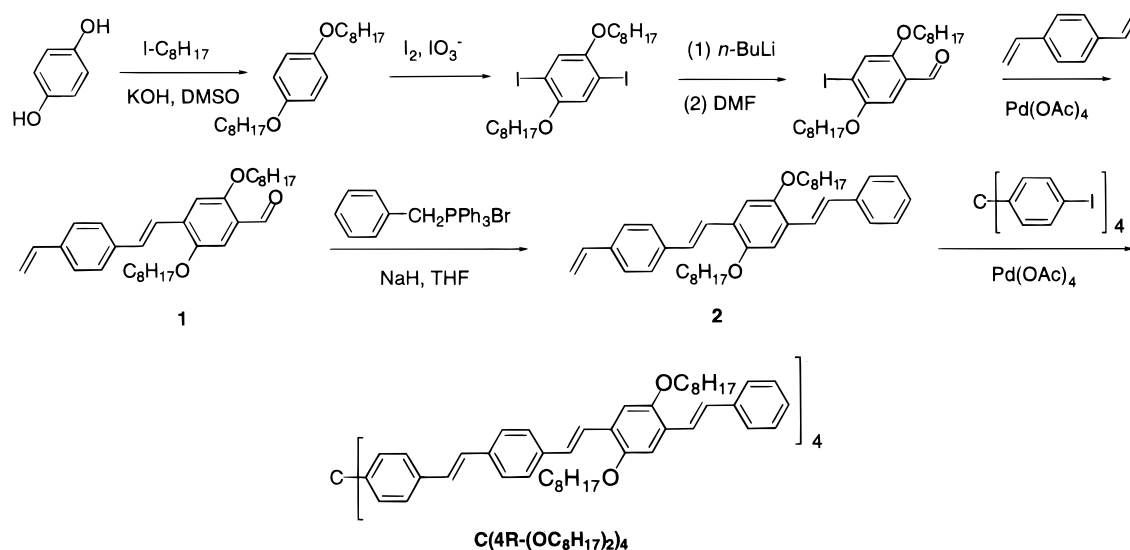
(32) Beller, M.; Fischer, H.; Herrmann, W. A.; Öfele, K.; Brossmer, C. *Angew. Chem., Int. Engl.* **1995**, *34*, 1848–1849.

(33) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.

Scheme 2



Scheme 3



Metathesis of the bromine atom for boronpinacolate proceeds in good yield using the method of Miyaura.<sup>34</sup> In this case metathesis of bromine using the *n*-BuLi/B(OiPr)<sub>3</sub> protocol is not compatible with the sensitive cyano functionality. Five equivalents of 2-(4-pinacolatoboron-phenyl)-3,3-diphenylacrylonitrile react smoothly with tetrakis(4-bromophenyl)methane using the optimized Pd(dppf)Cl<sub>2</sub> catalyzed coupling conditions to yield tetrakis(4,4'-(3,3-diphenylacrylonitrile)-1,1'-biphenyl)-methane, **C(DPAB)<sub>4</sub>** in 82% yield, following purification by flash chromatography. Compound **C(DPAB)<sub>4</sub>** has been fully characterized and the details can be found in the Experimental Section.

**Extension of Conjugation Length.** Another important question is whether the ability of the tetrahedral arrangement to discourage crystallization extends to longer chromophores. It is noteworthy that for linear molecules extending the linear axis results in less soluble and more crystalline materials. To resolve this issue, the four ring tetramer tetrakis(4-(4'-(4'-*tert*-butylstyryl)styryl)stilbenyl)methane (**C(4R-1Bu)<sub>4</sub>**) was synthesized as shown in Scheme 2. The requisite 1-(4'-*tert*-butylstyryl)-4-(4'-vinylstyryl)benzene can be obtained readily by olefination of 4-(4'-vinylstyryl)benzaldehyde using (4-*tert*-butyl)benzyltriphenylphosphonium bromide. Four equivalents of 1-(4'-*tert*-butylstyryl)-4-(4'-vinylstyryl)benzene react with **C(C<sub>6</sub>H<sub>4</sub>I)<sub>4</sub>** to

give **C(4R-1Bu)<sub>4</sub>**, albeit in only ~20% yield. As in previous examples, we suspect that the low yield of the reaction is due to the poor solubility of partly coupled intermediates.

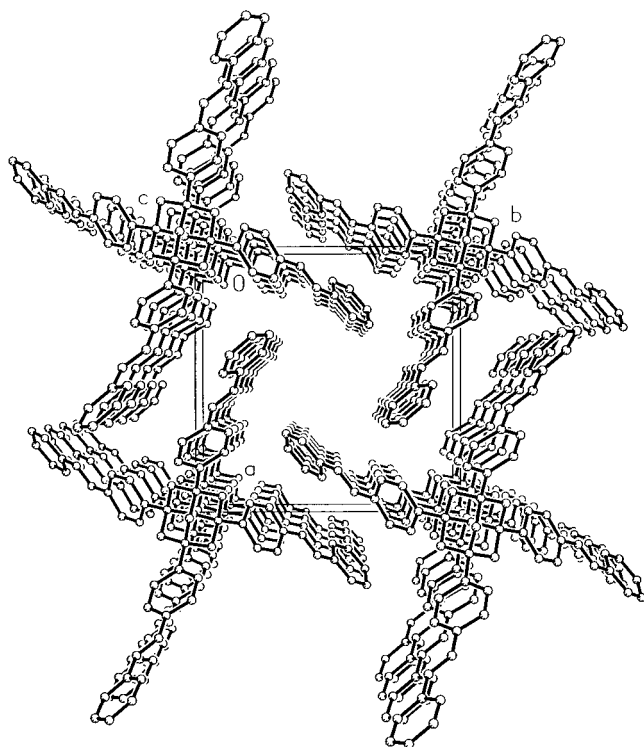
Improved solubility for processability and higher reaction yields were expected for tetrakis(4-(4'-(3'',5''-di-*tert*-butylstyryl)styryl)stilbenyl)methane (**C(4R-2Bu)<sub>4</sub>**), by virtue of the eight *tert*-butyl groups around the periphery of the molecule, and this molecule was prepared as shown in Scheme 2. Coupling of 1-(3',5'-di-*tert*-butylstyryl)-4-(4'-vinylstyryl)benzene with **C(C<sub>6</sub>H<sub>4</sub>I)<sub>4</sub>** under phase transfer conditions affords **C(4R-2Bu)<sub>4</sub>** in 80% yield. For both **C(4R-1Bu)<sub>4</sub>** and **C(4R-2Bu)<sub>4</sub>**, the products are obtained as a mixture of isomers which can be converted to the all-*trans* isomers by irradiation using a mercury lamp.

The four-ring tetramer tetrakis(4-(2',5'-dioctyloxy-4'-styryl)styryl)stilbenyl)methane, **C(4R-(OC<sub>8</sub>H<sub>17</sub>)<sub>2</sub>)<sub>4</sub>** in Scheme 3, was obtained by reaction of **C(C<sub>6</sub>H<sub>4</sub>I)<sub>4</sub>** with 12 equiv of 2,5-dioctyloxy-1-styryl-4-(4'-vinylstyryl)benzene, **2**, under Heck coupling conditions (Scheme 3). Olefin **2** is used as a mixture of *cis/trans* isomers. The requisite, 2,5-dioctyloxy-4-(4'-vinylstyryl)benzaldehyde, **1**, for making the subunit was synthesized in four steps from hydroquinone by using a procedure that is a modification of previous methods.<sup>35</sup> Analysis by HPLC showed data consistent with a mixture of five *cis-trans* C—C double bond isomers in **C(4R-(OC<sub>8</sub>H<sub>17</sub>)<sub>2</sub>)<sub>4</sub>**. The five isomers were

(34) Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508–7510.

(35) Maddux, T.; Li, W.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 844–845.

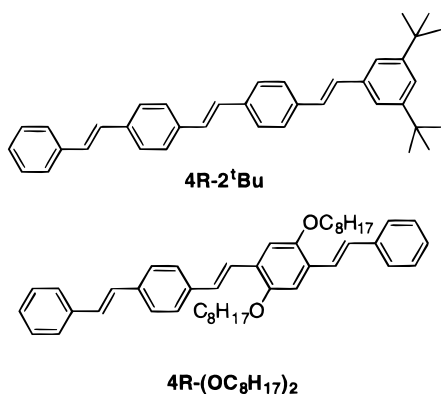




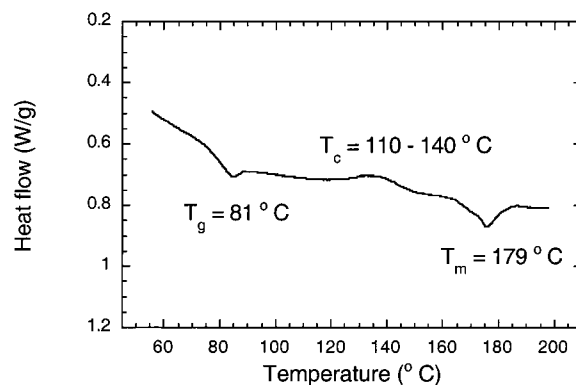
**Figure 4.** Packing diagram of  $\text{Ad}(\text{STB})_4$  unit cell as viewed down the  $c$  axis.

isolated by preparative HPLC and identified with  $^1\text{H}$  NMR spectroscopy and mass spectrometry. The five peaks collapse into a single peak upon irradiation in degassed benzene solution. After workup, the all-trans isomer was obtained in 73% isolated yield.

The “arm” of the tetramers,  $4\text{R}-2^t\text{Bu}$  and  $4\text{R}-(\text{OC}_8\text{H}_{17})_2$ , serve as model compounds and are easily synthesized by reaction of 4-iodobenzene with 1-(3',5'-di-*tert*-butylstyryl)-4-(4'-vinylstyryl)benzene and 2,5-dioctyloxy-1-styryl-4-(4'-vinylstyryl)benzene, respectively. The “arm” of tetramer  $\text{C}(4\text{R}-^t\text{Bu})_4$  was not examined due to its low solubility.



**Morphology.** We recently reported the single-crystal X-ray study of  $\text{C}(\text{STB})_4$ .<sup>20</sup> Two independent molecules were located on special positions (0, 0, 0 and  $1/2, 1/2, 0$ ) in the tetragonal unit cell  $\text{P}\bar{4}$ . A similar study was undertaken with  $\text{Ad}(\text{STB})_4$  using single crystals grown from methylene chloride and the results are shown in Figure 4. In the case of  $\text{Ad}(\text{STB})_4$ , the solution to the structure was also done in the  $\text{P}\bar{4}$  space group. There is an increase in the volume occupied per molecule from 1101.6(2)  $\text{\AA}^3$  to 1257.36(7)  $\text{\AA}^3$  as a result of the larger adamantane core. The intramolecular metrical parameters and the separation



**Figure 5.** DSC analysis of  $\text{Si}(\text{STB})_4$ .

**Table 1.** Thermal Analysis Data by DSC

compound	$T_g$ , °C	$T_m$ , °C
$\text{C}(\text{STB})_4$		274
$\text{Si}(\text{STB})_4$	81	179
$\text{Ad}(\text{STB})_4$		306
$\text{C}(^t\text{BuSSB})_4$	190	
$\text{Si}(^t\text{BuSSB})_4$	191	
$\text{Ad}(^t\text{BuSSB})_4$	165	
$\text{C}(\text{DPVBi})_4$	142	
$\text{C}(\text{DPAB})_4$	174	
$\text{C}(4\text{R}-^t\text{Bu})_4$	230	
$\text{C}(4\text{R}-2^t\text{Bu})_4$	181	
$4\text{R}-2^t\text{Bu}$		320
$4\text{R}-(\text{OC}_8\text{H}_{17})_2$		117

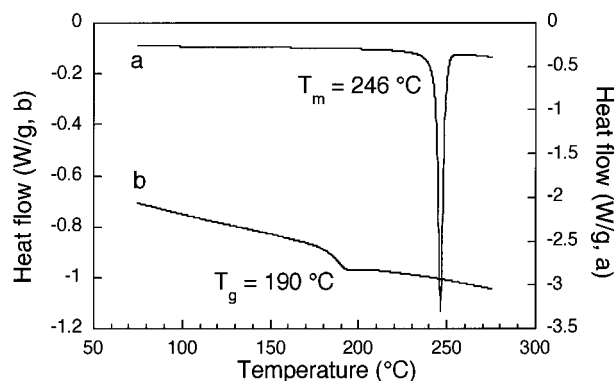
between molecules observed for  $\text{Ad}(\text{STB})_4$  are normal. Thus, the two complexes have similar geometry and choose to pack in an isomorphous fashion. Both  $\text{C}(\text{STB})_4$  and  $\text{Ad}(\text{STB})_4$  show melting transitions by DSC at 274 and 306 °C, respectively. Table 1 compares the thermal transitions determined for all compounds.

Compound  $\text{Si}(\text{STB})_4$  has interesting intermediate properties. Figure 5 shows the DSC trace for thermally annealed  $\text{Si}(\text{STB})_4$ . There is clear evidence of a glass transition at approximately 81 °C. As the sample continues to be heated, a broad crystallization exotherm occurs in the 110–140 °C range. Finally melting occurs at approximately 179 °C. Note that melting occurs at considerably lower temperatures than for  $\text{C}(\text{STB})_4$  or  $\text{Ad}(\text{STB})_4$  (Table 1). Similar melting point depressions for silicon-centered materials have been observed before. For example, the melting points of tetraphenylmethane and tetraphenylsilane are 285–286 and 224 °C, respectively.

Thermally annealed compounds with  $^t\text{BuSSB}$  substituents give kinetically stable amorphous phases (Table 1). These compounds are initially obtained as microcrystalline powders when precipitated from solution following synthesis and purification. Accordingly pristine samples typically show a weak and broad melting endotherm on the first heating cycle of a DSC experiment. Once residual solvent molecules are removed only amorphous phases are observed. Spin casting films directly from chloroform solution results in transparent homogeneous films.

For  $\text{C}(^t\text{BuSSB})_4$ , we previously reported a glass transition at 175 °C. More recent syntheses of this compound have yielded materials that gave an even higher glass transition at 190 °C (Figure 6b). While NMR data and elemental analysis obtained for different batches seem indistinguishable, GPC analysis indicates that the samples with  $T_g = 175$  °C contain a slightly higher fraction of *cis*-vinyl groups (15% compared to batches with  $T_g = 190$  °C that have a *cis*-fraction of only about 5%). It is likely that greater disorder is expected in samples with a larger

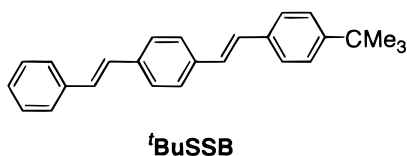




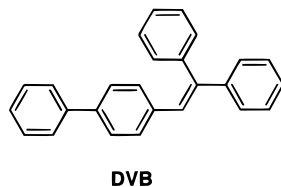
**Figure 6.** DSC analysis of (a) 4-*tert*-butyl-distyrylbenzene and (b) **C(BuSSB)<sub>4</sub>**.

population of randomly distributed *cis*-linkages results in a reduction of  $T_g$ . The isomeric purity of the arms therefore is an important parameter for optimizing thermal stability. Compounds **Ad(BuSSB)<sub>4</sub>** and **Si(BuSSB)<sub>4</sub>** behave similarly with  $T_g$ s measured at 161 and 191 °C, respectively.

These observations made for the distyrylbenzene tetramers are in marked contrast to simple 4-*tert*-butyl-distyrylbenzene. In this case a distinctive melting endotherm is observed at 246 °C (Figure 6a). Attempts to trap this compound as an amorphous glass by rapidly quench freezing the melted sample in liquid nitrogen were unsuccessful. Thus, the basic distyrylbenzene chromophore shows a strong tendency to crystallize even when cooled extremely rapidly.

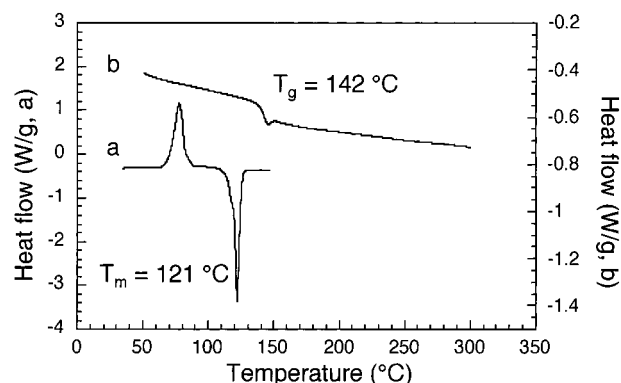


DSC analysis of **C(DPVBi)<sub>4</sub>** gives similar results to those obtained for the **tBuSSB** tetramers. The first heating cycle reveals a broad endothermic transition centered at ca. 270 °C. No transitions were observed upon cooling. Further heating cycles reveal only a step transition at 142 °C, assigned to the glass transition of the amorphous sample (Figure 7b). In comparison, 4-(2,2-diphenylvinyl)-1,1'-biphenyl (**DVB**) shows a melting endotherm on the first heating cycle at 121 °C (Figure 7a). Upon cooling this sample at 10 °C/min no crystallization transition was observed. Instead, in the next heating cycle the compound spontaneously crystallizes at 78 °C, then  $T_m$  is again observed at 121 °C. This pattern is continuously observed in further heating/cooling cycles.

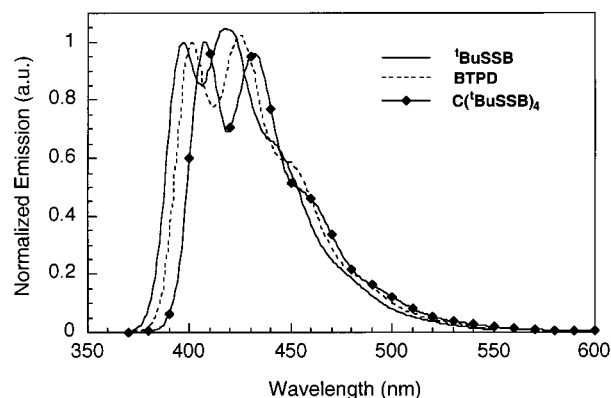


A slightly higher glass transition temperature was observed **C(DPAB)<sub>4</sub>** at 174 °C. The elevated  $T_g$  compared to **C(DPVBi)<sub>4</sub>**, is consistent with stronger intermolecular interactions as the result of the more polar cyano functionality.

Studies on the larger molecules **C(4R-tBu)<sub>4</sub>**, **C(4R-2tBu)<sub>4</sub>**, and **C(4R-(OC<sub>8</sub>H<sub>17</sub>)<sub>2</sub>)<sub>4</sub>**, confirm the observed trends. None shows a melting transition by DSC or evidence of crystalline



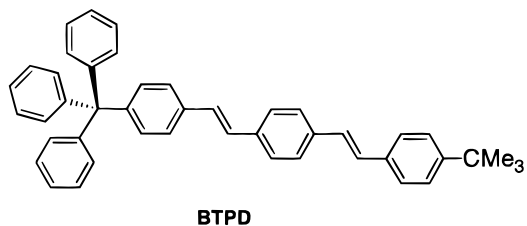
**Figure 7.** DSC analysis of (a) 4-(2,2-diphenylvinyl)-1,1'-biphenyl and (b) **C(DPVBi)<sub>4</sub>**.



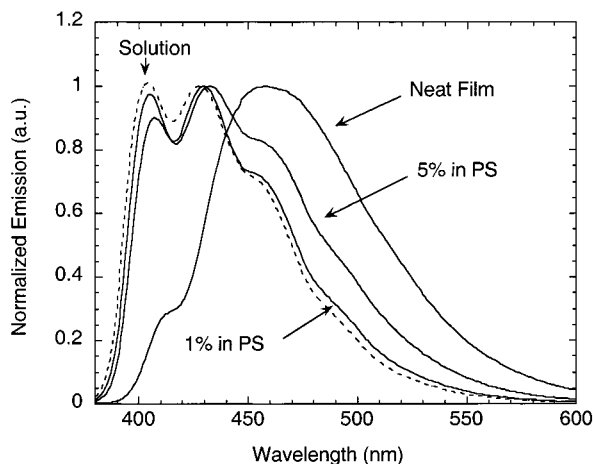
**Figure 8.** Fluorescence spectra of **tBuSSB**, **BTPD**, and **C(BuSSB)<sub>4</sub>** in  $\text{CHCl}_3$ .

regions by powder diffraction experiments. The component arms **4R-2tBu** and **4R-(OC<sub>8</sub>H<sub>17</sub>)<sub>2</sub>**, are crystalline (Table 1) and lead to opaque films. Therefore, the tetrahedral strategy as means to design organic glasses extends to more conjugated fragments. In fact, comparison of **C(BuSSB)<sub>4</sub>** ( $T_g = 165$  °C) against **C(4R-tBu)<sub>4</sub>** ( $T_g = 230$  °C) shows that considerably more stable films result when the chain length is extended by a single phenylenevinylene unit.

**Optical Properties.** Dilute solution phase optical data obtained for the *tert*-butyl-distyrylbenzene tetramers are each similar to the parent distyrylbenzene chromophore. We have examined the model compounds to compare the effect of placing four stilbenoid chromophores in close proximity. Thus, 4,4'-*tert*-butyl-triphenylmethyl-distyrylbenzene (**BTPD**) was prepared via palladium catalyzed Heck coupling of 4,4'-*tert*-butyl-vinylstilbene with  $\text{Ph}_3\text{C}(\text{C}_6\text{H}_4\text{I})$ . An even more simplified, 4-*tert*-butyl-distyrylbenzene chromophore was also prepared for comparison.



The fluorescence spectra observed for 4-*tert*-butyl-distyrylbenzene, **BTPD**, and **C(BuSSB)<sub>4</sub>** are shown in Figure 8. The highest energy emission bands are observed at 397, 401, and 407 nm, respectively. Thus, substitution of 4-*tert*-butyl-distyryl-



**Figure 9.** Fluorescence spectra of  $C(\text{BuSSB})_4$  measured for the neat film, solution phase sample and for solid-phase blends with polystyrene (PS) at 5 and 1 wt %/wt loading.

benzene with triphenylmethyl causes a red shift in the fluorescence spectrum of  $251\text{ cm}^{-1}$ . The fluorescence spectrum of the distyrylbenzene carbon-centered tetramer,  $C(\text{BuSSB})_4$  is further shifted to lower energy by an additional  $368\text{ cm}^{-1}$ . We conclude from these comparisons that linking four identical chromophores to a central carbon atom causes only a modest perturbation of the resulting electronic characteristics.

Although there are no distinctive differences in the absorption spectra of dilute chloroform solutions compared to neat films of  $C(\text{BuSSB})_4$ , the corresponding fluorescence spectra reveal a noteworthy contrast. The fluorescence spectrum of a neat film (spin cast from a chloroform solution onto a cleaned glass slide) is shown in Figure 9. The spectrum is broad and unstructured and is also significantly red shifted compared to the spectrum from a dilute solution. The optical properties of blends of  $C(\text{BuSSB})_4$  in a polystyrene host were subsequently measured. A 1 wt %/wt blend of  $C(\text{BuSSB})_4$  in polystyrene gives a fluorescence spectrum nearly indistinguishable from the solution spectrum. At 5% loading a noticeable broadening is observed. Thus, it is likely that spectral broadening is a result of interchromophore contacts rather than rigidity in the solid state. Since the environment around the periphery of  $C(\text{BuSSB})_4$  is

**Table 2.** Absorption and Fluorescence Emission Data

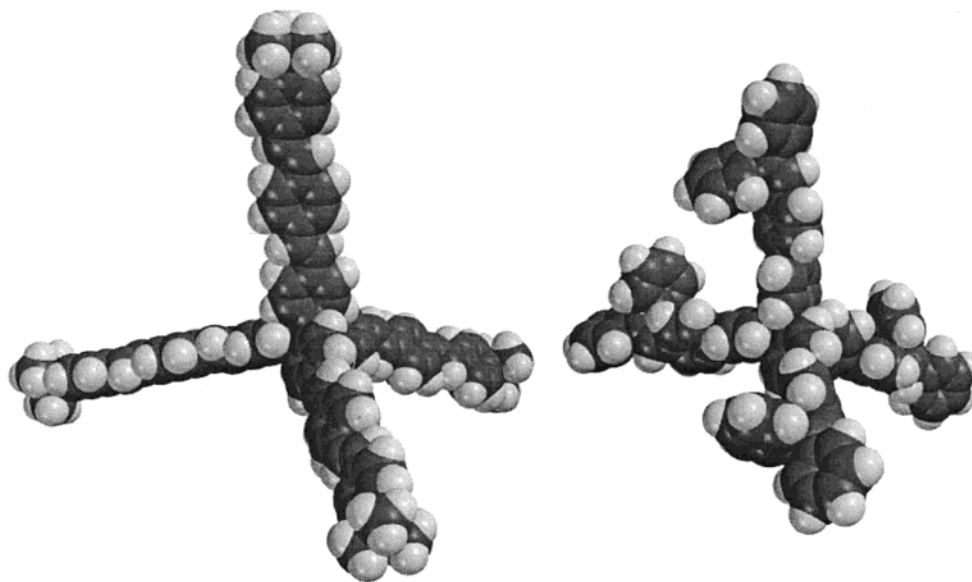
compound	$\lambda_{\text{max}}^{\text{abs}}$ , nm <sup>a</sup>	$\lambda_{\text{max}}^{\text{soln}}$ , nm <sup>b</sup>	$\lambda_{\text{max}}^{\text{film}}$ , nm <sup>c</sup>	$\lambda_{\text{max}}^{\text{annealed}}$ , nm <sup>d</sup>
$C(4R\text{-}^i\text{Bu})_4$	389	432	472	511
$C(4R\text{-}2^i\text{Bu})_4$	386	431	479	515
$4R\text{-}2^i\text{Bu}$	385	426	483	509
$C(4R\text{-}(\text{OC}_8\text{H}_{17})_2)_4$	412	470	482	544
$4R\text{-}(\text{OC}_8\text{H}_{17})_2$	407	466	482	510

<sup>a</sup> Absorption maximum in  $\text{CHCl}_3$ . <sup>b</sup> Emission maximum in  $\text{CHCl}_3$ . <sup>c</sup> Emission maximum of thin film. <sup>d</sup> Emission maximum of thermally annealed thin film.

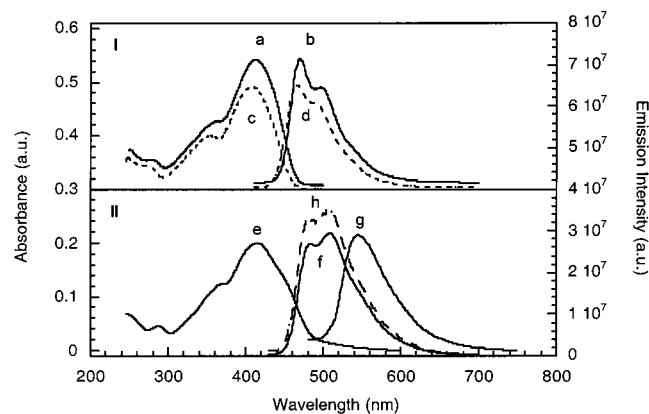
open (Figure 10, left),<sup>36</sup> it is likely that the distyrylbenzene chromophores in the solid are highly interpenetrated. Because energy transfer is quite efficient in the solid state, only a few excimer sites can make a significant impact on the fluorescence characteristics of the entire sample.<sup>37</sup>

The larger molecules  $C(4R\text{-}^i\text{Bu})_4$ ,  $C(4R\text{-}2^i\text{Bu})_4$ , and  $C(4R\text{-}(\text{OC}_8\text{H}_{17})_2)_4$  display optical properties which are dependent on sample history (Supporting Information and Table 2). Their behavior is largely similar and only that of  $C(4R\text{-}(\text{OC}_8\text{H}_{17})_2)_4$  will be discussed in detail as a representative example. As shown in Figure 11, part I, the fluorescence (Figure 11a) and absorption spectra of  $C(4R\text{-}(\text{OC}_8\text{H}_{17})_2)_4$  (Figure 11b) in solution are similar to those of the parent chromophore  $4R\text{-}(\text{OC}_8\text{H}_{17})_2$  (Figure 11c,d). Films have a broader absorption band (Figure 11e) and their emission is red-shifted, relative to samples in solution (Figure 11f). Heating films of  $C(4R\text{-}(\text{OC}_8\text{H}_{17})_2)_4$  to  $190\text{ }^\circ\text{C}$  for 5 min under a nitrogen atmosphere leads to a red shift in emission (Figure 11g). No changes occur in the absorption spectrum. Redissolving the annealed sample and recasting the film results in an emission spectrum identical to that of the original film (Figure 11h). Therefore, the process is reversible and is not likely to be due to impurities caused by thermal degradation. Our current thinking is that the “annealing” steps allows for the molecules to optimize interpenetration between chromophores and leads to environments suitable for excimer formation.

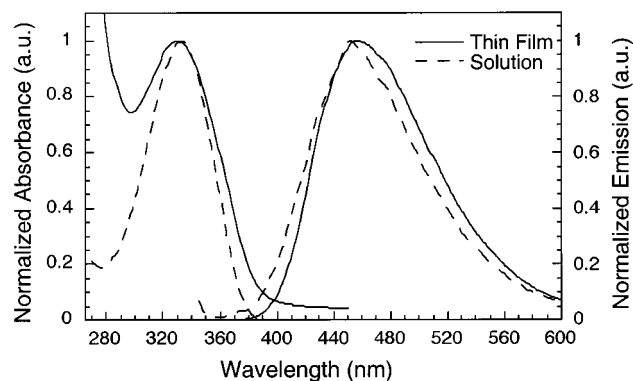
The absorption and fluorescence spectra of  $C(\text{DPVBi})_4$  is shown in Figure 12 for both a sample in dilute solution and a neat film. Little distinction can be made in the optical spectra between the two different samples. However, while the fluorescence in solution is barely detectable by eye, the solid film glows



**Figure 10.** Space filling model of  $C(\text{BuSSB})_4$  (left) and  $C(\text{DPVBi})_4$  (right).



**Figure 11.** Part I: (a) absorption spectrum of  $C(4R-(OC_8H_{17})_2)_4$  in  $CHCl_3$ , (b) fluorescence spectrum of  $C(4R-(OC_8H_{17})_2)_4$  in  $CHCl_3$ , (c) absorption spectrum of  $4R-(OC_8H_{17})_2$  in  $CHCl_3$ , (d) fluorescence spectrum of  $4R-(OC_8H_{17})_2$  in  $CHCl_3$ . Part II: (e) absorption spectrum of  $C(4R-(OC_8H_{17})_2)_4$  (thin film), (f) fluorescence spectrum of  $C(4R-(OC_8H_{17})_2)_4$  (thin film), (g) fluorescence spectrum of  $C(4R-(OC_8H_{17})_2)_4$  (thermally annealed film), (h) fluorescence spectrum of  $C(4R-(OC_8H_{17})_2)_4$  (thin film obtained after dissolving a thermally annealed sample).



**Figure 12.** Absorption and emission spectra for  $C(DPVBi)_4$  measured as dilute solutions or neat films on glass.

with a brilliant blue fluorescence when excited with a hand held UV lamp. As is the case with  $DPVBi$ , the tetramer shows a large Stokes shift and an unstructured absorption and fluorescence curve. In fact the spectra of  $DPVBi$  and  $C(DPVBi)_4$  are virtually superimposable. As shown by the space filling model in Figure 10 (right) the rings on the periphery of the  $C(DPVBi)_4$  molecule seal effectively the chromophores from interdigitation and prevent interchromophore contacts that lead to excimer formation.

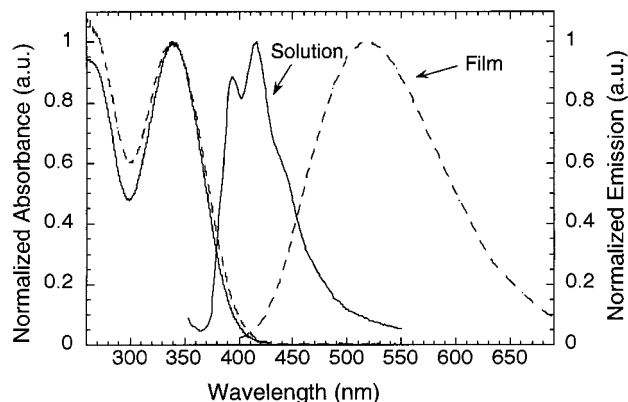
Very little difference can be discerned in the absorption spectra of solution phase samples or neat films of  $C(DPAB)_4$  (Figure 13). The corresponding fluorescence data are remarkably different. Emission in solution is centered at ca. 416 nm and shows distinct vibronic coupling. The neat film gives a broad red-shifted fluorescence centered at ca. 519 nm that is reminiscent of exciplex emission. These data suggest interactions between the carbonitrile functionality and the chromophore in the excited state.

### Summary and Conclusion

In summary, we have shown that it is possible to minimize the tendency of conjugated organic fragments to crystallize by

(36) Geometry optimization was performed using Spartan 5.01, Beilstein Database.

(37) Guillet, J. E. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, U.K., 1985.



**Figure 13.** Absorption and emission spectra for  $C(DPAB)_4$  measured as dilute solutions and neat films on glass.

coordinating them around a tetrahedral junction site. The length of the monomeric unit needs to reach a minimum length to obtain a stable amorphous phase. For the relatively small stilbene arms, the materials crystallize readily. It is interesting in this respect that the methane and adamantane cores give isomorphous crystal lattices with an increase in cell dimensions commensurate with the core volume. Compound  $Si(STB)_4$  is an intermediate case and displays thermal transitions corresponding to glassy and crystalline phases.

Kinetically stable amorphous morphologies are obtained with the distyrylbenzene arms. The series  $C(^iBuSSB)_4$ ,  $Ad(^iBuSSB)_4$ , and  $Si(^iBuSSB)_4$  shows that the choice of tetrahedral core determines the glass transition temperature. Exactly how the chemical and dimensional qualities of the inner core influences  $T_g$ , even for a family of closely related set of compounds, remains unanswered at the present time. Nonetheless, the molecular qualities of the inner core are a useful parameter to optimize the stability of the resulting films for a specific application. As the conjugation length of the monomeric unit is further increased, only amorphous materials are obtained. The compounds  $C(4R-^iBu)_4$ ,  $C(4R-2^iBu)_4$ , and  $C(4R-(OC_8H_{17})_2)_4$  display the highest glass transition temperatures and have excellent film forming properties.

The thermal properties of  $C(DPVBi)_4$  and  $C(DPAB)_4$  illustrate nicely how the tetrahedral approach discourages crystallization without the need to substitute the basic chromophore skeleton with aliphatic side groups. It is noteworthy that each of these compounds is initially obtained as a crystalline material following conventional organic solvent crystallization procedures. In the case of  $C(DPVBi)_4$ , solvent molecules are incorporated in the crystal lattice. For example colorless crystals that have only been briefly exposed to vacuum analyze correctly for  $C_{105}H_{76} \cdot 1/3 CHCl_3$  (see Experimental Section for details). During the first heating cycle of the DSC analysis, solvent is removed and the long range order in the crystalline material is disrupted to give an amorphous solid. The melted material becomes trapped in a disordered state upon cooling because reversible molecular associations that are conducive to crystal growth are hindered in the absence of solvent.

Comparison of solution and solid-state optical data indicates that multiple environments are present in the solid state. In particular, the broad emission from films of  $^iBuSSB$  containing tetramers strongly suggests formation of excimer sites. The reversible red shift in emission observed for films of  $C(4R-^iBu)_4$ ,  $C(4R-2^iBu)_4$ , and  $C(4R-(OC_8H_{17})_2)_4$  upon heating is consistent with this idea. It is likely that the molecules are capable to interdigitate better with the additional thermal energy and these enhanced mixing gives excimer forming sites. Because



of energy migration, it is not possible to quantitate the fraction of chromophores that participate in excimer formation. In the case of the **DPVBi** fragment, the terminal phenyl rings enclose the outer surface of the tetrahedral molecule and prevent close contacts along the long axis of the chromophore. Each chromophore is thus insulated from its partners and behaves independently.

The synthetic methods described herein provide a suitable platform for accessing a wide range of chemical structures with properties appropriate for inclusion in optoelectronic devices. Addition of electron withdrawing or releasing substituents is easily envisioned for fine-tuning charge injection properties, charge migration and emission color. The use of these compounds as active device components is next in our study agenda.

## Experimental Section

**General Details.** All manipulations involving air-sensitive organometallic reagents were carried out as described previously.<sup>38</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer operating at 400.1 and 100.6 MHz, respectively. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer and photoluminescence spectra on a Spex Fluorolog 2 spectrometer in spectral grade chloroform. High-resolution mass spectrometry was performed by the Nebraska Center for Mass Spectrometry at the University of Nebraska-Lincoln. Elemental analyses were performed by Desert Analytics. Reagents were obtained from Aldrich and used as received. Flash chromatographic separations were carried out using the Biotage Flash 40 system. Differential scanning calorimetry experiments were carried out using a TA Instruments model 2920 DSC.

**Tetrastilbenylmethane (C(STB)<sub>4</sub>).** In an inert atmosphere glovebox, a 25 mL round-bottom flask was charged with a Teflon coated stir bar, tetrakis(4-iodophenyl)methane<sup>39</sup> (414 mg, 0.502 mmol), styrene (0.5 mL, 4.4 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), K<sub>2</sub>CO<sub>3</sub> (354 mg, 2.56 mmol), *n*-Bu<sub>4</sub>NBr (679 mg, 2.11 mmol), and dimethylacetamide (DMA) (6 mL), then the flask was sealed with a rubber septum, which was secured with copper wire. The reaction mixture was heated at 110 °C for 2 days. The crude product mixture was then diluted with methanol to give an off-white solid that was filtered off. This solid material was then heated in 50 mL of benzene and filtered hot over Celite. The filtrate was allowed to cool and was then diluted with 50 mL of methanol and allowed to stand to afford a collection of colorless needles, which were filtered off and washed with methanol, then dried under vacuum. Yield 316 mg (86%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.52 (d, *J* = 7.4 Hz, 2 H), 7.47, 7.31 (AA'BB' pattern, *J* = 8.5 Hz, 2 H each), 7.36 (t, *J* = 7.4 Hz, 2 H), 7.26 (t, *J* = 7.4 Hz, 1 H), 7.13 (s, 2 H, vinylene). Low solubility precludes obtaining a <sup>13</sup>C NMR spectrum. Anal. Calcd for C<sub>57</sub>H<sub>44</sub>: C, 93.92; H, 6.08. Found: C, 94.00; H, 5.99.

**Tetrastilbenyladamantane (Ad(STB)<sub>4</sub>).** In an inert atmosphere glovebox, a round-bottom flask (25 mL) equipped with a magnetic stir bar was charged with tetrakis(4-iodo-phenyl)adamantane<sup>24</sup> (250 mg, 0.265 mmol, 1.0 equiv), styrene (243 μL, 2.12 mmol, 8 equiv), Pd(OAc)<sub>2</sub> (5 mg, 0.008 mmol, 0.04 equiv), K<sub>2</sub>CO<sub>3</sub> (150 mg, 1.09 mmol, 4 equiv), *n*-Bu<sub>4</sub>NBr (340 mg, 1.05 mmol, 4 equiv) and DMA (5 mL), then sealed with a rubber septum that was secured with copper wire. The reaction mixture was heated at 105 °C for 4 days. The crude product mixture was then diluted with methanol to give an off-white solid that was collected by filtration. The precipitate was suspended in hot benzene for 30 min, filtered, and then cooled prior to dilution with methanol. The precipitate was collected via centrifuge to afford 0.054 g (24%) of the desired product. <sup>1</sup>H NMR(CD<sub>2</sub>Cl<sub>2</sub>): δ 7.54 (m, 24 H), 7.36 (t, *J* = 7.4 Hz, 8 H), 7.26 (tt, *J*<sub>1</sub> = 7.4 Hz, *J*<sub>2</sub> = 1.2 Hz, 4 H), 7.14 (br s, 8 H), 2.21 (br s, 12 H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 149.7, 137.9, 135.7, 129.2, 128.7, 128.6, 128.1, 127.0, 126.9, 126.0, 47.6, 39.8. Exact mass (FAB, NBA) for M+H<sup>+</sup>. Anal. Calcd for C<sub>66</sub>H<sub>56</sub>: 848.4382. Found: 898.4361.

(38) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L.; Darrensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

(39) Su, D.; Menger, F. M. *Tett. Lett.* **1997**, *38*, 1485-1488.

**Tetrastilbenylsilane (Si(STB)<sub>4</sub>).** A round-bottom flask (50 mL) equipped with a Teflon coated stir bar was charged with tetrakis(4-bromophenyl)silane (326 mg, 0.5 mmol), styrene (2.0 g, 12 mmol), Pd(OAc)<sub>2</sub> (14 mg, 12 mol %), K<sub>2</sub>CO<sub>3</sub> (690 mg, 5 mmol), *n*-Bu<sub>4</sub>NBr (645 mg, 2 mmol), and DMA (10 mL). The flask was fitted with a rubber septum and purged with nitrogen prior to heating (80 °C) with stirring for 48 h. The reaction mixture was allowed to cool to room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub>, and washed five times with brine. The organic phase was dried with MgSO<sub>4</sub>, filtered through silica gel and the solvent was evaporated under reduced pressure. The residue was dissolved in CHCl<sub>3</sub> and precipitated with hexanes. The colorless needlelike crystals were collected (52% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.61 (d, *J* = 8.0 Hz, 8H), 7.55 (m, 16H), 7.38 (t, *J* = 7.3 Hz, *J* = 8.0 Hz, 8H), 7.29 (t, *J* = 7.3 Hz, 4H), 7.17 (AA'BB' pattern, *J* = 16.4 Hz, 8H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 138.5, 137.1, 136.7, 133.4, 129.5, 128.6, 128.4, 127.7, 126.5, 125.9.

**Tetrakis(4-*tert*-butylstyrylstilbenyl)methane (C'(BuSSB)<sub>4</sub>).** In an inert atmosphere glovebox, a round-bottom flask (25 mL) equipped with a Teflon coated stir bar was charged with tetrakis(4-iodophenyl)methane (0.510 g, 0.62 mmol), 4,4'-vinyl-*tert*-butylstilbene (0.966 g, 3.52 mmol), Herrmann's catalyst<sup>23</sup> (26 mg, 0.28 mmol), Na<sub>2</sub>OAc (0.261 g, 3.18 mmol), and DMA (15 mL). The flask was sealed with a rubber septum that was then secured with copper wire. Outside of the glovebox, the reaction mixture was heated at 140 °C while stirring for 4 days to give a brown solution containing significant amounts of precipitate. After it was cooled to room temperature, the mixture was diluted with water and the tan solid was filtered off. This solid was then dissolved in warm chloroform and filtered through a short plug of silica gel. Upon standing, an off-white solid precipitated from solution, which was then filtered off. The filtrate was then diluted with diethyl ether and the resulting precipitate was also filtered off. The combined solids were dried under vacuum. Yield 420 mg (50%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.48 (s, 4 H); 7.44, 7.37 (AA'BB' pattern, *J* = 8.6 Hz, 2 H each); 7.42 (AA'BB' pattern, *J* = 8.5 Hz, 2 H each); 7.08 (s, 2 H); 7.10, 7.04 (second-order AB pattern, *J* = 16 Hz, 1 H each); 1.32 (s, 9H). FABMS: *m/z* 1362 (M<sup>+</sup>), 1101, 1024, 763 amu. Anal. Calcd for C<sub>105</sub>H<sub>100</sub>: C, 92.6; H, 7.4. Found: C, 91.44; H, 7.42.

**Tetrakis(4-*tert*-butylstyrylstilbenyl)adamantane (Ad'(BuSSB)<sub>4</sub>).** A dry round-bottom flask (50 mL) was charged with tetrakis(4-iodo-phenyl)adamantane (213 mg, 0.230 mmol, 1.0 equiv) and 4,4'-*tert*-butyl-vinylstilbene (375 mg, 1.40 mmol, 6.0 equiv) prior to sealing with a rubber septum and purging with argon. To the flask was added dry DMA (6 mL) via syringe. In an inert atmosphere glovebox, a 25 mL round-bottom flask equipped with a magnetic stir bar was charged with Na<sub>2</sub>OAc (120 mg, 1.0 mmol, 4.5 equiv) and Herrmann's catalyst (10 mg, 0.01 mmol, 0.05 equiv) prior to sealing with a rubber septum. The solution was transferred from the first flask to the second flask via syringe and then heated to 140 °C using an oil bath for 5 days. The slurry was cooled to room temperature prior to quenching with water. The resulting precipitate was collected via filtration. The filtrate was diluted with more water and the filtrate collected. The precipitate was dried under vacuum to afford 104 mg (31%) of the desired product. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.52 (m, 32 H), 7.48 (d, *J* = 8.5 Hz, 8 H), 7.40 (d, *J* = 8.5 Hz, 8 H), 7.14 (d, *J* = 16.3 Hz, 4 H), 7.13 (m, 8 H), 7.08 (d, *J* = 16.3 Hz, 4 H), 2.22 (m, 12 H), 1.35 (s, 36 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 151.0, 149.1, 137.0, 136.8, 135.6, 134.8, 128.8, 128.5, 128.2, 127.7, 127.0, 126.9, 126.8, 126.4, 125.8, 125.7, 47.4, 39.5, 34.8, 31.5. Anal. Calcd for C<sub>114</sub>H<sub>112</sub>: C, 92.38; H, 7.62. Found: C, 92.26; H, 7.64. FABMS: (M+H)<sup>+</sup> 1482.

**Tetrakis(4-*tert*-butylstyrylstilbenyl)silane (Si'(BuSSB)<sub>4</sub>).** A round-bottom flask (50 mL) equipped with a Teflon coated stir bar was charged with tetrakis(4-bromophenyl)silane (0.652 g, 1.00 mmol), 4,4'-*tert*-butylvinylstilbene (1.57 g, 5.98 mmol), Pd(OAc)<sub>2</sub> (27 mg, 12 mol %), K<sub>2</sub>CO<sub>3</sub> (1.38 g, 10 mmol), *n*-Bu<sub>4</sub>NBr (1.29 g, 4 mmol), and DMA (30 mL). The flask was fitted with a rubber septum and purged with nitrogen prior to heating (80 °C) with stirring for 72 h. The reaction mixture was allowed to cool to room temperature, diluted with CH<sub>2</sub>-Cl<sub>2</sub>, and washed five times with brine. The organic phase was dried with MgSO<sub>4</sub>, filtered and solvent evaporated under reduced pressure. The crude residue was dissolved in CHCl<sub>3</sub> and precipitated with methanol. The solid material was filtered off then further purified



by silica gel chromatography (chloroform:hexanes = 1:3) to give Si(BuSSB)<sub>4</sub> as a greenish white solid (40% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.59 (d, *J* = 8 Hz, 4H), 7.52 (s, 4H), 7.43 (d, *J* = 8 Hz, 4H), 7.17 (d, *J* = 17 Hz, 2H), 7.10 (dd, *J* = 16 Hz, 2H), 1.34 (s, 9 H). FABMS: *m/z* = 1378 (M+H<sup>+</sup>).

**4,4'-tert-Butyl-(triphenylmethyl)distyrylbenzene.** In an inert atmosphere glovebox, a round-bottom flask (25 mL), equipped with a Teflon coated stir bar, was charged with 4-iodo-tetraphenylmethane<sup>40</sup> (462 mg, 1.04 mmol), 4,4'-vinyl-*tert*-butylstilbene (313 mg, 1.14 mmol), *n*-Bu<sub>4</sub>NBr (346 mg, 1.07 mmol), K<sub>2</sub>CO<sub>3</sub> (184 mg, 1.33 mmol), Pd(OAc)<sub>2</sub> (3 mg, 0.013 mmol), and DMA (10 mL). The flask was sealed with a rubber septum that was then secured with a copper wire. Outside of the glovebox, the reaction mixture was heated with stirring to 110 °C for 5 h. The reaction mixture was diluted with water, and the gray solids were filtered off. The isolated solid material was dissolved in chloroform and filtered. The filtrate was dried (MgSO<sub>4</sub>) then concentrated and layered with hexanes. The resulting slightly yellowish crystals were filtered off and dried under vacuum. Yield 550 mg (92%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.52 (s, 4 H); 7.47, 7.40 (AA'BB' pattern, *J* = 8 Hz, 2 H each); 7.44(AA' part of an AA'BB' pattern, *J* = 8 Hz, 2 H); 7.28–7.20 (m, 17 H); 7.15, 7.08 (second-order AB pattern, *J* = 16 Hz, 1 H each); 7.13 (s, 2 H); 1.31 (s, 9 H). MS: *m/z* 580 (M<sup>+</sup>). Anal. Calcd for C<sub>45</sub>H<sub>40</sub>: C, 93.06; H, 6.94. Found: C, 91.73; H, 6.99.

**4-tert-Butyldistyrylbenzene.** Working in an inert atmosphere glovebox, a round-bottom flask (10 mL) equipped with a Teflon coated stir bar, was charged 4,4'-vinyl-*tert*-butylstilbene (312 mg, 1.19 mmol), *n*-Bu<sub>4</sub>NBr (418 mg, 1.30 mmol), K<sub>2</sub>CO<sub>3</sub> (189 mg, 1.37 mmol), Pd(OAc)<sub>2</sub> (5 mg, 0.022 mmol), and DMA (5 mL). The flask was sealed with a rubber septum that was then secured with a copper wire. Outside of the box, bromobenzene (130 μL, 1.23 mmol) was added via syringe. The reaction mixture was heated with stirring at 105 °C for 19 h. After cooling to room temperature, the reaction mixture was diluted with water and the solids were filtered off. The solid was then dissolved in chloroform, dried (MgSO<sub>4</sub>), and refiltered. The filtrate was concentrated by warming on a hot plate, then allowed to stand at –30 °C overnight. The resulting bright yellow needles were filtered off and collected. The filtrate was concentrated with warming and allowed to cool again to afford a second crop of bright yellow crystals. Combined yield: 270 mg (67%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.54 (complex d, 2H); 7.53 (s, 4H); 7.47, 7.40 (AA'BB' pattern, *J* = 8 Hz, 2 H each); 7.36 (complex d, *J* = 8 Hz, 2 H); 7.27 (tt, *J* = 8 Hz, 1 Hz, 1 H); 7.15, 7.09 (second-order AB pattern, *J* = 16 Hz, 1 H each); 7.15 (s, 2 H); 1.34 (s, 9H).

**1,1-Diphenyl-2-(4-bromophenyl)ethene.** The following procedure was adapted from that described by Baker and Sims.<sup>41</sup> In an inert atmosphere glovebox, a round-bottom flask (250 mL), equipped with a Teflon coated stir bar, was charged with 4-bromobenzyl(diethylphosphonate) (10.0 g, 32.56 mmol), benzophenone (5.93 g, 32.54 mmol), NaH (0.927 g, 38.6 mmol), 15-crown-5 (0.2 mL, 1 mmol), and THF (50 mL). The flask was capped with a rubber septum and vented with a needle. The reaction mixture was allowed to stir at room temperature for 24 h, upon which time a gelatinous goo had formed in the bottom of the flask. Outside of the glovebox, water was added to give a homogeneous solution that was extracted with diethyl ether. The combined ether extracts were washed with NaHSO<sub>3</sub> (2 × 100 mL), brine (2 × 100 mL), and dried (MgSO<sub>4</sub>). A slight impurity of benzophenone was removed by flash chromatography (silica gel, hexanes, *R<sub>f</sub>* = 0.49). The hexanes solution was concentrated under vacuum to give a clear oil, that upon standing at –30 °C, crystallized to yield 8.5 g (78%) of colorless crystals. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 7.37–7.29 (complex m, 8H); 7.55, 6.90 (AA'BB' pattern, *J* = 8.8 Hz, 2 H each); 7.18 (m, 2H); 6.93 (s, 1 H). MS: *m/z* 336, 334 (M<sup>+</sup>, 1:1 rel intensity).

**1,1-Diphenyl-2-(4-dihydroxyboronphenyl)ethene (DDE).** In an inert atmosphere glovebox, a round-bottom flask (250 mL) equipped with a Teflon coated stir bar, was charged with 1,1-diphenyl-2-(4-bromophenyl)ethene (8.45 g, 25.2 mmol) and then fitted with a vacuum

line adapter. Diethyl ether (50 mL) was then vacuum transferred into the flask and allowed to warm to 0 °C. To the clear solution was added *n*-BuLi (1.6 M in THF, 18 mL, 28.8 mmol) dropwise over 10 min. The mixture was then allowed to warm to room temperature and stirred an additional 30 min. The mixture was then cooled again to 0 °C, and B(O*i*Pr)<sub>3</sub> (7.3 mL, 31.6 mmol) was added dropwise and then allowed to warm to room temperature and stirred for 90 min. A solution of H<sub>2</sub>SO<sub>4</sub> (7 mL of concentrated H<sub>2</sub>SO<sub>4</sub> in 100 mL of water) was added carefully and stirred briefly. The mixture was diluted with more diethyl ether and the organic layer separated. The aqueous phase was extracted with more diethyl ether (100 mL), and the organic fractions were combined. The diethyl ether was removed under vacuum to give a waxy oily solid that was dissolved in warm aqueous base (KOH) and filtered and allowed to cool. Neutralization with aqueous HCl then gives a flocculent white solid, which was filtered off and then dried under vacuum. Yield 2.3 g (30%). The isolated white solid is poorly soluble in chlorinated solvents, but did dissolve in methanol. <sup>1</sup>H NMR (CD<sub>3</sub>OD): 7.47 (d, *J* = 7.6 Hz, 2 H), 7.35–7.25 (complex m, 8H), 7.13 (br, 2 H), 7.0–6.95 (overlapping m, 3 H).

**Tetrakis(4,4'-(2,2-diphenyl-vinyl)-1,1'-biphenyl)methane (C-(DPVBi)<sub>4</sub>).** In an inert atmosphere glovebox, a round-bottom flask (25 mL), equipped with a Teflon coated stir bar, was charged with tetrakis-(4-bromophenyl)methane<sup>42</sup> (0.500 g, 0.786 mmol), 1,1-Diphenyl-2-(4-dihydroxyboronphenyl)ethene (1.184 g, 3.94 mmol), Pd(dppf)Cl<sub>2</sub> (24 mg, 0.033 mmol), and THF (13 mL). The flask was then sealed with a rubber septum that was then secured with copper wire. A saturated aqueous solution of N<sub>2</sub> sparged NaHCO<sub>3</sub> (10 mL) was then added via syringe into the sealed flask. The reaction mixture was then heated with stirring to 70 °C for 3 days. Upon cooling to room temperature, the mixture was diluted with chloroform and brine. The organic layer was separated and washed with brine (three times), then dried (MgSO<sub>4</sub>). The crude product was then purified by flash chromatography (silica gel, hexanes/CHCl<sub>3</sub>). Colorless needles were obtained upon diffusion of methanol into a concentrated chloroform solution. Yield 0.893 g (85%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.44 (AA' portion of an AA'BB' pattern, *J* = 9.2 Hz, 2H); 7.37, 7.05 (AA'BB' pattern, *J* = 8.4 Hz, 2 H each); 7.34–7.21 (complex overlapping m, 10 H); 6.98 (s, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 146.0, 143.7, 143.0, 140.7, 138.9, 138.3, 136.8, 131.7, 130.7, 130.3, 129.0, 128.6, 128.1, 127.93, 127.86, 127.8, 126.7, 126.2, 64.4. FABMS: *m/z* 1338 (M<sup>+</sup>), 1083, 1006, 751, 673. Anal. Calcd for C<sub>105</sub>H<sub>76</sub><sup>1/3</sup>CHCl<sub>3</sub>: C, 91.84; H, 5.59; Cl, 2.57. Found: C, 91.55; H, 5.49; Cl, 2.66. Same batch of TPET was further dried under vacuum and reanalyzed: Calcd for C<sub>105</sub>H<sub>76</sub><sup>1/4</sup>CHCl<sub>3</sub>: C, 92.14; H, 5.62; Cl, 1.94. Found: C, 92.34; H, 5.47; Cl, 1.89.

**4-(2,2-Diphenylvinyl)-1,1'-biphenyl.** In an inert atmosphere glovebox, a round-bottom flask (25 mL) equipped with a Teflon coated stir bar was charged with 1,1-diphenyl-2-(4-dihydroxyboronphenyl)ethene (200 mg, 0.67 mmol), Pd(dppf)Cl<sub>2</sub> (5 mg, 0.007 mmol), and THF (6 mL). The flask was then sealed with a rubber septum, which was then secured with copper wire. Bromobenzene (100 μL, 0.95 mmol) was added via syringe outside the glovebox. A saturated aqueous solution of N<sub>2</sub> sparged NaHCO<sub>3</sub> (2 mL) was then added via syringe into the sealed flask. The reaction mixture was then heated with stirring to 75 °C for 24 h. To the cooled reaction mixture was then added diethyl ether and water. The organic phase was separated and extracted with brine (three times), then dried (MgSO<sub>4</sub>). The crude product was purified by flash chromatography (silica gel, 3:1 hexanes:chloroform). The combined fractions were then concentrated under vacuum and allowed to slowly evaporate to afford clear colorless needles. Yield 170 mg (77%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.55 (complex d, 2 H); 7.42–7.23 (complex overlapping m, 15H); 7.10 (complex d, 2 H); 7.03 (s, 1 H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 143.7, 143.1, 140.9, 140.8, 139.5, 136.9, 130.7, 130.4, 129.1, 128.6, 128.0, 127.9, 127.6, 127.1, 126.8.

**2-(4-Bromophenyl)-3,3-diphenylacrylonitrile.** The synthetic procedure used to prepare this compound was adapted from a general scheme reported to yield triarylcyanoethenes.<sup>43</sup> A three neck flask (500 mL) equipped with a Teflon coated stir bar was charged with benzophenone (16.2 g, 91.7 mmol), NaH (2.5 g, 104 mmol), and

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benzene (100 mL) while working in an inert atmosphere glovebox. A separate liquid addition funnel was charged with 4-bromobenzonitrile (18.7 g, 95.4 mmol) and benzene (150 mL). The funnel and the round-bottom flask were temporarily sealed with rubber septa, then assembled outside of the box against a counter flow of dry N<sub>2</sub>. While maintaining the inert atmosphere, a reflux condenser was then added to the assembly. The benzophenone/NaH mixture was heated to reflux for 10 min, then the 4-bromobenzonitrile was added dropwise over 60 min while maintaining reflux. Evolving gas (H<sub>2</sub>) was observed at the oil bubbler and the reaction was allowed to proceed for 20 h. Upon cooling to room temperature, the reaction mixture was diluted with water and the organic phase was separated and washed with brine (4 × 100 mL). The organic phase was then dried (MgSO<sub>4</sub>) and concentrated under vacuum. Addition of methanol gives a pale yellow powder that was filtered off and washed with additional methanol, then dried under vacuum. Yield 25.6 g (80%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.32 (m, 2H); 7.06 (m, 3H); 6.94 (AA' part of an AA'BB' pattern, 2 H); 6.84 (BB' part of an AA'BB' pattern overlapping with a multiplet, 3H); 6.76 (complex t, *J* = 8 Hz, 2H); 6.70 (complex d, *J* = 7 Hz, 2 H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 157.7, 140.5, 139.2, 134.4, 131.9, 131.6, 130.9, 130.2, 130.1, 129.1, 128.6, 128.4, 122.7, 119.6, 111.3. MS: *m/z* 359, 361 (M<sup>+</sup>, 1:1 rel int.).

**2-(4-Pinacoloboronophenyl)-3,3-diphenylacrylonitrile.** Working in an inert atmosphere glovebox, a round-bottom flask (25 mL) equipped with a Teflon coated stir bar, was charged with 1-Cyano-1-(4-bromophenyl)-2,2-diphenylethene (719 mg, 2.0 mmol), bis(pinacolato)-diborane (555 mg, 2.19 mmol), K<sub>2</sub>OAc (590 mg, 6.0 mmol), Pd(dppf)-Cl<sub>2</sub> (38 mg, 0.052 mmol), and dimethylacetamide (11 mL). The flask was then sealed with a rubber septum that was secured with copper wire. The reaction mixture was heated with stirring to 80 °C for 2 h. Upon cooling to room temperature the mixture was diluted with benzene and washed with water and brine, then dried (MgSO<sub>4</sub>). The resulting bright yellow filtrate was concentrated under vacuum, then diluted with methanol to afford an off white powder that was filtered off and dried under vacuum. Yield 670 mg (82%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.61 (AA' part of an AA'BB' pattern, *J* = 8.4 Hz, 2H), 7.47–7.43 (complex m, 5 H), 7.29–7.24 (BB' part of an AA'BB' pattern overlapping with another multiplet, 3 H), 7.20 (complex t, *J* = 7.4 Hz, 2 H), 7.01 (complex d, 2 H), 1.31 (s, 12 H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 158.6, 140.9, 139.4, 137.9, 135.0, 131.0, 130.2, 129.4, 129.3, 128.8, 128.6, 120.2, 112.1, 84.3, 25.0.

**Tetrakis(4,4'-(3,3-diphenylacrylonitrile)-1,1'-biphenyl)methane (C(DPAB)<sub>4</sub>).** Working in an inert atmosphere glovebox, a round-bottom flask (50 mL), equipped with a Teflon coated stir bar, was charged with tetrakis(4-bromophenyl)methane (220 mg, 0.346 mmol), 1-cyano-1-(4-boronpinacolato-phenyl)-2,2-diphenylethene (667 mg, 1.64 mmol), Pd(dppf)Cl<sub>2</sub> (10 mg, 0.014 mmol), and THF (16 mL). The flask was then sealed with a rubber septum, which was then secured with copper wire. A saturated aqueous solution of N<sub>2</sub> sparged NaHCO<sub>3</sub> (7 mL) was then added via syringe into the sealed flask. The reaction mixture was then heated with stirring to 70 °C for 2 days. Upon cooling to room temperature, the mixture was diluted with chloroform and brine. The organic layer was separated and washed with brine (3 x), then dried (MgSO<sub>4</sub>). The crude product was then purified by flash chromatography (silica gel, hexanes/CHCl<sub>3</sub>). The combined fractions were then concentrated and layered with methanol to afford a pale off-white powder upon standing, which was filtered off and dried under vacuum. Yield 410 mg (82%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.55–7.48 (complex overlapping m, 4H), 7.47 (s, 4 H), 7.41–7.33 (complex overlapping m, 4 H), 7.31–7.20 (complex overlapping m, 4 H), 7.06 (complex d, *J* = 8 Hz, 2 H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 158.0, 146.7, 141.0, 139.5, 137.8, 134.3, 131.8, 131.1, 130.5, 130.2, 129.4, 128.8, 128.7, 127.1, 126.5, 126.4, 120.3, 111.8, 64.8. FABMS: *m/z* 1437 (M<sup>+</sup>), 1158, 1080, 801. Anal. Calcd for C<sub>109</sub>H<sub>72</sub>N<sub>4</sub>: C, 91.06; H, 5.05; N, 3.90. Found: C, 90.76; H, 4.95; N, 3.62.

**4-(4'-Vinylstyryl)benzaldehyde.** Solid NaH (360 mg, 15 mmol) was added in small portions into a suspension of terephthalaldehyde mono-(diethylacetal) (1.95 g, 9.09 mmol) and 4-vinylbenzyltriphenylphosphonium chloride (4.13 g, 10 mmol). The reaction mixture was stirred under nitrogen at room temperature for 24 h. The reaction was quenched slowly with water, extracted with CHCl<sub>3</sub>, washed with brine, dried over

MgSO<sub>4</sub>, and the solvent was evaporated under reduced pressure. The oily light yellow solid was dissolved in a mixture of 10 mL THF, 10 mL water and 5 mL acetic acid and stirred for 30 min at room temperature. The solvents was removed to dryness. The crude product was purified on a silica gel column (20–40 CH<sub>2</sub>Cl<sub>2</sub>/hexanes) to give a light yellow solid. Yield 2.0 g (94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.87 (d, *J* = 8.0 Hz, 2 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 16.0 Hz, 1 H), 7.14 (d, *J* = 16.0 Hz, 1 H), 6.73 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 11.2 Hz, 1 H), 5.80 (d, *J* = 11.2 Hz, 1 H), 5.29 (d, *J* = 11.2 Hz, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 191.54, 143.31, 137.67, 136.19, 135.94, 131.66, 130.17, 127.08, 127.02, 126.79, 126.58, 114.27.

**1-(4'-tert-Butylstyryl)-4-(4'-vinylstyryl)benzene.** Solid NaH (396 mg, 16.5 mmol) was added in small portions into a suspension of 4-(4'-vinylstyryl)benzaldehyde (703 g, 3.0 mmol) and 4-tert-butylbenzyltriphenylphosphonium bromide (1.61 g, 3.3 mmol). The reaction mixture was stirred under nitrogen at room temperature for 24 h. The reaction was quenched slowly with water, extracted with CHCl<sub>3</sub>, washed with brine, and the solvent was evaporated under reduced pressure to dryness. To the residue, 100 mL of dry toluene was added and evaporated to dryness. The light yellow solid was triturated with ethanol, filtered to give light yellow solid (which is the all-trans isomer by NMR). The filtrate was concentrated and purified with silica gel chromatography (10–20% CHCl<sub>3</sub>/hexanes) to give another portion of product (a mixture of cis and trans isomers). Yield: 1.1 g (>99%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) of the all-trans isomer: δ 7.51 (s, 4 H), 7.49, 7.47 (d, *J* = 8.46 Hz, 4 H), 7.41, 7.39 (d, *J* = 8.45 Hz, 4 H), 7.13, 7.07 (d, *J* = 16.28 Hz, 2 H), 7.11 (s, 2 H), 6.72 (dd, *J*<sub>1</sub> = 10.85 Hz, *J*<sub>2</sub> = 17.55 Hz, 1 H), 5.78 (d, *J* = 17.55 Hz, 1 H), 5.26 (d, *J* = 10.85 Hz, 1 H), 1.34 (s, 9 H). The compound is too insoluble for <sup>13</sup>C NMR spectroscopy.

**Tetrakis(4-(4'-(4'-tert-butylstyryl)styryl)stilbenyl)methane (C(4R-Bu)<sub>4</sub>).** A 50 mL round-bottom flask was charged with a Teflon coated stir bar, tetrakis(4-iodophenyl)methane (154.5 mg, 0.1875 mmol), 1-(4'-tert-butylstyryl)-4-(4'-vinylstyryl)benzene (1.1 g, 3.0 mmol), Pd(OAc)<sub>2</sub> (8.4 mg, 10 mol %), K<sub>2</sub>CO<sub>3</sub> (258 mg, 1.875 mmol), *n*-Bu<sub>4</sub>NBr (249 mg, 0.75 mmol), and *N,N*-dimethylformamide (DMF) (25 mL). The mixture was degassed with four freeze–pump–thaw cycles and heated at 90 °C for 72 h. The reaction was cooled to room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, dried over MgSO<sub>4</sub>, and the solvent was removed under reduced pressure. The low solubility of the product makes it difficult to extract the product from the reaction. A small amount of crude material was purified on a silica gel column (30% CHCl<sub>3</sub>/hexanes) to give a yellow solid which is a mixture of cis–trans isomers. The isomers were dissolved in 80 mL of benzene and degassed with four freeze–pump–thaw cycles. The solution was irradiated with Blak-Ray long UV lamp for 30 min, and the solvent was removed under reduced pressure. The isomerized product was triturated with chloroform and filtered to give a yellow solid (yield 39 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.06–7.55 (aromatic and vinylic –CH=, complex, 21 H), 1.38 (s, 18 H). The compound was too insoluble for <sup>13</sup>C NMR spectroscopy. Anal. Calcd for C<sub>137</sub>H<sub>124</sub>: C, 92.94; H, 7.06. Found: C, 92.73; H, 7.21.

**1-(3',5'-Di-tert-butylstyryl)-4-(4'-vinylstyryl)benzene.** Solid NaH (396 mg, 16.5 mmol) was added in small portions into a suspension of 4-(4'-vinylstyryl)benzaldehyde (703 g, 3.0 mmol) and 3,5-di-tert-butylbenzyltriphenylphosphonium bromide (2.09 g, 3.3 mmol). The reaction mixture was stirred under nitrogen at room temperature for 22 h. The reaction was quenched slowly with water, extracted with CHCl<sub>3</sub>, washed with brine, dried over MgSO<sub>4</sub>, and the solvent was evaporated under reduced pressure. The crude product was purified on a silica gel column (20% CHCl<sub>3</sub>/hexanes) to give a greasy yellow solid which is a mixture of cis–trans isomers. Yield 1.30 g (>99%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.00–7.56 (complex, 14 H), 6.50–6.77 (complex, 2 H), 5.71–5.81 (complex, 1 H), 5.22–5.30 (complex, 1 H), 1.45, 1.39, 1.38, 1.34, 1.26 (s, 18 H).

**Tetrakis(4-(4'-(3',5'-Di-tert-butylstyryl)styryl)stilbenyl)methane (C(4R-2'Bu)<sub>4</sub>).** A 100 mL round-bottom flask was charged with a magnetic stir bar, tetrakis(4-iodophenyl)methane (206 mg, 0.25 mmol), 1-(3',5'-di-tert-butylstyryl)-4-(4'-vinylstyryl)benzene (1.3 g, 3.0 mmol), Pd(OAc)<sub>2</sub> (12 mg, 0.0535 mmol), K<sub>2</sub>CO<sub>3</sub> (345 mg, 2.5 mmol), *n*-Bu-



NBr (332 mg, 1.0 mmol), and DMF (30 mL). The mixture was degassed with four freeze–pump–thaw cycles and heated at 90 °C for 63 h. The reaction was cooled to room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified on a silica gel column (20–40% CH<sub>2</sub>Cl<sub>2</sub>/hexanes) to give a yellow greasy solid which is a mixture of cis–trans isomers. The isomers were dissolved in 100 mL of benzene and degassed with 4 freeze–pump–thaw cycles. The solution was irradiated with Blak-Ray long UV lamp for 30 min and the solvent was removed under reduced pressure. The isomerized product was repurified on a silica gel column (30% CH<sub>2</sub>Cl<sub>2</sub>/hexanes) to give a yellow solid (yield 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.06–7.55 (overlapping aromatic and vinylic signals, 21 H), 1.38 (s, 18 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 151.27, 146.28, 136.94, 136.70, 136.64, 135.28, 131.51, 129.94, 129.50, 128.43, 128.20, 127.76, 127.06, 127.00, 126.51, 126.04, 123.59, 122.39, 121.10, 94.60, 31.55. Anal. Calcd for C<sub>153</sub>H<sub>156</sub>: C, 92.12; H, 7.88. Found: C, 91.87; H, 8.11.

**4-(4-(3',5'-Di-tert-butylstyryl)styryl)stilbene (4R-2'Bu).** A 50 mL round-bottom flask was charged with a Teflon coated stir bar, 4-iodophenylmethane (408 mg, 2.0 mmol), 1-(3',5'-di-tert-butylstyryl)-4-(4'-vinylstyryl)benzene (0.84 g, 2.0 mmol), Pd(OAc)<sub>2</sub> (22.45 mg, 0.1 mmol), K<sub>2</sub>CO<sub>3</sub> (690 mg, 5.0 mmol), *n*-Bu<sub>4</sub>NBr (665 mg, 2.0 mmol), and DMF (16 mL). The mixture was degassed with four freeze–pump–thaw cycles and heated at 90 °C for 48 h. The reaction was cooled to room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, dried over MgSO<sub>4</sub>, and the solvent was removed under reduced pressure. The crude product was purified on a silica gel column (20% CH<sub>2</sub>Cl<sub>2</sub>/hexanes) to give a yellow greasy solid which contains cis–trans isomers. The isomers were dissolved in 150 mL of benzene and degassed with four freeze–pump–thaw cycles. The solution was irradiated with Blak-Ray long UV lamp for 60 min, and the solvent was removed under reduced pressure. The isomerized product was repurified on a silica gel column (20% CH<sub>2</sub>Cl<sub>2</sub>/hexanes) to give a yellow solid (yield 71%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.51–7.54 (overlapping signals, 9 H), 7.35–7.39 (overlapping signals, 5 H), 7.28 (t, *J* = 7.50 Hz, 1 H), 7.19 (d, *J* = 16.3 Hz, 1 H), 7.13 (complex, 4 H), 7.10 (d, *J* = 16.3 Hz, 1 H), 1.37 (s, 18 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 151.28, 137.54, 136.66, 129.96, 128.93, 128.78, 128.49, 128.20, 127.76, 127.09, 127.04, 127.01, 126.73, 121.09, 31.69. Exact mass (FAB, NBA) for M<sup>+</sup> (C<sub>38</sub>H<sub>40</sub>): calculated 496.3143; found 496.3189.

**2,5-Dioctyloxy-4-(4'-vinylstyryl)benzaldehyde.** To a round-bottom flask was added *p*-divinylbenzene (9.28 g, 71.2 mmol), 2,5-dioctyloxy-4-iodobenzaldehyde (11.6 g, 23.8 mmol), Pd(OAc)<sub>2</sub> (65 mg, 0.288 mmol), *n*-Bu<sub>3</sub>NBr (6.42 g, 34.6 mmol), tri-*o*-tolylphosphine (0.707 g, 2.32 mmol), and DMF (200 mL). The mixture was degassed with three freeze–pump–thaw cycles and heated to 80 °C for 27 h. The reaction was cooled to room temperature and diluted with ether. The organic layer was washed with water, dried with MgSO<sub>4</sub> and concentrated. The crude product was purified on a silica gel column (hexanes/ethyl acetate) to give a yellow solid (yield: 57%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.45 (s, 1 H), 7.51 (d, *J* = 8.06 Hz, 2 H), 7.48 (d, *J* = 16.49 Hz, 1 H), 7.43 (d, *J* = 8.04 Hz, 2 H), 7.32 (s, 1 H), 7.23 (d, *J* = 16.49 Hz, 1 H), 7.17 (s, 1 H), 6.73 (dd, *J*<sub>1</sub> = 17.58 Hz, *J*<sub>2</sub> = 11.35 Hz, 1 H), 5.80 (d, *J* = 17.58 Hz, 1 H), 5.27 (d, *J* = 11.35 Hz, 1 H), 4.11 (t, *J* = 6.60 Hz, 2 H), 4.03 (t, *J* = 6.59 Hz, 2 H), 1.85 (m, 4 H), 1.50 (m, 4 H), 1.24–1.42 (m, 16 H), 0.89 (m, 6 H). FABMS: *m/z* 490 (M<sup>+</sup>).

**2,5-Dioctyloxy-1-styryl-4-(4'-vinylstyryl)benzene.** Solid NaH (300 mg, 12.4 mmol) was added in small portions into a suspension of 2,5-dioctyloxy-4-(4'-vinylstyryl)benzaldehyde (1.27 g, 2.59 mmol) and benzyltriphenylphosphonium bromide (1.35 g, 3.11 mmol). The reaction mixture was stirred under nitrogen at room temperature for 24 h. The reaction was quenched slowly with water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, dried over MgSO<sub>4</sub>, and the solvent was evaporated under reduced pressure. The crude product was purified on a silica gel column (25–40% CHCl<sub>3</sub>/hexanes) to give a greasy yellow solid which is a mixture of cis and trans isomers. Yield 1.2 g (82%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.51 (d, *J* = 9.26 Hz, 2 H), 7.47 (d, *J* = 9.25 Hz, 1 H), 7.42 (s, 2 H), 7.29 (d, *J* = 7.36 Hz, 2 H), 7.25 (dd, *J*<sub>1</sub> = 6.38 Hz, *J*<sub>2</sub> = 7.36 Hz, 2 H), 7.18 (t, *J* = 7.34 Hz, 1 H), 7.14 (s, 1 H), 6.76 (d, *J* = 11.97 Hz, 1 H), 6.72 (dd, *J*<sub>1</sub> = 17.72 Hz, *J*<sub>2</sub> = 10.85 Hz, 1 H),

6.34 (d, *J* = 12.00 Hz, 1 H), 5.78 (d, *J* = 17.72 Hz, 1 H), 5.25 (d, *J* = 10.85 Hz, 1 H), 4.02 (t, *J* = 6.54 Hz, 2 H), 3.55 (t, *J* = 6.87 Hz, 2 H), 1.78 (m, 4 H), 1.64 (m, 4 H), 1.23–1.42 (m, 16 H), 0.90 (m, 6 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 151.34, 150.35, 137.89, 137.79, 136.81, 136.72, 130.24, 129.12, 128.49, 128.36, 127.14, 126.84, 126.73, 126.70, 125.62, 123.74, 114.81, 113.71, 110.37, 69.56, 69.16, 32.06, 29.61, 29.51, 26.33, 22.90, 14.35. FABMS: *m/z* 564 (M<sup>+</sup>).

**Tetrakis(4-(2',5'-dioctyloxy-4'-styryl)styryl)stilbenyl)methane (C(4R-(OC<sub>8</sub>H<sub>17</sub>)<sub>2</sub>)<sub>4</sub>).** A 50 mL round-bottom flask was charged with a Teflon coated stir bar, tetrakis(4-iodophenyl)methane (145.6 mg, 0.177 mmol), 2,5-dioctyloxy-1-styryl-4-(4'-vinylstyryl)benzene (1.2 g, 2.12 mmol), Pd(OAc)<sub>2</sub> (8 mg, 0.035 mmol), K<sub>2</sub>CO<sub>3</sub> (244 mg, 1.77 mmol), *n*-Bu<sub>4</sub>NBr (235 mg, 0.708 mmol), and DMF (20 mL). The mixture was degassed with three freeze–pump–thaw cycles and heated at 90 °C for 3 days. The crude product mixture was then diluted with methanol and filtered to give a yellow greasy solid. The crude was purified on a silica gel column (30% CH<sub>2</sub>Cl<sub>2</sub>/hexanes) to give a yellow greasy solid which is a mixture of five cis–trans isomers (by HPLC). The isomers were dissolved in 100 mL of benzene and degassed with three freeze–pump–thaw cycles. The solution was irradiated with Blak-Ray long UV lamp for 60 min and concentrated under reduced pressure. The residue was diluted with methanol and filtered off to give a yellow solid (yield: 330 mg, 72%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.49–7.56 (m, 28 H), 7.47 (d, *J* = 6.70 Hz, 8 H), 7.45 (s, 4 H), 7.36 (dd, *J*<sub>1</sub> = 7.50 Hz, *J*<sub>2</sub> = 7.66 Hz, 8 H), 7.29 (d, *J* = 8.46 Hz, 8 H), 7.25 (t, *J* = 7.66 Hz, 4 H), 7.16 (s, 4 H), 7.13 (s, 8 H), 7.12 (s, 12 H), 4.06 (t, *J* = 6.38 Hz, 16 H), 1.88 (m, 16 H), 1.19–1.43 (m, 80 H), 0.90 (m, 24 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 151.34, 137.88, 137.65, 136.72, 131.52, 130.21, 129.14, 128.86, 128.65, 128.37, 128.11, 127.15, 127.03, 126.74, 126.03, 125.64, 123.71, 114.84, 69.80, 69.20, 32.05, 29.74, 29.50, 26.52, 22.91, 14.35. Anal. Calcd for C<sub>185</sub>H<sub>250</sub>: C, 86.40; H, 8.62. Found: C, 86.09; H, 8.92.

**4-(2',5'-Dioctyloxy-4'-styryl)styrylstilbene (4R-(OC<sub>8</sub>H<sub>17</sub>)<sub>2</sub>).** A 25 mL round-bottom flask was charged with a Teflon coated stir bar, 4-iodophenylmethane (120 mg, 0.59 mmol), 2,5-dioctyloxy-1-styryl-4-(4'-vinylstyryl)benzene (1.2 g, 2.12 mmol), Pd(OAc)<sub>2</sub> (6.6 mg, 0.03 mmol), K<sub>2</sub>CO<sub>3</sub> (203 mg, 1.475 mmol), *n*-Bu<sub>4</sub>NBr (190 mg, 0.59 mmol), and DMF (7 mL). The mixture was degassed with four freeze–pump–thaw cycles and heated at 90 °C for 29 h. The crude product mixture was then diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, dried over MgSO<sub>4</sub>, and the solvent was evaporated under reduced pressure. The crude product was purified on a silica gel column (20% CH<sub>2</sub>Cl<sub>2</sub>/hexanes) to give a yellow greasy solid which contains cis–trans isomers. The isomers were dissolved in 100 mL of benzene and degassed with four freeze–pump–thaw cycles. The solution was irradiated with Blak-Ray long UV lamp for 30 min and the solvent was removed under reduced pressure. The isomerized product was repurified on a silica gel column (20% CH<sub>2</sub>Cl<sub>2</sub>/hexanes) to give a yellow solid (yield 65%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.50–7.58 (m, 10 H), 7.37 (2t, *J*<sub>1</sub> = 7.34 Hz, *J*<sub>2</sub> = 7.81 Hz, 4 H), 7.28 (2t, *J*<sub>1</sub> = 7.34 Hz, *J*<sub>2</sub> = 7.81 Hz, 4 H), 7.16, 7.12 (d, *J* = 16.40 Hz, 2 H), 7.14 (s, 2 H), 7.13 (s, 2 H), 7.12 (s, 12 H), 4.07 (2t, *J* = 6.39 Hz, 4 H), 1.89 (m, 4 H), 1.56 (m, 4 H), 1.24–1.47 (m, 16 H), 0.90 (m, 6 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 151.34, 138.17, 137.58, 136.66, 129.00, 128.92, 128.86, 128.61, 128.57, 128.54, 127.82, 127.62, 127.16, 127.05, 126.74, 126.71, 123.71, 123.62, 110.88, 110.78, 69.82, 32.05, 29.74, 29.56, 29.66, 26.54, 22.91, 14.36. Exact mass (FAB, NBA) for M<sup>+</sup> (C<sub>46</sub>H<sub>56</sub>O<sub>2</sub>): calculated 640.4289; found 640.4280.

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**Supporting Information Available:** Complete experimental details for the preparation for the X-ray crystallographic determination of Ad(STB)<sub>4</sub>. Absorption and fluorescence spectra of C(4R-'Bu)<sub>4</sub>, C(4R-2'Bu)<sub>4</sub>, and 4R-2'Bu (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.