Synthesis, Spectroscopy, and Morphology of Tetrastilbenoidmethanes

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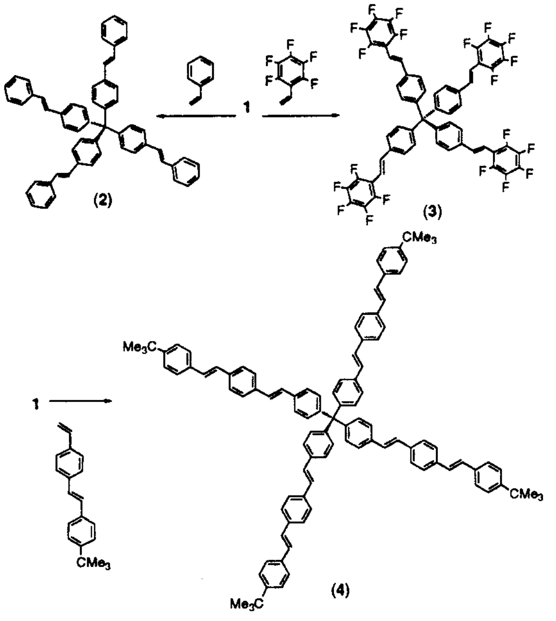
Low band gap molecular and polymeric organic materials are currently being considered for the active component in a variety of optoelectronic devices, most notably as the emissive layer in light-emitting diodes.[1] It is generally believed that the morphology adopted by these materials plays a fundamental role in defining their bulk performance. For example, completely amorphous and ultrapure thin films appear to provide the longest device lifetimes, combined with the highest efficiency and emissive brightness.[2] While sufficiently pure films of low molecular weight fluorescent compounds can be obtained by sublimation under high vacuum, these tend to recrystallize over time, thus precipitating device failure.[3] Luminescent polymeric materials can be designed to remain amorphous, even at elevated temperatures, but they are more difficult to obtain in high purity.[4,5] Furthermore, the close association of polymer chains in the solid state can lead to crystalline domains.[6] Ordered polymer regions appear to reduce emission efficiency by promoting low-energy non- or weakly emissive excimer or aggregate states.[7] Ultimately, because of facile energy migration, these low-energy sites can dominate the optical properties, even when present in small concentration.[8]

In this paper, we describe a strategy to obtain precisely defined and readily purified luminescent materials of intermediate molecular size with amorphous morphology. For this purpose, new molecules containing a tetrahedral array of four stilbenoid units coupled to a central sp^3-hybridized carbon atom have been prepared.[9] The rigid tetrahedral framework orients the chromophores such that the possibility of intramolecular π-stacking is minimized. These molecules are highly symmetrical and might be expected to favor a crystalline morphology, as observed for most structures which incorporate a tetraphenylmethane core.[10] However, we show that when the stilbenoid units are sufficiently long, crystalline packing becomes unfavorable and a stable amorphous phase is obtained.[11]

Scheme 1. Products Obtained from the Reaction of **1** with Different Stilbenoid Compounds in the Presence of $Pd(OAc)_2/NBu_4Br/DMF/K_2CO_3$



The parent compound in this series, tetrastilbenylmethane (**2**), is obtained via palladium-catalyzed Heck coupling of tetrakis(4-iodophenyl)methane[12] (**1**) with styrene (see Scheme 1).[13] Reactions carried out under phase-transfer conditions[14] were found to give the highest yields (86%), and this procedure was used exclusively in subsequent coupling reactions. Slightly reduced yields (70%) were obtained using the Herrmann catalyst,[15] and only traces of **2** were observed using the traditional catalyst system[16] composed of a mixture of $Pd(OAc)_2$ and $P(o\text{-tol})_3$. Incomplete reaction was observed, even under optimized conditions, if tetrakis(4-bromophenyl)methane[11] was substituted for **1**. Reactions carried out with pentafluorostyrene gave tetrakis(pentafluorostilbenyl)methane (**3**), which is only slightly soluble in aromatic or chlorinated solvents.[17]

Longer stilbenoid arms were obtained by coupling 4,4′-*tert*-butylvinylstilbene[18] with **1** to yield the pale yellow and freely soluble tetrakis(4-*tert*-butylstyrylstilbenyl)methane (**4**).[19] Compounds **3** and **4** were isolated in yields of 31 and 17%, respectively. The low yields for these two reactions are attributed to the insolubility of partially coupled intermediates, which were observed to precipitate from solution during early reaction times. Appropriate NMR and analytical data were obtained for each compound. Importantly, ^1H NMR signals attributed to unreacted 4-iodophenyl groups were not observed.

The absorption and emission spectra for **2** and **4** dissolved in $CHCl_3$ are shown in Figure 1. The respective absorbance and

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(13) Data for **2**: ^1H NMR (CD_2Cl_2) 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). Anal. Calcd for $C_{57}H_{44}$: C, 93.9; H, 6.1. Found: C, 94.00; H, 5.99.

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(17) Data for **3**: ^1H NMR (C_6D_6) 7.42, 7.26 (AA′BB′ pattern, J = 8.4 Hz, 2 H each), 7.29, 6.82 (AB pattern, J = 16.4 Hz, 1 H each). Anal. Calcd for $C_{57}H_{24}F_{20}$: C, 62.9; H, 2.22; F, 34.90. Found: C, 63.17; H, 2.07; F, 34.00.

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S0002-7863(97)04209-1 CCC: $15.00

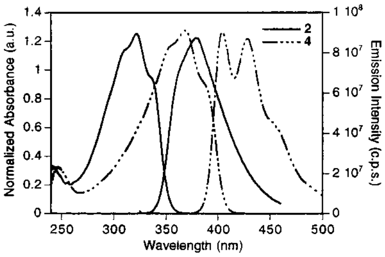


Figure 1. Absorption and emission data for **2** and **4** in $CHCl_3$. Excitation frequencies correspond to the absorption maxima.

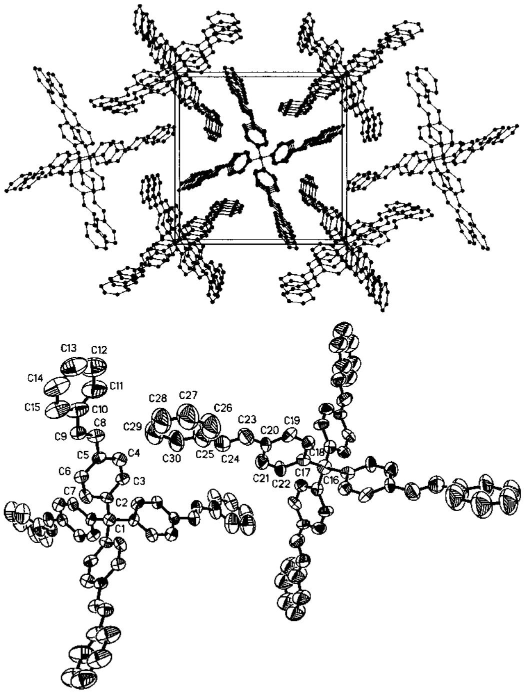


Figure 2. (a) Packing diagram of the unit cell as viewed down the *c* axis. (b) 50% ORTEP diagram, with H atoms omitted for clarity.

emisson maxima are noted at 322 and 379 nm for **2**, compared to 368 and 427 nm for **4**.[20] Interestingly, the spectra for both **2** and **4** are red shifted with respect to stilbene and distyrylbenzene, respectively (ca. 26 nm for **2** and ca. 16 nm for **4**). This observation indicates delocalization through the sp^3-hybridized carbon center. The absorption and emission data of **3** are nearly identical to that shown for **2** in Figure 1, indicating that the HOMO−LUMO gap is largely unaffected by fluorine substitution.

Crystals of **2** suitable for X-ray diffraction studies were obtained from a MeOH/benzene solution.[21] As shown in Figure 2, two independent molecules lie on special positions (0, 0, 0 and $^1/_2$, $^1/_2$, 0) in the tetragonal unit cell ($P\bar{4}$). The results of this study reveal a molecular structure with normal intramolecular metrical parameters as compared to those of *trans*-stilbene.[22] All intermolecular C···C interactions were greater than the sum of their van der Waals radii. The closest contact is ca. 3.54 Å between C4 and C15 on a symmetry-related molecule (see Figure 2). In sharp contrast to **2**, the solid samples of **4** were consistently obtained as amorphous powders as detailed below.

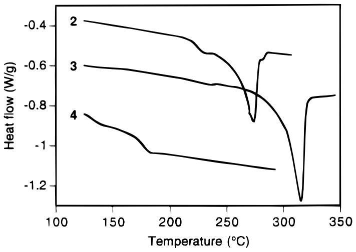
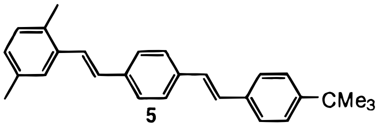


Figure 3. DSC curves for compounds **2**−**4**.

Analysis by differential scanning calorimetry (DSC) provides important information concerning solid-state morphology (Figure 3).[23] Both **2** and **3** are cystalline compounds and accordingly show distinct melting endotherms at 274 and 316 °C, respectively. However, a similar phase transition was not observed for **4** up to 400 °C, at which point the onset of thermal decomposition was evident. Careful inspection of the heating cycle for **4** (Figure 3) shows a step transition at 175 °C which we assign to a glass transition.[24] The absolute change in heat capacity (ΔC_p) at the glass transition is proportional to the fraction of amorphous material in a sample. In addition, ΔC_p for **4** was found to be independent of thermal history, which suggests that this material has few if any crystalline domains. Thus, samples which were annealed at 300 °C and then rapidly air cooled to 100 °C gave DSC heating curves very similar to those of samples which had been annealed at 300 °C and then slowly cooled to 100 °C (ΔT = 1 °C/min). In the latter experiment, if crystalline regions had been formed during the slow cooling cycle, then ΔC_p at T_g would have been reduced.[25]

A comparison of the thermal behavior of **4** against that of 2,5-dimethyl-4′-*tert*-butyldistyrylbenzene (**5**) highlights how bringing together four molecular fragments at a tetrahedral junction changes the morphology of the bulk material. Instead of a glass transition, compound **5** displays a sharp melting endotherm at 133 °C.[26]



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In summary, the results described herein provide a versatile strategy for controlling the morphology of organic materials. This approach should be useful in designing suitable materials for application in optoelectronic devices by combining the advantages of small molecules (e.g., high purity and volatility) with those of polymers (e.g., amorphous morphology). A detailed study of the photophysical properties of the new stilbenoid compounds and the effect of structural diversity on their morphology is underway.

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Supporting Information Available: Complete experimental details for the preparation of all new compounds and for the X-ray crystallographic determination of **2** (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[19] Data for **4**: ^{1}H NMR ($CDCl_3$) 7.48 (s, 4 H, arene), 7.45, 7.37 (AA′BB′ pattern, *J* = 8.5 Hz, 2 H each, arene), 7.41, 7.26 (m, 2 H each, arene), 7.10, 7.04 (AB pattern, *J* = 16.3 Hz, 1 H each, vinylene), 7.09 (br s, 2 H, vinylene); $^{13}C\{^1H\}$ NMR ($CDCl_3$) 150.8, 146.08, 146.04, 136.9, 136.5, 135.1, 134.5, 131.3, 128.6, 128.4, 127.9, 127.5, 126.8, 126.7, 126.3, 125.8, 125.6, 34.6, 31.3. Anal. Calcd for $C_{105}H_{100}$: C, 92.6; H, 7.4. Found: C, 92.50; H, 7.19.

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[21] Crystal data for $C_{57}H_{44}$: colorless needles, tetragonal, (*P*4), a = 17.5046(5), c = 7.1921(4) Å, V = 2203.1(2) Å^3, Z = 2, R = 10.10%, GOF = 1.389.

[22] Hoekstra, A.; Meertens, P.; Vos, A. *Acta Crystallogr.* **1975**, *B31*, 2813−2817.

[23] Data shown in Figure 3 were obtained as follows. Samples were annealed by heating to 300−350 °C (depending on T_m) and then cooled to 100 °C (ΔT = 10 °C/min). Subsequent heating cycles (shown in figure) were measured at rates of 10 °C/min for **2** and **3** and at 20 °C/min for **4**.

[24] Low molecular weight organics can exhibit glass transition phenomena. See: Eisenberg, A. *Physical Properties of Polymers*; American Chemical Society: Washington, DC, 1993.

[25] Powder diffraction experiments show no peaks for **4**, confirming its amorphous nature. A pattern is obtained for **2** which matches the reflections calculated from the single-crystal data. Bazan, G. C.; Lachicotte, R. J. Work in progress.

[26] **5** was available from a previous study. A similar sharp endotherm was measured for *trans*-stilbene at 126 °C, consistent with literature values.