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Unsymmetrically substituted four-armed tolanes: new multichromophoric molecules

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Abstract—The selective synthesis of a four-armed tolane with different fluorescent chromophores that are asymmetrically distributed is described. Its optical absorption and emission properties were examined. This multichromophoric molecule exhibits a charge-transfer pathway that has a pronounced effect on the overall optical properties, together with an energy transfer process. Appropriate basic centers are present, meaning that the energy transfer processes can be stopped by the addition of acid—a process that makes this system a fluorescent pH-sensor.
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Multichromophoric systems are interesting research targets due to their ability to undergo cascade energy transfer[1]—the main characteristic of light-harvesting antenna molecules[2] used to mimic biological photosynthesis—and for the synthesis of nanomolecules for optoelectronic devices.[3] Moreover, fluorescent multichromophoric molecules may be used as sensors.[4] Thus, the development of simple synthetic routes to wavelength-tunable fluorophores is of great interest, which in turn is essential for obtaining materials with tunable optoelectronic properties.

It has been demonstrated that the presence of both double and triple bonds in a conjugated structure has a strong influence on the resulting optoelectronic properties. For example, poly(p-phenylenevinylene)s (PPVs) with tolane-bis-benzyl moieties,[5] conjugated oligomers and polymers with double and triple bonds,[6,4c] and dithiafulvene-acetylene hybrid chromophores[7] have been studied as PLEDs, fluorophores, and materials with electronic properties of interest, respectively. Derivatives of tetraethynylethene and diethynylethene have also provided a unique class of π-conjugated building blocks, being promising candidates for manifold applications in material sciences.[8,6a]

In this context, and as a part of our research program aimed at the construction of extended and cross-conjugated π-electronic systems,[9] we report here a new methodology for the selective synthesis of new multichromophoric molecules. Concretely, we have prepared, as a model, the unsymmetrically substituted four-armed tolane **1** with *meta*-connectivities that incorporates up to five independent chromophores. The optical absorption and emission characteristics of this system were examined for structure–function relationships.

The target molecule **1** contains four different substituents and these were selected to satisfy several objectives: (i) to obtain a wide range of absorption wavelengths (greater than 150 nm), (ii) to have two different acid-sensitive chromophores, and (iii) to improve the solubility of the system. Moreover, the amino-containing chromophores were placed in different halves of the molecules in order to compare the behavior between the whole molecule and each separate half.

The synthetic approach to the target molecule is based on our previous experience in the synthesis of dendrons[10] and a recent report describing the preparation of differently substituted bisarylethynes.[11] Compound **1** was prepared in good yield following the reaction sequence outlined in Scheme 1. An initial Horner–Wadsworth–Emmons (HWE) reaction between biphosphonate **2a**[12] and the corresponding benzaldehyde derivative (1 equiv) forms compounds **3a,b**. The

synthesis was carried out by using only 1.2 equiv of KBu^{t}O in THF at 0 °C. Although the presence of the starting material **2a** and the corresponding di-coupled products were also observed in the crude mixture, all the monophosphonates **3** could be easily separated by column chromatography (silica gel, EtAcO) in good yields (68–86%). A second HWE reaction with a different benzaldehyde derivative (1 equiv) gave the desired asymmetrical compounds **4a,b**. Ultimately, two different functional groups are located at the periphery or the chain end of the final branched molecules. Similarly, using **2b** as a starting reagent, compounds **3c,d** and **4c,d** could be synthesized. Compounds **3** and **4** were obtained as single all-trans isomers, as determined by ^{1}H NMR spectroscopy. Finally, compound **1**† was prepared by a double Pd-catalyzed alkynylation involving reaction of **4b** with trimethylsilylacetylene, removal of the SiMe$_3$ protecting group and subsequent coupling with **4a**. This approach allows accurate control over the placement of different functionalities (electron-donating and electron-withdrawing groups) in two segregated and opposed parts of the molecule, while avoiding the need for the introduction of additional functional group protection/deprotection steps.

First, we recorded the absorption and emission spectra of each separate half of the target molecule, that is, **4c** and **4d**. The absorption spectrum of **4c**—the half bearing the electron-withdrawing group (CF$_3$)—consists of the superposition of each chromophores showing two maxima at 317 and 364 nm. The emission spectrum in CH$_2$Cl$_2$, exciting at 317 nm, is characterized by two bands (inset Fig. 1). One is centered at approximately 407 nm, while the maximum of the more intense band appears around 548 nm. When exciting at 364 nm, the band at 407 nm disappears, showing a shoulder at ca. 430 nm instead. In comparison to those of models taken for a single arm, such as *trans*-4-trifluoromethyl-

(361 nm) and *trans*-4-dibutylaminostilbene (432 nm), the emission spectrum is not due to the addition of both fluorophore responses. The maximum of the low-energy band has experienced a bathochromic shift with respect to those of the individual fluorophores. This red shift may be attributed to a charge separation effect because of the presence of both electron-withdrawing and electron-donating groups, in spite of the *meta*-arrangement, as indicated by the bathochromically shifted and lower bands observed upon increasing solvent polarity (λ_{max} toluene: 458 nm; dichloromethane: 548 nm; acetonitrile: 615 nm). The smaller bands at 407 and 430 nm should be the residual fluorescence from a second excited state for each individual chromophore.

The study of **4d**, the other half of the molecule, indicates a *quasi*-complete identity (453 nm) of the fluorescent response when compared with the *trans*-4-diphenylaminostilbene (448 nm). The response is independent of the excitation wavelength. This fact suggests that the emission occurs only from the *trans*-4-diphenylaminostilbene unit (the emission maximum for *trans*-4-hexyloxystilbene is 379 nm), indicating an efficient energy transfer from the *trans*-4-hexyloxystilbene moiety (Fig. 1). Here, the charge separation does not take place, as expected, between the two electron-releasing NPh$_2$ and OC$_6$H$_{13}$ groups.

The absorption spectrum of the four-armed tolane **1** is a simple superposition of the absorptions due to the five independent chromophores (stilbene and tolane moieties) and shows a continuous absorption from 250 to 440 nm. The absorption maxima are observed at 308 nm ($\varepsilon = 97,500$) and 373 nm ($\varepsilon = 65,500$). The emission spectra obtained by irradiation at different wavelengths are the same regardless of the excitation frequency, with a maximum at 536 nm and a shoulder at ca. 470 nm (Figs. 1 and 2). In comparison to those of models taken for a single arm, such as tolane (318 nm), *trans*-4-trifluoromethyl- (361 nm), *trans*-4-hexyloxy- (379 nm), *trans*-4-dibutylamino- (432 nm), and *trans*-4-diphenylaminostilbene (448 nm), the emission maximum of the longest-wavelength transition of **1** is again red-shifted. This behavior can be interpreted in terms of significant electronic interaction between the fluorophores in the excited state. The absorbing and emitting states are not the same, something that has been previously demonstrated in phenylacetylene derivatives with *meta*-arrangements.[13]

In any case, the four-armed tolane shows a single characteristic response upon excitation over a wide spectral range. The obtained profiles indicate that some energy transfer must occur from one half of the molecule to the other. However, in this case the energy transfer is not as efficient as in compound **4d**. Emission occurs mainly at 536 nm, a band, which resembles that of compound **4c**, while the shoulder at ca. 470 nm is the residual fluorescence of the half related with **4d**.

Excitation spectra of **1** observed at different emission wavelengths reveal more evidence for energy transfer. Thus, for example, observing fluorescence at 610 nm,

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† Selected data for compound **1**: ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.91 (pseudo t, 3H, $J = 7.0$ Hz, CH$_3$), 0.97 (t, 6H, $J = 7.5$ Hz, CH$_3$), 1.32–1.42 (m, 8H, 4 × CH$_2$), 1.43–1.53 (m, 2H, CH$_2$), 1.56–1.62 (m, 4H, 2 × CH$_2$), 1.76–1.83 (m, 2H, CH$_2$), 3,30 (t, 4H, $J = 7.5$ Hz, 2 × NCH$_2$), 3.99 (t, 2H, $J = 7.0$ Hz, OCH$_2$), 6.65 (A of ABq, 2H, $J = 9.0$ Hz, ArH), 6.87 (A of ABq, 1H, $J = 16.0$ Hz, CH=), 6.91 (A of ABq, 2H, $J = 8.5$ Hz, ArH), 6.97 (A of ABq, 1H, $J = 16.0$ Hz, CH=), 7.00 (A of ABq, 1H, $J = 16.5$ Hz, CH=), 7.03–7.10 (m, 4H), 7.10–7.17 (m, 7H), 7.20 (s, 2H, 2 × CH=), 7.25–7.30 (m, 4H), 7.39–7.43 (m, 4H), 7.47 (B of ABq, 2H, $J = 8.5$ Hz, ArH), 7.53–7.59 (m, 5H), 7.61–7.64 (m, 5H). ^{13}C NMR and DEPT (CDCl$_3$, 125 MHz): δ 159.1 (C), 148.1 (C), 147.6 (C), 147.5 (C), 140.6 (C), 139.1 (C), 138.3 (C), 138.2 (C), 137.1 (C), 131.1 (C), 130.5 (CH), 130.3 (CH), 129.6 (C), 129.4 (q, $J = 32$ Hz, C), 129.4 (CH), 129.3 (CH), 129.2 (CH), 129.2 (CH), 128.6 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 126.7 (CH), 126.0 (CH), 125.7 (q, $J = 4$ Hz, CH), 125.4 (CH), 124.6 (CH), 124.5 (CH), 124.5 (CH), 124.2 (q, $J = 270$ Hz, CF$_3$), 124.0 (C), 123.9 (C), 123.8 (C), 123.4 (CH), 123.1 (CH), 123.0 (CH), 122.2 (CH), 114.8 (CH), 111.6 (CH), 89.4 (C≡), 89.2 (C≡), 68.1 (OCH$_2$), 50.8 (NCH$_2$), 31.6 (CH$_2$), 29.5 (CH$_2$), 29.2 (CH$_2$), 25.7 (CH$_2$), 22.6 (CH$_2$), 20.4 (CH$_2$), 14.0 (CH$_3$), 14.0 (CH$_3$). MALDI-TOF, *m/e* 1049.5 (M$^+$+1). Anal. Calcd for C$_{73}$H$_{71}$F$_3$N$_2$O: C, 83.55; H, 6.82; N, 2.67. Found: C, 83.80; H, 6.62; N, 2.71.
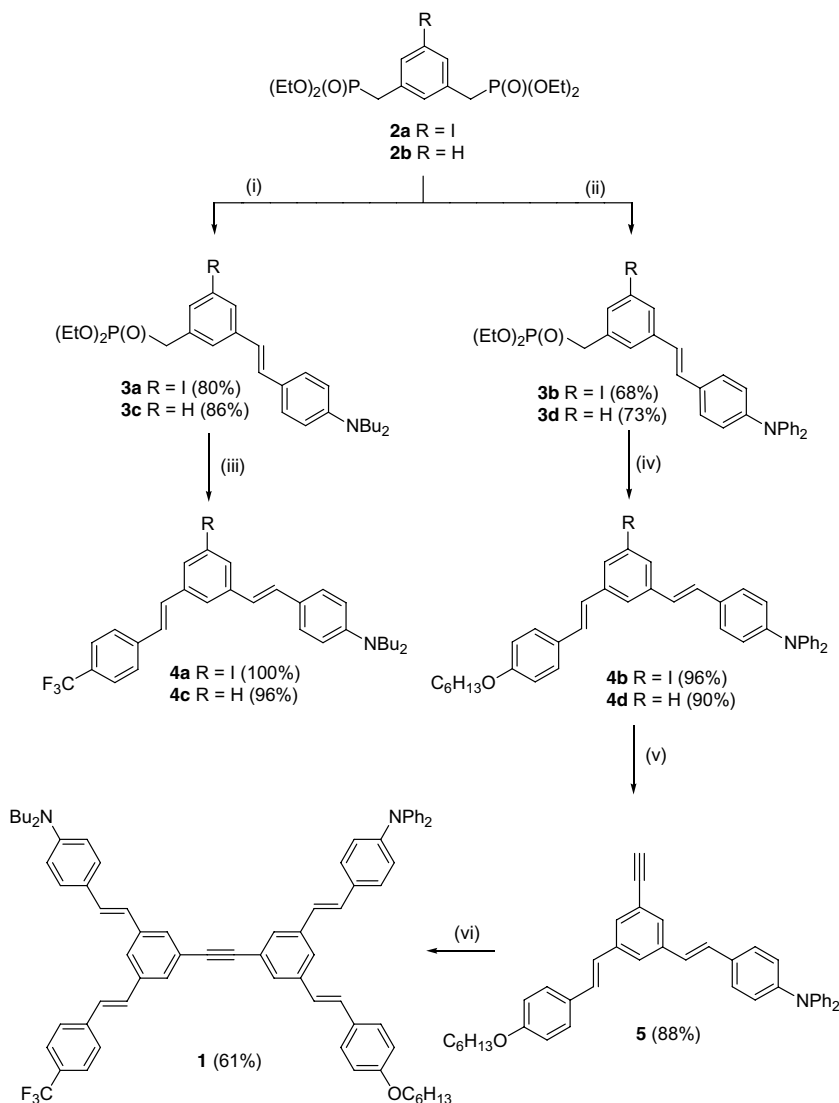
Scheme 1. Synthesis of the four-armed tolane **1** with four different stilbenoid chromophores. Reagents and conditions: (i) KBu^{t}O (1.2 equiv), THF, *p*-Bu$_2$N–C$_6$H$_4$–CHO, 0 °C; (ii) KBu^{t}O (1.2 equiv), THF, *p*-Ph$_2$N–C$_6$H$_4$–CHO, 0 °C; (iii) KBu^{t}O (1.2 equiv), THF, *p*-F$_3$C–C$_6$H$_4$–CHO, rt; (iv) KBu^{t}O (1.2 equiv), THF, *p*-C$_6$H$_{13}$O–C$_6$H$_4$–CHO, rt; (v) **4b**, HC≡C–TMS, PdCl$_2$(PPh$_3$)$_2$/CuI/Et$_3$N cat., DMF/Et$_3$N 1:1, 55 °C; then K$_2$CO$_3$, CH$_2$Cl$_2$/MeOH; (vi) **4a**, PdCl$_2$(PPh$_3$)$_2$/CuI/Et$_3$N cat., DMF/Et$_3$N 1:1, 60 °C.

the excitation spectrum exhibits peaks at 372, 340, and 287 nm, which correspond to the different chromophores, all of them giving rise to emission (Fig. 3).

As indicated above, the four-armed tolane has two basic centers that can be protonated. The addition of successive aliquots (0.1 equiv) of trifluoroacetic acid provokes the protonation of the stronger basic Bu$_2$N– group. This avoids the charge separation state in this half, resulting in a continuous decrease in the fluorescence intensity at 536 nm, while increasing the emission of the shoulder. After the addition of 3 equiv of acid, only a single band from the other half with $\lambda_{max} = 470$ nm is observed (Fig. 4). A larger excess of acid begins to protonate the Ph$_2$N– group until complete quenching is achieved. These results demonstrate that the low-energy band in the emission spectrum of compound **1** is consistent with an excited state that is more polarized than the ground

state, that is, with a lower-lying intramolecular charge-transfer state.

In summary, the synthetic methodology to prepare new multichromophoric four-armed tolanes bearing an unsymmetrical distribution of functional groups is presented. We have selectively synthesized compound **1**. Absorption and fluorescence measurements demonstrate that the absorbing and emitting states of this molecule are not the same, developing a strong charge-transfer band in the fluorescence spectrum. This material also exhibits energy transfer and is a blue-fluorescence H$^+$-sensor that works over a wide spectral range (250–440 nm).

The synthesis of new four-armed tolanes bearing a different disposition of donor and acceptor groups as well as different chromophores and recognition elements is in
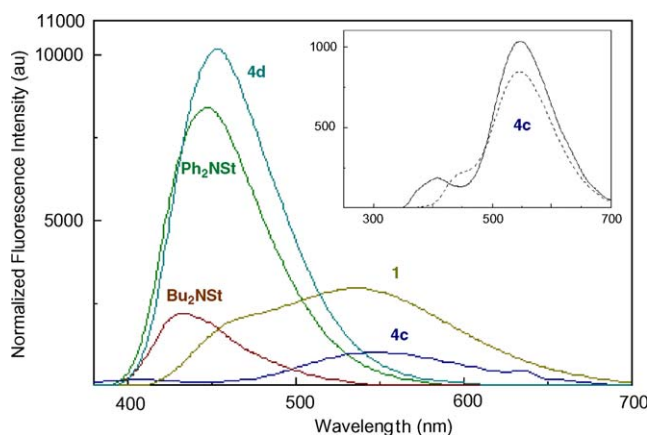
Figure 1. Normalized fluorescence spectra of **1** ($\lambda_{exc} = 300$ nm), *trans*-4-diphenylaminostilbene (Ph$_2$NSt, $\lambda_{exc} = 360.5$ nm), *trans*-4-dibutyl-aminostilbene (Bu$_2$NSt, $\lambda_{exc} = 345$ nm), **4c** ($\lambda_{exc} = 317$ nm), and **4d** ($\lambda_{exc} = 304$ nm) in CH$_2$Cl$_2$ at room temperature ($c = 1 \times 10^{-5}$ M in all cases). Inset: normalized fluorescence spectra of **4c** (solid line, $\lambda_{exc} = 317$ nm; dotted line, $\lambda_{exc} = 364$ nm).
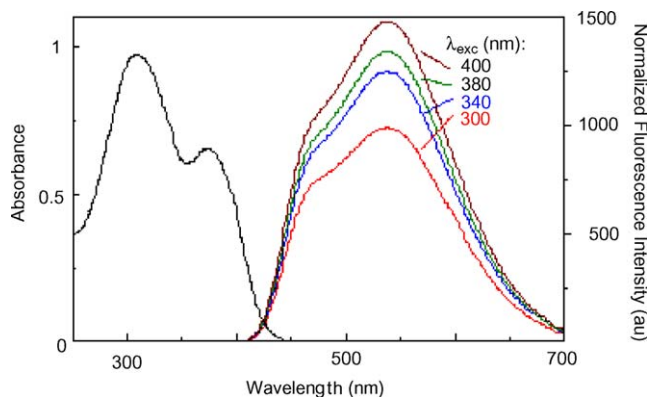

Figure 2. UV–vis absorption and normalized fluorescence spectra of **1** at different excitation wavelengths ($c = 1 \times 10^{-5}$ M in CH$_2$Cl$_2$ at room temperature).
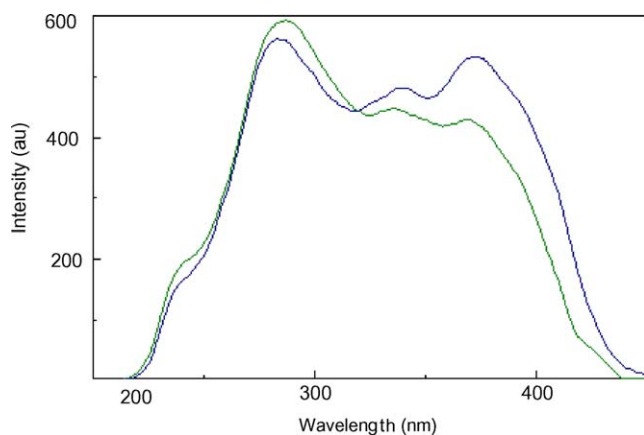

Figure 3. Excitation spectra of **1** at room temperature in CH$_2$Cl$_2$ (blue, monitored at 610 nm; green, monitored at 450 nm).

progress. Such compounds can be made starting from different aldehydes. They will be investigated with
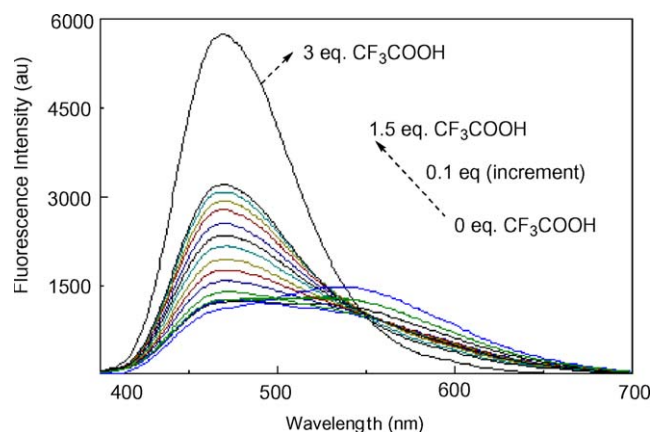

Figure 4. Spectrophotometric behavior at room temperature of **1** upon addition of successive aliquots (0.1 equiv) of trifluoroacetic acid to 3 mL of the solution. The concentration of **1** in CH$_2$Cl$_2$ was kept at 1×10^{-5} M. The excitation wavelength was 300 nm.

respect to the change of their optical properties in order to modulate desired spectral features.

Acknowledgments

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