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Nanosized π-Conjugated Molecules Based on Truxene and Porphyrin: Synthesis and High Fluorescence Quantum Yields

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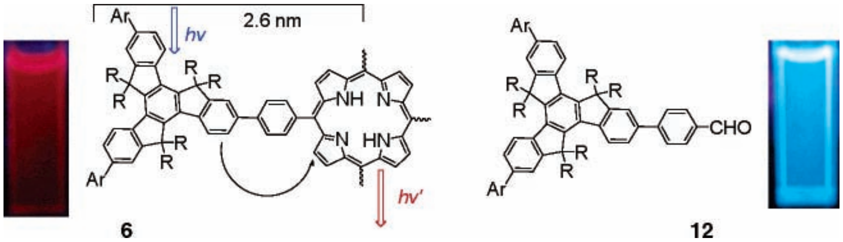
ABSTRACT



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A series of novel nanosized π-conjugated molecules based on both truxene and porphyrin moieties with high fluorescence quantum yields have been prepared via the Suzuki cross-coupling and the Lindsey reactions. The investigation of optical properties demonstrates that various aryl groups as the antenna efficiently enhance the intramolecular and intermolecular energy transfer. These nanosized macromolecules emitting intense red light might be good candidates for photonic and electronic devices.

Recently, the design and synthesis of nanosized π-conjugated macromolecules has rapidly become a vigorous research topic as a result of their momentous applications, such as active components in advanced materials.[1] π-Conjugated dendrimers have received particular attention in this field because of their regularly branched three-dimensional architectures, nanosized rigid structures, and monodisperse nature, as well as the ease of introduction of functional groups.[2] Such features of π-conjugated dendrimers are therefore appropriate for various applications in material science, including organic light-emitting diodes (OLED),[3] nonlinear optics,[4] and nanofibers by self-assembly.[5]

Porphyrins as building blocks provide an extensively conjugated two-dimensional π-system with a relatively facile synthetic approach.[6] Importantly, their biological activity as antennas and the efficient light-harvesting abilities in photo-

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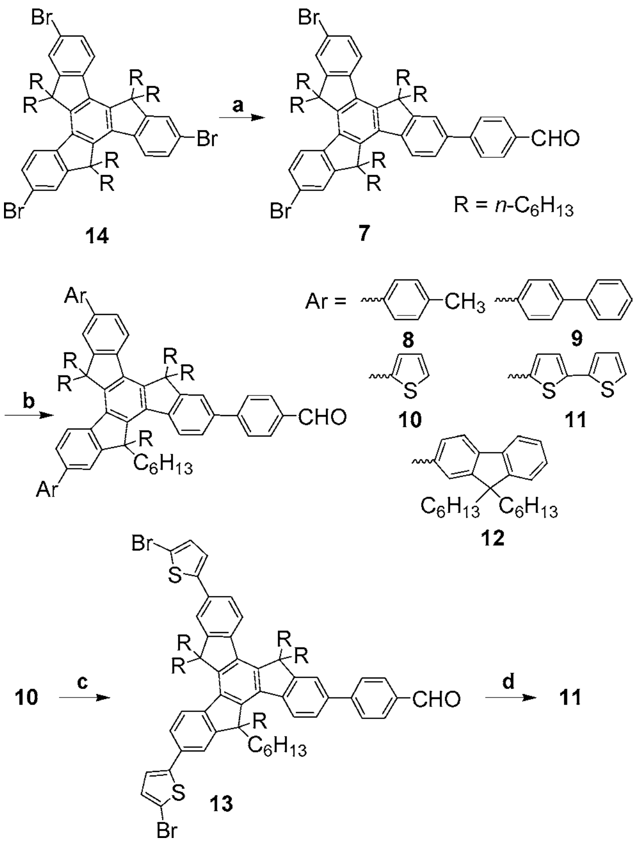
synthetic bacteria as well as the use in molecular conductive wires and optoelectronic devices have received extensive attention.[7] Although considerable efforts have been made for exploration of multiporphyrin arrays with flexible[8] and rigid dendrons,[9] to develop π-conjugated porphyrin-containing dendrimers as the core and/or as the bridge for the nanomaterials has still been of recent concern.

In this contribution, we present a series of π-conjugated nanosized macromolecules containing two chromophores (porphyrin and truxene moieties). For example, the diameter of **3** is ca. 5.2 nm (see SI S19−S21), which represents one of the largest known conjugated dendrimers based on prophyrin.[9] We also develop a highly convenient diversity approach to such porphyrin-containing π-conjugated dendrimers through the Suzuki coupling and the Lindsey reactions. We achieve highly intense red light emission from **1**−**6**, because truxene moieties with long alkyl chains radically enhance the solubility and suppress the aggregation in solid states and obviously reduce the self-quench of porphyrin's fluorescence.

The readily available starting material **14** was reported in our previous contributions.[10] Scheme 1 shows the approach to **7**−**12** as the precursors of **1**−**6**. The Suzuki cross-coupling reaction of tribromotruxene with 4-formylbenzeneboronic acid catalyzed by Pd(PPh$_3$)$_4$ in a mixture of THF and aqueous sodium carbonate solutions provided **7** in moderate yield (70%). Finally, we obtained **8**, **9**, **10**, and **12** from **7** and **11** from **13** in good yields (70−90%) by using various arylboronic acids. Bromination of **10** with NBS in CH$_2$Cl$_2$ and acetic acid (v/v = 1:1) afforded **13** (90%).

Scheme 1[a]



[a] Reagents and conditions: (a) 4-formylbenzeneboronic acid, Pd(PPh$_3$)$_4$, THF, reflux; (b) arylboronic acid, Pd(PPh$_3$)$_4$, THF, reflux; (c) NBS, CH$_2$Cl$_2$/acetic acid, 0 °C; (d) 2-thiophenylboronic acid, Pd(PPh$_3$)$_4$, THF, reflux.

As outlined in Scheme 2, the products through the Adler reaction using propionic acid as the catalyst and solvent were too difficult to be purified.[11] Trifluoroacetic acid was not powerful enough to construct such large molecules.[12] Fortunately, the condensation of **7**−**12** with distilled pyrrole using BF$_3$·Et$_2$O and ethanol as catalyst and CH$_2$Cl$_2$ as solvent in an aerobic dark environment, following by DDQ oxidation and Et$_3$N neutralization, afforded porphyrins **1**−**6** at about 20% yields.[13] We also employed the Suzuki reaction of **1** with various arylboronic acid to produce **2**−**6**; however, the yields were quite low and it was difficult to purify the desired products.[14] Therefore, such fairly convenient and highly diversified convergent strategy provides us the possibility to develop nanosized π-conjugated porphyrins with various aromatic substituents at outermost.

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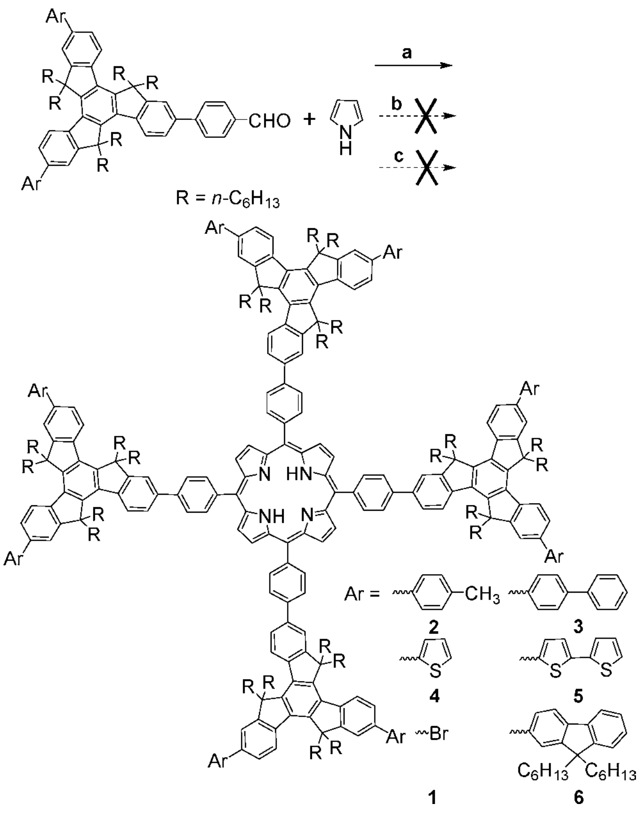
Scheme 2[a]



[a] Reagents and conditions: (a) (i) $BF_3{\cdot}Et_2O$, Ethanol, CH_2Cl_2, (ii) DDQ, (iii) NEt_3; (b) propionic acid, reflux; (c) (i) trifluoroacetic acid, (ii) DDQ, (iii) NEt_3.

Porphyrins **1**−**6** were readily soluble in common organic solvents such as toluene, CH_2Cl_2, chloroform, and THF. The structure and purity of all new compounds was characterized clearly with ^1H and ^{13}C NMR spectra and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy (see SI S22−S60). ^1H NMR spectra showed expected signals for the inner proton of porphyrin moiety at around −2.50 ppm together with the aromatic protons (at about 9.10 ppm) corresponding to porphyrin moieties.

The absorption and photoluminescent (PL) spectra of porphyrin derivatives **1**−**6** were recorded both in dilute THF solutions (10^{-6} M) and in thin films as shown in Figures 1 and 2. Table S1 summarizes their physical properties. In Figure 1, **1**−**6** show the main features of absorption spectra including four Q-bands in the region of 500−700 nm (which were consistent with a free-base porphyrin), the Soret band at 425 nm, and the truxene moiety at 315−380 nm, respectively. We also observed that to introduce the different aryl groups resulted in a red-shift of the absorption peaks of truxene moieties (328 nm for **2**, 334 nm for **3**, 340 nm for **4**, 375 nm for **5** and 341 nm for **6**, respectively) due to the increase of the effective conjugation length through $\pi-\pi^*$ delocalization. In comparison with TPP (tetraphenylporphyrin),[9h] the Soret band of **2**−**6** exhibited slight red-shift (about 9 nm).

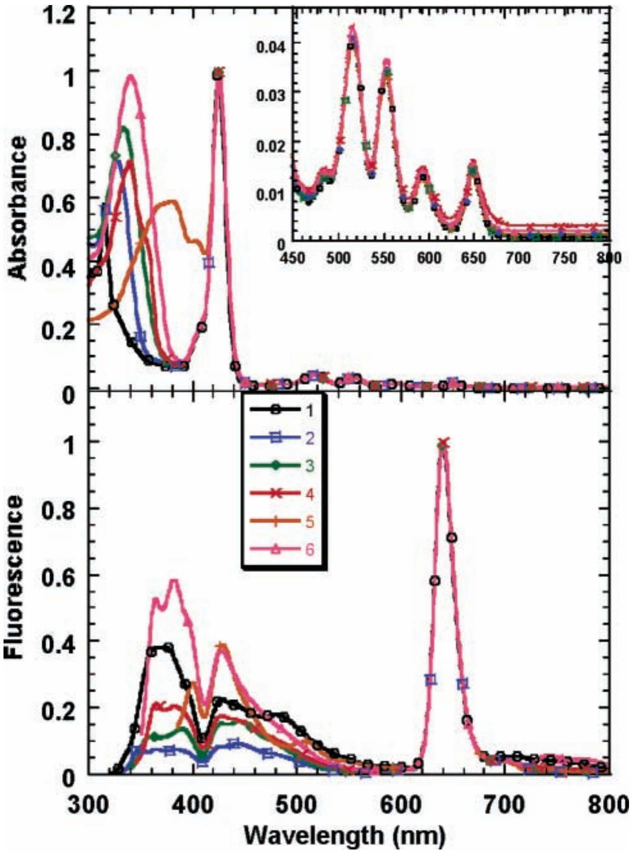


Figure 1. Normalized absorbance (top) and fluorescence (bottom) spectra of **1**−**6** in solution states at room temperature. Emission spectra were obtained upon excitation at the absorption maxima.

All PL spectra in dilute THF solutions exhibited characteristics of the porphyrin chromophore (at about 650 nm) and truxene derivatives (at about 300−400 nm) as well as another peak at 400−500 nm, respectively. The fluorescence quantum yields (ΦF) of **1**−**6** were from 0.19 to 0.30, which was much higher than lots of porphyrin derivatives; for example, the quantum yield of TPP was about 0.11.[15] Compound **6** exhibited strong red light emission with high fluorescence quantum yield (ΦF = 0.30), indicating that it could be a good candidate for red-emitting materials.

To understand the energy transfer we first carried out the PL measurement at the absorption maximum of the dendron and the core. The photoluminescent excitation (PLE) spectra of **1**−**6** were also recorded under excitation at 650 nm across the absorption spectrum (see SI S15−S17). Both PL and PLE results demonstrated that highly efficient energy transfer from the truxene moieties to the porphyrin core was achieved owing to the antenna effect of eight aryl branches at the outer space.

Solid films of **1**−**6** on quartz plates were spin-coated with 10 mg/mL THF solutions at 1000 rpm and recorded in Figure 2. We observed that absorption behaviors of **1**−**6** in films were almost identical with those in solutions, which implied

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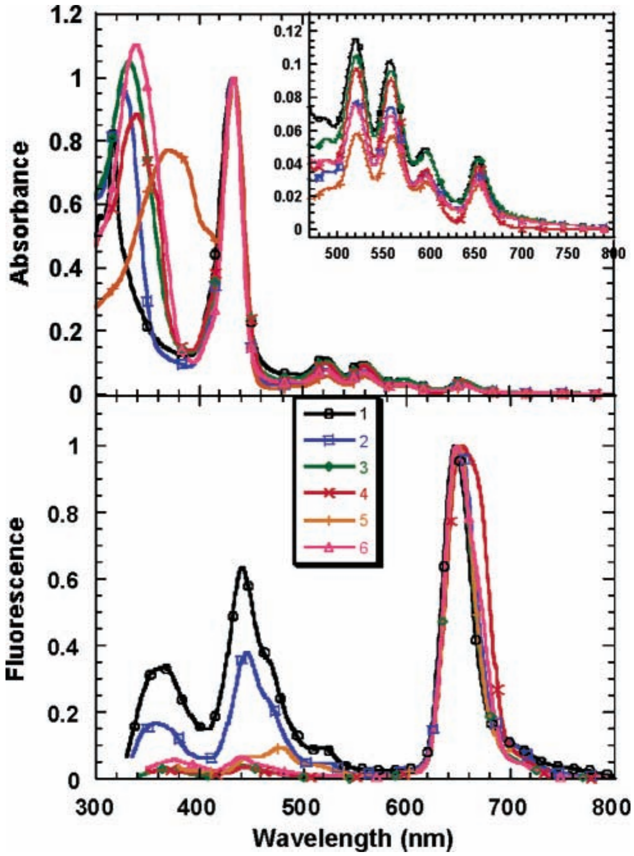

Figure 2. Normalized absorbance (top) and fluorescence (bottom) spectra of **1**−**6** in film states at room temperature. Emission spectra were obtained upon excitation at the absorption maxima.

that intermolecular $\pi-\pi$ aggregation was suppressed in films owing to the long alkyl chains. However, the Soret band of the porphyrin core red-shifted about 8 nm (433 nm) relative to those in solutions (425 nm).

In thin films, **1**−**6** exhibited intense light emission at about 650 nm, which blue-shifted about 10 nm compared with TPP as a result of the large torsion angle between the porphyrin core and the truxene moieties. All results indicated that the large steric effect of the truxene skeleton significantly reduced the $\pi-\pi$ aggregation of the porphyrin core. Interestingly, we observed that emission peaks in the blue region were obviously decreased from **1** to **6**, which were identical with the red-shift of the absorption behaviors from **1**−**6**. We also found more efficient energy transfer in films than in solutions, because it was enhanced in solid films and the torsion angle between porphyrin and truxene moieties was smaller in films than in solutions.[16] With alteration of the outermost aryl units, irradiation of the truxene segments resulted in the intensity of emission bands between 350 and 500 nm weakening and the one of the porphyrin at around 650 nm increasing. This indicated that the efficiency of energy transfer from truxene arms to the porphyrin core enhanced with the increase of the effective conjugation length from benzene to the fluorene units. The remaining emission in blue region accounted for the competition between the direct emission from truxene moieties and energy transfer from truxene to porphyrin core.

In summary, we have developed a convenient and highly diversified route to construct novel, monodispersed, nanosized π-conjugated dendrimers based on truxene and porphyrin segments. These nanosized molecules show intense red light emitting properties with high fluorescence quantum yields both in solutions and in films. We also demonstrate that excitation of the truxene moieties leads to energy transfer to the luminescent core, and such energy transfer relies on the aromatic units at the outermost. Evaluating new materials based on this molecular backbone and applications in optoelectronic devices are still in investigation in our laboratory.

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Supporting Information Available: Experimental procedures, additional data and details. This material is available free of charge via the Internet at http://pubs.acs.org.

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