

## Porphyrins with Four Monodisperse Oligofluorene Arms as Efficient Red Light-Emitting Materials

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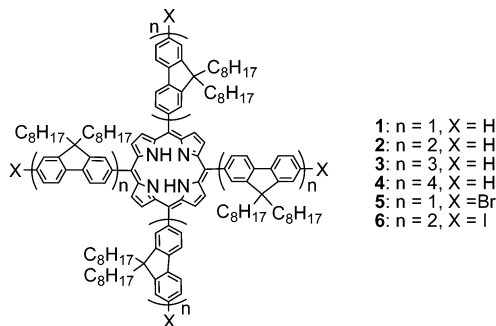
Organic and polymeric light-emitting materials have attracted considerable scientific and industrial attention due to their potential application in large area flat-panel displays.<sup>1</sup> For full-color displays three primary colors, i.e., blue, green, and red light-emitting materials are required. Green light-emitting materials have already been achieved with high brightness and efficiency, while red and blue light-emitting materials, which fully meet the requirements for commercial application, are scarce.<sup>2</sup> The main problem with red is its relatively low efficiency. Usually red light emitting is achieved by doping red dyes into host materials with a large band gap.<sup>3</sup> Red dyes are normally small organic molecules, which are prone to aggregate and end up self-quenching their luminescence. Organic dyes used as red emission doping materials are limited. Porphyrin is one, which exhibits reasonable fluorescence efficiency and good thermal stability. Examples of porphyrins used as red emitting materials include: tetraphenylporphyrin (TPP)<sup>3a,d</sup> and porphyrin platinum (II),<sup>3b,c</sup> which were used as dopants dispersed into host matrix such as AlQ<sub>3</sub> or poly(9,9-dioctylfluorene-2,7-diyl)s (POFs). (POFs are very promising blue light-emitting materials with exceptionally high solution- and solid-state quantum yields and excellent chemical and thermal stabilities.) Additionally, TPP as pendant groups attached to PPV polymer backbones with an alkylene spacer were also investigated.<sup>4</sup>

The idea in this communication is to bond the porphyrin (guest) and polyfluorenes (host) with conjugated chemical connections, which would lead to through-bond energy transfer. The rate of through-bond energy transfer is normally a hundred times faster than that of through-space energy transfer (Föster).<sup>6</sup> Furthermore, these kinds of structures should also help to form homogeneous amorphous films and prevent the porphyrin rings from aggregating and self-quenching their fluorescence. For this purpose, we synthesized a series of well-defined star-shaped porphyrins with four oligofluorene arms at their *meso* positions and investigated the relationships of their structures and optical properties.

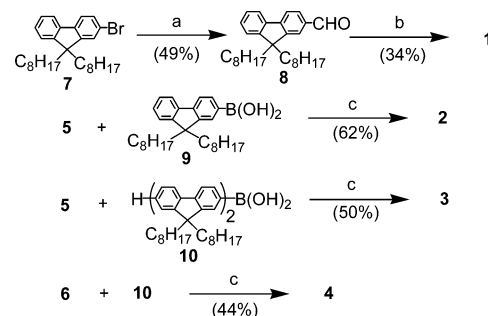
The chemical structures of the four-arm oligofluorene porphyrins 1–6 are outlined in Chart 1. The oligofluorene arms not only conjugate with the porphyrin rings but also provide good solubility for the whole molecules. The key reactions involved in the synthesis are “Lindsey condensation” for porphyrin synthesis and Pd-mediated Suzuki–Miyaura cross coupling (SMCC) reactions for the attachment of the oligofluorene arms. The synthetic routes to porphyrins 1–4 are outlined in Scheme 1.

The synthesis of the monofluorene porphyrin 1 was started from 2-bromo-9,9-dioctylfluorene 7, with treatment of 7 with 1.2-fold of *n*-BuLi and followed by quenching with DMF to give 8 in a yield of 49%. Lindsey condensation of 8 with equimolar amount of pyrrole in chloroform with trifloroacetic acid (TFA) as a catalyst afforded 1 in a yield of 34%. Porphyrins 2 and 3 were prepared by SMCC of tetrabromo-monofluorene-porphyrin 5 (vide infra) with corresponding mono- and difluoreneboronic acid 9 and 10, respec-

Chart 1

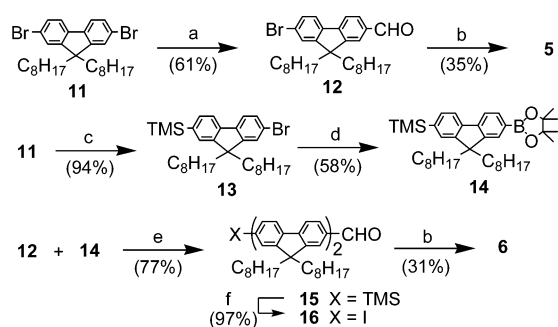


Scheme 1<sup>a</sup>

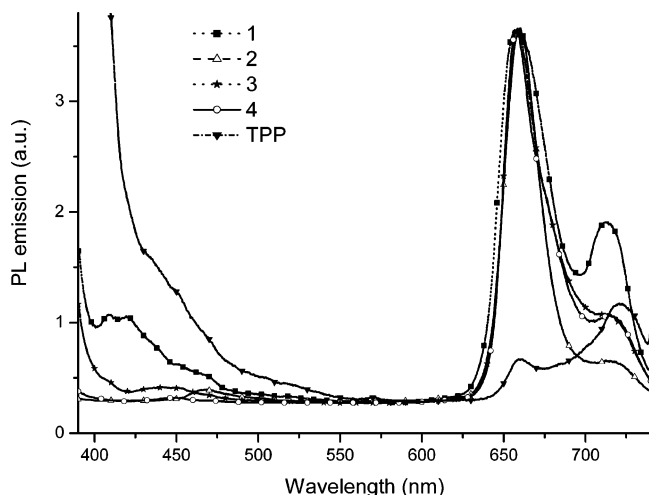


<sup>a</sup> (a) (i) *n*-BuLi,  $-78\text{ }^{\circ}\text{C}$  to rt; (ii) DMF,  $-78\text{ }^{\circ}\text{C}$  to rt. (b) (i) pyrrole, TFA,  $\text{CHCl}_3$ , rt, 12 h; (ii) DDQ. (c) Pd(PPh<sub>3</sub>)<sub>4</sub>, NaHCO<sub>3</sub>, THF, H<sub>2</sub>O, N<sub>2</sub>, reflux, 2 d.

tively. Porphyrin 4 was obtained by coupling of tetraiodo-bifluorene-porphyrin 6 (vide infra) with bi-fluoreneboronic acid 10. The SMCC reactions were done with Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst in the biphasic system THF/NaHCO<sub>3</sub>, and afforded the final products in moderate yields (44–62%). The synthesis of two key intermediate porphyrins 5 and 6 is shown in Scheme 2. Monolithium–halogen exchanging of 11 and quenching with DMF accomplished 7-bromofluorene-2-carbaldehyde 12 in a yield of 61%. Condensation of 12 with pyrrole afforded 5 in a yield of 35%. The synthesis of tetraiodo-porphyrin 6 started from 11, which was converted to 2-bromo-7-trimethylsilyl-9,9-dioctylfluorene 13 by treatment with *n*-BuLi and followed by quenching with TMSCl. Halogen–lithium exchange followed by quenching with B(O-*i*-Pr)<sub>3</sub> affording 14 in a 58% yield. SMCC of 12 and 14 in standard conditions furnished 15 in a yield of 77%. The TMS group was readily converted to the iodo group by treatment with ICl in CH<sub>2</sub>-Cl<sub>2</sub>. 16 was obtained in a yield of 97%. Condensation of 16 with pyrrole afforded porphyrin 6 in a yield of 31%. All intermediates and final products were purified with column chromatography on silica gel and characterized unambiguously with <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, combustion analysis, or matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy.

Scheme 2<sup>a</sup>

<sup>a</sup> (a) (i) *n*-BuLi,  $-78\text{ }^{\circ}\text{C}$  to rt; (ii) DMF,  $-78\text{ }^{\circ}\text{C}$  to rt. (b) (i) pyrrole, TFA,  $\text{CHCl}_3$ , rt, 12 h; (ii) DDQ. (c) (i) *n*-BuLi,  $-78\text{ }^{\circ}\text{C}$  to rt; (ii) TMSCl,  $-78\text{ }^{\circ}\text{C}$  to rt. (d) (i) *n*-BuLi,  $-78\text{ }^{\circ}\text{C}$  to rt; (ii)  $\text{B}(\text{O}-i\text{-Pr})_3$ ,  $-78\text{ }^{\circ}\text{C}$  to rt; (iii) HCl; (iv) pinacol,  $\text{CH}_2\text{Cl}_2$ . (e)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{NaHCO}_3$ , THF,  $\text{H}_2\text{O}$ , reflux, 2 d. (f) ICl,  $\text{CH}_2\text{Cl}_2$ ,  $0\text{ }^{\circ}\text{C}$  to rt, 12 h.



**Figure 1.** Normalized PL spectra of spin-coated thin films of **1–4** and TPP.

Porphyrins **1–4** are readily soluble in common organic solvents such as THF,  $\text{CH}_2\text{Cl}_2$ , chloroform, and toluene.

The gel permeation chromatography (GPC) eluting curves of **1–4** exhibited a symmetrical narrow peak with a polydispersity of 1.02, which indicated a high purity. MALDI-TOF mass measurements were done with all porphyrins **1–4**, and the results fitted the calculated values very well.

In the UV–visible absorption spectra, all porphyrins **1–4** exhibited an intense Soret band with absorption maximum at around 425–430 nm together with four weak Q-bands between 500 and 700 nm. The Soret bands were markedly red-shifted and broadened compared with those of TPP. Increasing the number of fluorene units, the absorption peaks of the oligofluorene segments red-shifted from 290 to 365 nm along with increasing the intensity. The normalized emission spectra of **1–4** in THF solution showed emissions in blue and red regions (see SI). The emission spectra of spin-coated films of **1–4** and TPP are shown in Figure 1. All oligofluorene-armed porphyrins **1–4** films exhibited an intense red emission peak at around 658 nm and a shoulder at 715 nm, while TPP showed two relatively weak emission peaks at around 660 and 720 nm. Energy transfer from fluorene segments to porphyrin core is more efficient in films than in solution. This is probably

because the torsion angle between porphyrin and fluorene is smaller in films than in solution.<sup>7</sup> From the efficiency gain and the blue shift in the emission we would conclude that the degree of aggregation of the porphyrins was significantly reduced. With an increase of the number of fluorene units, irradiation of the fluorene segments at 360 nm resulted in the intensity of fluorene emission bands between 380 and 500 nm weakening, and the intensity of the porphyrin Q-band emission at around 658 nm increasing. This indicated that the efficiency of energy transfer from oligofluorene arms to the porphyrin core increased with the conjugation length of oligofluorenes. The remaining emission from oligofluorenes accounted for the competition between the direct emission from oligofluorenes and energy transfer to porphyrin. However, energy transfer become predominant when  $n \geq 3$ , because the emission intensity from the oligofluorene segments decreased drastically from **1** to **4**. The fluorescence quantum yields ( $\Phi_F$ ) of **1–4** in toluene were measured in comparison to TPP ( $\Phi_F = 0.11$ )<sup>5</sup> and range from 0.16 (for **1**) to 0.22 (for **4**). The values are much higher than many other porphyrins; however, they do not show a trend and seem to be similar irrespective of the number of fluorene units.

In conclusion, a series of star-shaped porphyrins with four oligofluorene arms were prepared. The side octyl chains on the fluorene units can efficiently suppress the aggregation of the porphyrin rings. The star-shaped oligomers showed blue absorption, but emitted in red due to efficient energy transfer. The efficiency of light absorption and energy transfer was intensified with increased conjugated length of the oligofluorene arms.

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**Supporting Information Available:** Detailed experimental procedures and characterization of all compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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