

Soluble porphyrin–bisindolylmaleimides dyad and pentamer as saturated red luminescent materials

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Received 2 October 2006; revised 5 December 2006; accepted 6 December 2006
Available online 26 December 2006

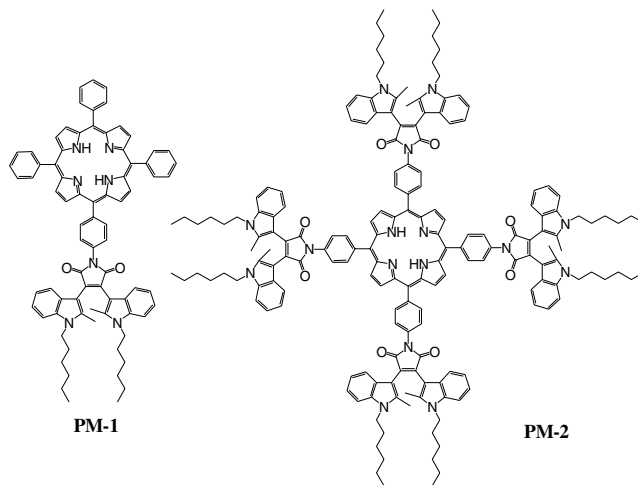
Abstract—Novel soluble porphyrin–bisindolylmaleimides dyad and pentamer have been prepared conveniently by coupling of amino-porphyrins and bisindolylmaleic anhydride. The bisindolylmaleimide groups function as the antenna to efficiently enhance the intramolecular energy transfer to the porphyrin core. These compounds may serve as good candidates of red-light emitting materials for organic light-emitting diodes.

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Light-emitting materials are the primary substances for organic light-emitting diodes (OLEDs) in flat panel display applications.¹ For full-colour displays, the development of red-, green-, and blue-emitting materials with a sufficiently high luminous efficiency and proper chromaticity is required. While green- and blue-emitting materials with good material strength (i.e., stability) have been achieved, red-emitting materials are usually achieved by doping red dyes (e.g., porphyrins) into host matrix materials with a large band gap.² Because that red dyes are normally organic molecules possessing π – π interaction or strong charge-transfer character, they are prone to aggregate and end up self-quenching their luminescence.³ Porphyrin exhibits reasonable fluorescence efficiency, saturated red luminescence, thermal stability and could be used as ideal doping materials.⁴ Many functional groups (e.g., oligo-fluorene,⁵ truxene⁶), which could act as efficient light-harvesting antenna and suppress the aggregation, have been introduced to porphyrin to achieve novel red light-emitting materials. Bisindolylmaleimides, as pure red luminescent materials, were also found effectively in the fabrication of OLEDs.⁷ Such conjugated chromophores have nonplanar conformation and could form amorphous glass in solid film

due to the steric hindrance of the two vicinal indole groups.

The idea in this Letter is to bond a porphyrin and bisindolylmaleimides with conjugated connections, which would lead to the through-bond energy transfer. The Förster mechanism would suggest that intramolecular through-bond mechanism is much faster.⁸ Furthermore, these kinds of structures should also help to form homogeneous amorphous films and prevent the porphyrin rings from aggregating and self-quenching their luminescence.



Keywords: Porphyrin; Bisindolylmaleimide; Intramolecular energy transfer; OLEDs.

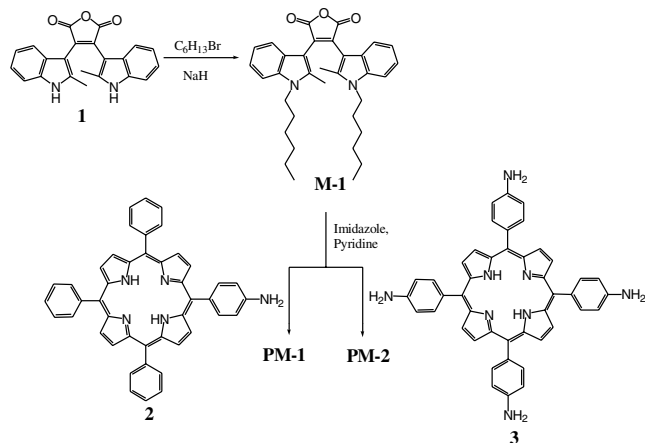
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Bisindolylmaleimide derivatives that incorporate porphyrins have been prepared through the imidization of bisindolylmaleic anhydride with aminoporphyrins (Scheme 1). The long hexyl chains on the bisindolylmaleimide units can improve the solubility and suppress the aggregation in solid states. The readily available starting material bis-2-methylindolylmaleic acid anhydride (**1**) was synthesized following the known procedure.⁷ Tetraphenylporphyrin⁹ (TPP) was synthesized for reference experiments.

Porphyrins **PM-1** and **PM-2** were readily soluble in common organic solvents such as toluene, CH₂Cl₂, THF and acetone. The structure and purity of **PM-1** and **PM-2** was characterized clearly with ¹H NMR, ¹³C NMR, ESI or MALDI-TOF mass spectroscopy. ¹H NMR showed expected signals for the inner proton of porphyrin moiety at around -2.70 ppm, and the signals of 5-, 6- positions of indole partially superpose the signals of water signals of CDCl₃ at 7.24 ppm (see Supplementary data).

The absorption spectra of **M-1**, **PM-1**, **PM-2** and TPP were recorded in dilute THF as shown in Figure 1. All porphyrins **PM-1** and **PM-2** exhibited an intense Soret band with four weak Q-bands between 500 and 700 nm. The Soret bands were slightly red shifted and broadened compared with those of TPP. The absorption in blue region and around 480 nm were due to the bisindolylmaleimide units. When the number of bisindolylmaleimide units was increased, the absorption at 290 nm and around 480 nm also increased.

All photoluminescence (PL) spectra in dilute THF solutions of the compounds exhibited characteristics of the porphyrin chromophore (at about 650 nm). The feature emission of bisindolylmaleimide could not be detected and virtually identical fluorescence spectra were obtained indicating an efficient energy transfer from the periphery bisindolylmaleimides to the porphyrin core. This is due to the overlaps between the emission spectrum of the isolated bisindolylmaleimide moiety and the Q-bands absorption of TPP via the Förster mechanism. The fluorescence quantum yields (Φ_F) of **PM-1** and **PM-2** in toluene were measured in comparison to



Scheme 1. Synthetic routes of compounds **PM-1** and **PM-2**.

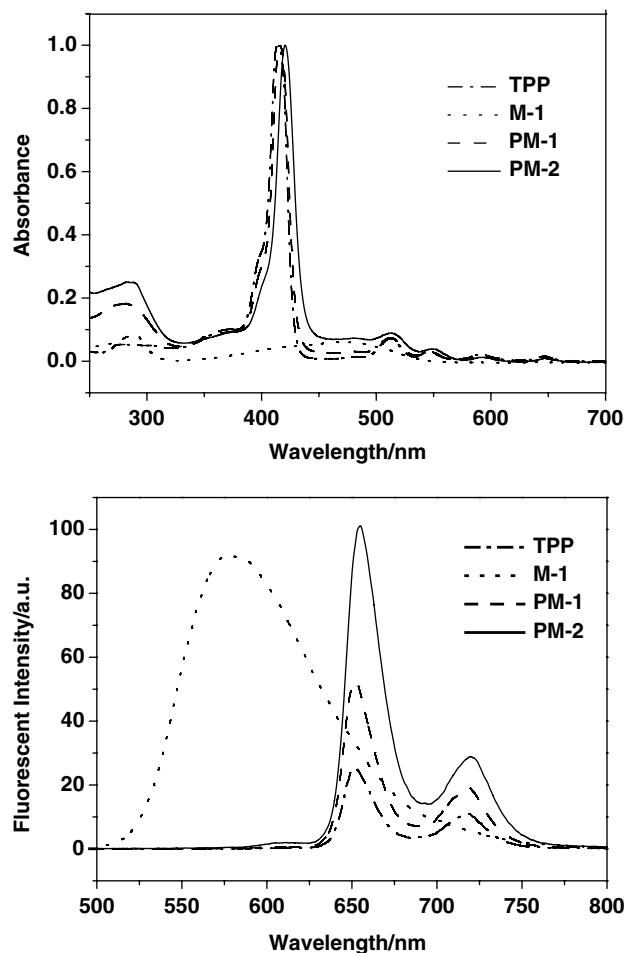


Figure 1. Normalized absorption spectra (top) and fluorescence spectra of **M-1**, **PM-1**, **PM-2** and TPP in THF (1.0×10^{-5} M in THF). Emission spectra were obtained upon excitation at the absorption maxima.

TPP ($\Phi_F = 0.11$ in toluene¹⁰) and ranged from 0.15 and 0.21, respectively. The values are much higher than many other porphyrin derivatives. The four bisindolylmaleimide armed porphyrin **PM-2** exhibited a stronger emission comparing to porphyrin-bisindolylmaleimide dyad **PM-1** due to the increased antennae harvesting energy.

Solid films of **PM-1** and **PM-2** on quartz plates were spin-coated with 10 mg/mL CH₂Cl₂ solutions at 1000 rpm and recorded in Figure 2. Similar spectra were obtained comparing to those in solutions. All results indicated that the import of bisindolylmaleimide skeleton significantly reduced the π - π aggregation of the porphyrin core. The excitation spectra of **PM-1** and **PM-2** in the film state were also recorded under excitation at 655 nm across the absorption spectrum (see in Supplementary data) and further demonstrated that highly efficiently energy transfer from the periphery bisindolylmaleimide to the porphyrin core.

Oxidation potentials of **PM-1** and **PM-2** were measured by cyclic voltammetry (CV) in CH₂Cl₂ using Ag/AgCl as a reference electrode. The reversible nature of

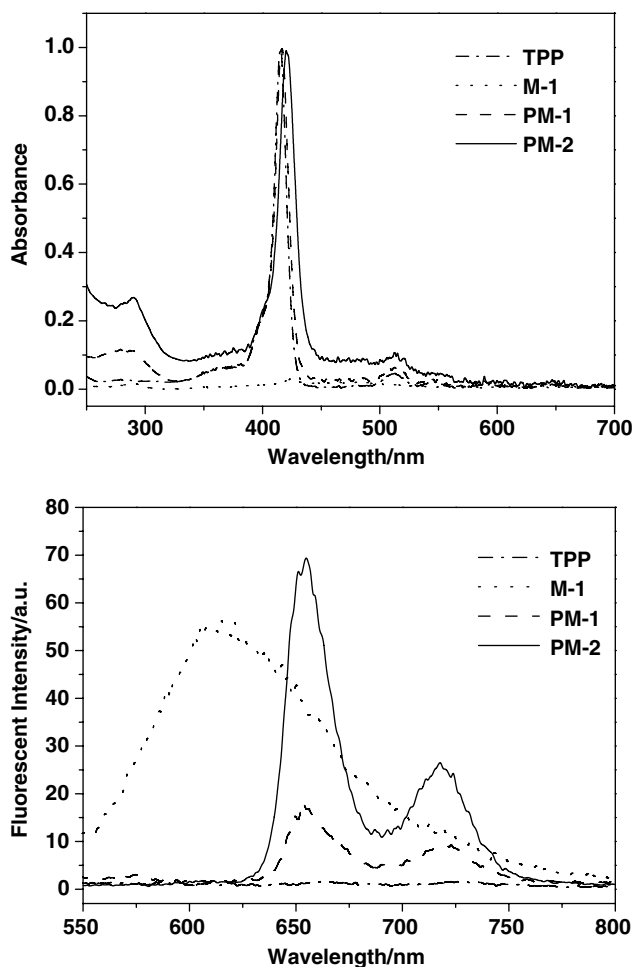


Figure 2. Normalized absorption spectra (top) and fluorescence spectra (bottom) of **M-1**, **PM-1** and **PM-2** in the film state at room temperature. Emission spectra were obtained upon excitation at the absorption maxima.

these peaks indicate the electrochemical stability of these compounds. The half-peak potentials ($E_{1/2} = 1/2(E_{pa} + E_{pc})$) of the first oxidation wave were estimated to be 0.96 and 1.14 V for **PM-1** and **PM-2**, respectively. The HOMO levels were estimated by a comparison with the ionization potential of ferrocene, which has been determined to be 4.8 eV.¹¹

The OLEDs (ITO/PEDOT/PVK/PFO+PBD: **PM-2** (5%)/Ba/Al) showed pure red (CIE $X=0.67$, $Y=0.30$) emission demonstrating effective energy transfer taking place in the emissive layer comprising of **PM-2** (see Fig. 3). The external quantum efficiency was found to be 0.13%. OLED devices 2.5% **PM-2** doped within the PFO + PBD host layer were also constructed. Although the luminance maximum was higher to 101 cdm^2 and the external quantum efficiency was up to 0.20%, the chromaticity coordinate ($X=0.52$, $Y=0.32$) was not pure enough due to inefficient energy transfer from PFO to **PM-2**.

In conclusion, two novel soluble bisindolylmaleimides functionalized porphyrins were prepared. Efficient energy transfer from the bisindolylmaleimides to the

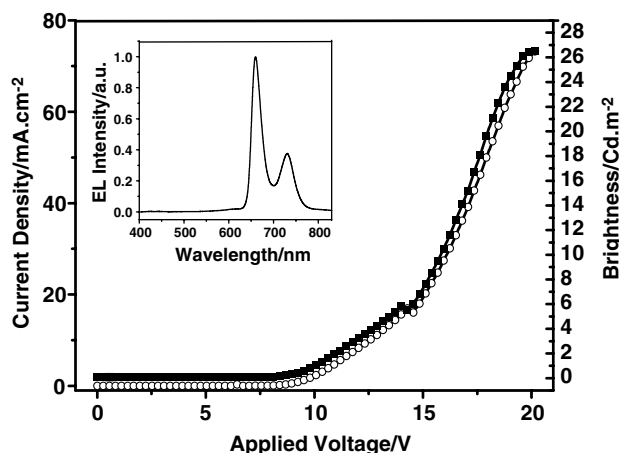


Figure 3. Current density–voltage–luminance curves of ITO/PEDOT/PVK/PFO + PBD: **PM-2** (5%)/Ba/Al.

porphyrin core was observed and increasing the number of bisindolylmaleimides could intensify the efficiency of light absorption and the energy transfer. In the OLEDs, the material of **PM-2** exhibits red emission with a high colour purity. Further modification of the compound as well as the device structure, aiming at the improvement of the physical performance of the devices is currently in progress.

Acknowledgement

This work was supported by NSFC/China and Scientific Committee of Shanghai.

Supplementary data

The experimental details, synthetic and spectroscopic data were available in [Supplementary data](#). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2006.12.013](https://doi.org/10.1016/j.tetlet.2006.12.013).

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