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Synthesis of *meso*-Coumarin-Conjugated Porphyrins and Investigation of Their Luminescence Properties

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A series of *meso*-coumarin-conjugated porphyrins **1a**–**e** were designed and synthesized. Condensation of 4-chloroacetoacetate ethyl ester with *m*-cresol or resorcin afforded 4-chloromethylcoumarins, which were then hydrolyzed to give coumarin alcohols, followed by oxidation to provide coumarin aldehydes. The reaction of coumarin aldehydes with pyrrole under Adler or Lindsey conditions afforded the *meso*-coumarin-conjugated porphyrins **1a**–**e**. Their UV/Vis absorption spectra and photoluminescent spectra were recorded both in dilute THF solution and as solid films. Analysis of the luminescence spectra indicate that the energy transfer from the coumarin substituents to the porphyrin core for **1a**–**e** is more efficient in solid film than in solution, and the energy transfer from the coumarin substituent to the porphyrin core for **1d** and **1e** is more efficient than that of **1a**, **1b** and **1c** in solid film.

Introduction

Light-emitting materials are the primary component used in the preparation of organic light-emitting diodes (OLEDs); these materials have attracted considerable scientific and industrial attention because of their potential applications in large area flat-panel displays.[1] Organic light-emitting materials for three primary colors, such as blue, green and red, are needed for full-color display. Among them, green and blue light-emitting materials have been fully developed,[2] but the development of red light-emitting materials is still at the early stage. Therefore, red light-emitting materials are urgently sought in order to realize full-color display of OLEDs.[3,4] Porphyrins have a large conjugated skeleton and may emit fluorescence with wavelengths around 650 nm; therefore, porphyrins are ideal candidates for red light-emitting materials. The coumarins are an important class of fluorescent compounds with outstanding optical properties, and they have been used as energy-transfer donors in dendrimers, transferring energy to acceptor cores by long-range förster-type resonance energy transfer.[5–9] In addition, it is known that electron-donating substituents in the 7-position of coumarins can make the coumarin fluorescent emission band redshift and enhance the emission intensity.[10] By taking advantage of the unique photochemical properties of both porphyrins and coumarins, in this contribution, we provided an example of *meso*-coumarin-conjugated porphyrins (Figure 1, **1a**–**e**) as red light-emitting materials. We envision that, upon excitation, coumarin substituents (donor) may act as an antenna, absorbing the energy and then transferring it to the porphyrin core (acceptor) to be reemitted by the porphyrin core as red fluorescence. The electron-donating groups, such as methyl,

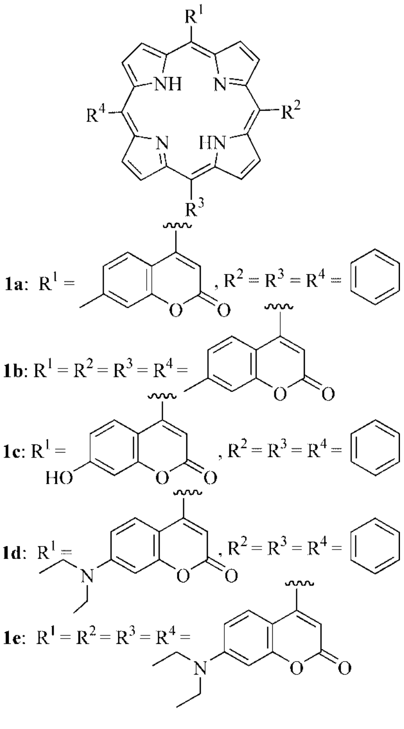

Figure 1. Molecular structure of *meso*-coumarin-conjugated porphyrins.

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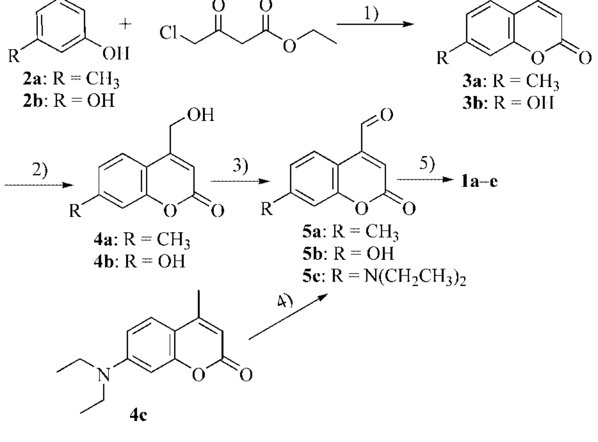
hydroxy, and diethylamino, in the 7-position of the coumarin moiety may promote the energy transfer from the coumarin substituent to the porphyrin core by electron-donating effects. In this communication, we presented the synthesis and luminescence studies of these novel red light-emitting materials.

Results and Discussion

The synthetic route of *meso*-coumarin-conjugated porphyrins (**1a**–**e**) is outlined in Scheme 1. Condensation of 4-chloroacetoacetate ethyl ester with *m*-cresol (**2a**) or resorcin (**2b**) in concentrated sulfuric acid at –5 °C afforded 4-chloromethyl-7-methylcoumarin (**3a**) or 4-chloromethyl-7-hydroxycoumarin (**3b**) in 72 or 85% yield, respectively. 4-Chloromethyl-7-hydroxycoumarin (**3b**) was hydrolyzed in boiling water overnight to give 7-hydroxy-4-(hydroxymethyl)coumarin (**4b**) in 92% yield. However, coumarin **3a** has limited solubility in water, so it was hydrolyzed in water/DMF (1:1) instead, and coumarin **4a** was obtained in 72% yield. Oxidation of **4a** or **4b** with manganese dioxide in refluxing THF for 3 d afforded 4-formyl-7-methylcoumarin (**5a**) or 4-formyl-7-hydroxycoumarin (**5b**) in yields of 81 or 41%, respectively. By contrast, 7-diethylamino-4-formylcoumarin (**5c**) was prepared from commercially available 7-diethylamino-4-methylcoumarin (**4c**), which was oxidized by selenium dioxide in refluxing *p*-xylene.



Scheme 1. Synthetic route of *meso*-coumarin-conjugated porphyrins. Reaction conditions: (1) Concentrated H_2SO_4, –5 °C; (2) for **4a**: DMF, H_2O, 100 °C; for **4b**: H_2O, 100 °C; (3) for **5a**: MnO_2, THF, reflux; for **5b**: MnO_2, ethyl acetate, reflux; (4) SeO_2, *p*-xylene, reflux; (5) for **1a**: benzaldehyde, pyrrole, **5a**, $BF_3{\cdot}OEt_2$, $CHCl_3$, room temp., 4 h, then *p*-chloranil, 61 °C, 2 h; for **1b**: pyrrole, **5a**, $BF_3{\cdot}OEt_2$, $CHCl_3$, room temp., 4 h, then *p*-chloranil, 61 °C, 2 h; for **1c**: benzaldehyde, pyrrole, **5b**, propionic acid, reflux, 45 min; for **1d**: benzaldehyde, pyrrole, **5c**, propionic acid, reflux, 45 min; for **1e**: pyrrole, **5c**, TFA, $CHCl_3$, room temp., 4 h, then *p*-chloranil, 61 °C, 2 h.

For the synthesis of porphyrin **1a**, coumarin **5a** was treated with pyrrole and benzaldehyde in a proportion of 1:5:4 in dry chloroform by using $BF_3{\cdot}OEt_2$ as the catalyst under a nitrogen atmosphere in the dark (Lindsey conditions[11]). Coumarin **5a** was also treated with pyrrole to give porphyrin **1b** by using the same Lindsey conditions. Because coumarin aldehyde **5b** is poorly soluble in chloroform, it was treated with benzaldehyde and pyrrole in refluxing propionic acid (Alder conditions[12]) to prepare porphyrin **1c**.

The synthesis of porphyrin **1d** was initially attempted by treating **5c** with benzaldehyde and pyrrole under the standard Lindsey conditions by using $BF_3{\cdot}OEt_2$ as the catalyst, but no desired product porphyrin **1d** was observed and most of **5c** remained intact. This could be due to the reaction of the strong lewis acid $BF_3{\cdot}OEt_2$ with the diethylamino group of **5c** to form a quaternary ammonium salt instead; therefore the $BF_3{\cdot}OEt_2$ catalyst became inactive.[13] Thus, the standard Adler method was then employed to prepare porphyrin **1d** by treating **5c** with benzaldehyde and pyrrole in refluxing propionic acid, and the desired product **1d** was successfully obtained. The success of the synthesis of porphyrin **1d** by employing the Adler conditions prompted us to attempt the preparation of porphyrin **1e** by using the same conditions; however, surprisingly, when **5c** was treated with pyrrole in refluxing propionic acid, a complex mixture was obtained. Alternatively, we decided to employ the Lindsey conditions by using TFA as a catalyst to prepare **1e**. Fortunately, after treating **5c** with pyrrole and TFA at room temperature for 4 h in the dark, we were able to isolate the desired product porphyrin **1e**.

Because the porphyrins synthesized as the potential emitting materials will ultimately be used in solid films in OLEDs, the absorption and photoluminescent spectra of **1a**–**e** were recorded both in dilute THF solutions (5×10^{-6} mol/L) and as solid films. The solid films of **1a**–**e** on quartz plates were spin-coated with 8 mg/mL dichloromethane solutions at 1000 rpm, and the thickness of these solid films is in the range of 100–120 nm.

The absorption spectra of **1a**–**e** in dilute THF solutions and solid films are shown in Figure 2. The absorption spectra of **1a**–**e** in solid films were almost identical to those in solutions except that they were redshifted by about 12–20 nm. The absorption spectra of **1a**–**e** both in solid film and THF solution show the main features of free-base porphyrins including an intense soret band and four weak Q bands. Interestingly, the Q bands of **1e** are redshifted, but the soret band of **1e** is blueshifted relative to those of **1a**, **1b**, **1c**, and **1d**. In addition, the soret band of **1e** appears significantly broader both in solution and film than that of **1a**, **1b**, **1c**, or **1d**. This is probably due to the overlap of the absorption soret band of the porphyrin core with that of the 7-diethylaminocoumarin substituent.

The photoluminescent spectra of **1a**–**e** in dilute THF solutions were recorded by exciting, in the soret band, the highest Q_y (0,1) transition or the corresponding coumarin-substituent absorption maxima, and all photoluminescent spectra exhibited characteristics of the porphyrin chromophore with intense red fluorescence emission: a peak maximum at about 650 nm and a weak shoulder at about 710 nm. Furthermore, in the photoluminescent spectra (Supporting Information, Figure S7) of **1a**–**e** obtained by

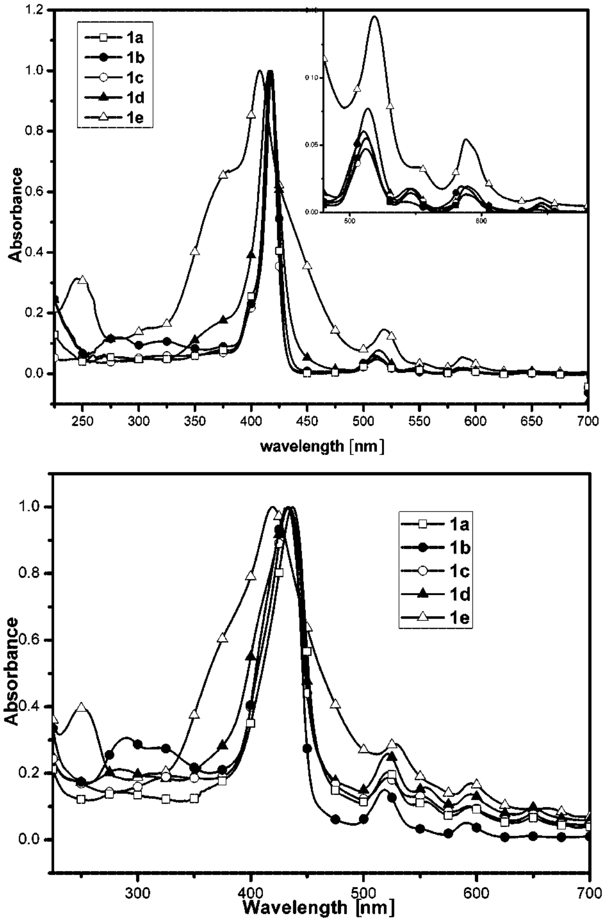


Figure 2. The normalized UV/Vis spectra of *meso*-coumarin-conjugated porphyrins in THF solution (top) and solid film (bottom).

exciting in the corresponding coumarin-substituent absorption maxima, besides the porphyrin chromophore emission at around 650 nm in the red range, there is still the residual emission of the coumarin substituents from 400 to 600 nm. This indicates that there is some extent of energy transfer from the coumarin substituent to the porphyrin core but that it is inefficient. The fluorescence quantum yields (Φ_F) of porphyrins **1a**–**e** in THF were measured by using tetraphenylporphyrin (Φ_F = 0.11 in benzene[14]) as a reference, and their fluorescence quantum yields range from 0.15 to 0.22.

The photoluminescent spectra of **1a**–**e** in solid film was also excited in the soret band, in the highest Q_y (0,1) transition or in the coumarin-substituent absorption, and all the photoluminescent spectra in solid film still exhibited the red fluorescence emission, the characteristics of the porphyrin chromophore. When compared with the emission bands of the photoluminescent spectra of **1a**–**e** in THF solution, those of **1a**–**e** in solid film exhibit a slight redshift. This is consistent with the redshift of the Q_X (0,0) absorption band in solid film.

The photoluminescent spectra of **1d** and **1e** in solid film, obtained by exciting in the corresponding coumarin-substituent absorption maxima, exhibit two significantly different characteristics when compared with those in THF solution (Figure 3). Firstly, in the photoluminescent spectra of **1d** and **1e** in solid film, besides the apparent porphyrin chromophore emission at around 670 nm in the red range, there is almost no residual emission of the coumarin substituents from 400 to 600 nm. This is in sharp contrast with the photoluminescent spectra of **1d** and **1e** in THF solution, which still, to some extent, exhibit emission of the coumarin substituents from 400 to 600 nm. To exclude the factor of the self-quenching effect of 7-diethylaminocoumarin substituent in the solid film, we further investigated the photoluminescent spectra of 7-diethylamino-4-formylcoumarin **5c** in the solid film. As shown in Figure S9 (Supporting Information), there is an apparently strong emission peak around 600 nm in the photoluminescent spectra of 7-diethylamino-4-formylcoumarin **5c**, this clearly indicates that 7-diethylamino-4-formylcoumarin **5c** does not self-quench in the solid film. Therefore, the lack of emission of the coumarin substituents in the photoluminescent spectra of **1d** and **1e** in solid film demonstrates that there is a good energy transfer between the 7-diethylaminocoumarin substituent and the porphyrin core. The energy absorbed by the coumarin antenna was apparently efficiently transferred to the porphyrin core and reemitted by the porphyrin chromophore as intense red fluorescence light. Secondly, the porphyrin chromophore emission peaks at around 670 nm in the photoluminescent spectra of **1d** and **1e** in solid film are markedly redshifted and broader relative to those in THF solution. This further supports that there is good energy transfer from the coumarin moiety to the porphyrin core for **1d** and **1e** in solid film, and the energy transfer for **1d** and **1e** in solid film is much more efficient than in THF solution. This is probably because, in the solid state, the stacking porphyrins reduce the torsion angle between the porphyrin core and the coumarin substituent, forcing them to be coplanar.[15] Thus, it enhances the conjugated extent of the porphyrin core and the coumarin substituent, facili-

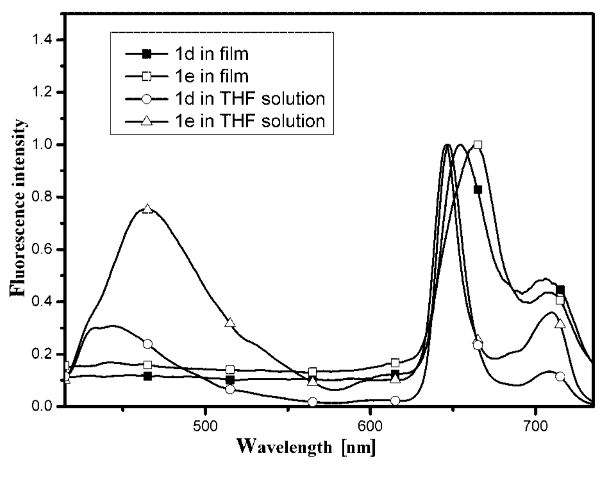


Figure 3. The normalized photoluminescent spectra of **1d**, **1e** in THF solution and solid film. The spectra were obtained upon excitation at the absorption of 7-diethylamino-4-formylcoumarin (380 nm).

tating the energy transfer from the coumarin substituent to the porphyrin core through bonds. Another line of evidence of efficient energy transfer between the 7-diethylaminocoumarin substituent and the porphyrin core of **1d** and **1e** in the solid film comes from the comparison of photoluminescent excitation spectra of **1d** and **1e** in the solid film with their absorption spectrum (Supporting Information, Figures S10–S13).

The photoluminescent spectra of porphyrins **1a**–**c** in solid film (Supporting Information, Figures S1–S3) still show the emission peaks of the corresponding coumarin substituents, but with the intensity of the emission peaks of the corresponding coumarin substituents decrease significantly relative to those in solution. In addition, the porphyrin chromophore emission peaks at around 670 nm of **1a**–**c** in solid film are broader and redshifted relative to those in THF solution. These lines of evidence indicate that, for **1a**–**c**, the energy transfer efficiency is still higher in solid film than in solution, but not very efficient. That is probably because the relatively weak electron-donating methyl and hydroxy groups at the 7-position of the coumarin substituents cannot efficiently promote the energy transfer from the coumarin substituent to the porphyrin core by electron donating effects.

Conclusions

A series of novel *meso*-coumarin-conjugated porphyrins, **1a**–**e**, were designed and synthesized as red fluorescent emitting materials. We also demonstrated that the energy transfer from the coumarin substituents to the porphyrin core for **1a**–**e** is more efficient in solid film than in solution, and the energy transfer from the coumarin substituent to the porphyrin core for **1d** and **1e** is more efficient than **1a**–**c** in solid film. In addition, the fluorescence quantum yields (Φ_F) of porphyrins **1a**–**e** in THF solution are higher than those of most other porphyrins.[14] The applications of **1d** and **1e** in organic light-emitting diodes (OLEDs) are in progress in our laboratory.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures and full characterization data for all compounds synthesized and some photoluminescent spectra of the porphyrin compounds.

Acknowledgments

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