

Highly Soluble Porphyrin (TPP)-Perylene Diimide (PDI) Dyad and Triad: Synthesis and Spectroscopic Studies

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Novel porphyrin-perylene diimide dyad (TPP-PDI) and porphyrin-perylene diimide-porphyrin triad (TPP-PDI-TPP) were synthesized and characterized. Their structure and properties were studied by UV, FL, ¹H NMR, MS, elemental analysis, *etc.* The variation of fluorescence feature and UV spectra of TPP-PDI-TPP triad were investigated at different concentration of CF₃COOH in THF. The incorporation of CF₃COOH leads to the closure of the efficient charge transfer decay. After protonation of porphyrin units, the fluorescence intensity of TPP-PDI-TPP triad increased greatly. The fluorescence intensity of TPP-PDI-TPP triad restored after addition of triethylamine into the solution. Thus, TPP-PDI-TPP triad was a proton-type fluorescence switch based on acid-base control. Moreover, different from porphyrin-perylene type molecular switches reported before, this TPP-PDI-TPP triad has wonderful solubility in organic solvents.

Keywords porphyrin, perylene diimide, protonation, fluorescence switch

Introduction

Perylene diimide (PDI) compounds¹⁻⁷ have been extensively investigated in donor-acceptor supramolecular systems because of their optical, redox and stability properties. On the other hand, porphyrins are well known as optoelectronic and biological materials because of their excellent photochemical and electronical properties.⁸⁻¹¹ In the past few years, porphyrin-PDI donor-acceptor systems¹²⁻²² attracted much attention in the fields of photosynthetic research and molecular photo/electro-active devices. Wasielewski and coworkers have reported an efficient synthetic route to prepare perylene-porphyrin array.¹²⁻¹⁴ However, the solubility of the expected array was very low because of the poor solubility of perylene unit. Here, we will introduce a donor-acceptor dyad and a donor-acceptor-donor triad consisting of porphyrin and PDI unit. The PDI unit in both compounds was modified by *tert*-butylphenoxy to increase their solubility. The mono-nitrified porphyrin was often prepared by condensing benzaldehyde, *p*-nitrobenzaldehyde and pyrrole, and the yield of this reaction was very low because there were six products which were difficult to separate. We modified the route to obtain mono-nitrified porphyrin through direct nitration of tetraphenylporphyrin with a yield of 70%. The fluorescence behavior of the TPP-PDI-TPP triad modulated by CF₃COOH and triethylamine was also dis-

cussed.

Experimental

Instruments and materials

¹H NMR spectra were obtained on BRUKER 500 spectrometer. Mass spectra were recorded using LCQ ADVANTAGE mass spectrometer. Elemental analyses were performed on Elementar Vario EL III C, H, N analyzer. Absorption spectra were measured with CARY 100 Conc UV-vis spectrophotometer. Fluorescence spectra were carried out with a CARY Eclipse Fluorescence spectrophotometer in a 1 cm quartz cell. All reagents were purchased from commercial sources and were distilled or dried when necessary using the standard procedures.

Synthesis

The synthetic route is shown in Scheme 1.

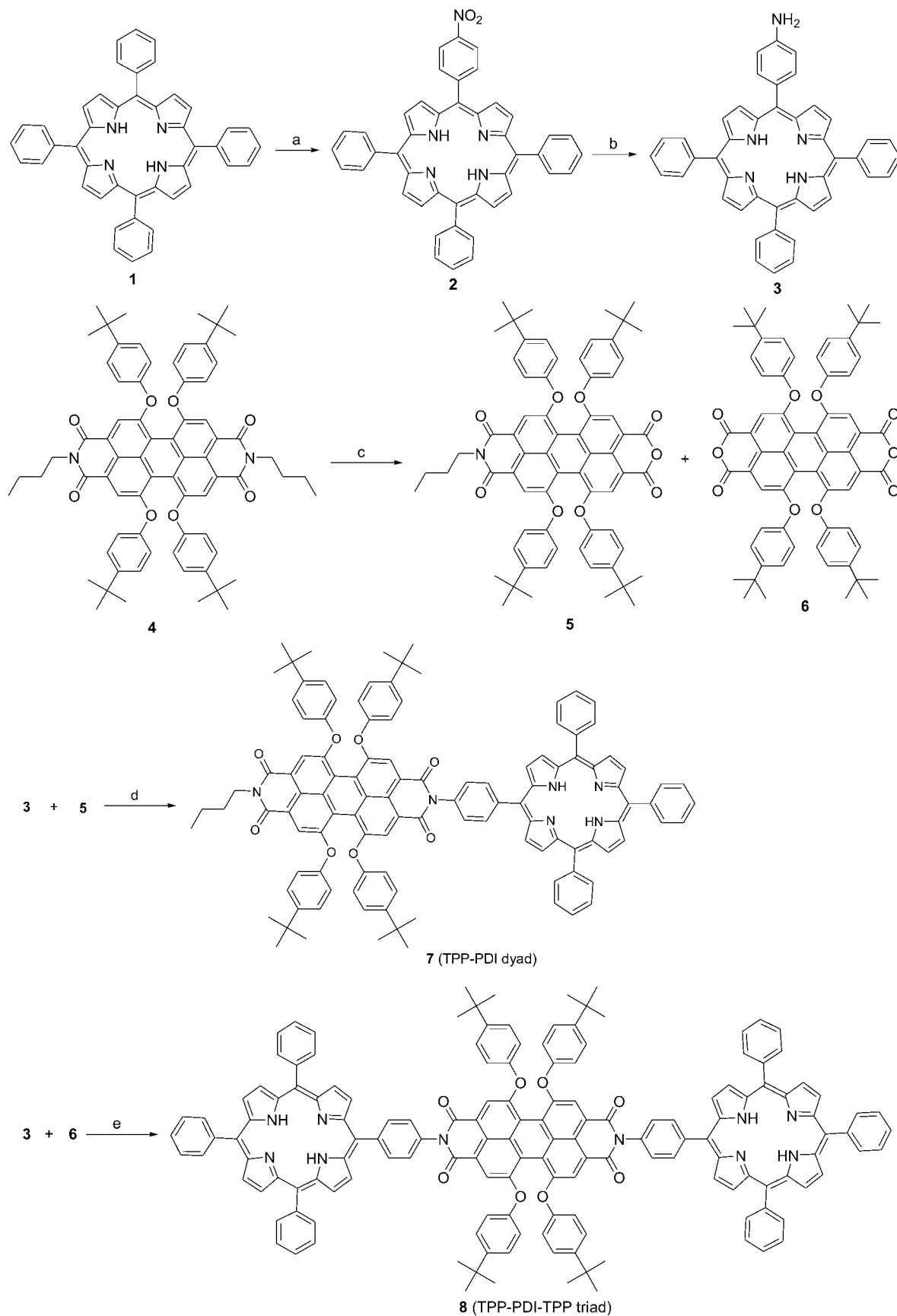
5-(4-aminophenyl)-10,15,20-triphenylporphyrin (3) (NH₂TPP) Compound **3** were synthesized according to the literature.²³ Yield: **1**, 40%; **2**, 70%; **3**, 81%. **3**: ¹H NMR (CDCl₃, 500 MHz) δ : 8.93 (d, *J*=4.5 Hz, 2H, H_{pyrrole}), 8.80–8.82 (m, 6H, H_{pyrrole}), 8.21 (d, *J*=6.5 Hz, 6H, H_{ar}), 7.97 (d, *J*=8.2 Hz, 2H, H_{ar}), 7.73–7.75 (m, 9H, H_{ar}), 6.95 (d, *J*=8.2 Hz, 2H, H_{ar}), 3.93 (s, 2H, NH₂), –2.75 (s, 2H, NH).

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Scheme 1 Synthetic route of TPP-PDI and TPP-PDI-TPP



Reagents and conditions: (a) 65% HNO₃, CHCl₃; (b) SnCl₂, HCl, N₂; (c) KOH, isopropanol, N₂; (d) imidazole, reflux in *m*-cresol for 24 h, yield 82%; (e) imidazole, reflux in *m*-cresol for 32 h, yield 74%.

***N*-butyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4-anhydride-9,10-tetracarboxylic imide (5) and 1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic bisanhydride (6)** Compound **5** and **6** were synthesized according to the literature.²⁴ Yield: **5**, 65%; **6**, 72%. **5**: ¹H NMR (500 MHz, CDCl₃) δ: 8.26 (d, *J*=2.47 Hz, 4H), 7.22 (d, *J*=8.32 Hz, 8H), 6.83 (d, *J*=7.34 Hz, 8H), 4.10 (t, *J*=7.53, 7.51 Hz, 2H), 1.64–1.66 (m, 2H), 1.34–1.36 (m, 2H), 1.29 (s, 36H), 0.84 (t, *J*=6.68, 7.09 Hz, 3H). **6**: ¹H NMR (CDCl₃, 500 MHz) δ: 8.28 (s, 4H, H_{per}), 7.25 (d, *J*=8.4 Hz, 8H, H_{ar}), 6.85 (d, *J*=8.8 Hz, 8H, H_{ar}), 1.3 (s, 36H, 4-C(CH₃)₃).

Porphyrin-perylene diimide dyad 7 (TPP-PDI) TPP-PDI dyad **7** was synthesized by the reaction of amino porphyrin **3** and compound **5**. Amino porphyrin **3** (650 mg 1.0 mmol), compound **5** (1.0 g, 1.0 mmol) and imidazole were added to 30 mL of *m*-cresol. The reaction mixture was heated to 170–175 °C under purified argon for 24 h with stirring. After the reaction mixture was cooled to room temperature, it was evaporated *in vacuo* to remove excess *m*-cresol. The residue was washed by methanol and filtered by silica gel. Then the residue was washed by hot 1% NaOH solution and hot water three times respectively. After drying, the residue was purified by chromatography on silica gel using a mixture of dichloromethane-petroleum ether (*V/V*, 2 : 1) as eluent, to give a purple solid **7** 1.31 g, yield 82%. m.p. > 300 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 8.85 (d, *J*=8.2 Hz, 2H, H_{pyrrole}), 8.60–6.64 (m, 6H, H_{pyrrole}), 8.29–8.34 (m, 4H, H_{per}+H_{ar}), 8.12–8.18 (m, 8H, H_{per}+H_{ar}), 7.88–7.92 (m, 9H, H_{ar}), 7.58 (d, *J*=8.3 Hz, 2H, H_{ar}), 7.20–7.24 (m, 8H, H_{ar}), 6.84–6.86 (m, 8H, H_{ar}), 4.08 (t, 2H, S-CH₂), 1.34–1.36 (m, 4H, CH₂), 1.21 (s, 36H, CH₃), 0.88–0.90 (m, 3H, CH₃), –2.85 (2H, NH); MS (ESI) *m/z*: 1652.8 [M]⁺ (calcd for C₁₁₂H₉₄N₆O₈ 1652.0). Anal. calcd for C₁₁₂H₉₄N₆O₈: C 81.43, H 5.74, N 5.09; found C 81.35, H 5.78, N 5.12.

Porphyrin-perylene diimide-porphyrin triad 8 (TPP-PDI-PDI) TPP-PDI-TPP triad **8** was synthesized by the reaction of NH₂TPP **3** (1.0 g, 16 mmol) and compound **6** (807 mg, 8.13 mmol) with imidazole in *m*-cresol (30 mL) according to the above working procedure. Compound **8** (1.33 g) was obtained in a yield of 74% with a byproduct porphyrin-perylene dyad in a yield of 5%. m.p. > 300 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 8.85 (d, *J*=4.5 Hz, 4H, H_{pyrrole}), 8.72–8.79 (m, 12H, H_{pyrrole}), 8.32 (s, 4H, H_{per}), 8.22 (d, *J*=8.5 Hz, 4H, H_{ar}), 8.09–8.15 (m, 12H, H_{ar}), 7.65–7.71 (m, 18H, H_{ar}), 7.57 (d, *J*=8.5 Hz, 4H, H_{ar}), 7.20 (d, *J*=8.9 Hz, 8H, H_{ar}), 6.90 (d, *J*=8.9 Hz, 8H, H_{ar}), 1.25 (s, 36H, CH₃), –2.85 (4H, NH); MS (MALDI-TOF) *m/z*: 2206.9 [M]⁺ (calcd for C₁₅₂H₁₁₄N₁₀O₈ 2206.8). Anal. calcd for C₁₅₂H₁₁₄N₁₀O₈: C 82.66, H 5.20, N 6.34; found C 82.71, H 5.18, N 6.38.

Results and discussion

UV absorption and fluorescent behavior

The UV-vis spectra of TPP-PDI **7** and

TPP-PDI-TPP **8** measured in THF (1.0 × 10^{−5} mol·L^{−1}) were presented in Figure 1. For comparison, the UV-vis spectra of model TPP **1**, and PDI **4** were also given. Their spectral data are listed in Table 1.

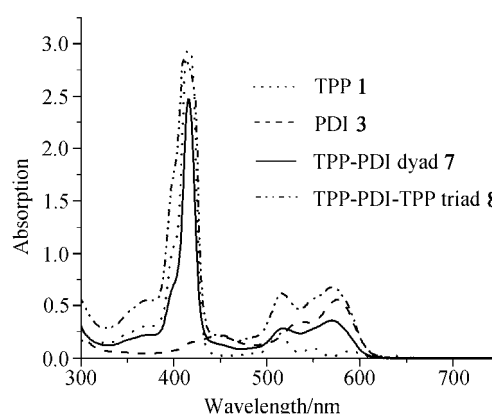


Figure 1 UV-vis absorption spectra of compounds **1**, **4**, **7** and **8** (1.0 × 10^{−5} mol·L^{−1} in THF).

The UV-vis spectra of **7** and **8** were almost the summation of UV-vis spectra of porphyrin chromophore and perylene diimide chromophore. Compounds **7** and **8** all showed intense absorption at about 418 nm which is the Soret band of porphyrin. The sharp Soret band was coincident with compound **1** and the Q-band of porphyrin overlaps with the first absorption band of perylene diimide in the region of 500–600 nm, this led to two absorption maxima at 516 and 571 nm. Since the perylene diimide moiety and porphyrin moiety in dyad **7** and triad **8** showed their individual characteristic absorption, it indicated that neither intramolecular nor intermolecular interaction took place between each electroactive moieties in the ground state.

Table 1 The UV-vis absorption data of compounds **1**, **4**, **7** and **8**

Compound	Absorption λ/nm ε × 10 ⁵ /(L·mol ^{−1} ·cm ^{−1})
1	418 (2.94), 515 (0.23), 549 (0.10), 589 (0.07)
4	450 (0.21), 537 (0.34), 576 (0.56)
7	417 (2.46), 518 (0.28), 570 (0.36)
8	415 (2.94), 516 (0.62), 571 (0.68)

Figure 2 showed the fluorescence spectra of **1**, **4**, **7** and **8** in THF. Compared to compounds **1** and **4**, dyad **7** and triad **8** showed a rather weak fluorescence. The maximum fluorescence intensity of TPP-PDI-TPP **8** which has porphyrin unit at both terminal of perylene diimide is much lower than TPP-PDI **7**. Thus, we chose TPP-PDI-TPP **8** to study its fluorescence switch performance.

UV-vis spectra (TPP-PDI-TPP triad) after addition of CF₃COOH

The UV-vis absorption of **8** and those after addition of different amounts of CF₃COOH are showed in Figure 3. After CF₃COOH was added, the absorption

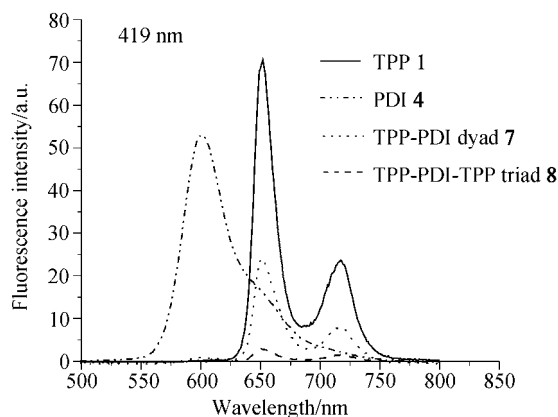


Figure 2 Fluorescence spectra of **1**, **4**, **7**, **8** ($4.5 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$, others $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, $\lambda_{\text{ex}} = 419 \text{ nm}$, THF).

band at 418, 516 and 571 nm decreased due to the protonation of porphyrin unit. The protonated porphyrin showed its new band at 441 and 655 nm. The spectra of **8** with $8.0 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1} \text{ CF}_3\text{COOH}$ showed that the Soret band of porphyrin at 418 nm was totally disappeared and the band between 500–600 nm was red-shifted. In contrast, the absorption of perylene diimide unit kept almost unchanged after addition of CF_3COOH .

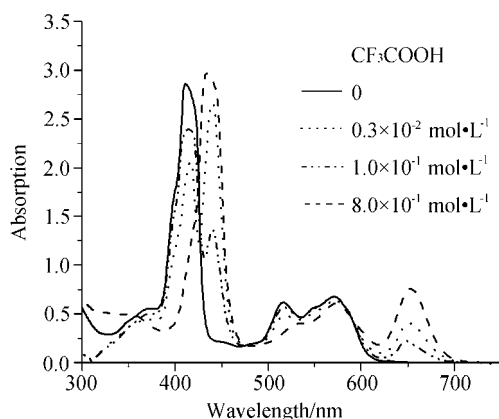


Figure 3 UV-vis absorption spectra of **8** in the presence of different amount of CF_3COOH ($1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ in THF).

Fluorescence spectrum (TPP-PDI-TPP) after addition of CF_3COOH

Figure 4 showed the fluorescence spectra of **8** in different concentration of CF_3COOH solution and further deprotonation by triethylamine. The fluorescence intensity began to increase when the concentration of CF_3COOH was larger than $10^{-2} \text{ mol} \cdot \text{L}^{-1}$. New fluorescence emission peak was produced by protonated porphyrin at 691 nm. The maximum fluorescence intensity increased about 34 times after $8.0 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1} \text{ CF}_3\text{COOH}$ was added. Obviously, the introduction of CF_3COOH interrupted the efficient charge transfer between porphyrin and perylene diimide unit at excited state. After react with excess triethylamine to the former

protonated solution, the fluorescence spectrum of compound **8** restored as expected. This indicated that the fluorescence of compound **8** could be modulated by reversible protonation and deprotonation of its porphyrin unit. Thus, TPP-PDI-TPP **8** was a fluorescence switch based on acid-base method.

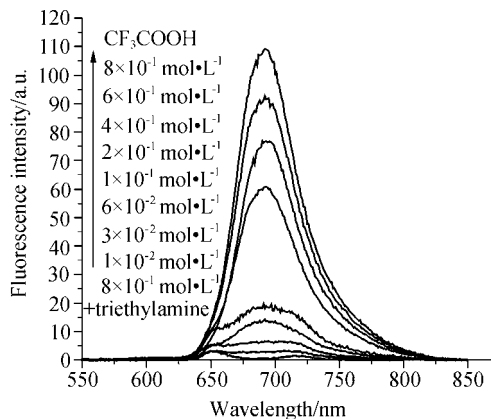


Figure 4 Fluorescence spectra of **8** in the presence of different amounts of CF_3COOH and further addition of triethylamine ($1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ in THF, $\lambda_{\text{ex}} = 419 \text{ nm}$).

Conclusion

We have synthesized novel TPP-PDI dyad **7** and TPP-PDI-TPP triad **8** which have wonderful solubility in organic solvents compared with former reported porphyrin-perylene diimide type fluorescence switches. The fluorescence of triad **8** quenched at a much larger extent compared with dyad **7**. What's more, its fluorescent behavior could be reversibly modulated by protonation and deprotonation of its porphyrin unit.

References

- Gómez, R.; Coya, C.; Segura, J. L. *Tetrahedron Lett.* **2008**, 49, 3225.
- Kohl, C.; Weil, T. J.; Qu, J. Q.; Müllen, K. *Chem. Eur. J.* **2004**, 10, 5297.
- Leroy-Lhez, S.; Perrin, L.; Baffreau, J.; Hudhomme, P. C. R. *Chimie* **2006**, 9, 240.
- Zheng, X. P.; Zhang, D. Q.; Zhu, D. B. *Tetrahedron Lett.* **2006**, 47, 9083.
- Guo, X. F.; Zhang, D. Q.; Zhang, H. J.; Fan, Q. H.; Xu, W.; Ai, X. C.; Fan, L. Z.; Zhu, D. B. *Tetrahedron* **2003**, 59, 4843.
- Bouquin, N.; Malininskii, V. L.; Haner, R. *Chem. Commun.* **2008**, 1974.
- Qvortrup, K.; Bond, A. D.; Nielsen, A.; Mckenzie, C. J.; Kilsa, K.; Nielsen, M. R. *Chem. Commun.* **2008**, 1986.
- Guo, X.-M.; Shi, Y.-H.; Zhang, Y.-H.; Yu, L.-X.; Shi, T.-S. *Chin. J. Org. Chem.* **2006**, 26, 247 (in Chinese).
- Liu, M. O.; Tai, C. H.; Chen, C. W.; Chang, W. C.; Hu, A. T. *J. Photochem. Photobiol. A* **2004**, 163, 259.
- Zhou, Z. C.; He, L.; Zhu, Y. Z.; Zheng, J. Y. *Chin. J. Chem.* **2007**, 25, 1632.

- 11 Sun, Y.; Chen, Y. H.; Li, Y. Z.; Li, Y. Q.; Ma, F. C. *Chin. J. Chem.* **2008**, *26*, 1011.
- 12 O'neil, M. P.; Niemezyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines III, G. L.; Wasielewski, M. R. *Science* **1992**, *257*, 63.
- 13 Debreczeny, M. P.; Svec, W. A.; Wasielewski, M. R. *Science* **1996**, *274*, 584.
- 14 Gosztola, D.; Niemczyk, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 5118.
- 15 Yang, S. I.; Lammi, R. K.; Prathapan, S.; Miller, M. A.; Seth, J.; Diers, J. R.; Lindsey, J. S.; Holten, D. *J. Mater. Chem.* **2001**, *11*, 2420.
- 16 Sun, J.-Z.; Yang, X.-G.; Li, H.-Y.; Huang, J.; Wang, M. *Chem. J. Chin. Univ.* **2004**, *25*, 2148 (in Chinese).
- 17 Scandola, F.; Chiorboli, C.; Prodi, A.; Iengo, E.; Alessio, E.; *Coord. Chem. Rev.* **2006**, *250*, 1471.
- 18 Li, Y.; Cao, L. F.; Tian, H. *J. Org. Chem.* **2006**, *71*, 8279.
- 19 You, C. C.; Würthner, F. *Org. Lett.* **2004**, *6*, 2401.
- 20 Boom, T.; Hayes, R. T.; Zhao, Y. Y.; Bushard, P. J.; Weiss, E. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 9582.
- 21 Xiao, X. W.; Xu, W.; Zhu, D. B. *J. Mater. Chem.* **2005**, *15*, 2557.
- 22 Li, X. Y.; Sinks, L. E.; Rybtchinski, B.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2004**, *126*, 10810.
- 23 Kruper, W. J.; Chamberlin, T. A.; Kochanny, M. *J. Org. Chem.* **1989**, *54*, 2753.
- 24 Li, Y. J.; Wang, N.; Gan, H. Y.; Liu, H. B.; Li, H.; Li, Y. L.; He, X. R.; Huang, C. S.; Cui, S.; Wang, S.; Zhu, D. B. *J. Org. Chem.* **2005**, *70*, 9686.

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