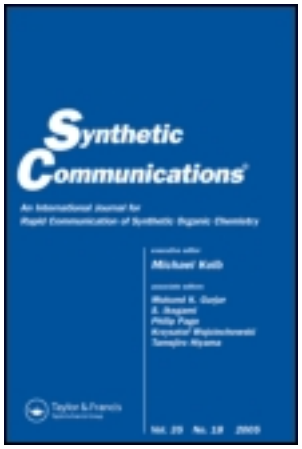

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Accepted author version posted online: 21 Oct 2011.Version of record first published: 25 Jan 2012.

To cite this article: Juanjuan Sun , Ming Wang , Ping Xu , Shuai Zhang & Zhiqiang Shi (2012): Synthesis of Water-Soluble Perylene Dicarboximide Derivatives Containing Pyridine Oxide Groups, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:10, 1472-1479

To link to this article: http://dx.doi.org/10.1080/00397911.2010.540731

Synthetic Communications®, 42: 1472–1479, 2012

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.540731

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SYNTHESIS OF WATER-SOLUBLE PERYLENE DICARBOXIMIDE DERIVATIVES CONTAINING PYRIDINE OXIDE GROUPS

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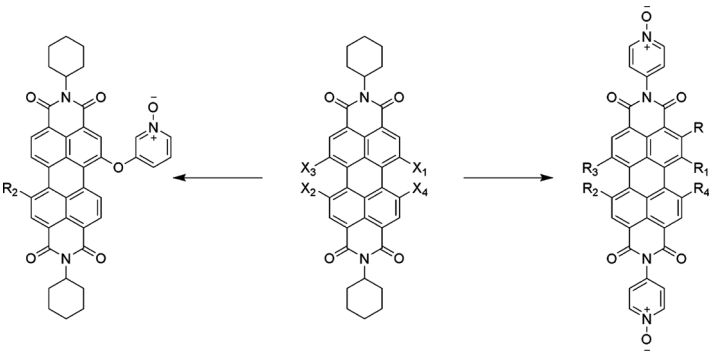
GRAPHICAL ABSTRACT



Abstract *Several water-soluble perylene dicarboximide derivatives were synthesized by indroducing pyridine oxide moieties to the perylene core or to imide groups.*

Keywords Fluorescence; perylene diimides; pyridine-N-oxide; water-soluble chromophore

INTRODUCTION

Although there are a large variety of water-soluble chromophores commercially available today, most of them exhibit relatively low fluorescence quantum yields and/or photochemical stabilities.[1,2] Perylene diimides (PDI) derivative is one outstandingly versatile organic chromophore.[3–6] PDI demonstrates exceptional thermal and photochemical stability, strongly absorbs visilble light, and shows high fluorescence quantum yield.[7,8] Because of the unique properties of PDI, it plays an important role in diverse fields such as biological applications,[9,10] where water solubility is an essential issue. Most PDI derivatives exhibit high fluorescence and good

Received January 7, 2010.

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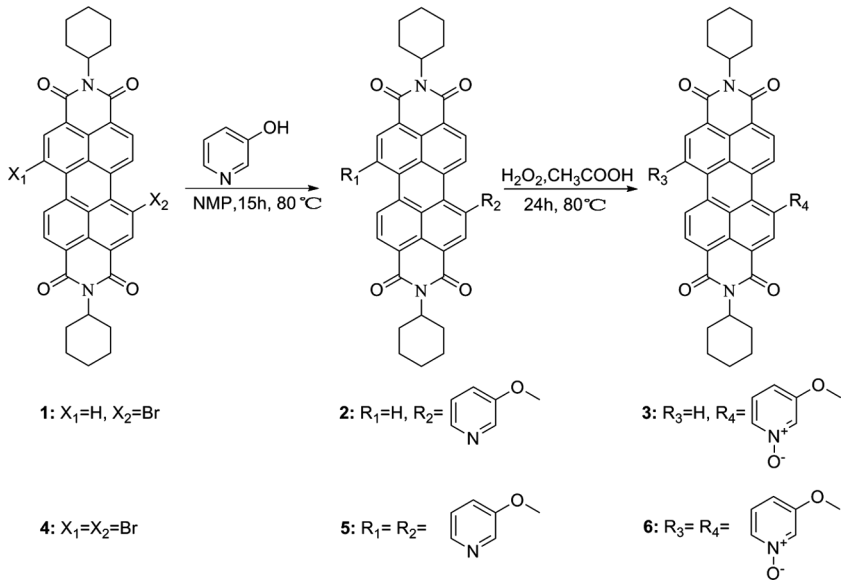
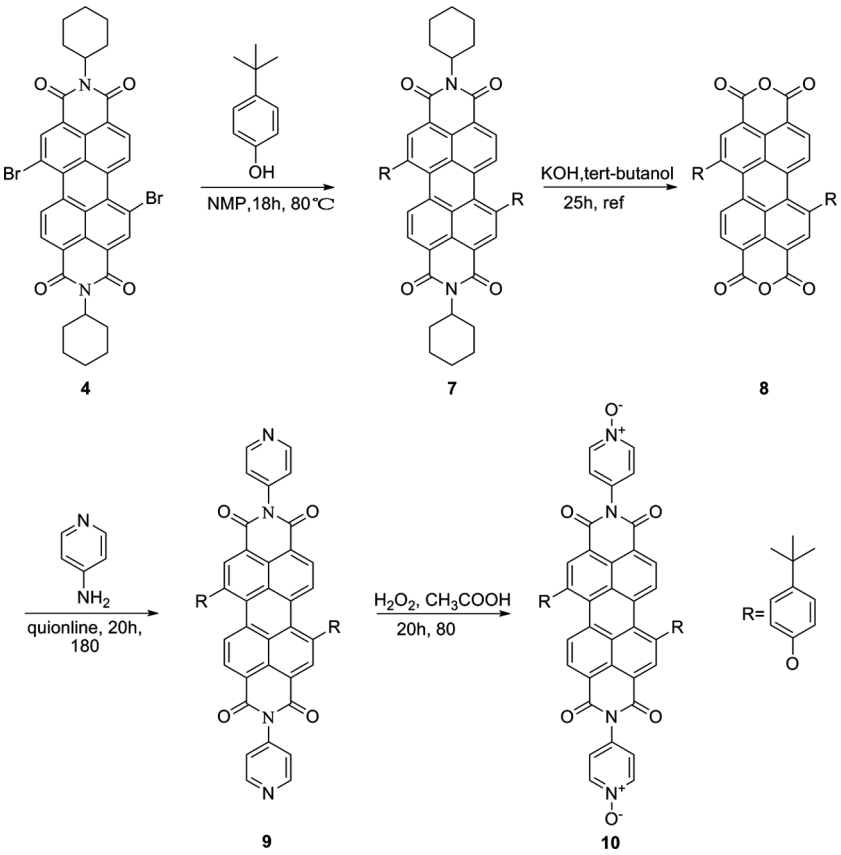
solubility in organic solvents but poor water solubility and very weak fluorescence in water because of aggregation of the perylene core.[11–13] Until now, only a few water-soluble PDI derivatives have been reported with hydrophilizing substituents, such as quaternized amine groups,[11] sulfonic acid moieties,[12] crown ethers[13] as part of the imide structure of the chromophore, polyethylene glycol,[14] or peptide chains[15] attached to the chromophore scaffold. In all cases these perylene chromophores show almost no fluorescence in water. Herein, several pyridine N-oxide groups were attached to the aromatic chromophore, which shown high fluorescence and good water solubility.

RESULTS AND DISCUSSION

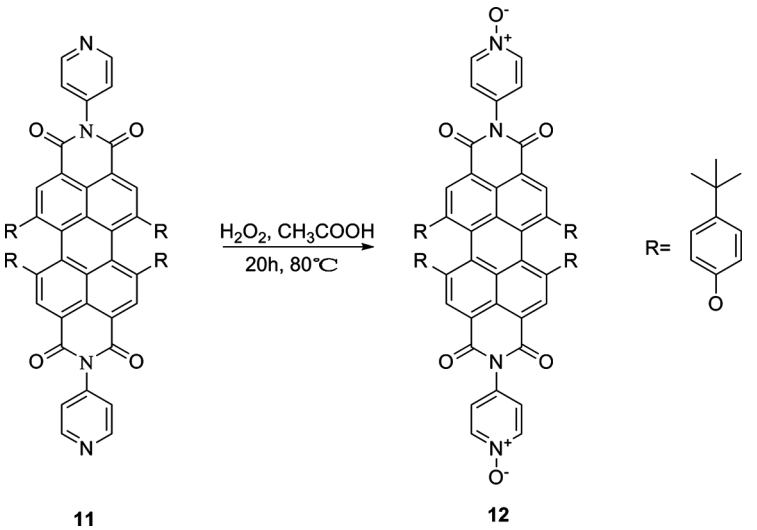
As we all know, the perylene core is rich in negative charge due to the π-stacking and results in aggregation behavior of perylene chromophores. There are two strategies to solve the solubility of perylene in water. One method introduces a hydrophilic group on the perylene, which can simultaneously twist the perylene core, and the group is like dendritic wedges that effectively shield the chromophores to suppress the effects of aggregation of the perylene, and the perylene core dispersed in water. However, the number of hydrophilic groups is not as much as we can predict. The other method, electron acceptors or positive group attached to the perylene core, could transfer the charge of perylene core itself, hence decreasing the degree of aggregation of perylene. Based on this concept, the synthesis of PDIs with one pyridine N-oxide substituent attached at the bay region was accomplished through treatment of (N,N′-dicyclohexyl-1-bromo)perylene-3,4:9,10-tetracarboxydiimide, which is available on a gram scale, with 3 equivalents of 3-hydroxypyridine in 1-methyl-2-pyrrolidone (NMP) (80% yield, Scheme 1). Because this chromophore



Scheme 1. Synthesis of compounds **3** and **6**.



Scheme 2. Synthesis of the compound **10**.



Scheme 3. Synthesis of the compound **12**.

is not soluble in water, N,N′-dicyclohexyl-1-(3-pyridine-N-oxide)perylene-3,4:9,10-tetracarboxylic acid bisimide **3** was prepared by oxidation of N,N′-dicyclohexyl-1-(3-pyridoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide **2** with H_2O_2 in CH_3COOH (54% yield). The synthesis of the two pyridine N-oxide-substituted PDI chromophores involved phenoxylation with 3-pyridinol by the same procedure as described previously, to yield N,N′-Dicyclohexyl-1,7-di(3-pyridine-N-oxide)-perylene-3,4:9,10-tetracarboxylic acid bisimide **6** (45% yield).

The N,N′-di(4-pyridine-N-oxide)-1,7-di(4-tert-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide **10** was derived from (N,N′-dicyclohexyl-1,7-dibromo)perylene-3,4:9,10-tetracarboxydiimide **4** in four steps via aryloxylation, saponification, imidation, and oxidation (Scheme 2). The purposed compound **12** was achieved by the means of oxidizing of compound **11**[16] with H_2O_2 in CH_3COOH (58% yield, Scheme 3).

CONCLUSION

In summary, facile synthesis routes of a kind of water-soluble chromophore based on PDI have been developed by indroducing pyridine oxide moieties to a perylene core or imide groups. This strategy results in good solubility in water and high fluorescence.

EXPERIMENTAL

N,N′-Dicyclohexyl-1-(3-pyridoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide 2. Compound **1** (0.50 g, 0.79 mmol), K_2CO_3 (0.49 g, 3.55 mmol), and 3-hydroxypyridine (0.30 g, 3.16 mmol) were dissolved in N-methyl-2-pyrrolidone (15 mL). The solution was stirred at 80 °C under argon for 13 h. The reaction mixture was chilled to room temperature, and aqueous HCl solution (2 N) was added. The solution was filtered, and the precipitate was washed with water. The red solid was dried at 50 °C under vacuum overnight. The product was purified by column chromatography over silica gel (CH_2Cl_2–acetone = 50:1) to yield a red solid (409 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.32–1.44 (m, 7H), 1.76 (m, 5H), 1.92 (m, 4H), 2.54 (m, 4H), 5.00 (m, 1H), 5.04 (m, 1H), 7.49–7.55 (m, 2H), 8.22 (s, 1H), 8.55–8.72 (m, 7H), 9.39 (d, 1H, $J = 8.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 25.42, 26.52, 29.10, 54.04, 54.22, 122.70, 123.61, 123.80, 124.49, 125.25, 126.32, 126.87, 127.48, 128.47, 128.60, 129.07, 130.39, 130.94, 131.78, 132.89, 134.03, 134.46, 140.19, 152.23, 154.32, 162.82, 163.57, 163.63, 163.88. MS (MALDI): 647 (M^+).

N,N′-Dicyclohexyl-1-(3-pyridine-N-oxide)perylene-3,4:9,10-tetracarboxylic acid bisimide 3. Compound **2** (0.3 g, 0.46 mmol) were dissolved in CH_3COOH (8 mL), and 0.5 mL H_2O_2 was added. The solution was stirred at room temperature for half an hour, and the temperature rose to 80 °C. About 3 h later, 0.5 mL H_2O_2 was added again, and the mixture continued to stir for 20 h. The reaction mixture was chilled to room temperature, and water was added. The solution was filtered, and the precipitate was washed with water. The red solid was dried at 50 °C under vacuum overnight. The product was purified by column chromatography over silica

gel ($CHCl_3$–THF–methanol = 250:50:3) to yield a red solid (166 mg, 54%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.37–1.51 (m, 6H), 1.78–1.91 (m, 10H), 2.52–2.60 (m, 4H), 5.04 (m, 2H), 7.45 (m, 1H), 8.23 (m, 2H), 8.31 (s, 1H), 8.63 (d, 1H, $J = 7.6$ Hz), 8.68–8.74 (m, 5H), 9.21 (d, 2H, $J = 7.6$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 25.39, 26.49, 29.08, 29.29, 29.67, 54.09, 54.29, 116.10, 122.95, 123.61, 123.95, 125.47, 126.30, 126.82, 127.91, 128.39, 129.05, 130.83, 131.04, 131.69, 132.29, 133.80, 134.56, 135.76, 141.59, 152.48, 154.40, 162.62, 163.44, 163.50, 163.77. MS (MALDI): 663 (M^+). Anal. calc. for $C_{41}H_{33}N_3O_6$: C, 74.19; H, 5.01; N, 6.33. Found: C, 73.98; H, 4.89; N, 6.20.

N,N′-Dicyclohexyl-1,7-di(3-pyridoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide 5. Compound **4** (0.50 g, 0.70 mmol), K_2CO_3 (0.49 g, 3.50 mmol), and 3-hydroxypyridine (0.34 g, 3.58 mmol) were dissolved in 1-methyl-2-pyrrolidone (15 mL). The solution was stirred at 80 °C under argon for 15 h. The reaction mixture was chilled to room temperature, and aqueous HCl solution (2 N) was added. The solution was filtered, and the precipitate was washed with water. The red solid was dried at 50 °C under vacuum overnight. The product was purified by column chromatography over silica gel (CH_2Cl_2–acetone = 20:1) to yield a red solid (414 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.25–1.45 (m, 8H), 1.61–1.91 (m, 8H), 2.44–2.52 (m, 4H), 4.96 (m, 2H), 7.40–7.48 (m, 4H), 8.26 (s, 2H), 8.54 (m, 4H), 8.64 (d, 2H, $J = 8.3$ Hz), 9.47 (d, 2H, $J = 8.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 25.36, 26.46, 29.06, 54.21, 123.22, 123.91, 124.19, 124.95, 125.62, 126.73, 127.91, 129.07, 130.52, 131.06, 132.61, 153.94, 162.82, 163.34. MS (MALDI): 740 (M^+).

N,N′-Dicyclohexyl-1,7-di(3-pyridine-N-oxide)perylene-3,4:9,10-tetracarboxylic acid bisimide 6. Compound **5** (0.30 g, 0.40 mmol) were dissolved in CH_3COOH (8 mL), and 0.5 mL H_2O_2 was added. The solution was stirred at room temperature for half an hour, and the temperature rose to 80 °C. About 3 h later, 0.5 mL H_2O_2 was added again, and the mixture continued to stir for 24 h. The reaction mixture was chilled to room temperature, and water was added. The solution was filtered, and the precipitate was washed with water. The red solid was dried at 50 °C under vacuum overnight. The product was purified by column chromatography over silica gel (CH_2Cl_2–methanol = 100:2) to yield a red solid (140 mg, 45%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.25–1.51 (m, 8H), 1.63–1.92 (m, 8H), 2.48–2.53 (m, 4H), 4.98 (m, 2H), 7.13–7.37 (m, 4H), 8.12 (m, 4H), 8.36 (s, 2H), 8.65 (d, 2H, $J = 8.3$ Hz), 9.29 (d, 2H, $J = 8.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 23.90, 25.33, 26.43, 29.02, 54.31, 67.60, 107.87, 116.47, 123.65, 125.05, 125.16, 125.47, 126.37, 129.05, 131.07, 131.20, 132.12, 152.11, 162.56, 163.14. MS (MALDI): 770 (M^+). Anal. calc. for $C_{46}H_{36}N_4O_8$: C, 71.49; H, 4.70; N, 7.25. Found: C, 71.12; H, 4.56; N, 7.16.

N,N′-Dicyclohexyl-1,7-di(4-*tert*-butylphenoxy)perylene-3,4:9,10-tetracarboxydiimide 7. Compound **4** (1.00 g, 1.40 mmol), K_2CO_3 (0.97 g, 7.03 mmol), and 4-*tert*-butylphenol (0.87 g, 5.80 mmol) were dissolved in 1-methyl-2-pyrrolidone (NMP) (30 mL). The solution was stirred at 80 °C under argon for 18 h. The mixture was chilled to room temperature, and aqueous HCl solution (2 N) was added. The solution was filtered, and the precipitate was washed with water. The red solid

was dried at 50 °C under vacuum overnight. The product was purified by column chromatography over silica gel (CH_2Cl_2–petroleum ether = 1:1) to yield a red solid (1.01 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.18 (m, 6H), 1.28 (s, 18H), 1.60 (m, 6H), 1.75 (m, 4H), 2.53 (m, 4H), 5.01 (m, 2H), 7.10 (d, 4H, $J = 8.2$ Hz), 7.48 (d, 4H, $J = 8.2$ Hz), 8.29 (s, 2H), 8.53 (d, 2H, $J = 8.3$ Hz), 9.54 (d, 2H, $J = 8.3$ Hz).^{13}C NMR (75 MHz, $CDCl_3$, ppm) : δ 25.44, 26.52, 29.10, 29.68, 31.46, 31.92, 34.53, 54.02, 119.23, 122.55, 123.35, 123.54, 124.15, 124.88, 127.41, 128.61, 128.96, 129.94, 133.15, 148.10, 152.53, 155.36, 163.30, 163.67. MS (MALDI): 850 (M^+).

N,N′-Di(4-pyridyl)-1,7-di(4-*tert*-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide 9. Compound **7** (0.50 g, 0.59 mmol) was added to 4-*tert*-butanol (30 mL), potassium hydroxide (1.65 g, 29.50 mmol), and water (2.6 mL), and the resulting solution was refluxed for 25 h. Then the crude mixture was cooled to room temperature, and aqueous HCl solution (2 M) and water were added. The solution was filtered, and the precipitate was washed with water and dried. The product **8** was not handled further as the next step's materials.

A mixture of compound **8** (0.4 g, 0.58 mmol), 4-aminopyridine (0.19 g, 2.02 mmol), and zinc acetate (0.10 g, 0.45 mmol) in quinoline (20 mL) was stirred under argon at 180 °C for 20 h. After the solution was chilled, 2 M hydrochloric acid (150 mL) was added to precipitate the product, which was collected by suction filtration, washed thoroughly with a large amount of water and methanol and dried in a vacuum. The crude product was purified by column chromatography silica gel (CH_2Cl_2–THF = 50:1) to yield a dark purple powder (341 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.37 (s, 18H), 7.13 (d, 4H, $J = 7.8$ Hz), 7.47 (d, 4H, $J = 7.8$ Hz), 7.50 (d, 4H, $J = 7.1$ Hz), 8.41 (s, 2H), 8.69 (d, 2H, $J = 8.4$ Hz), 8.86 (d, 4H, $J = 7.1$ Hz), 9.73 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 31.41, 34.61, 119.36, 121.36, 122.73, 123.22, 123.81, 124.55, 125.59, 127.68, 128.07, 128.89, 131.33, 132.04, 134.42, 149.00, 152.06, 157.15, 161.92, 162.60. MS (MALDI): 841 (M^+).

N,N′-Di(4-pyridine-N-oxide)-1,7-di(4-*tert*-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide 10. Compound **9** (0.25 g, 0.30 mmol) were dissolved in CH_3COOH (6 mL), and 0.5 mL H_2O_2 was added. The solution was stirred at room temperature for half an hour, and the temperature rose to 80 °C. About 3 h later, 0.5 mL H_2O_2 was added again and stirred for 20 h. The reaction mixture was chilled to room temperature, and water was added. The solution was filtered, and the precipitate was washed with water. The red solid was dried at 50 °C under vacuum overnight. The product was purified by column chromatography over silica gel ($CHCl_3$–THF–CH_3OH = 100:10:3) to yield a red solid (143 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 1.38 (s, 18H), 7.14 (d, 4H, $J = 8.4$ Hz), 7.51 (d, 4H, $J = 8.4$ Hz), 7.63 (d, 4H, $J = 7.2$ Hz), 8.44 (s, 2H), 8.71 (d, 2H, $J = 8.5$ Hz), 8.75 (d, 4H, $J = 7.2$ Hz), 9.74 (d, 2H, $J = 8.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 31.41, 34.62, 119.21, 121.44, 123.01, 124.14, 124.98, 127.70, 129.19, 130.77, 134.03, 139.96, 148.99, 152.11, 155.98, 162.08, 162.38. MS (MALDI): 872 (M^+). Anal. calc. for $C_{54}H_{40}N_4O_8$: C, 74.30; H, 4.62; N, 6.42. Found: C, 74.18; H, 4.55; N, 6.31.

N,N′-Di(4-pyridine-N-oxide)-1,6,7,12-tetra(4-*tert*-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide 12. Compound **11**[16] (0.25 g, 0.22 mmol)

Table 1. Solubility in H_2O and UV-visible absorption and fluorescence emission spectral data of 10^{-5} M perylene dicarboximide derivatives containing pyridine oxide groups in 20% THF/H_2O (v/v)

Compound	Solubility (M)	UV-vis (λ_{max})	Emission ($\lambda_{Ex}/\lambda_{Em}$)	Quantum yields (Φ)
3	4×10^{-5}	479	526/551	0.31
6	10^{-4}	540	529/566	0.48
10	2×10^{-5}	490	545/567	0.35
12	8×10^{-6}	602	584/617	0.22

was dissolved in CH_3COOH (6 mL), and 0.5 mL H_2O_2 was added. The solution was stirred at room temperature for half an hour, and the temperature rose to 80 °C. About 3 h later, 0.5 mL H_2O_2 was added again, and the mixture continued to stir for 20 h. The reaction mixture was chilled to room temperature, and water was added. The solution was filtered, and the precipitate was washed with water. The red solid was dried at 50 °C under vacuum overnight. The product was purified by column chromatography over silica gel (CH_2Cl_2–THF–methanol = 250:50:3) to yield a red solid (150 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 1.29 (s, 36H), 6.84 (d, 8H, $J = 8.3$ Hz), 7.26 (d, 8H, $J = 8.3$ Hz), 7.58 (d, 4H, $J = 6.3$ Hz), 8.26 (s, 4H), 8.71 (d, 4H, $J = 6.3$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 31.39, 34.41, 119.25, 119.50, 120.31, 121.18, 121.58, 126.85, 127.24, 133.13, 139.72, 147.95, 152.46, 156.28, 162.38. MS (MALDI): 1168 (M^+). Anal. calc. for $C_{74}H_{64}N_4O_{10}$: C, 76.01; H, 5.52; N, 4.79. Found: C, 75.92; H, 5.46; N, 4.71.

All of the perylene dicarboximide derivatives containing pyridine oxide groups are soluble in water. As shown in Table 1, the water solubility of the compounds **3** and **6** with pyridine oxide groups incorporated at the bay positions is better than that of the compounds **10** and **12** incorporating pyridine oxide groups at the imide nitrogens. The number of pyridine oxide groups improves the water solubility, whereas the number of phenol groups reduces the water solubility. The solubility increases significantly in a mixture of solvents H_2O/THF or H_2O/EtOH. Ultraviolet-visible absorption and fluorescence emission intensity also increase obviously before the THF up to 30% (v/v) in the mixture of solvents and then change slowly. UV-visible absorption and fluorescence emission spectral data of compounds **3**, **6**, **10**, and **12** in 20% THF/H_2O (v/v) are listed in Table 1. The data indicate the quantum yields increase with the solubilites.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (20771067) and the Natural Science Foundation of Shandong Province (2008BS02004).

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