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Non-conjugated dendrimers with a porphyrin core and coumarin chromophores as peripheral units: Synthesis and photophysical properties

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ABSTRACT

Three porphyrin-cored dendrimers with non-conjugated coumarins as dendrons have been synthesized and characterized. The photophysical properties of the title compounds were investigated by means of UV/Vis absorption and fluorescence spectroscopy in dilute CH_2Cl_2 solutions and in thin neat films. The intramolecular energy transfer from the coumarin units to the porphyrin core clearly reveals two factors influencing energy-transfer efficiency. Firstly, a better spectral overlap between the absorption spectrum of porphyrin core and the emission spectrum of the coumarin moiety results in high energy-transfer efficiency. Secondly, a long alkyl side-chain improves solubility of dendrimers, but also prevents the coumarins from self-quenching. Hence, the dendrimer with *N*-octyl groups possesses a higher efficiency than that with *N*-ethyl groups. The dendrimers emit red light with higher fluorescence quantum yields over the free porphyrin.

1. Introduction

Natural photosynthetic systems employ several light-harvesting complexes containing many chromophores that efficiently transfer absorbed radiation unidirectionally over nanometer distances [1–3]. Dendritic materials inspired by this energy transfer element of the photosynthetic pathway, have been designed and prepared, utilizing fluorescence resonance energy transfer (FRET) to concentrate absorbed energy at a single center [4–10]. In donor-bridge-acceptor type dendrimers, when donor chromophores are attached to the end points of the dendritic branches, a high-energy flux may occur from the periphery to the core, leading to efficient concentration of energy. The difficult functionalization of the interior of the dendrimer constitutes a serious obstacle to the full exploitation of the dendritic scaffold. For example, internally functionalized layered structures are desirable to achieve high Förster energy-transfer efficiency between core and periphery or to tailor specific properties of the dendritic interior. There has been continuous interest in the synthesis of porphyrins because of their wide potential applications in catalysis, medicine, photochemical energy conversion, switches, and molecular electronics [11–13]. To encapsulate a porphyrin core in the interior of a dendritic structure with various peripheral substituents can not only modulate the physical properties, but also impart the desired chemical characteristics to the macrocycle. 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 FRET [5,14–16].

Lin et al. [17] have reported a series of *meso*-coumarin-conjugated porphyrins as light antenna, in which energy transfer from the coumarin moiety to the porphyrin core can occur. The energy transfer is relative inefficient especially in solutions. Because of maximum only four coumarin units in these molecules their molar extinction coefficients in UV region are low relative to that of the porphyrin.

In this work, we have synthesized three dendrimers that contain a porphyrin core and multi-coumarin units as branches through non-conjugation linking (Chart 1), which have high molar extinction coefficients and good solubility. Efficient intramolecular energy transfer from coumarin moieties to the porphyrin core has been observed, and two factors determining their efficiency have been demonstrated.

2. Experimental

2.1. Reagents and instrumentation

Solvents for organic synthesis were reagent grade, and were dried prior to use, but all were HPLC grade for measurements of

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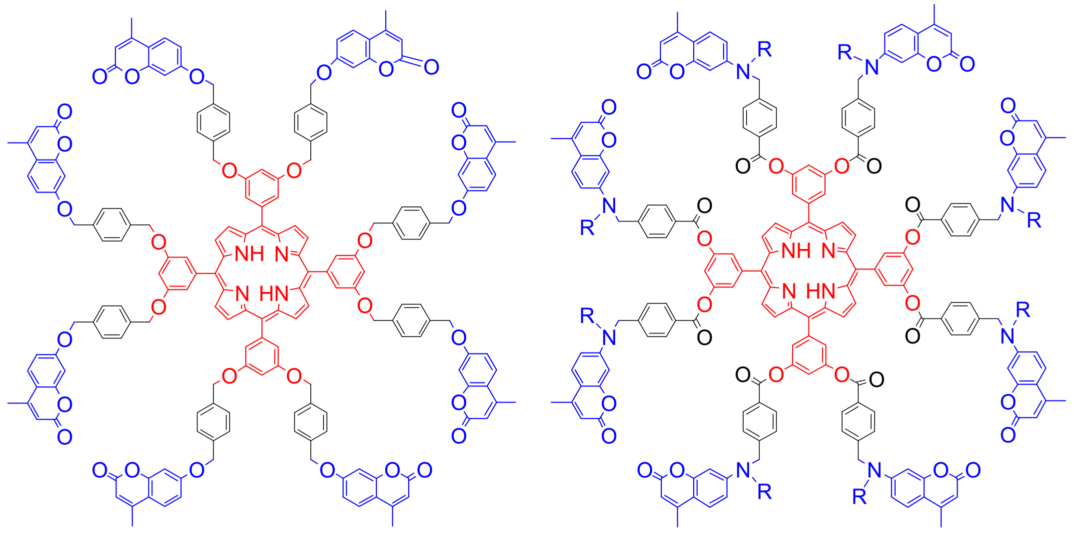


1

2: R = C_2H_5
3: R = n-C_8H_{17}

Chart 1. Molecular structures of dendrimers **1**–**3**.

spectroscopy and fluorescence quantum yield. All other compounds were purchased from commercial sources and used as received. 7-Hydroxy-4-methylcoumarin [18], 7-amino-4-methylcoumarin [19], 5, 10, 15, 20-tetrakis(3′,5′-dihydroxyphenyl)porphyrin [20] were prepared as described in the literature. NMR spectra were recorded on Bruker AV spectrometer (300 MHz for ^{1}H NMR, 75 MHz for ^{13}C NMR). Mass spectra were measured on a Bruker BIFLTMEX III Mass spectrometer or matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS). FTIR spectra were acquired on a Bruker VECTOR22 Infrared spectrophotometer. UV/vis absorption spectra were recorded with a Shimadzu UV/vis 2450 spectrophotometer. Fluorescence emission spectra were carried out on a Perkin-Elmer Instruments LS55 Luminescence spectrophotometer. Thin neat films were prepared by spin-coating CH_2Cl_2 solutions of dendrimers (2 wt %) on SiO_2/Si substrate at a spin speed of 2000 rpm.

2.2. Synthesis procedures and characterization data of new compounds

2.2.1. 7-(4-Bromomethyl-benzyloxy)-4-methylcoumarin (**4** [21])

7-Hydroxy-4-methylcoumarin (0.58 g, 3.3 mmol) in dry acetone (10 mL) was added during 2 h to the mixture of 1,4-bis (bromomethyl) benzene (1.32 g, 5.0 mmol), K_2CO_3 (0.92 g, 6.7 mmol) and 18-crown-6 (0.17 g, 0.7 mmol) in dry acetone (40 mL). The reaction mixture was heated under reflux for 5 h. The hot solution was then filtered, evaporated to dryness in *vacuo* and purified by means of chromatography to give **4** (0.96 g, 81%) as a white solid. $R_f = 0.42$ (CH_2Cl_2). Mp 115–116 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3 H, CH_3), 4.50 (s, 2 H, CH_2Br), 5.12 (s, 2 H, CH_2O), 6.14 (s, 1 H, ArH), 6.87 (d, J = 2.4 Hz, 1 H, ArH), 6.94 (dd, J = 8.7 Hz, 2.4 Hz, 1 H, ArH), 7.38–7.45 (m, 4 H, ArH), 7.50 (d, J = 8.7 Hz, 1 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.7, 33.0, 70.0, 102.0, 112.2, 112.8, 113.9, 125.7, 127.9, 129.5, 136.2, 138.0, 152.5, 155.2, 161.2, 161.5. IR (KBr, cm^{-1}): 1733 (s), 1613 (s), 1509 (m), 1385 (m), 1278 (m), 1226 (m), 1155 (m), 1071 (m), 826 (m). TOFMS (EI) calcd for (M^+) $C_{18}H_{15}BrO_3$: 358.0205, found 358.0202.

2.2.2. 7-[N-(p-toluenesulfonyl)-amino]-4-methylcoumarin (**5**)

7-Amino-4-methylcoumarin (1.85 g, 10.60 mmol) was dissolved in CH_2Cl_2 (20 mL), then *p*-toluenesulfonyl chloride (3.40 g, 17.85 mmol) in pyridine (20 mL) were slowly added to the solution. The mixture was stirred overnight at room temperature. CH_2Cl_2 (150 mL) was added and the solution was washed with 10% citrate aq. three times and brine once. The solution was dried with sodium sulfate and evaporated. The crude solid was washed with a small portion of EtOH and dried in vacuo to give a colorless solid **5** (3.20 g, 92%). $R_f = 0.08$ (CH_2Cl_2). Mp 218–219 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.33 (s, 6 H, CH_3), 6.23 (s, 1 H, ArH), 7.03 (d, J = 2.1 Hz, 1 H, ArH), 7.09 (dd, J = 8.7 Hz, 2.1 Hz, 1 H, ArH), 7.38 (d, J = 8.1 Hz, 2 H, ArH), 7.63 (d, J = 8.4 Hz, 1 H, ArH), 7.74 (d, J = 8.1 Hz, 2 H, ArH), 10.89 (s, 1 H, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 18.4, 21.4, 105.5, 113.0, 115.1, 115.7, 127.0, 127.2, 130.4, 136.8, 141.9, 144.3, 153.4, 154.1, 160.1. IR (KBr, cm^{-1}): 3163 (s), 1694 (s), 1614 (s), 1562 (s), 1393 (s), 1336 (s), 1162 (s), 1149 (s), 1090 (m), 846 (m). TOFMS (EI) calcd for (M^+) $C_{17}H_{15}NO_4S$: 329.0722, found 329.0729.

2.2.3. 7-[Ethyl-(4-methanesulfonyl-phenyl)-amino]-4-methylcoumarin (**6a**)

Compound **5** (0.37 g, 1.11 mmol) was dissolved in distilled CH_3CN (50 mL). Then Cs_2CO_3 (0.54 g, 1.66 mmol) and excessive ethyl iodide was added to the solution under confined condition, and the reaction was stirred overnight at 80 °C. After filtration the solution was evaporated and purified by means of silica gel column chromatography to give a colorless solid **6a** (0.36 g, 90%). $R_f = 0.38$ (CH_2Cl_2). Mp 141–142 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.01 (t, J = 7.0 Hz, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 2.43 (d, J = 0.9 Hz, 3 H, CH_3), 3.67 (q, J = 7.0 Hz, 2 H, CH_2), 6.41 (d, J = 1.2 Hz, 1 H, ArH), 7.13–7.17 (m, 2 H, ArH), 7.40 (d, J = 8.1 Hz, 2 H, ArH), 7.49 (d, J = 8.1 Hz, 2 H, ArH), 7.78 (d, J = 8.4 Hz, 1 H, ArH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.2, 18.5, 21.5, 45.1, 114.9, 115.7, 119.1, 124.3, 126.2, 127.7, 130.3, 135.1, 142.1, 144.2, 153.2, 153.5, 160.0. IR (KBr, cm^{-1}): 1721 (s), 1613 (s), 1392 (m), 1339 (s), 1324 (s), 1165 (s), 1083 (m), 1056 (m), 865 (m). TOFMS (EI) calcd for (M^+) $C_{19}H_{19}NO_4S$: 357.1035, found 357.1029.

*2.2.4. 7-[(4-Methanesulfonyl-phenyl)-octyl-amino]-4-methylcoumarin (**6b**)*

Based on an analogous method with **6a, 6b** was obtained as a colorless solid (0.42 g) in a yield 85%. $R_f = 0.63$ (CH_2Cl_2). Mp 68–69 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, $J = 6.3$ Hz, 3 H, CH_3), 1.21–1.28 (m, 10 H, CH_2), 1.43–1.36 (m, 2 H, CH_2), 2.43–2.44 (m, 6 H, CH_3), 3.54 (t, $J = 6.9$ Hz, 2 H, CH_2), 6.29 (s, 1 H, ArH), 6.86 (d, $J = 2.1$ Hz, 1 H, ArH), 7.23–7.24 (m, 1 H, ArH), 7.27 (d, $J = 8.1$ Hz, 2 H, ArH), 7.46 (d, $J = 8.1$ Hz, 2 H, ArH), 7.58 (d, $J = 8.4$ Hz, 1 H, ArH). ^{13}C NMR (75 MH_Z, $CDCl_3$): δ 13.7, 18.3, 21.2, 22.2, 26.0, 27.7, 28.6, 28.8, 31.3, 49.9, 114.8, 115.3, 118.8, 124.6, 127.2, 129.3, 134.5, 142.2, 143.6, 151.6, 153.2, 160.0. IR (KBr, cm^{-1}): 2930 (s), 1730 (s), 1610 (s), 1388 (m), 1344 (s), 1162 (s), 1091 (m), 670 (m). TOFMS (EI) calcd for (M^+) $C_{25}H_{31}NO_4S$: 441.1974, found 441.1980.

*2.2.5. 7-Ethylamino-4-methylcoumarin (**7a**)*

Compound **6a** (0.63 g, 1.75 mmol) was added to conc. sulfuric acid (5 mL) and the solution was stirred for 12 h at 90 °C. The reaction mixture was cooled and carefully poured into water. The mixture was neutralized with saturated sodium bicarbonate aq. and extracted with CH_2Cl_2 three times. The organic solution was dried and evaporated to give a yellow powder **7a** (0.33 g, 94%). $R_f = 0.31$ (CH_2Cl_2). Mp 147–149 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 1.29 (t, $J = 6.9$ Hz, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 3.21–3.23 (q, $J = 6.9$ Hz, 2 H, CH_2), 4.14 (br, 1 H, NH), 5.97 (s, 1 H, ArH), 6.44 (s, 1 H, ArH), 6.49 (d, $J = 7.8$ Hz, 1 H, ArH), 7.34 (d, $J = 7.8$ Hz, 1 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4, 18.5, 38.0, 97.9, 109.1, 110.3, 125.5, 151.7, 153.1, 162.1. IR (KBr, cm^{-1}): 3338 (s), 1692 (s), 1632 (s), 1601 (s), 1504 (m), 1403 (m), 1347 (m), 1169 (m), 850 (m). TOFMS (EI) calcd for (M^+) $C_{12}H_{13}NO_2$: 203.0946, found 203.0952.

*2.2.6. 7-Octylamino-4-methylcoumarin (**7b**)*

Similarly, **7b** was obtained as a yellow powder (0.40 g) in a yield 80%. $R_f = 0.41$ (CH_2Cl_2). Mp 109–110 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.87–0.89 (m, 3 H, CH_3), 1.29–1.39 (m, 10 H, CH_2), 1.58–1.67 (m, 2 H, CH_2), 2.34 (d, $J = 0.9$ Hz, 3 H, CH_3), 3.16 (t, $J = 6.9$ Hz, 2 H, CH_2), 4.20 (br, 1 H, NH), 5.97 (s, 1 H, ArH), 6.43 (d, $J = 2.4$ Hz, 1 H, ArH), 6.49 (dd, $J = 8.7$ Hz, 2.4 Hz, 1 H, ArH), 7.34 (d, $J = 8.7$ Hz, 1 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 18.4, 22.5, 26.9, 29.0, 29.1, 29.2, 31.7, 43.4, 97.7, 108.9, 110.1, 125.3, 151.7, 152.9, 155.9, 162.0. IR (KBr, cm^{-1}): 3332 (s), 2925 (s), 2851 (s), 1695 (s), 1637 (s), 1603 (s), 1504 (m), 1404 (m), 1347 (m), 831 (m). TOFMS (EI) calcd for (M^+) $C_{18}H_{25}NO_2$: 287.1885, found 287.1893.

*2.2.7. 4-{[Ethyl-(4-methylcoumarin-7-yl)-amino]-methyl}-benzoic acid methyl ester (**8a**)*

7a (0.35 g, 1.75 mmol), 4-(bromomethyl)benzoate (0.54 g, 2.34 mmol) and K_2CO_3 (1.21 g, 8.76 mmol) were mixed in freshly distilled CH_3CN (50 mL) and refluxed for 72 h. The solvent was evaporated in *vacuo* and the residue was purified by column chromatography to give product as pale yellow syrup **8a** (0.52 g, 85%). $R_f = 0.26$ (CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 1.28 (t, $J = 7.0$ Hz, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 3.56–3.58 (q, $J = 7.0$ Hz, 2 H, CH_2), 3.91 (s, 3 H; CH_3), 4.64 (s, 2 H, CH_2), 5.96 (s, 1H, ArH), 6.53–6.58 (m, 2 H, ArH), 7.27 (d, $J = 7.5$ Hz, 1 H, ArH), 7.36 (d, $J = 8.7$ Hz, 2 H, ArH), 7.99 (d, $J = 7.8$ Hz, 2 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.8, 18.0, 45.7, 51.7, 53.5, 98.1, 108.6, 109.0, 110.0, 125.3, 125.9, 128.9, 130.0, 142.9, 150.7, 152.5, 155.4, 161.5, 166.4. IR (KBr, cm^{-1}): 1695 (s), 1631 (s), 1604 (s), 1525 (m), 1407 (s), 1350 (m), 1278 (s), 1107 (m). TOFMS (EI) calcd for (M^+) $C_{21}H_{21}NO_4$: 351.1471, found 351.1479.

*2.2.8. 4-{[(4-Methylcoumarin-7-yl)-octyl-amino]-methyl}-benzoic acid methyl ester (**8b**)*

According to similar method, **8b** was prepared as pale yellow syrup (0.53 g) in a yield 70%. $R_f = 0.30$ (CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 0.86–0.90 (m, 3H, CH_3), 1.28–1.32 (m, 10 H, CH_2), 1.69 (m, 2 H, CH_2), 2.31 (s, 3 H, CH_3), 3.46 (t, $J = 7.5$ Hz, 2 H, CH_2), 3.91 (s, 3 H, CH_3), 4.65 (s, 2 H, CH_2), 5.96 (s, 1 H, ArH), 6.51–6.55 (m, 2 H, ArH), 7.24 (d, $J = 8.1$ Hz, 2 H, ArH), 7.34 (d, $J = 8.7$ Hz, 1 H, ArH), 7.98 (d, $J = 8.1$ Hz, 2 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.11, 18.4, 22.6, 27.1, 27.2, 29.3, 29.4, 31.8, 52.0, 52.1, 54.4, 98.6, 108.9, 109.5, 110.0, 125.5, 126.2, 129.3, 130.2, 143.1, 151.1, 152.8, 155.8, 162.0, 166.8. IR (KBr, cm^{-1}): 2926 (s), 1721 (s), 1630 (s), 1606 (s), 1525 (m), 1407 (s), 1369 (m), 1279 (s), 1170 (m). TOFMS (EI) calcd for (M^+) $C_{27}H_{33}NO_4$: 435.2410, found 435.2408.

*2.2.9. 4-{[Ethyl-(4-methylcoumarin-7-yl)-amino]-methyl}-benzoic acid (**9a**)*

8a (0.33 g, 0.95 mmol) and tetrabutylammonium hydroxide (TBA^+OH^-, 40% w/w, 1.56 mL, 2.40 mmol) were added to a mixture of THF (10 mL) and water (10 mL) and stirred overnight. The reaction mixture was acidified with aq. HCl to pH = 4, and extracted with dichloromethane three times. The organic solution was evaporated in vacuo and the residue was purified by column chromatography to give product as a white powder **9a** (0.28 g, 89%). Mp 147–149 °C. $R_f = 0.16$ (CH_2Cl_2/EtOAc 4:1). Mp 180–181 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.29 (t, $J = 7.1$ Hz, 3 H, CH_3), 2.33 (d, $J = 0.9$ Hz, 3 H, CH_3), 3.58 (q, $J = 7.1$ Hz, 2 H, CH_2), 4.66 (s, 2 H, CH_2), 5.98 (d, $J = 1.2$ Hz, 1 H, ArH), 6.53–6.59 (m, 2 H, ArH), 7.31 (d, $J = 8.4$ Hz, 2 H, ArH), 7.37 (d, $J = 8.7$ Hz, 1 H, ArH), 8.07 (d, $J = 8.4$ Hz, 2 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.1, 18.3, 46.0, 53.8, 98.5, 108.9, 109.6, 110.1, 125.6, 126.3, 128.4, 130.8, 144.1, 150.9, 152.7, 155.8, 162.0, 171.3. IR (KBr, cm^{-1}): 1714 (s), 1700 (s), 1576 (m), 1525 (m), 1410 (s), 1288 (s), 1174 (m), 1070 (m), 816 (m). TOFMS (EI) calcd for (M^+) $C_{20}H_{19}NO_4$: 337.1314, found 337.1284.

*2.2.10. 4-{[(4-Methylcoumarin-7-yl)-octyl-amino]-methyl}-benzoic acid (**9b**)*

9b was prepared by an analogous method with **9a**, as a white powder (0.33 g) in a yield 87%. $R_f = 0.24$ (CH_2Cl_2/EtOAc 4:1). Mp 134–135 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 0.86–0.89 (m, 3 H, CH_3), 1.28–1.33 (m, 10 H, CH_2), 1.68–1.70 (m, 2 H, CH_2), 2.32 (s, 3 H, CH_3), 3.47 (t, $J = 7.8$ Hz, 2 H, CH_2), 4.67 (s, 2 H, CH_2), 5.97 (s, 1 H, ArH), 6.48–6.55 (m, 2 H, ArH), 7.28 (d, $J = 8.1$ Hz, 2 H, ArH), 7.35 (d, $J = 8.7$ Hz, 1 H, ArH), 8.06 (d, $J = 8.1$ Hz, 2 H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 18.3, 22.6, 27.0, 27.1, 29.2, 29.4, 31.7, 52.0, 54.4, 98.5, 108.9, 109.4, 110.0, 125.5, 126.3, 128.5, 130.7, 144.0, 151.1, 152.8, 155.7, 162.0, 171.3. IR (KBr, cm^{-1}): 2923 (s), 1721 (s), 1697 (s), 1620 (s), 1606 (s), 1525 (m), 1408 (s), 1296 (m), 1170 (m). TOFMS (EI) calcd for (M^+) $C_{26}H_{31}NO_4$: 421.2253, found 421.2251.

*2.2.10.1. Dendrimer **1**.* **11** (37 mg, 0.05 mmol) and **4** (0.21 g, 0.60 mmol) were dissolved in 2 mL of dry DMF, and K_2CO_3 (0.11 g, 0.80 mmol) and 18-crown-6 (20 mg) were added, and heated to 60 °C, stirring overnight. The reaction mixture was poured into CH_2Cl_2 (50 mL), and filtered and washed with 0.1 M $NaHSO_4$ three times, brine once, dried over $MgSO_4$, filtered, and the solvent in the filtrate was removed in vacuo. Purification by means of silica gel column chromatography (CH_2Cl_2/THF = 10:1) afforded purple power **1** (0.12 g, 85%). $R_f = 0.33$ (CH_2Cl_2/THF 20:1). ^1H NMR (300 MHz, $CDCl_3$): δ −2.89 (s, 2 H, NH), 2.34 (s, 24 H, CH_3), 5.12 (s, 16H, CH_2), 5.24 (s, 16 H, CH_2), 6.10 (s, 8 H, ArH), 6.85–6.90 (m, 16 H, ArH), 7.05 (s, 4 H, ArH), 7.43–7.51 (m, 48 H, ArH), 8.84 (s, 8 H, pyrrole-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.6, 70.0, 70.2, 101.9, 112.1, 112.9, 113.8, 115.4, 119.7, 125.6, 127.9, 128.0, 135.8, 137.1, 144.0, 152.4, 155.2, 157.9, 161.2, 161.6. IR (KBr, cm^{-1}): 1724 (s), 1612 (s), 1388 (s), 1368 (m), 1279 (m), 1146 (s), 1107 (s). MALDI–TOF MS: calcd for (M^+) $C_{188}H_{142}N_4O_{32}$: 2968.9674, found 2968.4294.

*2.2.10.2. Dendrimer **2**.* **11** (37 mg, 0.05 mmol), **9a** (0.20 g, 0.60 mmol) and DPTS were dissolved in THF solution (5 mL), and then DCC (0.12 g, 0.60 mmol) in THF (1 mL) was added into above mixture solution under N_2 at room temperature. The reaction mixture was stirred overnight at room temperature and then solvent was removed in *vacuo*. Purification by means of silica gel column chromatography (CH_2Cl_2/THF = 15:1) afforded a purple power **2** (0.12 g, 75%). $R_f = 0.29$ (CH_2Cl_2/THF 20:1). ^1H NMR (300 MHz, $CDCl_3$): δ −2.89 (br, 2 H, NH), 1.26 (t, $J = 6.9$ Hz, 24 H, CH_3), 2.28 (s, 24 H, CH_3), 3.56 (q, $J = 6.9$ Hz, 16 H, CH_2), 4.66 (s, 16 H, CH_2), 5.92 (s, 8 H, ArH), 6.52–6.57 (m, 16 H, ArH), 7.32–7.35 (m, 24 H, ArH), 7.65 (t, $J = 2.1$ Hz, 4 H, ArH), 8.01 (d, $J = 2.1$ Hz, 8 H, ArH), 8.22 (d, $J = 8.1$ Hz, 16 H, ArH), 9.12 (s, 8 H, pyrrole-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.2, 18.4, 46.0, 53.9, 98.6, 108.9, 109.6, 110.1, 115.4, 118.3, 125.6, 126.6, 128.4, 130.9, 143.8, 144.3, 149.7, 150.9, 152.7, 155.8, 161.8, 164.6. IR (KBr, cm^{-1}): 1724 (s), 1606 (s), 1524 (m), 1407 (s), 1353 (m), 1255 (s), 1171 (m), 1067 (s). MALDI–TOF MS: calcd for (M^+) $C_{204}H_{166}N_{12}O_{32}$: 3297.1798, found 3297.3702.

*2.2.10.3. Dendrimer **3**.* According the same procedure with **2**, the dendrimer **3** was obtained as a purple power in yield 73%. $R_f = 0.83$ (CH_2Cl_2/THF 20:1). ^1H NMR (400 MHz, $CDCl_3$): δ −2.91 (br, 2 H, NH), 0.85 (m, 24 H, CH_3), 1.25–1.33 (m, 80 H, CH_2), 1.69 (m, 16 H, CH_2), 2.28 (s, 24 H, CH_3), 3.47 (m, 16 H, CH_2), 4.68 (s, 16 H, CH_2), 5.92 (s, 8 H, ArH), 6.5 (m, 16 H, ArH), 7.31–7.33 (m, 24 H, ArH), 7.63 (t, $J = 2.0$ Hz, 4H, ArH), 8.00 (s, 8 H, ArH), 8.21 (d, $J = 8.4$ Hz, 16 H, ArH), 9.11 (s, 8 H, pyrrole-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 18.2, 22.5, 26.9, 27.0, 29.1, 29.3, 31.6, 51.9, 54.4, 98.5, 108.8, 109.4, 109.9, 125.5, 126.4, 128.2, 130.8, 143.6, 144.1, 149.6, 150.9, 152.6, 155.7, 161.7, 164.5. IR (KBr, cm^{-1}): 2924 (s), 1736 (s), 1718 (s), 1606 (s), 1524 (m), 1407 (m), 1257 (m), 1170 (m), 1068 (m). MALDI–TOF MS: calcd for (M^+) $C_{252}H_{262}N_{12}O_{32}$: 3969.9310, found 3969.6828.

3. Result and discussion

3.1. Synthesis of dendrimers 1–3

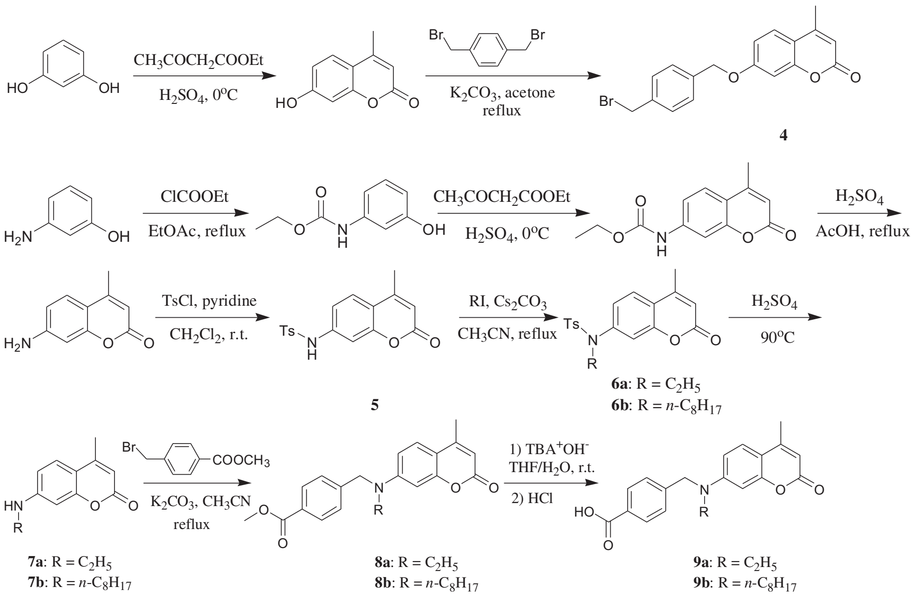
Three coumarin components **4**, **9a** and **9b** were synthesized according to procedures shown in Scheme 1. 1,4-Bis(bromomethyl) benzene was used to link 7-hydroxy-4-methylcoumarin to the porphyrin (**11**). The substitution reaction between 7-hydroxy-4-methylcoumarin and 1,4-bis(bromomethyl)benzene afforded compound **4** [21]. However, another coupling mode with 4-(bromomethyl)benzoate instead of 1,4-bis(bromomethyl)benzene was employed in the preparation of **9a** and **9b** [22,23], because of very low yield in the reaction of 1,4-bis(bromomethyl)benzene with 7-amino-4-methylcoumarin in acetonitrile under reflux.

The coumarin **5** was prepared through four reactions with 3-hydroxy aniline as the starting material. The coumarin **5** reacted with ethyl iodide in the presence of Cs_2CO_3 to yield a *N*-Ts amine **6a**. Deprotection of the *N*-Ts amine in the presence of H_2SO_4 yielded the secondary amine **7a**. Under catalysis of potassium carbonate, the coumarin **7a** reacted with 4-(bromomethyl)benzoate in acetonitrile under reflux to generate **8a**. Finally, **9a** was obtained by hydrolysis using tetrabutylammonium hydroxide in the solvent mixtures of THF and H_2O. To improve the solubility of dendrimers, *N*-alkylation of **5** with *n*-octyl iodide instead of ethyl iodide gave **6b**. According to the same procedures, **9b** was prepared.

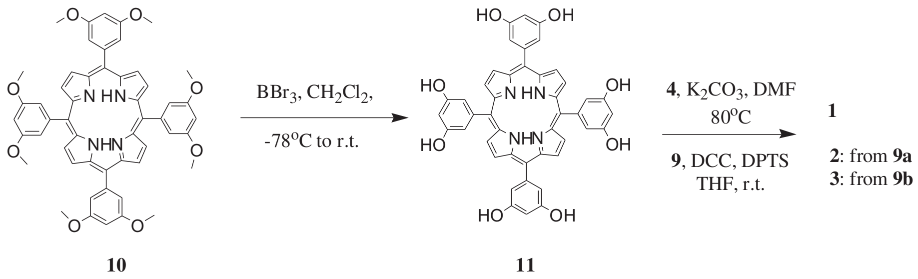
The synthesis of dendrimers **1**–**3** is shown in Scheme 2. Dendrimer **1** was prepared through a coupling reaction of 12 equivalents of **4** with one equivalent of the porphyrin **11** in DMF at 80 °C. Dendrimers **2** and **3** were synthesized by DCC-mediated coupling of carboxylic acid terminated coumarin **9** with the porphyrin **11**. The presence of all eight coumarin units in dendrimers **1**–**3** was confirmed by ^1H, ^{13}C NMR spectra and MALDI–TOF MS. Dendrimers **1**–**3** are soluble in common solvents, such as toluene, THF and dichloromethane, and the solubility becomes better in order of **1** < **2** < **3**. For example, concentrations of **1**–**3** in saturated dichloromethane solutions are 0.012, 0.015 and 0.030 mol L^{-1}, respectively.

3.2. Spectral properties

Fig. 1 shows UV/Vis absorption spectra of dendrimers **1**–**3** in CH_2Cl_2. The visible region with an intense Soret band (420 nm) and four weak Q-bands in the 500–700 nm of the porphyrin core is consistent with the free porphyrin, and absorption bands from 250 nm to 400 nm are mainly absorption of the peripheral coumarin dendrons, and these spectral data are listed in Table 1. Thin solid films of **1**–**3** have been prepared by spin-coating CH_2Cl_2 solutions of dendrimers (2 wt %) on SiO_2/Si substrate at a spin speed of 2000 rpm. The absorption bands for the porphyrin cores of



Scheme 1. Synthesis routes of compounds **4**, **9a** and **9b**.



Scheme 2. Synthesis routes of dendrimes **1**–**3**.

dendrimers **1**–**3** in solid films exhibit a bathochromic shift of about 10 nm in relation to those in solution, due to the aggregation effect (Fig. 2). As shown in Fig. 3, the absorption spectra of the non-conjugated dendrimers **1**–**3** are in agreement with simple sum of the spectra of the corresponding components, the coumarin **4** or **9** and the tetraphenylporphyrin **10**. This implies no conjugation interaction between the two chromophores.

Fig. 4 shows the absorption and fluorescence spectra for two coumarins **4**, **9a** and the porphyrin **10**. The emission peak of **9a** and the absorption peak of **10** are the same value 420 nm. In contrast to this, there is only part overlap for the corresponding spectra of **4** and **10**, $\lambda^{ab}_{max} = 380$ nm (**4**), and $\lambda^{em}_{max} = 420$ nm (**10**).

The fluorescence efficiencies of **4**, **9** are much higher than that of **10**. When coumarin units in the dendrimers are excited at 320 nm for **1** and 365 nm for **2** and **3**, significant fluorescence emission derives from the porphyrin, and fluorescence of the coumarins is almost quenched completely (Fig. 5). This indicates that energy transfer from the coumarins to the porphyrin occurs efficiently. The fluorescence resonance energy-transfer efficiencies (Φ_{FRET}) was calculated by comparing the donor emission in the presence of the acceptor relative to that in the absence of the acceptor, and the Φ_{FRET} values for **1**–**3** were calculated to be 86%, 99% and 99%, respectively. In addition, the excellent spectroscopic consistency between the excitation and absorption spectra of **1**–**3** results in an effective energy transfer shown in Fig. 6. This indicates that light energy collected by peripheral coumarin chromophores for **2** and **3** transfers almost quantitatively to the porphyrin core. Therefore, **2** and **3** are efficient light-harvesting antennae, with the porphyrin acting as the energy trap. By contrast, the fluorescence spectra of **1** obtained by exciting in the corresponding coumarin units absorption maxima 320 nm, besides the porphyrin emission at around 660 nm, there is still the residual emission (340–500 nm) of the coumarin moiety. The fluorescence of **1** was quenched by 86% relative to the emission of **4**. Hence, the energy transfer from the coumarin moiety to the porphyrin core for **1** is less efficient than those of **2** and **3**. This obeys one of the key requirements for Förster energy-transfer: spectral overlap between the absorption spectrum of an acceptor and the emission spectrum of the donor [24]. The fluorescence quantum yields (Φ_F) of the dendrimers **1**–**3** in benzene were measured with tetraphenylporphyrin ($\Phi_F = 0.11$ in benzene [25]) as a standard, and are listed in Table 1.

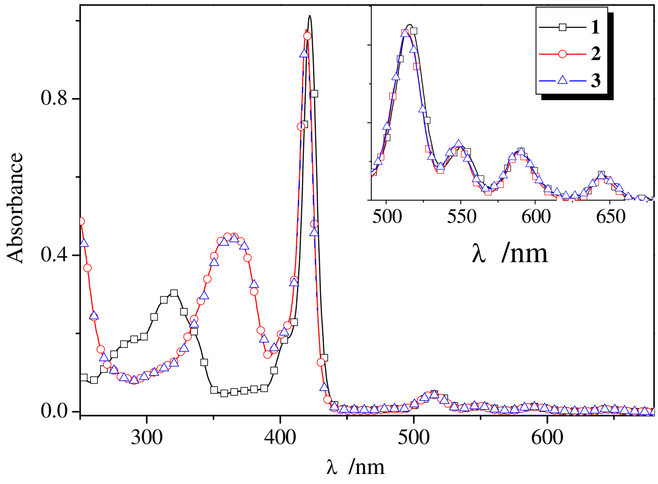


Fig. 1. The normalized UV/Vis spectra of dendrimers **1**–**3** in CH$_2$Cl$_2$ solutions.

The fluorescence spectra of **1**–**3** were also recorded in thin films (Fig. 5). Compared to the data from the CH$_2$Cl$_2$ solutions, the fluorescence spectra of dendrimers **1**–**3** in thin films exhibit two significant differences. First, the emission peaks at around 660 (Q(0,0)) and 718 nm (Q(0,1)) in thin films have a red-shifted of about 10 nm relative to those in CH$_2$Cl$_2$ solutions. The ratios of Q(0,0) to Q(0,1) of thin films decrease relative to those in solutions. However, these ratios are much lower than those of the literature [14]. Second, almost no residual fluorescence of the coumarin moieties in fluorescence spectra of **1**–**3** in thin films was observed, especially for **3**. This is a sharp contrast with the fluorescence spectra of **1**–**3** in CH$_2$Cl$_2$ solutions, which still, to some extent, exhibit emission of the coumarin unit. It demonstrates that energy transfer from coumarin units to the porphyrin core is more efficient in thin films than in solutions. This is probably because the torsion angle between porphyrin and coumarin is smaller in film than in solution [26]. In addition, the energy-transfer efficiency is better for **3** than **2** in both solid film and solution, that is, the *N*-octyl group is more favorable for the energy transfer than the *N*-ethyl group. This may be because the longer octyl chain can efficiently suppress the self-quenching of coumarin units. On the other hand, **3** has better solubility than other two dendrimers in common solvents, such as toluene, THF, and CH$_2$Cl$_2$. This is important for application as a light-harvesting antenna.

Fréchet and co-works have designed and synthesized a porphyrin-centered dendrimer with eight naphthopyranone and 16 coumarin chromophores as a light-harvesting system, which achieves excellent FRET from the coumarin through naphthopyranone to the porphyrin core when the coumarin moiety in the dendrimer is excited ($\lambda_{ex} = 335$ nm), and when the naphthopyranone is excited ($\lambda_{ex} = 358$ nm), efficient energy transfer occurs

Table 1
Photophysical data of dendrimers **1**–**3** in CH$_2$Cl$_2$ solutions and as thin neat films.

Compound	λ^{ab}_{max}/nm (solution)	λ^{ab}_{max}/nm (film)	λ^{em}_{max}/nm (solution)	λ^{em}_{max}/nm (film)	Φ_F[a]	Φ_{FRET} (solution)
1	320, 422	323, 435	648, 712	658, 720	0.13	86%
2	364, 420	375, 430	649, 710	661, 717	0.15	99%
3	365, 420	375, 430	649, 710	659, 718	0.15	99%

[a] The Φ_F values from benzene solutions with tetraphenylporphyrin (0.11 in benzene [25]) as a standard, excitation at 420 nm.

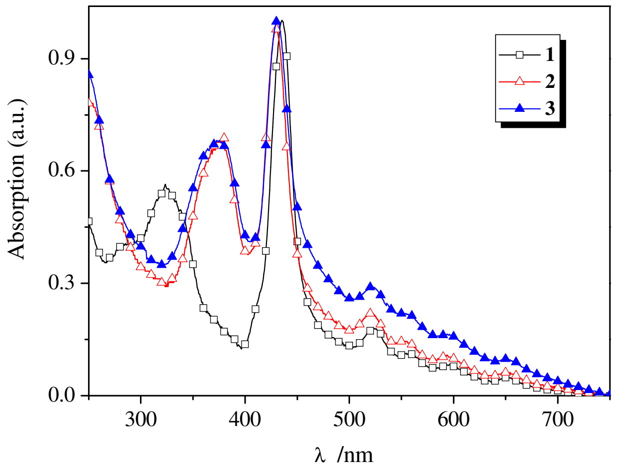


Fig. 2. The normalized UV/Vis spectra of **1**–**3** in thin films prepared by spin-coating CH_2Cl_2 solutions of dendrimers (2 wt %) on SiO_2/Si substrate at a spin speed of 2000 rpm.

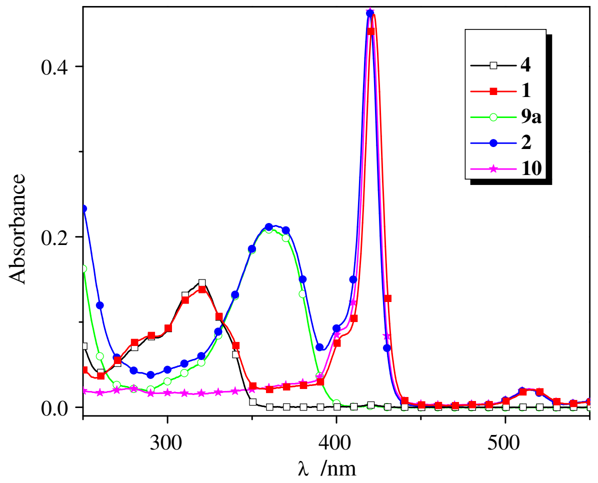


Fig. 3. Absorption spectra of compounds **4**, **9a** (8×10^{-6} M), **10**, **1**, and **2** (1×10^{-6} M) in CH_2Cl_2 solutions.

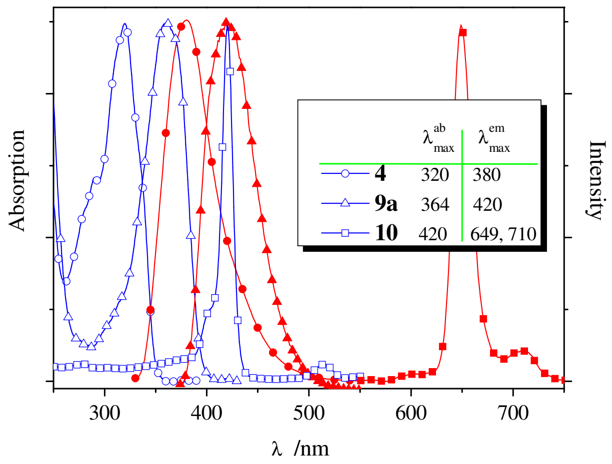


Fig. 4. Normalized UV/Vis spectra (open) and emission spectra (full) of **4** (cycle), **9a** (triangle) and **10** (square) in CH_2Cl_2 solutions.

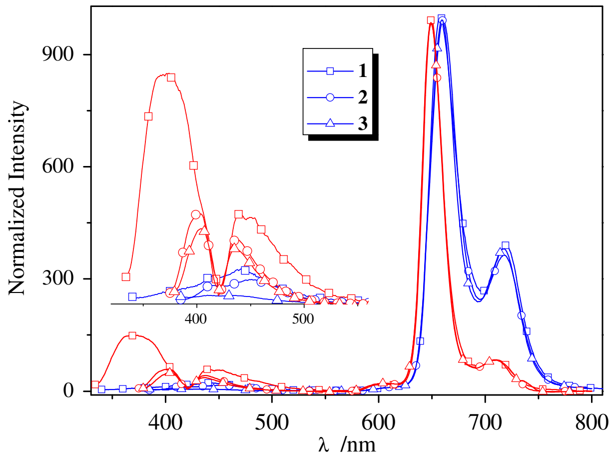


Fig. 5. Normalized fluorescence spectra of **1** (square), **2** (cycle) and **3** (triangle) in CH_2Cl_2 solutions (red) and thin films (blue), excitation at 320 nm for **1**, excitation at 365 nm for **2** and **3**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

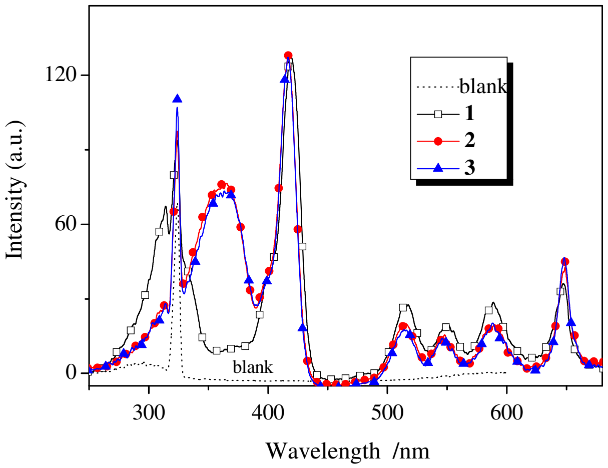


Fig. 6. Fluorescence excitation spectra of **1**–**3** in CH_2Cl_2 solutions.

from the naphthopyranone to the porphyrin core, in THF solution [14]. In the two processes, there is residual naphthopyranone emission due to a very broad fluorescence emission (400–650 nm, half-emission maximum (fwhm) of ~113 nm for a model compound **7** [14]) of the naphthopyranone unit and a narrow absorption band (400–440 nm) of the porphyrin core. In contrast, the fluorescence emission band of **9a** is a narrow band (390–480 nm, fwhm: ~56 nm) with a peak of 420 nm, which is the same value with absorption peak of the porphyrin core. Hence, almost quantitative FRET from the coumarin to the porphyrin core in dendrimers **2** and **3** were observed in both solution and neat film. Compared to the coumarin-conjugated porphyrins [17], dendrimers **1**–**3** have higher molar extinction coefficients in UV region and more effective FRET.

4. Conclusions

Three dendritic coumarin-based porphyrins **1**–**3** were prepared. Their photophysical properties reveal that intramolecular energy transfer occurs in these non-conjugated dendrimers from coumarin moieties to the porphyrin core. The energy-transfer efficiency depends on the degree of overlap between the emission spectrum of the coumarin units and the absorption spectrum of the porphyrin moiety. Due to a better spectral overlap, dendrimers **2** and **3** have higher energy-transfer efficiencies over the dendrimer **1**. In addition, a long side-chain, *N*-*n*-octyl group for **3** plays a role in preventing the self-quenching of coumarin units, as well as improving solubility and film-forming ability. These dendrimers emit single red light with high fluorescence quantum yields, and may be applied as light-harvesting antennae.

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