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SUPPORTING INFORMATION

Title: Synthesis of *meso*-Coumarin-Conjugated Porphyrins and Investigation of Their Luminescence Properties
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Ref. No.: O200700475

Experimental section

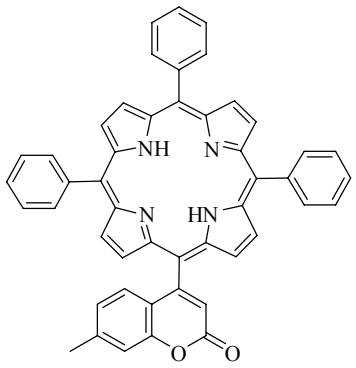
General: Low temperature reactions were undertaken in a low temperature cyclic pump; Melting point of the intermediates and porphyrins were measured on a Beijing taike XT-4 microscopy melting point apparatus, all melting points were uncorrected; LC-MS analyses were performed using a Waters Micromass ZQ-4000 spectrometer; 1HNMR spectra were recorded on an INOVA-400 spectrometer, using TMS as an internal standard; Elementary analyses were obtained on a Vario El III Elemental Analyzer; Electronic absorption spectra were obtained on a labtech UV-Visible spectrometer; Photoluminescent spectra were recorded at 293K with a HITACHI F4500 fluorescence spectrophotometer; TLC analyses were performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200–300), both of which were obtained from the Qingdao Ocean Chemicals. Tetrahydrofuran (THF) was distilled over sodium and benzophenone; pyrrole and propionic acid were redistilled before use. Unless otherwise noted, reagents were commercially available and used as received.

4-chloromethyl-7-methylcoumarin (3a): To a well stirred solution of concentrated sulfuric acid (40ml) cooled to –5^{o}C was slowly added m-cresol (4.35g, 40.2mmol) by dropwise, followed by slowly adding 4-chloroacetoacetate ethyl ester (6.61g, 40.1mmol). After overnight reaction at –5^{o}C, the reaction mixture was poured into 360ml of ice cold water and stirred for 1 h. The resulting white precipitate was collected by filtration, washed with ice water until the filtrate was neutral and dried under reduced pressure to afford a solid, which was then subjected to recrystallization from ethanol to give **3a** as a white powder (6.05g, yield 72.3%). M.p. 216–218 ℃. Ms m/z: 208.5 [M^+]. ^{1}HNMR (400MHz, $CDCl_3$) δ = 7.55 (d, *J* = 8.4Hz, 1H), 7.19 (s, 1H), 7.15 (d, *J* = 8.4Hz, 1H), 6.51 (s, 1H), 4.66 (d, *J* = 1.2Hz, 2H), 2.47 (s, 3H) ppm.

4-hydroxymethyl-7-methylcoumarin (4a): A suspension of 4-chloromethyl-7-methylcoumarin **3a** (3g, 14.38mmol) in a mixture of water and DMF (400 ml, V_{H2O}: V_{DMF}=1:1,) was heated to reflux, and the reaction mixture became clear after half hour refluxing. After overnight reaction, the resulting solution was cooled and evaporated under reduced pressure to afford a brown residue, which was then purified by silica gel column chromatography (petroleum ether/acetone 3:1) to afford **4a** as a white powder (1.97g, yield 72%). M.p. 173.8–175℃. Ms m/z: 190 [M^+]. ^{1}HNMR (400MHz, [D_6]DMSO): δ = 7.58 (d, *J* = 8 Hz, 1H), 7.24 (s, 1H), 7.18 (d, *J* = 8 Hz, 1H), 6.40 (s, 1H), 4.75 (s, 2H), 2.41 (s, 3H) ppm.

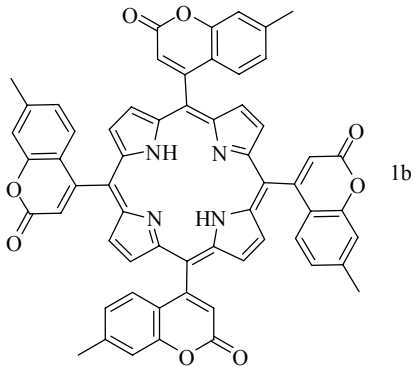
4-formyl-7-methylcoumarin (5a): To a solution of 4-hydroxymethyl-7-methylcoumarin **4a** (1.96g, 10.3mmol) in THF (30 ml) under a nitrogen atmosphere was added manganese dioxide (9.45 g, 108.69 mmol) in portions. After the suspension was stirred under refluxed for three days, the black solid was removed by filtration. The filtrate was evaporated under reduced pressure, and the resulting crude product was purified by chromatography on silica gel (CH_2Cl_2) to afford **5a** as a yellow solid (1.59g, yield 81.6%). M.p. 201–202℃. Ms m/z: 188[M^+]. ^{1}HNMR (400MHz, $CDCl_3$): δ = 10.11 (s, 1H), 8.46 (d, *J* = 8 Hz, 1H), 7.20 (s, 1H), 7.17 (S, 1H), 6.83 (s, 1H), 2.48 (s ,3H) ppm. UV/Vis (THF) λ_{max} (logε): 330.5 (3.69) nm.

5-(7-methylcoumarin-4-yl)-10,15,20-triphenylporphyrin (1a): To a solution of 4-formyl-7-methyl coumarin **5a** (118.9mg, 0.63mmol), benzaldehyde (265.3mg, 2.5mmol) and pyrrole (212.8mg, 3.17mmol) in dried $CHCl_3$ (313.5ml) at room temperature under nitrogen was added BF_3-etherate (85μl, 0.31mmol), and the reaction mixture was stirred at room temperature for 4 h in the dark. Then p-chloranil (462.5mg, 1.881mmol) was added and heated at 61℃ for 2 h. The reaction mixture was cooled to room temperature. After removal of the solvent under reduced pressure, the residue was purified on silica gel column chromatography (CH_2Cl_2/petroleum ether: 50:1) to afford **1a** as a purple solid (56.9mg, yield 12.9%). M.p. > 300℃. Ms m/z: 696.9 [M^+]. ^{1}HNMR (400MHz, $CDCl_3$): δ = 8.93 (d, *J* = 4.4Hz, 2H), 8.87 (d, *J* = 7.6Hz, 6H), 8.20 (m, 6H), 7.76 (m, 9H), 7.46 (s, 1H), 7.25 (S, 1H), 6.68 (d, *J* = 8.4Hz, 1H), 6.57 (d, *J* = 8.4Hz, 1H), 2.43 (s, 3H), -2.73 (s, 2H) ppm. UV/Vis (THF) λ_{max} (logε): 417 (5.66), 512.5 (4.41), 546 (3.83), 588.5 (3.80), 644.5 (3.34) nm. $C_{48}H_{32}N_4O_2$: calcd. C 82.74, H 4.63, N 8.04; found C 82.36, H 4.91 , N 7.73.



1a

***Meso*-tetra(7-methylcoumarin-4-yl)porphyrin (1b):** To a solution of 4-formyl-7-methylcoumarin **5a** (480.7mg, 2.55mmol), pyrrole (171.5mg, 2.56mmol) in dried $CHCl_3$ (250ml) at room temperature under nitrogen was added BF_3-etherate (68μl, 0.25mmol), and the reaction solution was stirred at room temperature for 4 h in the dark. Then p-chloranil (470.2mg, 1.91mmol) was added and heated at 61℃ for 2 h. The reaction mixture was cooled to room temperature. After removal of the solvent under reduced pressure, the residue was purified on silica gel column chromatography (CH_2Cl_2/Ethyl acetate 50:1), collected the main red fraction to afford **1b** as a purple solid (32.1mg, Yield 5.34%). M.p. > 300℃. Ms m/z: 943[M^+]. ^{1}HNMR (400MHz, $CDCl_3$): δ = 9.04 (d, *J* = 3.2Hz, 8H), 7.49 (s, 4H), 7.23 (m, *J* = 7.2Hz, 4H), 6.77 (d, *J* = 8.8Hz, 4H), 6.58 (m, 4H), 2.48 (t, *J* = 3.6Hz, 12H), -2.67 (s, 2H) ppm. UV/Vis (THF) λ_{max} (logε): 418.5 (5.46), 510.5 (4.24), 542.5 (3.36), 584.5 (3.75), 640.5(2.82) nm. $C_{60}H_{38}N_4O_8$: calcd. C 76.42, H 4.06, N 5.94; found C 76.09, H 4.42, N 5.56.



1b

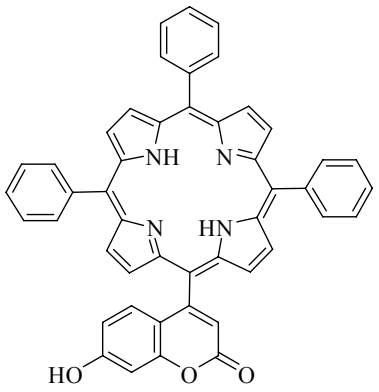
4-chloromethyl -7-hydroxylcoumarin (3b): To a well stirred solution of concentrated sulfuric acid (43ml) cooled to –5℃ was slowly added grinded resorcinol powder (5.6g, 50.9mmol), followed by slowly adding 4-chloroacetoacetate ethyl ester (7.0g, 42.5mmol). After overnight reaction at –5℃, the reaction mixture was poured into 360ml of ice cold water and stirred for 1 h. The resulting white precipitate was collected by filtration, washed with ice water until the filtrate was neutral and dried under reduced pressure to afford a solid, which was then subjected to recrystallization from ethanol to give **3b** as a white powder (7.621g, yield 85.1%). M.p. 185–186℃. Ms m/z: 210.6 [M^+]. ^{1}HNMR (400MHz, [D_6]DMSO): δ = 7.69 (d, *J* = 8.8Hz, 1H), 6.86 (dd, *J* = 2Hz, 8.8Hz, 1H), 6.78 (d, *J* = 2.4Hz, 1H), 6.44 (s, 1H), 4.96 (s, 2H) ppm.

7-hydroxyl-4-(hydroxymethyl)coumarin (4b): A suspension of 4-chloromethyl-7-hydroxylcoumarin **3b** (4.9g, 23.26mmol) in water (1300ml) was refluxed for 28h, the resulting solution was cooled and evaporated under reduced pressure to afford **4b** as a white powder (4.1g,92%), which is pure enough to use in the next step without further purification. M.p. 216–218℃. Ms m/z: 192 [M^+]. ^{1}HNMR (400MHz, [D_6]DMSO): δ = 7.53 (d, *J* = 8.8Hz, 1H), 6.79 (dd, *J* = 2.4Hz, 8.8Hz, 1H), 6.74 (d, *J* = 2.4Hz, 1H), 6.24 (s, 1H), 4.70 (S ,1H) ppm.

4-formyl-7-hydroxylcoumarin (5b): To a solution of 7-hydroxyl-4-(hydroxymethyl)coumarin **4b** (2.55g, 13.2mmol) in ethyl acetate(60 ml) under a nitrogen atmosphere was added manganese dioxide (12 g, 138.6 mmol) in portions. After the suspension was stirred under refluxed for five days, the black solid was removed by filtration. The filtrate was evaporated under reduced pressure, and the resulting crude product was purified by chromatography on silica gel (CH_2Cl_2) to afford **5b** as a yellow solid (1.037g, yield 41%) M.p. 223–225℃. Ms m/z: 190 [M^+]. ^{1}HNMR (400MHz, D-acetone): δ = 10.05 (s, 1H), 8.28 (d, *J* = 8.8Hz, 1H), 6.79 (dd, *J* = 2.4Hz, 8.8Hz, 1H), 6.73 (S ,1H), 6.69 (d, *J* = 2.4Hz, 1H) ppm. UV/Vis (THF) λ_{max} (logε): 344 (3.72), 362.5 (3.73) nm.

5-(7-hydroxylcoumarin-4-yl)-10, 15, 20-triphenylporphyrin (1c): A three necked round-bottomed flask fitted with a reflux condenser was filled with propionic acid (21ml), and 4-formyl-7-hydroxylcoumarin **5b** (193.2mg, 1.0mmol) and benzaldehyde (439.3mg, 4.1mmol) were then added. After stirring for five minutes, freshly distilled pyrrole (341.9mg, 5.1mmol) was added by dropwise. The reaction mixture was then refluxed for 45 min. After removal of the solvent under reduced pressure, the residue was purified on silica gel column chromatography (CH_2Cl_2/ethanol 200:1) to afford **1c** as a

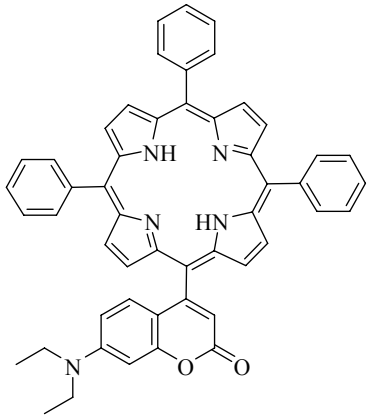
purple solid (38.2mg, yield 5.38%). M.p. > 300℃. Ms m/z: 698.9 [M^+]. ^{1}HNMR (400MHz, [D_6]DMSO) δ = 8.84 (s, 8H), 8.22 (t, *J* = 6.8 Hz, 6H), 7.85 (s, 9H), 7.12 (s, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.42 (dd, *J* = 2 Hz, 8.8 Hz, 1H), 6.35 (d, *J* = 8.8 Hz, 1H), -2.89 (s, 2H) ppm. UV/Vis (THF) λ_{max} (logε): 417 (5.6), 512 (4.28), 544.5 (3.85), 588.5 (3.73), 645 (3.43) nm. $C_{47}H_{30}N_4O_3$: calcd. C 80.79, H 4.33, N 8.02; found C 80.41, H 4.72, N 7.73.



1c

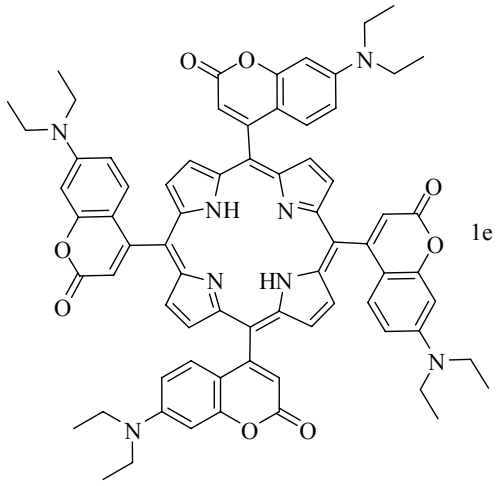
7-diethylamino-4-formylcoumarin (5c): Selenium dioxide (2.66g, 24mmol) was added to a solution of 7-diethylamino-4-methylcoumarin (3.7g, 16mmol) in p-xylene (120ml), and the mixture was heated to reflux with vigorous stirring. After refluxing for one day, the reaction mixture was filtered to remove black Solid, and the deep orange filtrate was concentrated under reduced pressure to afford a dark brown residual oil, which was further subjected to chromatography on silica gel twice (CH_2Cl_2: petroleum ether=3:1 for the first time, and petroleum ether: acetone=6:1 for the second time) to afford **5c** as a red crystal (1.57g, yield 40%). M.p. 84–85℃. Ms m/z: 245 [M^+]. ^{1}HNMR (400MHz, $CDCl_3$) δ = 10.03 (s, 1H), 8.32 (d, *J* = 9.2 Hz, 1H), 6.65 (dd, *J* = 2 Hz, 9.2 Hz, 1H), 6.55 (d, *J* = 2Hz, 1H), 6.47 (s, 1H), 3.44 (q, *J* = 7.2 Hz, 4H), 1.23 (t, *J* = 7.2 Hz, 6H) ppm. UV/Vis (THF) λ_{max} (logε): 380 (4.40), 441.5 (4.47) nm.

5-(7-diethylaminocoumarin-4-yl)-10, 15, 20-triphenylporphyrin (1d): A three necked round-bottomed flask fitted with a reflux condenser was filled with propionic acid (16ml), and 7-diethylamino-4-formyl coumarin (156.8mg, 0.64mmol) and benzaldehyde (268mg, 2.525mmol) were then added. After stirring for five minutes, freshly distilled pyrrole (216.8mg, 3.23mmol) was added by dropwise. The reaction mixture was refluxed for 45 min. After removal of the solvent under the reduced pressure, a black residue was obtained, which was further purified on silica gel column chromatography (CH_2Cl_2/petroleum ether 10:1) to afford **1d** as a purple solid (37.8mg, yield 7.84%). M.p. >300℃. Ms m/z: 753.9 [M^+]. ^{1}HNMR (400MHz, $CDCl_3$): δ = 9.04 (d, *J* = 4.8 Hz, 2H), 8.86 (m, 6H), 8.20 (m, 6H), 7.73 (m, 9H), 6.96 (s, 1H), 6.79 (d, *J* = 2Hz ,1H), 6.46 (d, *J* = 9.2 Hz, 1H), 6.13 (dd, *J* = 2.4 Hz, 9.2 Hz, 1H), 3.32 (q, *J* = 6.8 Hz, 4H), 1.13 (t, *J* = 6.8 Hz, 6H), -2.72 (s, 2H) ppm. UV/Vis (THF) λ_{max} (logε): 416 (5.29), 513.5 (4.18), 547 (3.53), 589 (3.58), 645.5 (3.14) nm. $C_{51}H_{39}N_5O_2$: calcd. C 81.25, H 5.21, N 9.29; found C 80.86, H 5.61, N 9.01.



1d

***Meso*-tetra(7-diethylaminocoumarin-4-yl)porphyrin (1e):** To a solution of 7-diethylamino-4-formyl coumarin **5c** (506.4mg, 2.065mmol), pyrrole (345.5mg, 5.15mmol) in dried $CHCl_3$ (210ml) at room temperature under nitrogen was added CF_3COOH (0.25ml, 3.37mmol). The mixture was stirred at room temperature for 4 h in the dark. Then p-chloranil (380mg, 1.55mmol) was added and heated at 61℃ for 2h. The reaction mixture was cooled to room temperature. After removal of the solvent under reduced pressure, the residue was purified on silica gel column chromatography (CH_2Cl_2/acetone 20:1) to afford **1e** as a purple solid (16mg, yield 2.67%). M.p. > 300℃. Ms m/z: 1171[M^+]. ^{1}HNMR (400MHz, $CDCl_3$): δ = 9.06 (m, 8H), 6.90 (s,3H), 6.85 (s,1H), 6.81 (d, *J* = 2 Hz, 4H), 6.46 (dd, *J* = 4 Hz, 9 Hz, 4H), 6.21 (dd, *J* = 2 Hz, 9.6 Hz, 4H), 3.40 (q, *J* = 6.8 Hz, 16H), 1.21 (t, *J* = 6.8 Hz, 24H), -2.71 (s, 2H) ppm. UV/Vis (THF) λ_{max} (logε): 407.5 (5.22), 518.5 (4.38), 552 (375), 588.5 (3.95), 644.5(3.25) nm. $C_{72}H_{66}N_8O_8$: calcd. C 73.83, H 5.68, N 9.57; found C 73.49, H 5.92, N 9.33.



1e

The fluorescence quantum yields (Φ_f) of **1a**–**1e** in THF solution were measured according to the reference[1], and used tetraphenylporphyrin (Φ_F = 0.11 in benzene[2]) as standard. The area under corrected emission curve was recorded from 600nm to 750nm. And the results of fluorescence quantum yield are outlined in Table S1.

Table S1. The fluorescence quantum yields (ΦF) of the porphyrins (1a-1e)

Compound	Φ_F	Compound	Φ_F
TPP	0.11	1c	0.16
1a	0.15	1d	0.21
1b	0.16	1e	0.22

Reference:

[1] a) C. A. Parker, W. T. Rees, *Analyst*. **1960**, 85, 587-600; b) Suzanne Fery-Forgues, Dominique Lavabre, *J. Chem. Educ.* **1999**, 76, 1260-1264.

[2] P. G. Seybold , M. Gouterman, *J. Mol. Spectrosc.* **1969**, 31, 1–13.

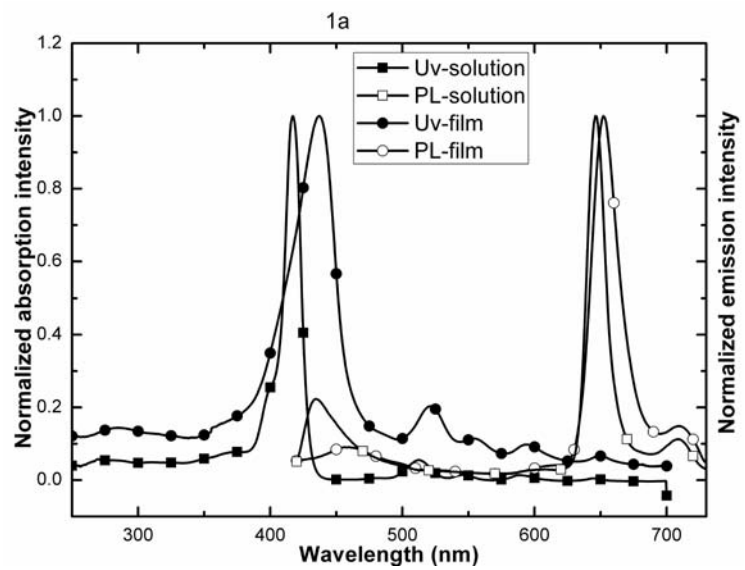


Figure S1. Normalized absorption (left) and photoluminescent (PL) (right) spectra of **1a** in THF solution and film state.Photoluminescence spectra were obtained upon excitation at the absorption of corresponding coumarin substituent at 330nm.

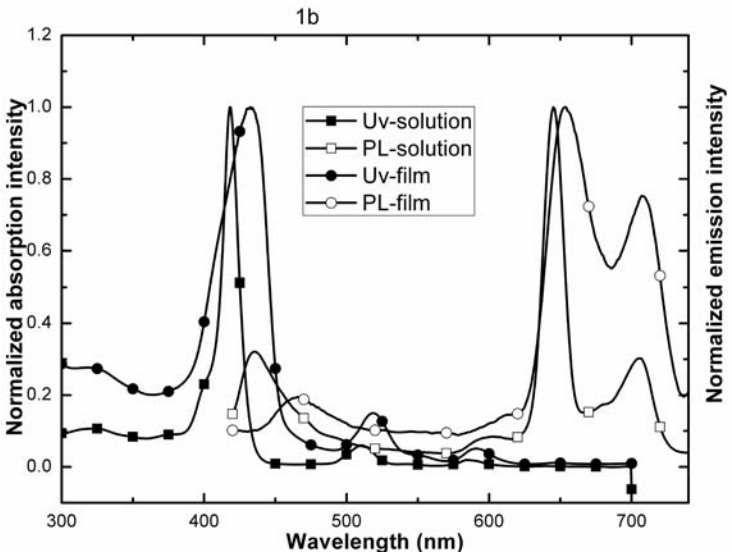


Figure S2. Normalized absorption (left) and photoluminescent (PL) (right) spectra of **1b** in THF solution and film state.Photoluminescence spectra were obtained upon excitation at the absorption of corresponding coumarin substituent at 330nm.

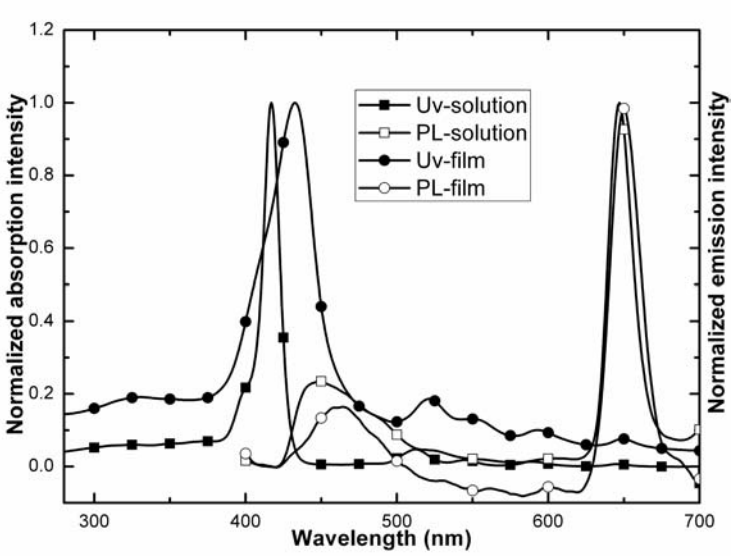


Figure S3. Normalized absorption (left) and photoluminescent (PL) (right) spectra of **1c** in THF solution and film state. Photoluminescence spectra were obtained upon excitation at the absorption of corresponding coumarin substituent at 362nm.

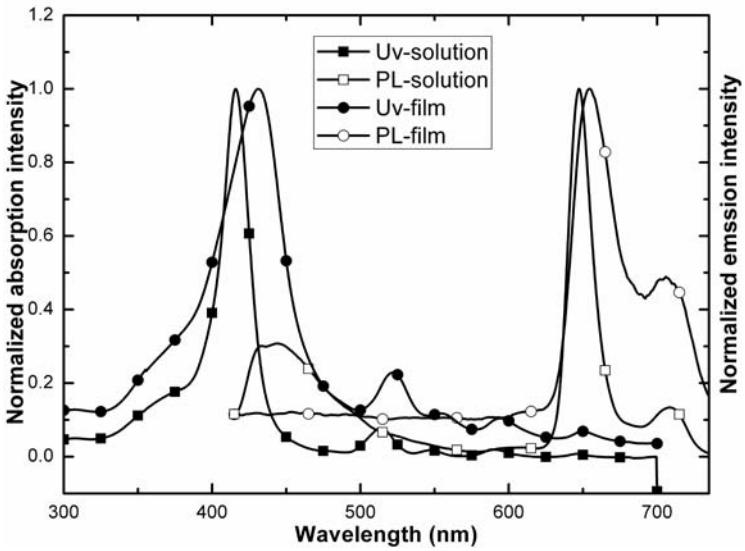


Figure S4. Normalized absorption (left) and photoluminescent (PL) (right) spectra of **1d** in THF solution and film state.Photoluminescence spectra were obtained upon excitation at the absorption of corresponding coumarin substituent at 380nm.

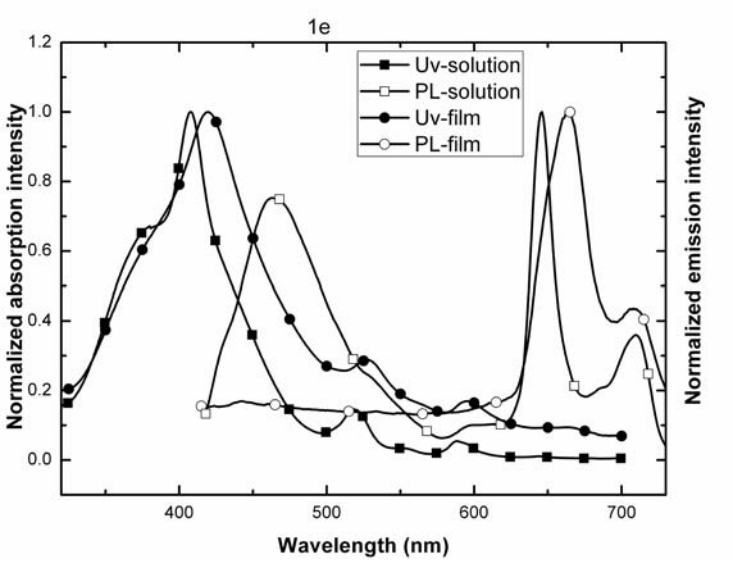


Figure S5. Normalized absorption (left) and photoluminescent (PL) (right) spectra of **1e** in THF solution and film state. Photoluminescence spectra were obtained upon excitation at the absorption of corresponding coumarin substituent at 380nm.

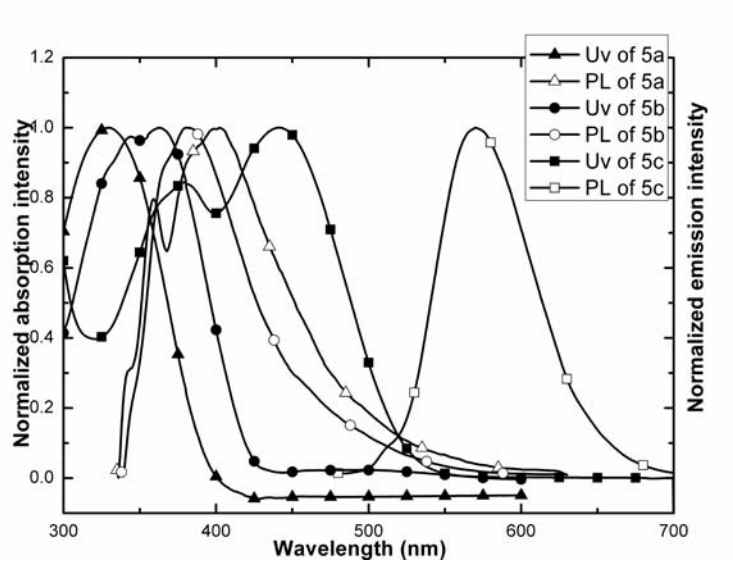


Figure S6. Normalized absorption (left) and photoluminescent (PL) (right) spectra of coumarin aldehyde **5a**, **5b** and **5c** in THF solution. photoluminescent spectra were obtained upon excitation at the absorption maxima (330nm, 362nm, 380nm respectively).

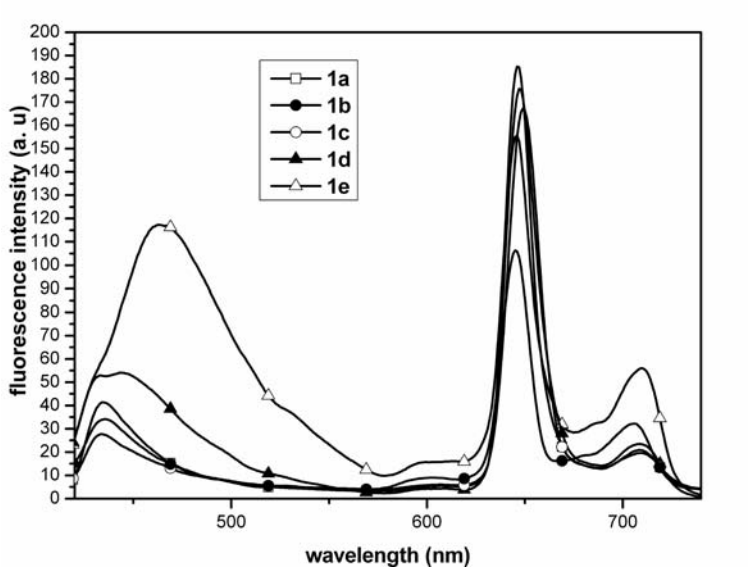


Figure S7. The photoluminescent spectra of *meso*-coumarin substituted Porphyrins (**1a**–**1e**) in THF solution. The photoluminescent spectra were obtained upon excitation at the absorption maxima of the corresponding coumarin substituents (330nm for **1a** and **1b** , 362nm for **1c**, 380nm for **1d** and **1e**).

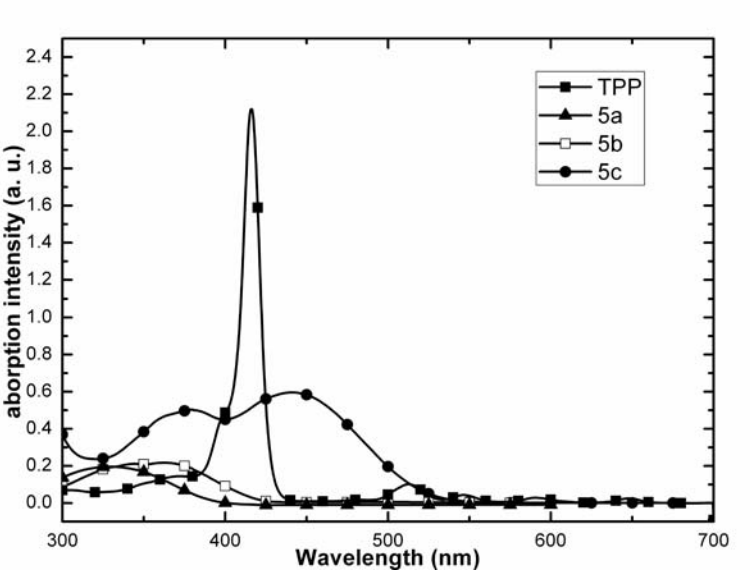


Figure S8. The absorption spectra of tetraphenyl porphyrin and coumarin **5a**, **5b** and **5c** in THF solution.

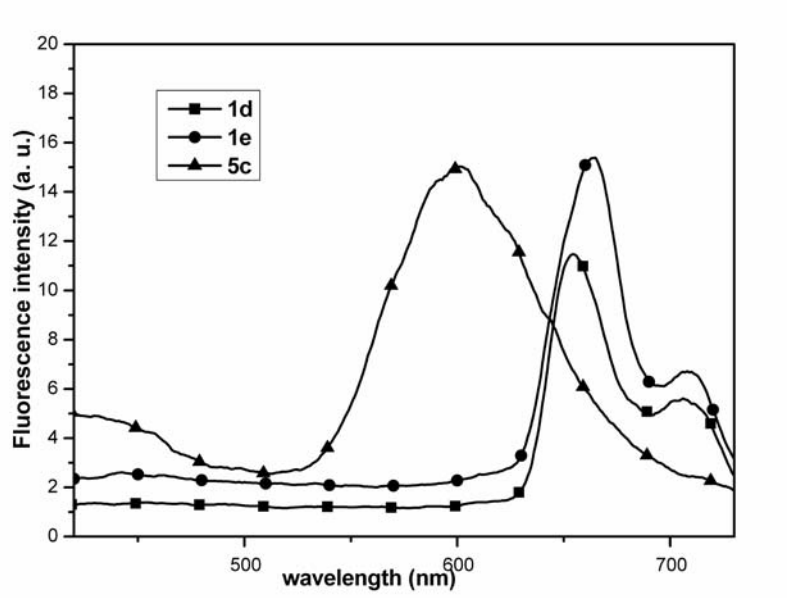


Figure S9. The photoluminescent spectra of **1d**, **1e** and 7-diethylamino-4-formyl-coumarin **5c** in solid film. Photoluminescent spectra were obtained upon excitation at the absorption of 7-diethylamino-4-formyl-coumarin (380nm).

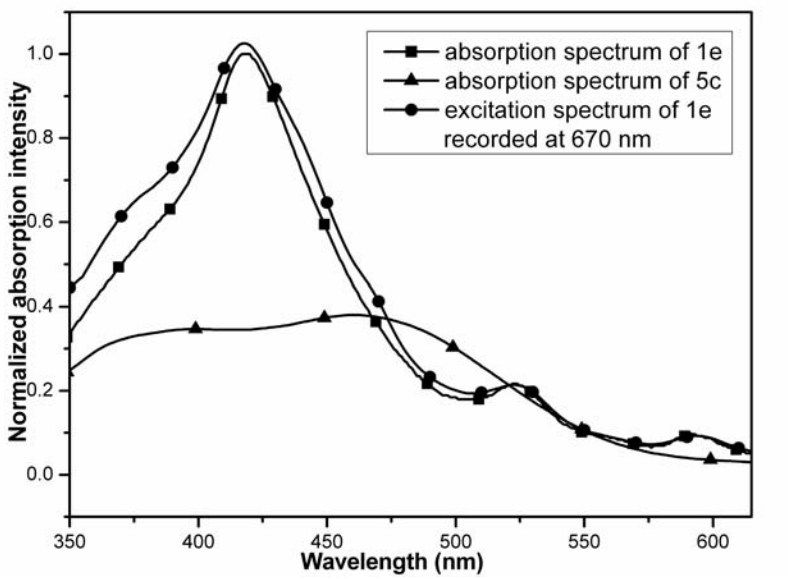


Figure S10. Overlays of the absorption spectra of **1e** and **5c**, and the excitation spectra of **1e** in solid film.

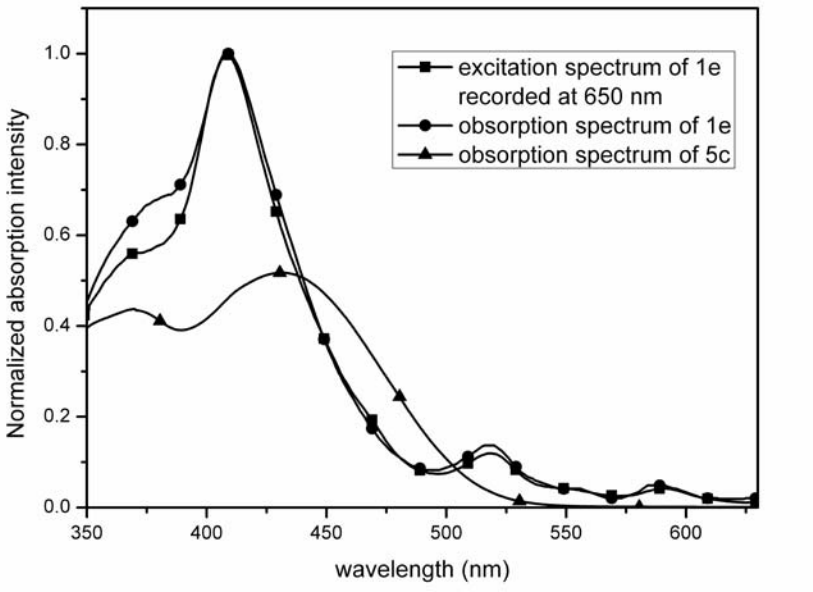


Figure S11. Overlays of the absorption spectra of **1e** and **5c**, and the excitation spectra of **1e** in THF solution.

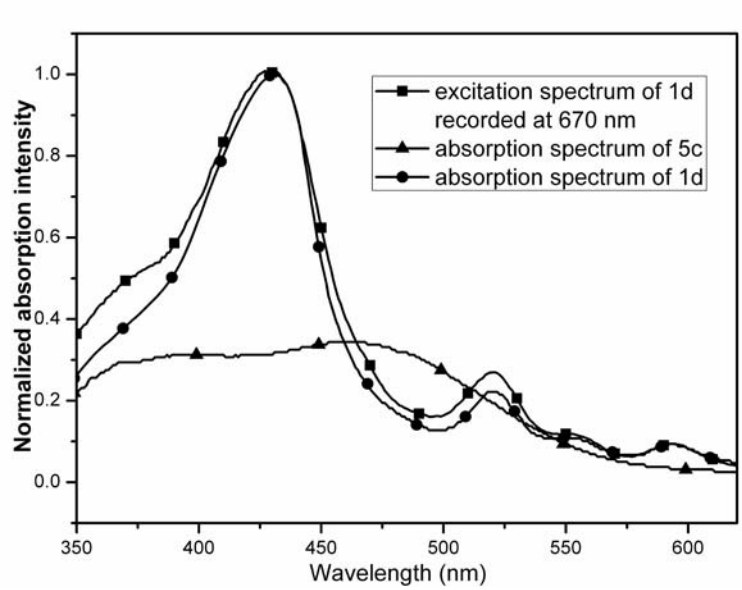


Figure S12. Overlays of the absorption spectra of **1d** and **5c**, and the excitation spectra of **1d** in solid film.

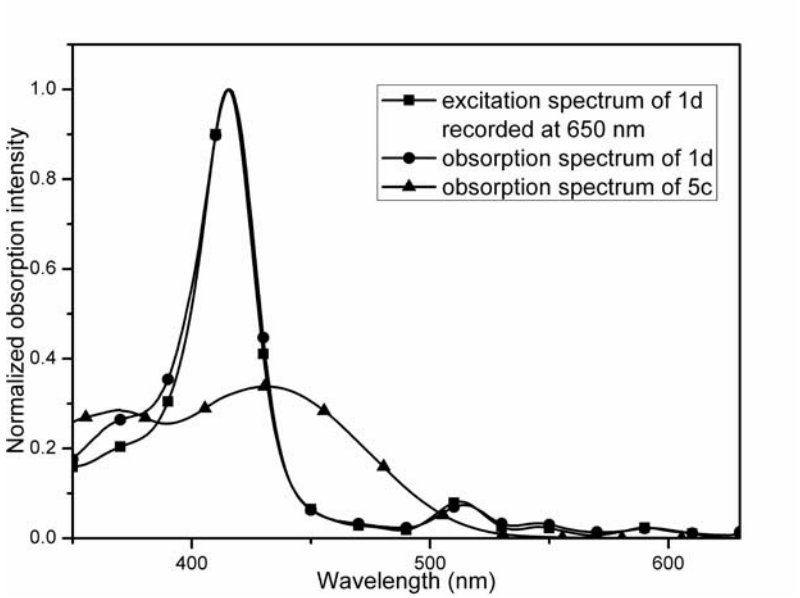


Figure S13. Overlays of the absorption spectra of **1d** and **5c**, and the excitation spectra of **1d** in solution.