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Electronic supplementary information

From Anthraquinone to Heterocoronene as Stable Red Chromophore

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1 Materials and method

All chemical reagents, solvents, catalysts and thin layer chromatography (TLC) were purchased from Sigma-Aldrich, Alfa-Aesar, Acros, Merck and TCI, unless stated otherwise. All of them were used as received without further purification.

1.1 NMR Spectroscopy

^{1}H-NMR, ^{13}C-NMR were recorded in CD_2Cl_2 solvents on a Bruker DPX 250 spectrometers. Chemical shifts (δ) were expressed in parts per million (ppm) referenced to residual signals of the deuterated solvents. The measurements were carried out at room temperature.

1.2 Mass Spectrometry

High-Resolution Mass Spectra (HR-MS) were recorded on a SYNAPT G2-Si high-resolution time-of-flight mass spectrometer (Water Crop., Manchester, UK) with Matrix-assisted laser desorption/ionization (MALDI).

1.3 Thermogravimetric Analysis and Differential Scanning Calorimetry

Thermogravimetric Analysis (TGA) was carried out on at Mettler 500 Thermogravimetry Analyzer with heating rates of 10 K/min under nitrogen atmosphere. Differential Scanning Calorimetry (DSC) was recorded on at Mettler DSC 30 with a heating/cooling rate of 10 ºC/min under nitrogen flow.

1.4 UV-Vis-NIR Spectroscopy

UV-Vis-NIR spectrum was measured Perkin Elmer Lambda 15 spectrophotometer.

1.5 Cyclic Voltammetry

Cyclic voltammetry was carried out on a computer controlled GSTAT 12 in a three electrodes cell in a dry dichloromethane solution of tetrabutylammonium hexafluorophosphate (0.1 M) with a scan rate 50 mV/s at room temperature under argon atmosphere. Glassy carbon, platinum wire and silver wire are work electrode, counter electrode and reference electrode respectively. Ferrocene/ferrocenium redox couple was used as the external standard.

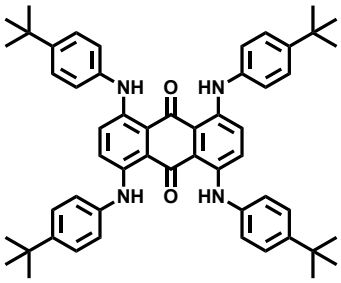
1.6 Fluorescence Quantum Yield

Fluorescence quantum yield of dilute solution was measured on fluorescence spectrometer IHR320 (Horiba Jobin Yvon company) match up integrating sphere. The excitation wavelength is 400 nm.

2. Synthesis and Structure Characterization:

2.1

1,4,5,8-Tetrakis((4-(*tert*-butyl)phenyl)amino)anthracene-9,10-dione (2a)



Under argon atmosphere 1,4,5,8-tetrachloro-9,10-anthracenedione (1.04 g, 3.00 mmol), *p-tert*butylaniline (2.70 g, 18.00 mmol) and Cs_2CO_3 (7.80 g, 24.00 mmol) were dissolved in dry toluene (50 mL). After argon bubbling for 20 minutes, $Pd_2(dba)_3$ (4% mol; 110 mg) and 2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene (BINAP,12% mol, 330 mg) were added into the solution. The reaction was stirred at 110 °C for 36 h. The reaction solution was cooled and the solvent was removed by rotary evaporation. The crude product was purified by silica column with petroleum ether/dichloromethane (7:3) as eluent. The pure product was obtained as dark green solid (1.6 g; 58%)

MALDI-TOF Ms (dithranol): m/*z* = 796.50; calculated: 796.50

^{1}H NMR (250 MHz, Methylene Chloride-d_2) δ [ppm] = 11.74 (s, 4H), 7.39 (s, 8H), 7.28 (d, 8H), 7.12 (d, 8H), 1.24 (s, 36H).

^{13}C NMR (62.5 MHz, Methylene Chloride-d_2) δ [ppm] = 186.16, 147.07, 142.35, 138.39, 126.64, 123.41, 122.87, 114.62, 34.66, 31.55.

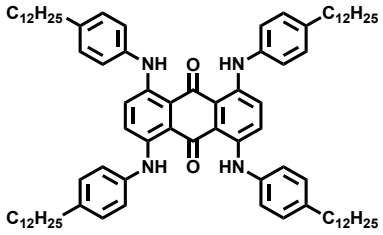
Elemental Analysis Cal. (%): C, 81.37; H, 7.59; N, 7.03

Found (%): C, 80.84; H, 7.57; N, 7.00

Melting point: 270 °C.

2.2

1,4,5,8-Tetrakis((4-dodecylphenyl)amino)anthracene-9,10-dione (2b)



Under argon atmosphere 1,4,5,8-tetrachloro-9,10-anthracenedione (692 mg, 2 mmol), 4-dodecylaniline (4.18g, 16 mmol) and Cs_2CO_3 (5.21 g, 24 mmol) were dissolved in dry toluene (50 mL). After argon bubbling for 20 min$Pd_2(dba)_3$ (7% mol, 128 mg) and BINAP (20% mol, 250 mg) were added into the solution. The reaction was stirred at 110 °C for 36 hours. The reaction solution was cooled and the solvent was removed by rotary evaporation. The crude product was purified by silica column chromatography with petroleum ether/dichloromethane (8:2) as eluent. The pure product was obtained as dark green solid in a yield of 44% .

MALDI-TOF Ms (dithranol): m/*z* =1245.03; calculated: 1244.97

^{1}H NMR (250 MHz, Methylene Chloride-d_2) δ [ppm] = 11.72 (s, 4H), 7.36 (s, 4H), 7.08 (s, 16H), 2.50 (t, 8H), 1.52 (m, 8H), 1.22 (m, 76H), 0.81 (t, 12H).

^{13}C NMR (62.5 MHz, Methylene Chloride-d_2) δ [ppm] = 186.11, 142.37, 138.98, 138.58, 129.67, 123.35, 123.23, 114.58, 54.71, 35.75, 32.34, 32.06, 30.10, 30.06, 29.95, 29.78, 29.73, 23.11, 14.31.

Elemental Analysis Cal. (%): C, 82.90; H, 10.03; N, 4.50

Found (%): C, 83.05; H, 10.36; N, 4.43

Melting point: 90 °C.

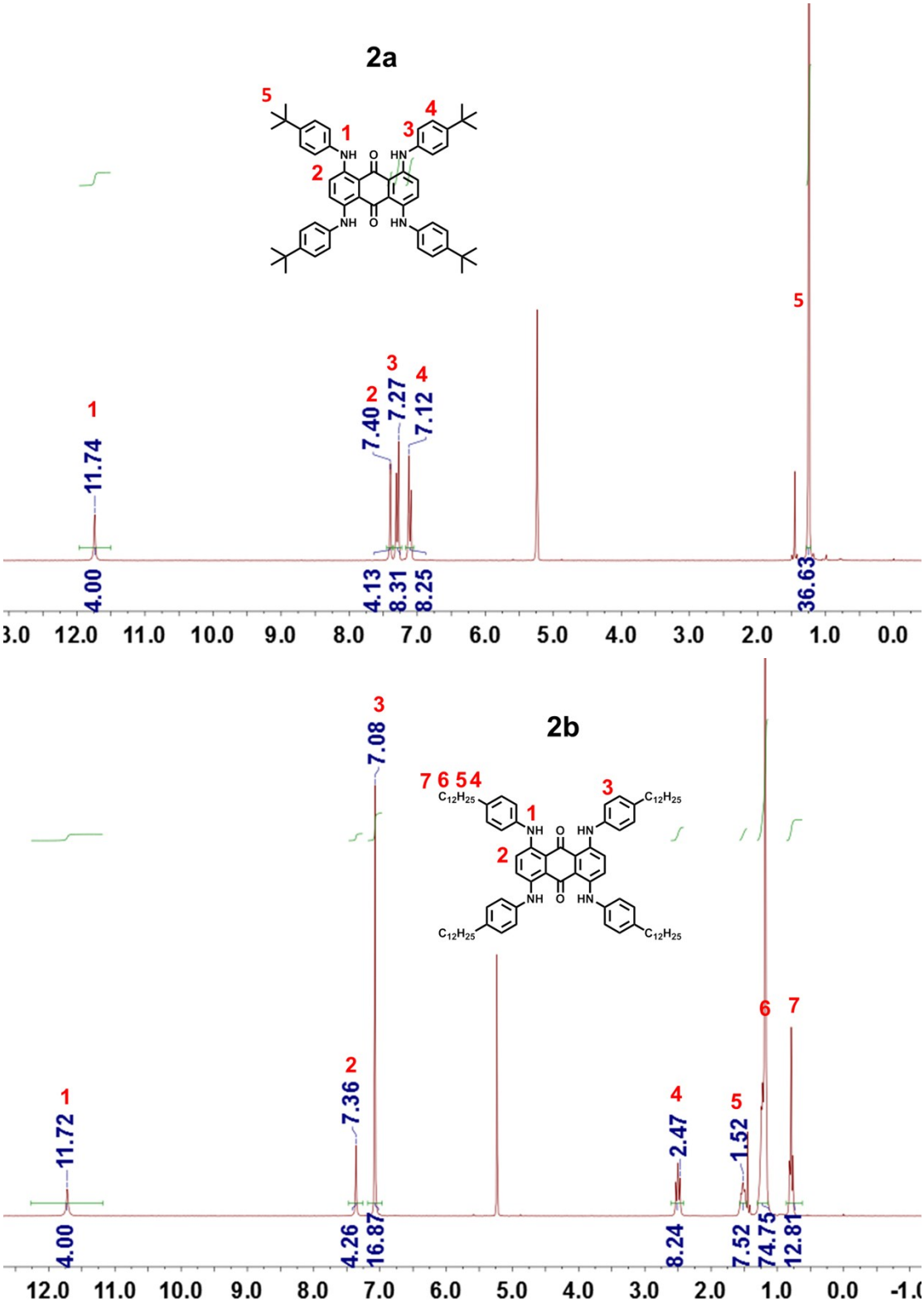


Figure S1. ^{1}HNMR spectra of **2a** (Top) and **2b** (bottom).

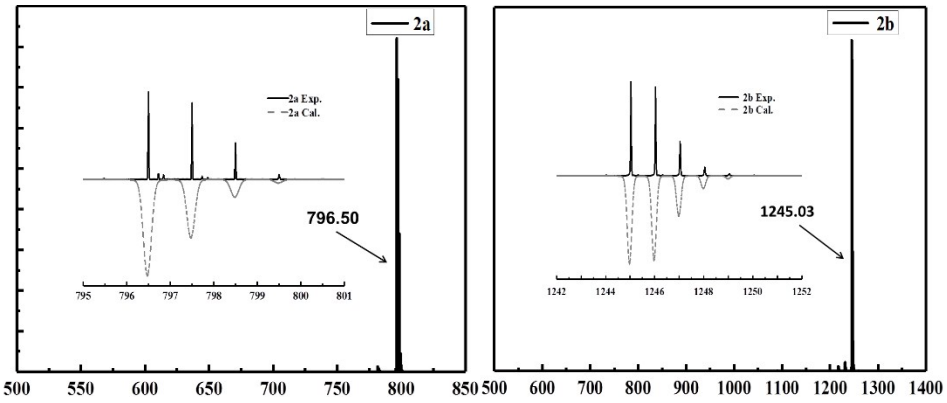
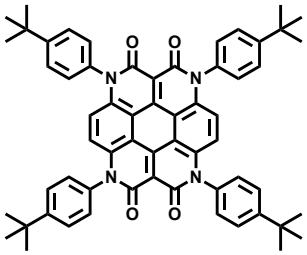


Figure S2. Mass measurement and calculation of **2a** (left) and **2b** (right)

2,3
1,4,7,10-Tetra(4-(*tert*-butyl)phenyl)-1,4,7,10-tetraazacoronene-2,3,8,9-tetraone (3a)



Under argon atmosphere 1,4,5,8-tetrakis((4-(*tert*-butyl)phenyl)amino)anthracene -9,10-dione (**2a**) (150 mg, 0.188 mmol)**,** diethyl malonate (600 mg, 3.76 mmol), potassium acetate (147 mg, 1.50 mmol) and DMF (3 mL) were placed in a microwave reaction tube. The reaction was heated by microwave at 170 °C for 30 min. The crude product was precipitated from hexane and purified by silica column chromatography with dichloromethane/ethyl acetate (1:1) as eluent and again by preparative GPC column with dichloromethane as eluent. The final product was dissolved in 3 mL dichloromethane and precipitated from methanol. The pure product was obtained as red powder (80 mg; 47%).

MALDI-TOF Ms (dithranol): m/*z* =897.46; calculated: 896.43

^{1}H NMR (250 MHz, Methylene Chloride-d_2) δ [ppm] = 7.69 (d, 8H), 7.36 (d, 8H), 7.06 (s, 4H), 1.45(s, 36H).

^{13}C NMR (62.5 MHz, Methylene Chloride-d_2) δ [ppm] = 158.94, 152.84, 138.85, 138.23, 135.21, 128.75, 127.70, 121.40, 114.51, 110.50, 35.19, 31.48.

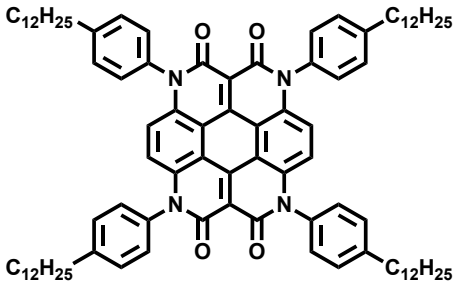
Elemental Analysis Cal. (%): C, 80.33; H, 6.29; N, 6.25

Found (%): C, 79.89; H, 6.33; N, 6.26

Melting point: 290 °C.

2.4

1,4,7,10-Tetra(4-dodecylphenyl)-1,4,7,10-tetraazacoronene-2,3,8,9-tetraone (3b)



Under argon atmosphere 1,4,5,8-tetrakis((4-dodecylphenyl)amino)anthracene -9,10-dione (**2b**) (150 mg, 0.120 mmol), diethyl malonate (385 mg, 2.41 mmol), potassium acetate (95 mg, 0.96 mmol) and DMF (3 mL) were placed in a microwave reaction tube. The reaction was heated by microwave irradiation to 170 °C for 30 min. The crude product was precipitated from hexane and purified by silica column chromatography (dichloromethane/ethyl acetate 1:1) and preparative gel permeation chromatography (DCM)**.** The final product was dissolved in 3 mL DCM and precipitated from methanol. The pure product was obtained as red powder (98 mg, 61%).

MALDI-TOF Ms (dithranol): m/*z* =1344.02 ; calculated: 1344.93

^{1}H NMR (250 MHz, Methylene Chloride-d_2) δ [ppm] = 7.48(d, 8H), 7.32 (d, 8H), 7.06 (s, 4H), 2.78 (t, 8H), 1.75 (t, 12H), 1.32 (m, 76H), 0.93 (t, 12H).

^{13}C NMR (62.5 MHz, Methylene Chloride-d_2) δ [ppm] = 158.92, 144.91, 138.83, 138.20, 135.35, 130.64, 129.01, 121.36, 114.53, 110.51, 36.08, 32.34, 31.83, 30.10, 30.06, 30.01, 29.92, 29.82, 29.78, 23.11, 14.32.

Elemental Analysis Cal. (%): C, 82.10; H, 8.99; N, 4.75

Found (%): C, 82.20; H, 8.36; N, 4.34

Melting point: 90 °C.

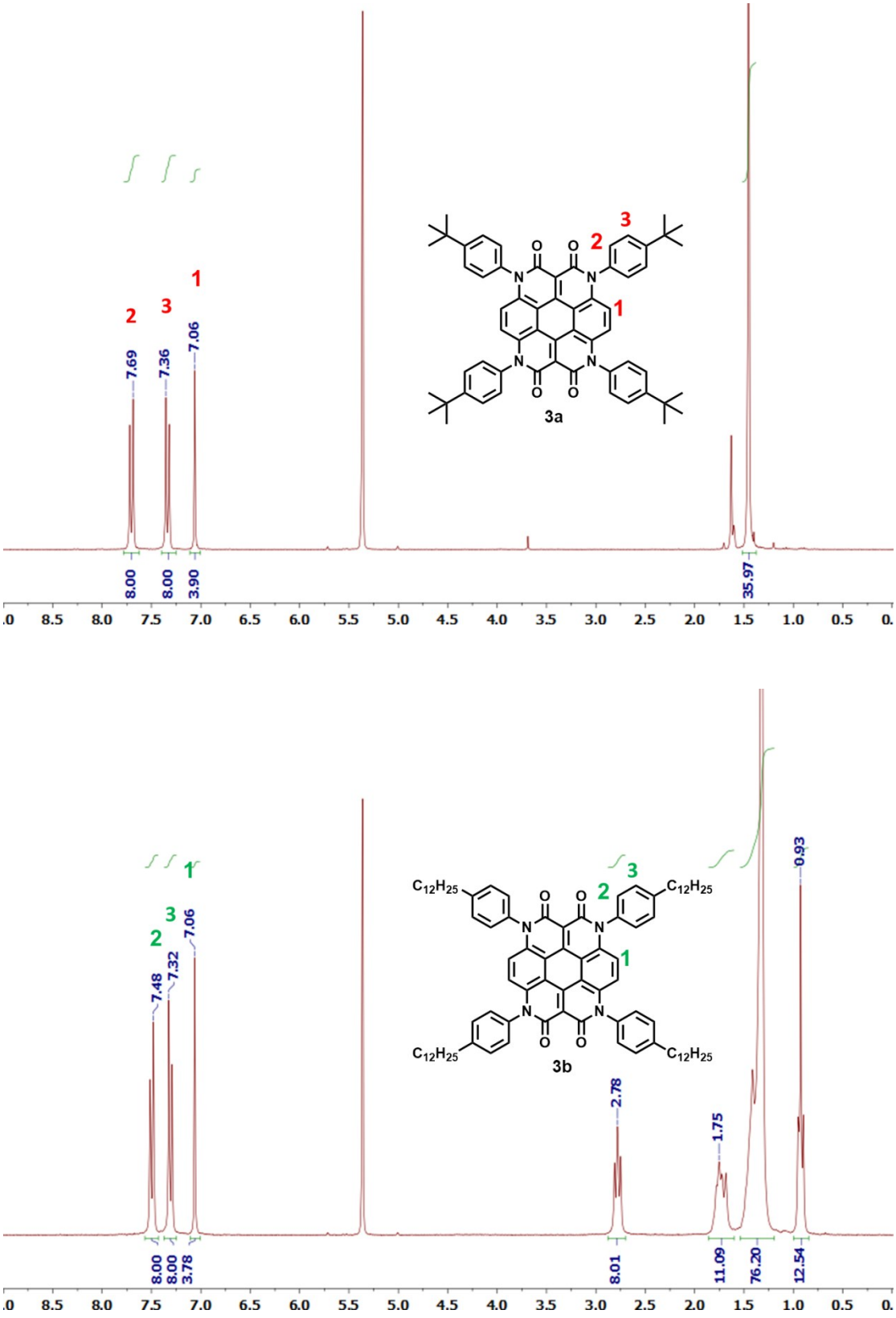


Figure S3. [1]HNMR spectra of **3a** (Top) and **3b** (bottom).

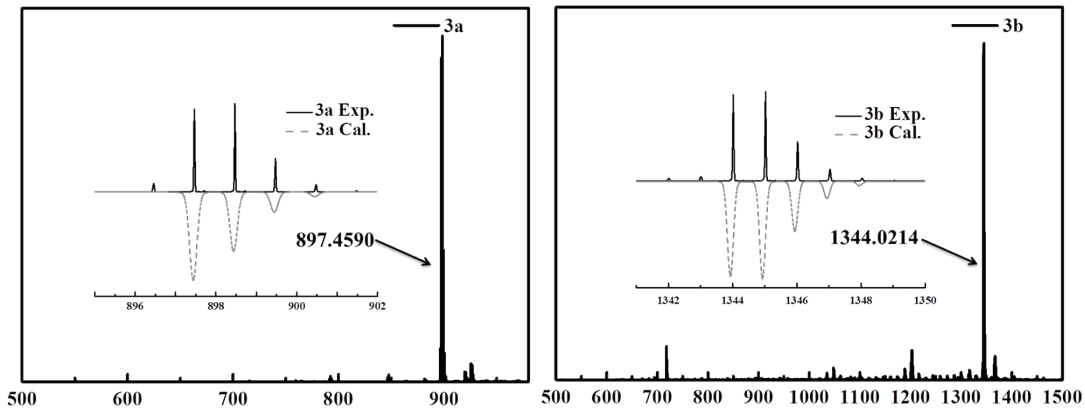


Figure S4. Mass measurement and calculation of **3a** (left) and **3b** (right)

3 Characterization of Physicl Property of 3a and 3b.

3.1 TGA and DSC Curves of 3a/b

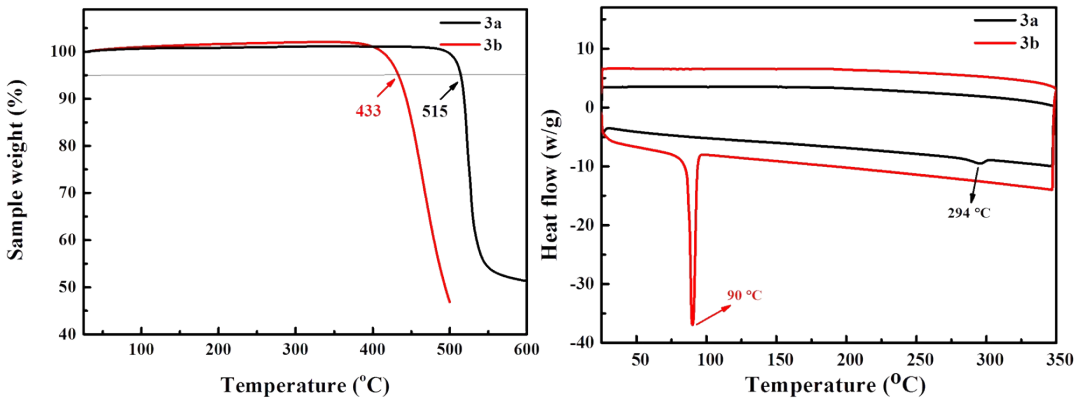


Figure S5. TGA (left) and DSC (right) curves of **3a**/**b**

3.2 Fluorescence Quantum Yield of 3a and PDI

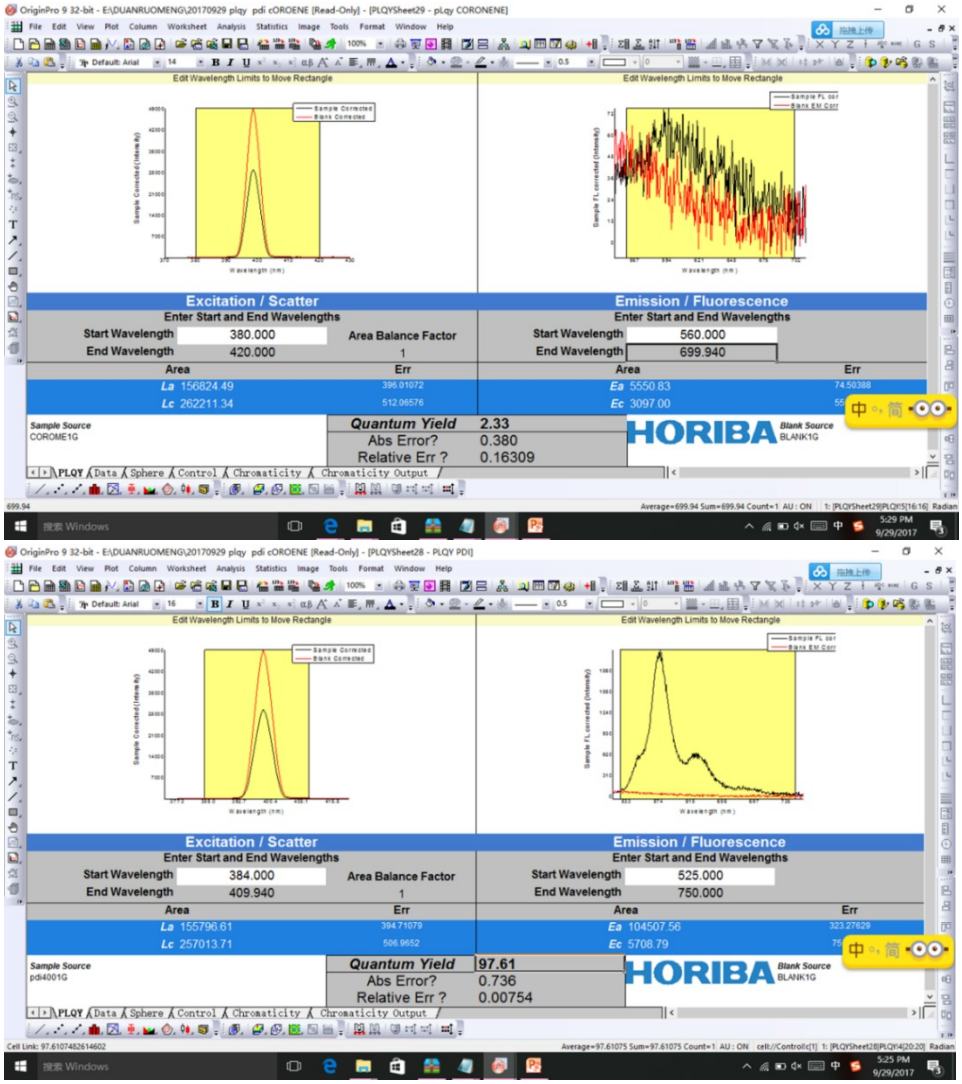


Figure S6. The measurement of quantum yield of **3a** (top) and PDI (bottom).

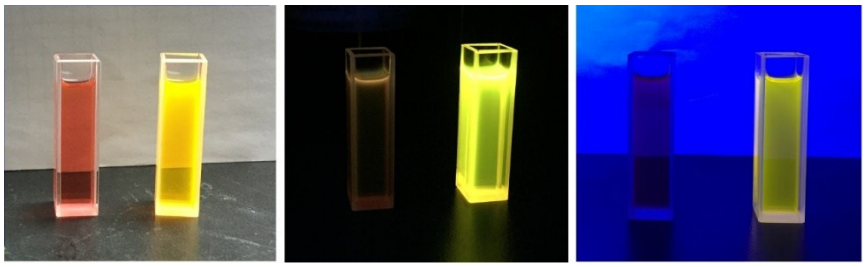


Figure S7. The comparison of fluorescence of **3a** and PDI.

Figure S8. The fluorescence spectrum of **3a** in solid, and the pictures of **3a** powder under nature light and under 365 nm UV lamp.

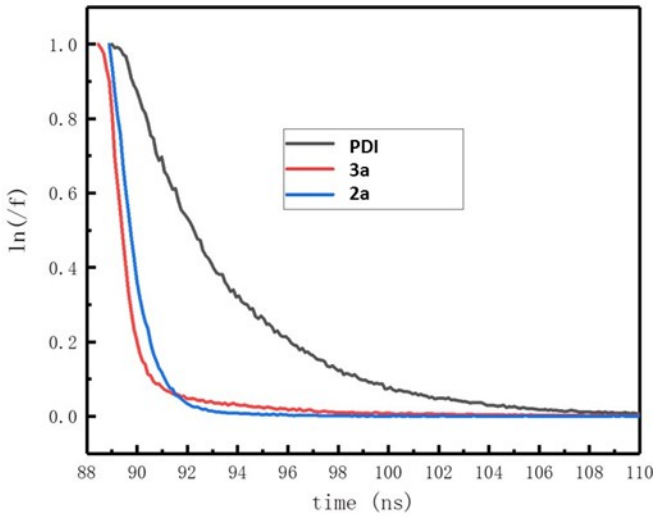


Figure S9. The fluorescence lifetime measurements of PDI (4.1 ns), **3a** (0.56 ns) and **2a** (0.53 ns).

Crystal data for **3a**

formula	$C_{60}H_{56}N_4O_4$, 6(CH_3OH)
molecular weight	1089.34 $gmol^{-1}$
absorption	μ = 0.078 mm^{-1}
crystal size	0.05 x 0.2 x 0.25 mm^3 red plate
space group	P -1 (triclinic)
lattice parameters	a = 11.3747(9)Å α = 93.969(2)°
(calculate from	b = 11.9787(10)Å β = 107.999(2)°
3170 reflections with	c = 12.5689(10)Å γ = 105.440(2)°
2.3° < θ < 27.2°)	V = 1548.4(4)$Å^3$ z = 1 F(000) = 584
temperature	-100°C
density	d_{xray} = 1.168 gcm^{-3}

data collection

diffractometer	Smart CCD
radiation	Mo-K_α graphit monochromator
scan type	ω-scans
scan – width	0.5°
scan range	2° ≤ θ < 28°
	-14 ≤ h ≤ 14 -15 ≤ k ≤ 15 -16 ≤ l ≤ 16
number of reflections:	
measured	22153
unique	7047 (R_{int} = 0.0411)
observed	4312 (|F|/σ(F) > 4.0)

data correction, structure solution and refinement

corrections	Lorentz and polarisation correction.
Structure solution	Program: SIR-2004 (Direct methods)
refinement	Program: SHELXL-2014 (full matrix). 388 refined parameters, weighting scheme: $w=1/[\sigma^2(F_o^2) + (0.1399*P)^2+0.63*P]$ with $(Max(F_o^2,0)+2*F_c^2)/3$. H-atoms at calculated positions and refined with isotropic displacement parameters, non H- atoms refined anisotropically.
R-values	wR2 = 0.2551 (R1 = 0.0752 for observed reflections, 0.1201 for all reflections)
goodness of fit	S = 1.037
maximum deviation of parameters	0.001 * e.s.d
maximum peak height in	

diff. Fourier synthesis	0.88, -0.49 eÅ^{-3}
remark	molecule has C_i symmetry, crystal contains 6 molecules methanol per main component, two are disordered

final coordinates and equivalent displacement parameters (Å^2)

$U_{äq}= (1/3)*\sum\sum_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

Atom	X	Y	Z	U_{eq}
C1	0.5452(3)	0.7457(2)	0.2210(2)	0.035(1)
C2	0.4846(2)	0.6232(2)	0.1925(2)	0.0278(9)
N3	0.4170(2)	0.5625(2)	0.2565(2)	0.0294(8)
C4	0.3597(2)	0.4403(2)	0.2357(2)	0.0286(9)
C5	0.3712(2)	0.3777(2)	0.1363(2)	0.0269(9)
C6	0.3139(2)	0.2491(2)	0.1094(2)	0.0291(9)
N7	0.3242(2)	0.1950(2)	0.0117(2)	0.0286(8)
C8	0.3858(2)	0.2545(2)	-0.0573(2)	0.0273(9)
C9	0.6084(3)	0.8048(2)	0.1554(2)	0.0342(10)
C10	0.4929(2)	0.5625(2)	0.0974(2)	0.0244(8)
C11	0.4346(2)	0.4377(2)	0.0696(2)	0.0238(8)
C12	0.4426(2)	0.3757(2)	-0.0290(2)	0.0242(8)
C13	0.3973(3)	0.6276(2)	0.3483(2)	0.0302(9)
C14	0.4870(3)	0.6540(2)	0.4561(2)	0.036(1)
C15	0.4683(3)	0.7206(3)	0.5403(2)	0.040(1)
C16	0.3600(3)	0.7593(2)	0.5197(2)	0.038(1)
C17	0.2700(3)	0.7295(3)	0.4112(3)	0.050(1)
C18	0.2882(3)	0.6641(3)	0.3249(2)	0.045(1)
C19	0.3444(3)	0.8345(3)	0.6160(3)	0.049(1)
C20	0.3683(4)	0.7773(3)	0.7222(3)	0.056(1)
C21	0.2079(5)	0.8474(4)	0.5843(3)	0.080(2)
C22	0.4495(6)	0.9536(3)	0.6451(4)	0.099(3)
O23	0.3042(2)	0.3952(2)	0.2979(2)	0.0384(8)
O24	0.2606(2)	0.1880(2)	0.1656(2)	0.0407(8)
C25	0.2682(2)	0.0674(2)	-0.0160(2)	0.0287(9)
C26	0.1406(3)	0.0177(2)	-0.0809(3)	0.048(1)
C27	0.0886(3)	-0.1032(2)	-0.1067(3)	0.050(1)
C28	0.1641(3)	-0.1769(2)	-0.0680(2)	0.0317(9)
C29	0.2928(3)	-0.1238(2)	-0.0034(2)	0.0329(10)
C30	0.3459(3)	-0.0017(2)	0.0236(2)	0.0329(9)
C31	0.1019(3)	-0.3108(2)	-0.0964(2)	0.037(1)
C32	-0.0043(3)	-0.3451(3)	-0.0432(3)	0.054(1)
C33	0.0386(3)	-0.3491(3)	-0.2253(3)	0.050(1)

C34	0.2010(3)	-0.3762(2)	-0.0514(3)	0.048(1)
O1L	0.1958(4)	0.3193(3)	0.5506(3)	0.110(2)
C2L	0.1944(6)	0.4327(4)	0.5376(5)	0.096(3)
O3L	0.0840(4)	0.2211(3)	0.6992(3)	0.116(2)
C4L	0.1048(5)	0.3189(5)	0.7762(4)	0.095(3)
O5L	0.1837(3)	0.1851(3)	0.3651(2)	0.045(1)
C6L	0.1697(9)	0.0681(5)	0.3602(8)	0.125(5)
O7L	0.1129(6)	-0.0646(5)	0.2974(4)	0.029(2)
C8L	0.1710(8)	-0.0832(7)	0.2171(6)	0.028(3)

anisotropic displacement parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	0.052(2)	0.023(1)	0.031(1)	0.007(1)	0.019(1)	-0.0020(10)
C2	0.036(1)	0.023(1)	0.027(1)	0.010(1)	0.013(1)	0.0034(9)
N3	0.040(1)	0.023(1)	0.028(1)	0.0081(9)	0.0179(9)	0.0016(8)
C4	0.033(1)	0.025(1)	0.030(1)	0.0084(10)	0.014(1)	0.0040(10)
C5	0.030(1)	0.022(1)	0.030(1)	0.0061(9)	0.013(1)	0.0030(9)
C6	0.033(1)	0.024(1)	0.032(1)	0.007(1)	0.015(1)	0.0047(10)
N7	0.035(1)	0.0164(9)	0.032(1)	0.0014(8)	0.0138(9)	0.0015(8)
C8	0.031(1)	0.020(1)	0.029(1)	0.0039(9)	0.011(1)	0.0022(9)
C9	0.046(2)	0.019(1)	0.035(1)	0.003(1)	0.018(1)	0.0001(10)
C10	0.028(1)	0.021(1)	0.024(1)	0.0073(9)	0.0092(9)	0.0009(9)
C11	0.024(1)	0.020(1)	0.027(1)	0.0057(9)	0.0081(9)	0.0020(9)
C12	0.027(1)	0.020(1)	0.025(1)	0.0065(9)	0.0092(10)	
0.0024(9)						
C13	0.041(1)	0.025(1)	0.029(1)	0.010(1)	0.018(1)	0.0025(10)
C14	0.039(1)	0.037(1)	0.034(1)	0.013(1)	0.014(1)	0.000(1)
C15	0.046(2)	0.043(2)	0.029(1)	0.013(1)	0.012(1)	-0.001(1)
C16	0.051(2)	0.037(1)	0.029(1)	0.014(1)	0.020(1)	0.002(1)
C17	0.057(2)	0.068(2)	0.039(2)	0.040(2)	0.018(1)	0.003(1)
C18	0.053(2)	0.057(2)	0.028(1)	0.027(1)	0.010(1)	-0.002(1)
C19	0.069(2)	0.047(2)	0.040(2)	0.021(2)	0.031(2)	0.000(1)
C20	0.060(2)	0.076(2)	0.034(2)	0.023(2)	0.020(1)	-0.001(1)
C21	0.116(3)	0.117(4)	0.047(2)	0.085(3)	0.039(2)	0.016(2)
C22	0.173(5)	0.045(2)	0.101(3)	0.013(3)	0.097(4)	-0.009(2)
O23	0.053(1)	0.0311(10)	0.0363(10)	0.0073(8)	0.0271(9)	0.0062(8)
O24	0.057(1)	0.0240(9)	0.047(1)	0.0041(8)	0.0313(10)	
0.0074(8)						
C25	0.036(1)	0.017(1)	0.033(1)	0.0023(10)	0.015(1)	0.0043(9)
C26	0.038(2)	0.022(1)	0.068(2)	0.008(1)	0.000(1)	0.008(1)
C27	0.032(2)	0.026(1)	0.073(2)	0.002(1)	-0.002(1)	0.007(1)

C28	0.034(1)	0.021(1)	0.038(1)	0.0032(10)	0.014(1)	0.0077(10)
C29	0.035(1)	0.024(1)	0.040(1)	0.011(1)	0.013(1)	0.007(1)
C30	0.031(1)	0.025(1)	0.038(1)	0.004(1)	0.010(1)	0.001(1)
C31	0.041(2)	0.018(1)	0.048(2)	0.003(1)	0.016(1)	0.007(1)
C32	0.054(2)	0.031(2)	0.082(2)	0.003(1)	0.037(2)	0.015(2)
C33	0.052(2)	0.027(1)	0.058(2)	0.001(1)	0.010(2)	0.001(1)
C34	0.050(2)	0.024(1)	0.068(2)	0.009(1)	0.019(2)	0.013(1)
O1L	0.171(4)	0.073(2)	0.102(3)	0.014(2)	0.087(3)	0.014(2)
C2L	0.124(4)	0.078(3)	0.099(4)	0.017(3)	0.067(3)	0.011(3)
O3L	0.166(4)	0.091(3)	0.119(3)	0.034(2)	0.088(3)	0.021(2)
C4L	0.120(4)	0.111(4)	0.073(3)	0.052(3)	0.045(3)	0.009(3)
O5L	0.043(2)	0.048(2)	0.034(1)	-0.010(1)	0.019(1)	0.018(1)
C6L	0.134(7)	0.130(6)	0.116(6)	0.037(5)	0.043(6)	0.056(5)
O7L	0.044(4)	0.016(3)	0.031(3)	0.005(2)	0.022(3)	0.008(2)
C8L	0.039(5)	0.019(4)	0.037(4)	0.008(3)	0.027(4)	0.011(3)

final coordinates and isotropic displacement parameters (Å^2) for H- atoms

Atom	X	Y	Z	U_{iso}
H1	0.54215	0.78772	0.28649	0.043
H9	0.64896	0.88716	0.17633	0.0411
H14	0.56096	0.62691	0.47257	0.044
H15	0.53137	0.74033	0.61430	0.048
H17	0.19434	0.75408	0.39516	0.060
H18	0.22601	0.64491	0.25048	0.054
H20A	0.30837	0.69738	0.70468	0.084
H20B	0.35412	0.82345	0.78198	0.084
H20C	0.45786	0.77435	0.74830	0.084
H21A	0.19524	0.89546	0.52421	0.121
H21B	0.19769	0.88535	0.65112	0.121
H21C	0.14334	0.76958	0.55737	0.121
H22A	0.53403	0.94125	0.65660	0.149
H22B	0.45160	0.99783	0.71455	0.149
H22C	0.43003	0.99792	0.58256	0.149
H26	0.08767	0.06608	-0.10836	0.057
H27	-0.00027	-0.13700	-0.15159	0.060
H29	0.34676	-0.17150	0.02339	0.0394
H30	0.43453	0.03303	0.06874	0.0394
H32A	-0.04474	-0.43040	-0.06087	0.082
H32B	-0.07016	-0.30610	-0.07391	0.082
H32C	0.03401	-0.32069	0.03927	0.082
H33A	0.10465	-0.32618	-0.26117	0.075

H33B	-0.02859	-0.31115	-0.25427	0.075
H33C	-0.00061	-0.43460	-0.24263	0.075
H34A	0.26791	-0.35667	-0.08680	0.072
H34B	0.15726	-0.46100	-0.06959	0.072
H34C	0.24144	-0.35278	0.03106	0.072
H1L	0.19112	0.28284	0.48909	0.166
H2L1	0.24261	0.48508	0.61051	0.144
H2L2	0.10461	0.43488	0.51148	0.144
H2L3	0.23517	0.45859	0.48164	0.144
H3L	0.07763	0.24036	0.63509	0.175
H4L1	0.10200	0.29484	0.84856	0.143
H4L2	0.03705	0.35621	0.74667	0.143
H4L3	0.18986	0.37472	0.78781	0.143
H5L	0.22253	0.21197	0.32103	0.067
H6L1	0.24911	0.05334	0.35646	0.188
H6L2	0.09640	0.02440	0.29256	0.188
H6L3	0.15334	0.04243	0.42810	0.188
H7L	0.10777	0.00415	0.30150	0.043
H8L1	0.16146	-0.02682	0.16447	0.042
H8L2	0.12876	-0.16325	0.17472	0.042
H8L3	0.26334	-0.07243	0.25580	0.042