Supplementary Information

Tetraphenylethylene Tetracylhydrazine Macrocycle with Ability for Discrimination of *n*-Propanol from *i*-Propanol and Highly Sensitive/Selective Detection of Nitrobenzene

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Materials and Methods

Materials: All reagents and solvents were chemical pure (CP) grade or analytical reagent (AR) grade and most of them were bought from China National Pharmaceutical Group Corporation, Aladdin (Shanghai) Bio-Chem Technology Co Ltd, and Meryer (Shanghai) Chemical Technology Co Ltd et al.. These reagents and solvents were used as received unless otherwise indicated.

Measurements: ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV 400 spectrometer at 298 K in $CDCl_3$. Infrared spectra were recorded on Bruker EQUINAX55 spectrometer. Absorption spectra were recorded on a Hewlett Packard 8453 UV–Vis spectrophotometer. Mass spectrum was measured on an Ion Spec 4.7 Tesla FTMS instrument. The single crystal data of TPE-BODIPY was collected on Rigaku Saturn diffractometer with CCD area detector. Powder X-ray diffraction (XRD) pattern were measured on a χ'Pert PRO diffraction instrument. Fluorescent emission spectra were collected on a Shimadzu RF-5301 fluorophotometer at 298 K. Transmission electron micrographs (TEM) were recorded on electron microscope at 200 kV. The gel diluted with hexane and the suspension was dropped onto a copper grid covered with a thin carbon film on a filter paper and air dried. The determination of fluorescence quantum yield of the TPE macroctcle using quinine sulfate (Φ_f = 0.546) in 0.50 M H_2SO_4 as standard.

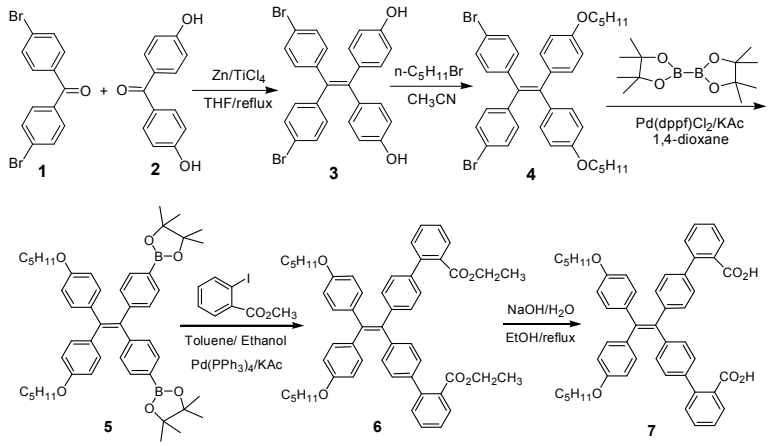
Detection of nitrobenzene vapor in air.

Preparation of nitrobenzene-saturating air: About 1 mL of TNT were added in a 0.5 L of bottle and let nitrobenzene fully evaporate into the air in the bottle by standing it at 25 ^{o}C for 4 h.

Preparation of nitrobenzene vapour diluted by air: Into the bottom of a 5 L of bottle was injected 50 mL of nitrobenzene-saturating air by syringe. Upon lidded, the bottle was standing for 1 h and nitrobenzene vapour diluted 100 times was obtained. Other nitrobenzene vapour samples with different dilution times were prepared in the same way.

The preparation of solid film: Solution of TPE macrocycle in THF (1.0×10^{-3} M) was dropped onto the surface of one quartz slide, let it fully spread on the surface, and air dried.

Synthesis of TPEtetracylhydrazine macrocyclic compounds



Synthesis of compound 3

One three-necked flask charged with a magnetic stirrer and zinc powder (8.9 g, 140 mmol) was vacuumed and filled by nitrogen for three times. Under nitrogen, THF (80 mL) was added and the mixture was cooled in a iced bath before $TiCl_4$ (7.61 mL, 70.1 mmol) was slowly added by a syringe to keep temperature under 10 °C. The suspending mixture was stirred for 0.5 h at room temperature and then was refluxed for 3 h. Again, the mixture was cooled to 0 °C before compound **1** (4.73 g, 14.0 mmol) and **2** (3.0 g, 14.0 mmol) were added. After finishing addition, the reaction mixture was refluxed until the carbonyl compounds disappeared (monitored by TLC, eluant: petroleum ether/ethyl acetate 2:1). The reaction mixture was cooled to room temperature, adjusted to pH 7 by 10% K_2CO_3 aqueous solution, and filtered through celite. The filtrate was extracted with ethyl acetate. The combined organic phase was washed two times with water and then with saturated brine. After dried over anhydrous Na_2SO_4 and filtered, the filtrate was evaporated to dryness. The obtained residue was subjected to column chromatography to give **3** as light yellow solid (1.5 g, 39%). Mp 116.6−117.8 ^oC; ^1H-NMR (400 MHz, $CDCl_3$) δ (ppm) 3.27 (d, J = 8.99 Hz, 4H), 3.51 (d, J = 8.58 Hz, 4H), 3.58 (d, J = 8.58 Hz, 4H), 3.92 (d, J = 8.17 Hz, 4H), 5.12 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 157.6, 155.4, 145.2, 142.2, 138.3, 137.9, 136.6, 134.5, 132.6, 130.6, 130.4, 130.3, 128.5, 127.3, 126.6, 124.3, 115.1, 113.5, 106.3, 77.2, 71.7, 67.8, 29.0, 28.2, 22.5, 14.0.

Synthesis of compound 4

To a flask was added **3** (2.0 g, 3.85 mmol), K_2CO_3 (2.2 g, 15.4 mmol) and CH_3CN (80

mL). The mixture was refluxed for 0.5 h before *n*-pentanebromide (1.16 mL, 9.23 mmol) was added. The mixture was continued to reflux for about 12 h until **3** disappeared (monitored by TLC, eluant: petroleum ether/ethyl acetate 5:1). After solvent was removed, water and dichloromethane were added. The organic phase was separated and washed with water. The solution was dried over Na_2SO_4, filtered, and evaporated to dryness. The obtained crude product was purified by column chromatography to offer **4** as white powder (1.89 g, 63%). Mp 114.2−115.3 ^oC; ^1H-NMR (400 MHz, $CDCl_3$) δ (ppm) 0.92 (t, *J* = 7.27 Hz, 6H), 1.37 (m, 8H), 1.75 (m, 4H), 3.88 (t, *J* = 6.73 Hz, 4H), 6.63 (d, *J* = 8.89 Hz, 4H), 6.87 (t, *J* = 9.70 Hz, 8H), 7.22 (d, *J* = 8.08 Hz, 4H)； ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm) 158.0, 142.9, 141.7, 136.4, 135.4, 133.0, 132.5, 131.0, 120.2, 113.7, 77.2, 67.9, 29.0, 28.2, 22.5, 14.0.

Synthesis of compound 5

To a flask was added **4** (3.0 g, 4.55 mmol), bis(pinacolato)diboron (2.8 g, 10.9 mmol), Bis(diphenylphosphino)ferrocenedichloropalladium(II) (200 mg, 0.27 mmol), and KAc (4.46 g, 45.5 mmol). After the flask was vacuumed and filled with nitrogen for three times, 1,4-dioxane (60 mL) was added and heated to reflux for about 12 h under nitrogen until **4** disappeared (monitored by TLC, eluant: petroleum ether/ethyl acetate 10:1). The mixture was filtered through celite and dichloromethane was added into the filtrate. The solution was washed with water, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by column chromatography to give **5** as solid powder (2.5 g, 73%). Mp 127.3−128.6 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.92 (t, *J* = 7.2 Hz, 6H), 1.31 (s, 24H), 1.37 (m, 8H), 1.75 (m, 4H), 3.86 (t, *J* = 6.7 Hz, 4H), 6.58 (d, *J* = 8.6 Hz, 4H), 6.87 (d, *J* = 8.6 Hz , 4H), 6.98 (d, *J* = 8.0 Hz, 4H), 7.50 (d, *J* = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 157.7, 147.3, 141.3, 138.7, 135.9, 134.1, 132.6, 130.8, 127.6, 113.5, 83.6, 67.7, 29.0, 28.2, 24.9, 22.4, 14.0.

Synthesis of compound 6

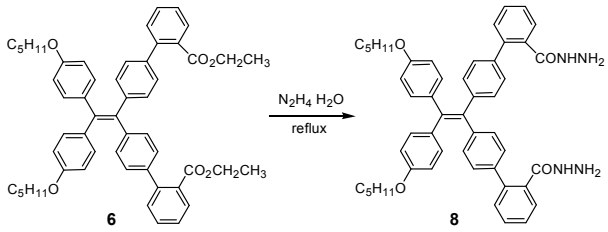
To a flask was added **5** (500 mg, 0.66 mmol), methyl-2-iodobenzoate (415 mg, 1.59 mmol), $Pd(PPh_3)_4$ (45.8 mg, 0.04 mmol), and K_2CO_3 (913 mg, 6.61 mmol). The flask was vacuumed and filled with nitrogen for three times before toluene (30 mL) and ethanol (15 mL) were added. The mixture was refluxed for about 12 h under nitrogen until **5** was consumed (monitored by TLC, eluant: petroleum ether/ethyl acetate 3:1). Dichloromethane and water was

added. The separated organic phase was wished with water, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by column chromatography to give **6** as yellow powder (0.42 g, 86%). Mp 105.4−106.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.91 (t, *J* = 6.90 Hz, 6H), 1.06 (t, *J* = 6.82 Hz, 6H) 1.33−1.42 (m, 8H), 1.73−1.74 (m, 4H), 3.88 (t, *J* = 4.64 Hz, 4H), 4.05−4.07 (m, 4H), 6.65 (d, *J* = 8.26 Hz, 4H), 6.99 (m, 4H), 7.08 (s, 8H), 7.36 (t, *J* = 7.47 Hz, 4H), 7.46−7.51 (m, 2H), 7.74 (d, *J* = 7.89 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 169.2, 157.7, 138.8, 132.6, 132.5, 131.5, 131.2, 131.0, 130.8, 130.5, 130.4, 129.6, 129.5, 127.8, 127.6, 126.9, 113.6, 67.7, 60.9, 51.8, 29.0, 28.2, 22.4, 14.0.

Synthesis of compound 7

To a flask was added **6** (1.0 g, 1.3 mmol), NaOH (1.2 g, 30 mmol) in H_2O (15 mL), and ethanol (20 mL). The mixture was refluxed for about 11 h under nitrogen until **6** disappeared (monitored by TLC, eluant: petroleum ether/ethyl acetate 3:1). After adjusted to pH 1−2 by addition of 2 M HCl, dichloromethane was added. The separated organic phase was washed with water, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by column chromatography to give **7** as yellow powder (0.47 g, 48%). Mp 207.1−208.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.89 (t, *J* = 7.2 Hz, 6H), 1.32 (m, 8 H), 1.63 (m, 4 H), 3.78 (t, *J* = 6.5 Hz, 4 H), 6.64 (d, *J* = 8.7 Hz, 4 H), 6.93−7.00 (m, 12 H), 7.23 (d, *J* = 7.55 Hz , 2 H), 7.36 (m, 2 H), 7.44 (m, 2 H), 7.89 (d, *J* = 7.91 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 174.1, 157.7, 143.7, 143.4, 140.3, 138.7, 138.2, 136.3, 132.7, 131.8, 131.2, 130.5, 130.1, 129.7, 127.7, 126.8, 113.6, 67.7, 29.0, 28.2, 22.4, 14.0; ESI$^+$ HRMS m/z calcd for $C_{50}H_{48}O_6$ 744.34 [M], found 744.34 [M].

Synthesis of compound 8

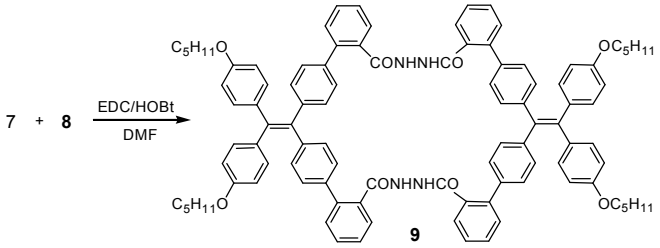


6 8

To a flask was added **6** (0.52 g, 0.67 mmol), ethanol (30 mL), and hydrazine hydrate (25 mL). The mixture was refluxed under nitrogen for about 24 h until **6** disappeared (monitored by TLC, eluant: dichloromethane/methanol 10:1). Upon cooled to room temperature, the precipitates were collected by filtering and were washed with ethanol to give **8** as yellow-green

solid (0.29 g, 55%). Mp 169.3−170.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.91 (t, *J* = 7.04 Hz, 6H), 1.38 (m, 8 H), 1.74 (m, 4 H), 3.14 (s, 4 H), 3.88 (t, *J* = 6.69 Hz, 4 H), 6.69 (d, *J* = 8.5 Hz, 4 H), 6.96 (d, *J* = 8.26 Hz , 4 H), 7.12 (m, *J* = 8.26 Hz, 8 H), 7.37 (m, 4 H), 7.47 (m, 2 H), 7.64 (d, *J* = 7.44 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.5, 157.9, 144.0, 141.7, 139.5, 137.6, 137.4, 135.7, 133.4, 132.6, 131.8, 130.5, 130.0, 129.0, 128.0, 127.5, 113.7, 67.8, 29.0, 28.2, 22.4, 14.0; ESI$^+$ HRMS m/z calcd for $C_{50}H_{53}N_4O_4$ 773.40 [M+1], found 773.40 [M+1].

Synthesis of compound 9



To a flask was added **7** (215 mg, 0.29 mmol), **8** (222 mg, 0.29 mmol), HOBt (117 mg, 0.86 mmol), EDC (165 mg, 0.86 mmol), and DMF (15 mL). The mixture was stirred at room temperature for about 24 h until **7** or **8** disappeared (monitored by TLC, eluant: petroleum ether/ethyl acetate 3:2). The solvent was removed under reduced pressure and chloroform was added. The solution was washed one time with 1M HCl and two times with water. Upon dried over anhydrous Na_2SO_4 and filtered, the solution was evaporated to dryness. The residue was subjected to column chromatography to give **9** as yellow-green powder (225 mg, 52%). Mp 282.6−283.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.91 (t, *J* = 6.99 Hz, 12H), 1.37 (m, 16H), 1.72 (m, 8H), 3.83 (t, *J* = 6.70 Hz, 8H), 6.62 (d, *J* = 8.82 Hz, 8H), 6.93 (d, *J* = 8.82 Hz, 8H), 6.99 (d, *J* = 8.11 Hz, 8H), 7.07 (d, *J* = 8.11 Hz, 8H), 7.21 (d, *J* = 7.47 Hz, 4H), 7.38−7.46 (m, 8H), 7.79 (d, *J* = 6.44 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.8, 157.9, 144.2, 141.1, 139.9, 137.2, 137.0, 135.7, 132.6, 131.9, 131.6, 130.9, 130.4, 129.6, 128.1, 127.5, 113.6, 67.7, 29.0, 28.2, 22.4, 14.0; ESI$^+$ HRMS m/z calcd for $C_{100}H_{96}N_4O_8$ 1481.72 [M], found 1481.71 [M].

Spectra of ^{1}H NMR, ^{13}C NMR, IR, and HRMS

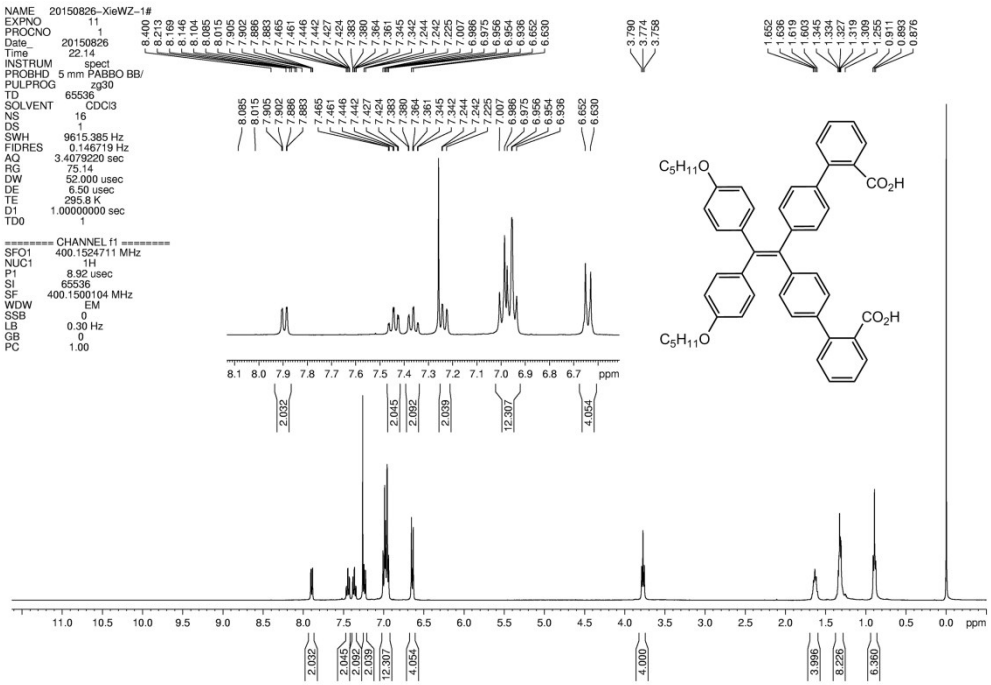


Fig. S1. ^{1}H-NMR spectrum of compound **7**.

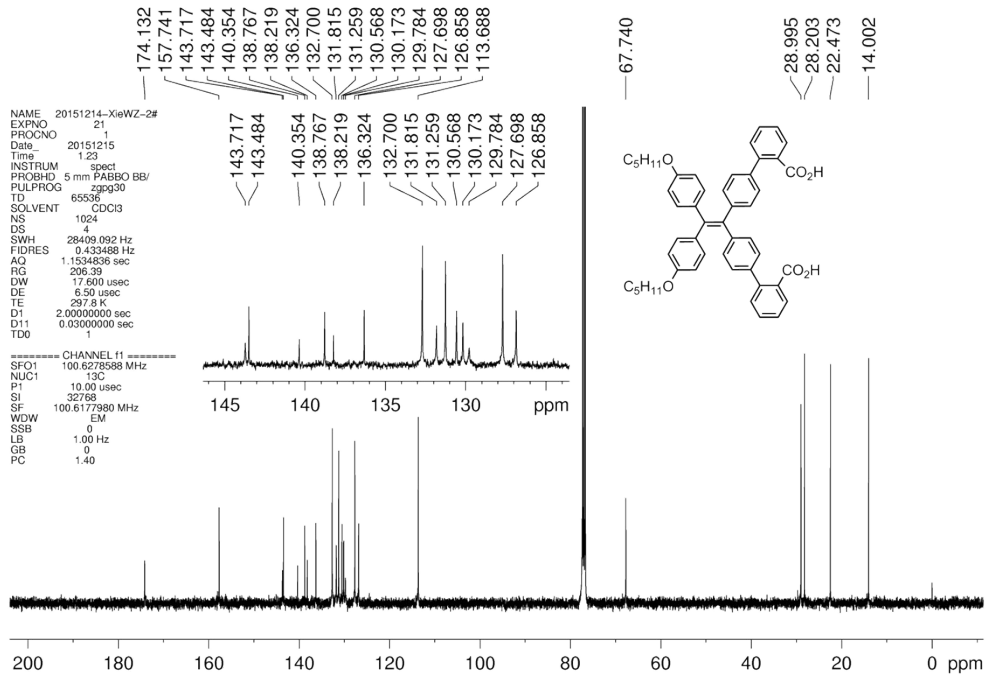
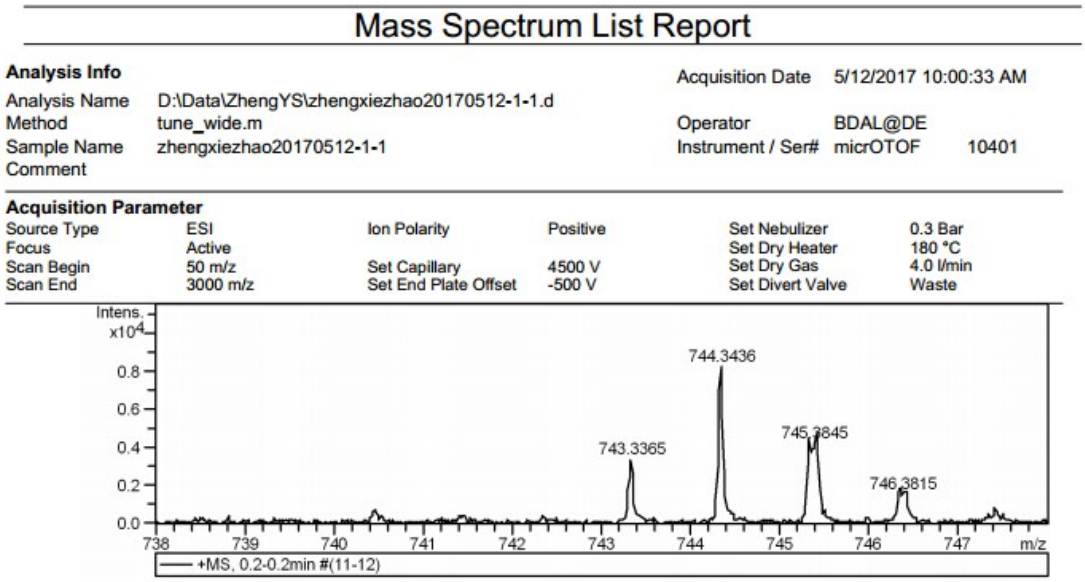


Fig. S2. ^{13}C-NMR spectrum of compound **7.**



#	m/z	Res.	S/N	I	FWHM
1	743.3365	11906	12.5	3427	0.0624
2	744.3436	13509	31.1	8131	0.0551
3	745.3845	5157	14.8	3852	0.1445
4	746.3815	5669	6.1	1588	0.1317

Fig. S3. HRMS spectrum of compound **7**.

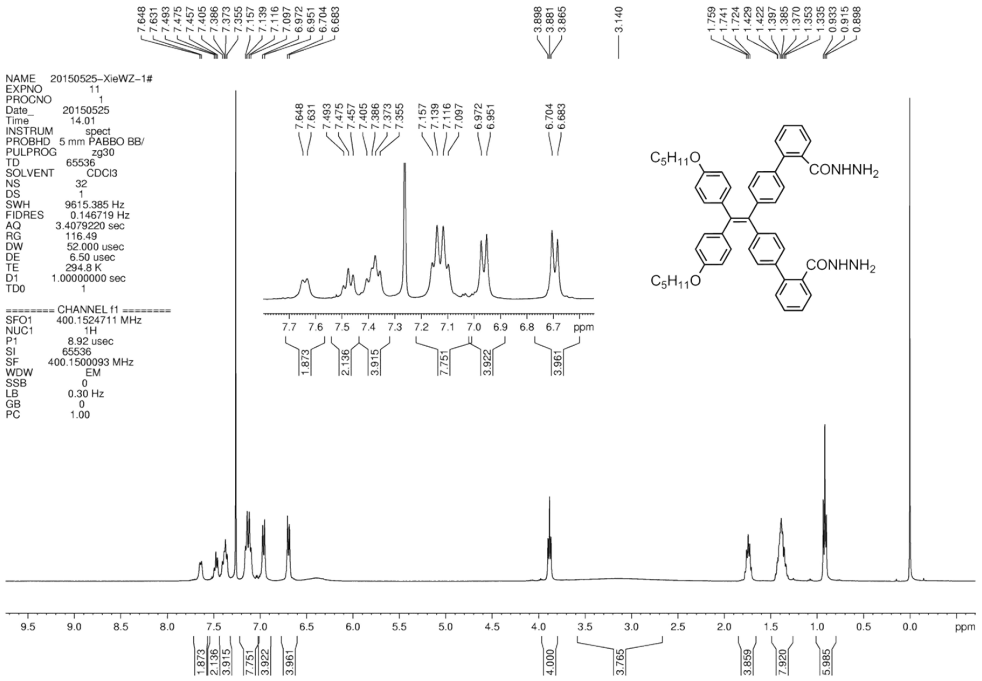


Fig. S4. ^{1}H-NMR spectrum of compound **8**.

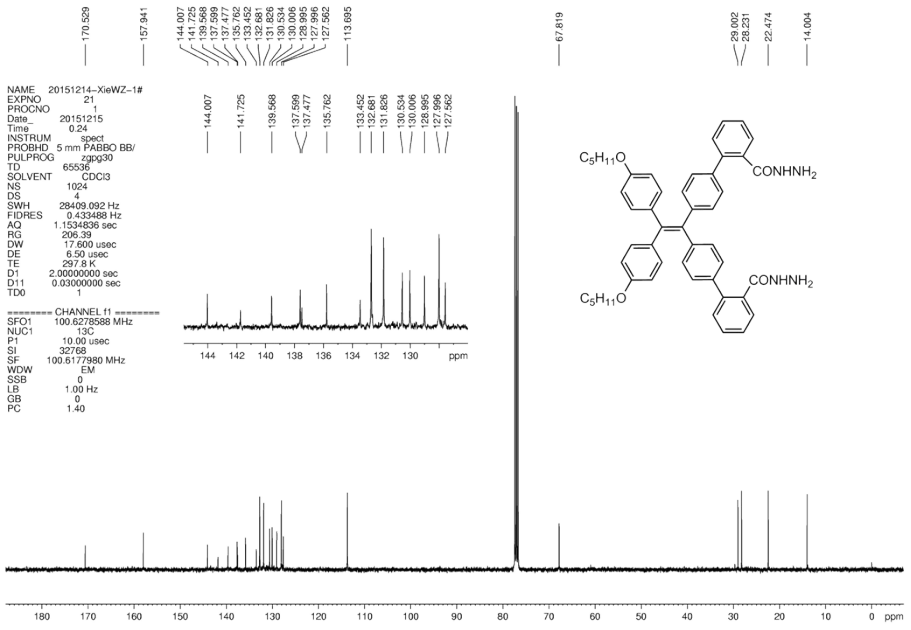
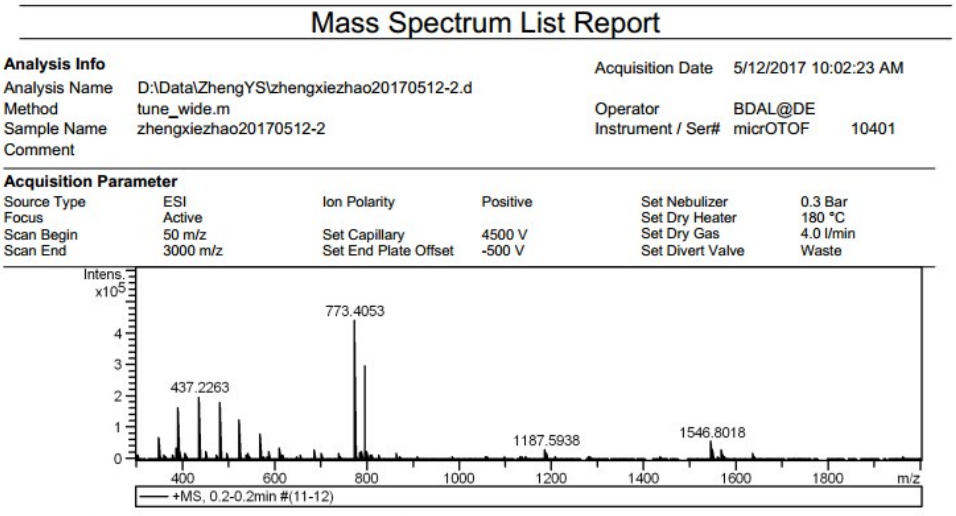


Fig. S5. ^{13}C-NMR spectrum of compound **8**.



#	m/z	Res.	S/N	I	FWHM
1	349.1833	11696	434.2	69838	0.0299
2	388.3928	12249	197.0	35975	0.0317
3	393.2093	12011	902.1	166772	0.0327
4	394.2138	11004	146.3	27195	0.0358
5	437.2263	9752	958.0	200190	0.0448
6	438.2270	7042	212.9	44692	0.0622
7	453.2025	9647	111.3	24336	0.0470
8	481.2618	12891	775.6	180806	0.0373
9	482.2647	11562	161.0	37731	0.0417
10	525.2866	12366	477.1	122776	0.0425
11	526.2908	12045	117.0	30282	0.0437
12	569.3133	12835	279.4	78891	0.0444
13	588.4100	12718	93.0	27414	0.0463
14	613.3400	12615	123.4	38055	0.0486
15	685.4328	12710	89.4	31329	0.0539
16	773.4053	15628	1225.0	443333	0.0495

Fig. S6. HRMS spectrum of compound **8**.

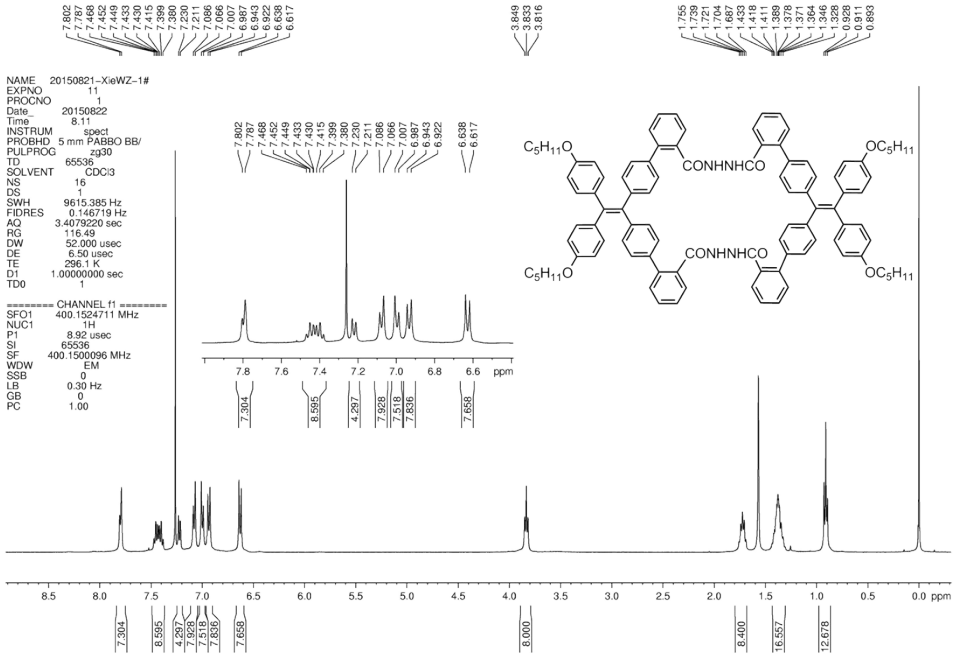


Fig. S7. [1]H-NMR spectrum of compound **9**.

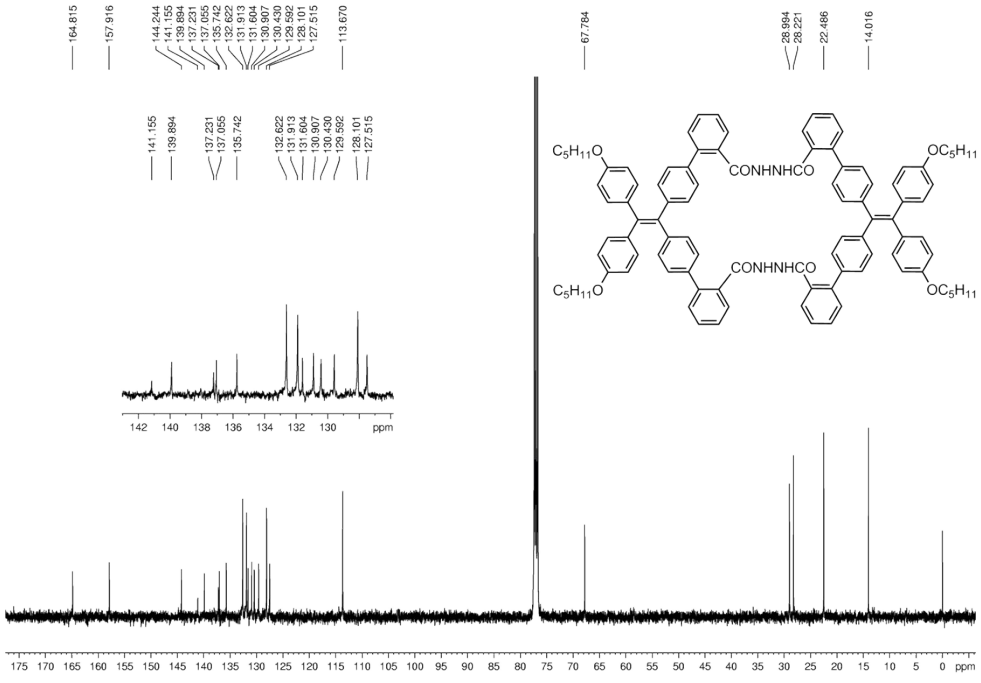


Fig. S8. [13]C-NMR spectrum of compound **9**.

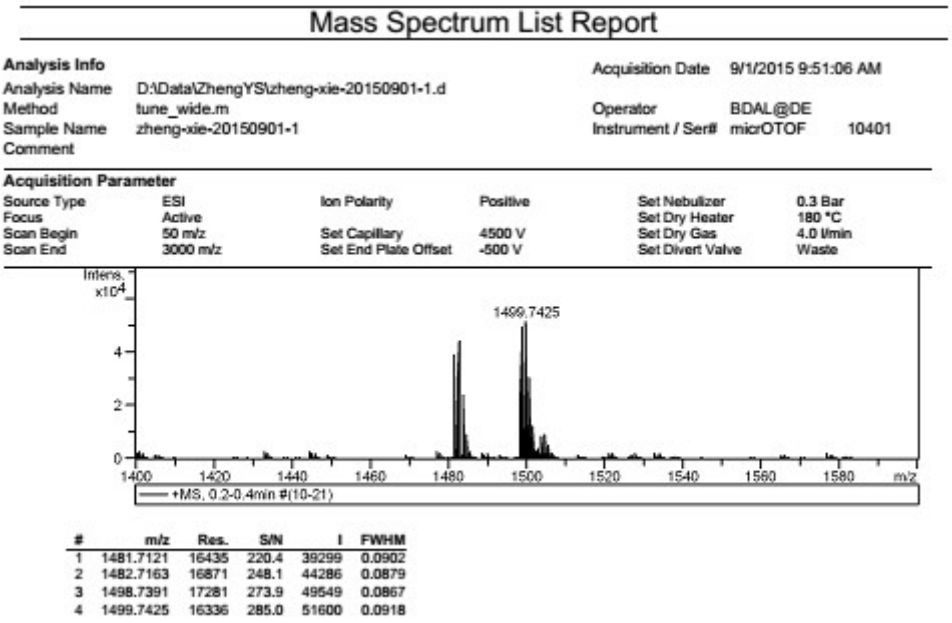


Fig. S9. HRMS spectrum of compound **9**.

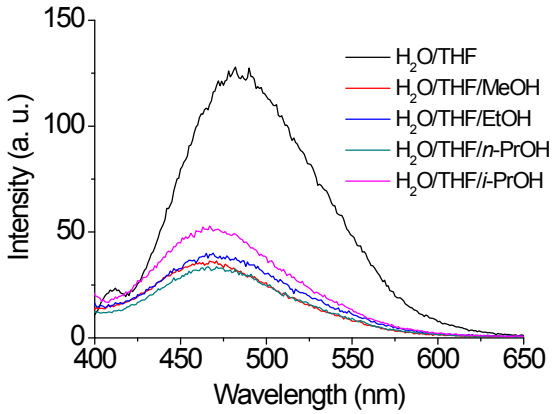


Fig. S10. Fluorescence spectra of **9** in 95:5 H_2O/THF, 85.5:4.5:10 H_2O/THF/MeOH, 85.5:4.5:10 H_2O/THF/EtOH, 85.5:4.5:10 H_2O/THF/*n*-PrOH, and 85.5:4.5:10 H_2O/THF/*i*-PrOH. [**9**] = 5×10^{-7} M.

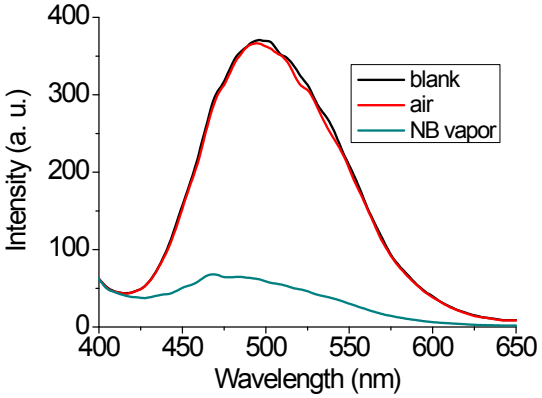


Fig. S11. Change in the fluorescence spectrum of ground powder of **9** with air bearing nitrobenzene vapor. λ_{ex} = 371 nm, ex/em slit widths = 3/3.

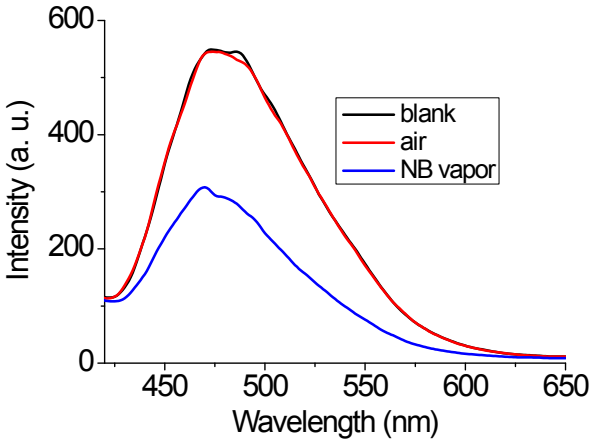


Fig. S12. Change in the fluorescence spectrum of powder of **9** with air bearing nitrobenzene vapor. λ_{ex} = 371 nm, ex/em slit widths = 3/3.