Supplementary Information

Synthesis of Tetraphenylethylene Pillar[4]arenes and the Selective Fast Quenching of Their AIE Fluorescence by TNT

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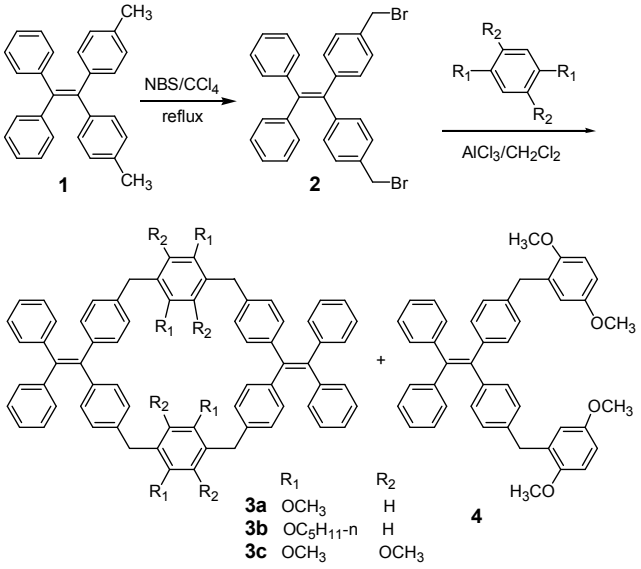
Materials and methods: All reagents and solvents were chemical pure (CP) grade or analytical reagent (AR) grade and were used as received unless otherwise specified. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV 400 spectrometer at 298 K in $CDCl_3$. Infrared spectra were recorded on BRUKER EQUINAX55 spectrometer. Mass spectrum was measured on an IonSpec 4.7 Tesla FTMS instrument. Fluorescent emission spectra were collected on a Shimadzu RF-5301 fluorophotometer at 298 K.

Synthesis of TPE pillar[6]arenes



Synthesis of the key intermediate 2: It was synthesized according to the known procedure (A. Qin, L. Tang, J. W. Y. Lam, C. K. W. Jim, Y. Yu, H. Zhao, J. Sun and B. Z. Tang, *Adv. Funct. Mater.* 2009, **19**, 1891–1900). To a flask was added 4,4'-dimethyltetraphenylethene **1**(1.08 g, 3 mmol), 1-bromosuccinimide (NBS, 1.18 g, 3.3 mmol), dibenzoyl peroxide (15 mg, 0.060 mmol) and CCl_4 (20 mL). The mixture was refluxed for 12 h, and then dichloromethane (20 mL) was added. After the solution was washed with water and brine, respectively, for three times, it was dried over anhydrous sodium sulfate, filtered and evaporated under vacuum to dryness. The residue was purified by flash chromatography (eluant, petroleum/dichloromethane 5:1 v/v) to give **2** as a slightly yellow power (1.15 g, 74%). Mp 219.7–220.8 ^{o}C; ^{1}H NMR(400 MHz, $CDCl_3$) 7.11 (m, 10 H), 7.00 (dt, J = 6.0, 2.3 Hz, 4 H), 6.97 (d, J =

8.3 Hz, 4 H), 4.41 (s, 4 H); ^{13}C NMR(100 MHz, $CDCl_3$) 143.7, 143.3, 142.1, 139.5, 135.9, 131.7, 131.2, 128.5, 127.8, 126.7, 33.5; IR (KBr) *v* 3070, 3026, 1659, 1604, 1507, 1488, 1440, 1410, 1226, 1205, 1129, 1099, 1072, 1024, 981, 839, 760, 697, 616 cm^{-1}.

Synthesis of TPE pillar[6]arene 3a: To a flask was added **2** (1.20 g, 2.30 mmol), 1,4-dimethyloxylbenzene (0.38 g, 2.80 mmol), anhydrous $AlCl_3$ (370 mg, 2.80 mmol) and dichloromethane (210 mL). The mixture was stirred at ambient temperature for 6 h, and the resultant dark green solution was quenched with water (30 mL) and became yellow. After the yellow solution was washed with 50 mL water for three times, it was dried over anhydrous sodium sulfate, filtered and evaporated under vacuum to dryness. The remained slurry-like solid was purified by flash chromatography (eluant, petroleum/dichloromethane 2:1 v/v). The obtained solid was recrystallized from a mixed solvent of $CHCl_3$ and methanol to give **3a** as a white solid (230 mg, 20%). Mp >300 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.08 (m, 12 H), 7.01 – 6.99 (m, 8 H), 6.87 (q, *J* = 12.4, 8.6 Hz, 16 H), 6.60 (s, 4 H), 3.78 (s, 8 H), 3.66 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.30, 144.29, 141.05, 140.95, 140.09, 139.37, 131.36, 131.23, 127.98, 127.79, 127.59, 126.09, 114.15, 55.15, 35.82; IR (KBr) *v* 3076.93, 3048.41, 3022.06, 2989.82, 2930.59, 2902.72, 2829.42, 1601.12, 1571.49, 1505.34, 1460.78, 1437.26, 1403.28, 1334.40, 1293.88, 1250.50, 1214.75, 1179.21, 1108.72, 1073.01, 1047.17, 977.72, 952.91, 925.70, 869.49, 801.97, 760.89, 736.30, 699.32, 620.82, 594.09, 540.73, 511.38, 486.78, 461.60, 428.21 cm^{-1}; ESI^{+} HRMS m/z calcd for $C_{72}H_{60}O_4$ 988.4492 [M^{+}], found 988.4496 [M^{+}].

Synthesis of TPE pillar[6]arene 3b: To a flask was added **2** (1.20 g, 2.30 mmol), 1,4-di(*n*-pentanoxy)benzene (0.70 g, 2.80 mmol), anhydrous $AlCl_3$ (370 mg, 2.80 mmol) and dichloromethane (210 mL). The mixture was stirred at ambient temperature for 12 h, and the resultant dark brown solution was quenched with 30 mL water and it became yellow. After the yellow solution was washed with water (50 mL) for three times, it was dried with anhydrous sodium sulfate, filtered and evaporated to dryness under vacuum. The remained slurry-like solid was purified with flash chromatography (eluant, petroleum/dichloromethane 7:1 v/v). The obtained solid was

recrystallized from $CHCl_3$ and methanol to give **3b** as a white solid (220 mg, 16%). Mp 270.8 – 271.4 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (m, 12 H), 7.01 – 6.99 (m, 8 H), 6.85 (q, *J* = 13.2, 8.5 Hz, 16 H), 5.57 (s, 4 H), 3.77 (s, 8 H), 3.75 (t, *J* = 6.7 Hz, 8 H), 1.63 (m, 8 H), 1.33 – 1.29 (m, 16 H), 0.88 (t, *J* = 5.9 Hz, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 144.4, 141.2, 140.9, 139.9, 139.5, 131.4, 131.2, 128.0, 127.9, 127.6, 126.1, 114.9, 68.7, 36.1, 29.2, 28.2, 22.4, 14.0; IR (KBr) *v* 3048.74, 3021.73, 2928.62, 1599.68, 1504.15, 1468.10, 1433.76, 1405.91, 1326.01, 1251.15, 1213.06, 1110.38, 1072.17, 1024.84, 929.95, 870.24, 800.84, 761.40, 699.97, 627.74 cm^{-1}; ESI^+ HRMS m/z calcd for $C_{88}H_{93}O_4$ 1213.7074 $[M+H]^+$, found 1213.7022 $[M+H]^+$.

Synthesis of TPE pillar[6]arene 3c: To a flask was added **2** (1.79 g, 3.46 mmol), 1,2,4,5-tetramethoxybenzene (0.82 g, 4.15 mmol), anhydrous $AlCl_3$ (0.55 mg, 4.15 mmol) and dichloromethane (320 mL). The mixture was stirred at reflux for 3 days, and the resultant dark brown solution was quenched with 50 mL water and became yellow. After the yellow solution was washed with water (70 mL) for three times, it was dried with anhydrous sodium sulfate, filtered and evaporated to dryness under vacuum. The remained slurry-like solid was purified with flash chromatography (eluant, petroleum/dichloromethane 1:3 v/v). Then the solid was recrystallized from $CHCl_3$ and methanol to give **3c** as a white solid (60 mg, 3.2%). Mp > 300 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (m, 12 H), 6.99 – 6.97 (m, 16 H), 6.87 (d, *J* = 8.0 Hz, 8 H), 3.80 (s, 8 H), 3.59 (s, 24 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 144.5, 141.0, 140.9, 140.5, 139.6, 131.4, 131.2, 128.3, 128.2, 127.6, 127.2, 126.1, 60.2, 30.0; IR (KBr) *v* 3075, 3052, 3022, 2991, 2968, 2934, 2828, 1600, 1507, 1460, 1407, 1327, 1299, 1253, 1184, 1110, 1064, 1018, 978, 959, 920, 860, 836, 811, 790, 758, 734, 698, 660, 638, 618, 577, 514, 480, 461 cm^{-1}; ESI^+ HRMS m/z calcd for $C_{76}H_{68}KO_8$ 1147.4551 $[M+K]^+$, found 1147.4528 $[M+K]^+$.

Synthesis of acyclic analogue 4: To a flask was added **2** (1.20 g, 2.30 mmol), 1,4-dimethoxylbenzene (1.92 g, 13.9 mmol), anhydrous $AlCl_3$ (370 mg, 2.80 mmol) and dichloromethane (70 mL). The mixture was stirred at ambient temperature for 2 h, and the resultant dark brown solution was quenched with water (30 mL) and became yellow. After the yellow solution was washed with water (70 mL) for three times, it

was dried with anhydrous sodium sulfate, filtered and evaporated to dryness under vacuum. The remained slurry-like solid was purified with flash chromatography (eluant, petroleum/dichloromethane 1:2 v/v). Then the solid was recrystallized from $CHCl_3$ and methanol to give **4** as a white solid (710 mg, 48%). Mp 67.1 – 68.3 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.06 (m, 6 H), 7.02 – 7.00 (m, 4 H), 6.91 (s, 8 H), 6.76 (d, J = 8.8 Hz, 2 H), 6.69 (dt, J = 8.8, 2.8 Hz, 2 H), 6.54 (d, J = 2.8 Hz, 2H), 3.83 (s, 4 H), 3.71 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 151.7, 144.0, 141.3, 140.9, 140.2, 138.7, 131.3, 131.2, 131.1, 128.3, 127.5, 126.1, 116.6, 111.5, 111.2, 56.1, 55.6, 35.6; IR (KBr) v 3021, 2993, 2953, 2901, 2830, 1598, 1498, 1464, 1436, 1412, 1314, 1297, 1275, 1219, 1178, 1155, 1108, 1076, 1046, 1025, 978, 949, 914, 852, 801, 756, 730, 700, 673, 636, 592, 578, 546, 486, 451 cm^{-1}; ESI^+ HRMS m/z calcd for $C_{44}H_{40}KO_4$ 671.2564 $[M+K]^+$, found 671.2550 $[M+K]^+$.

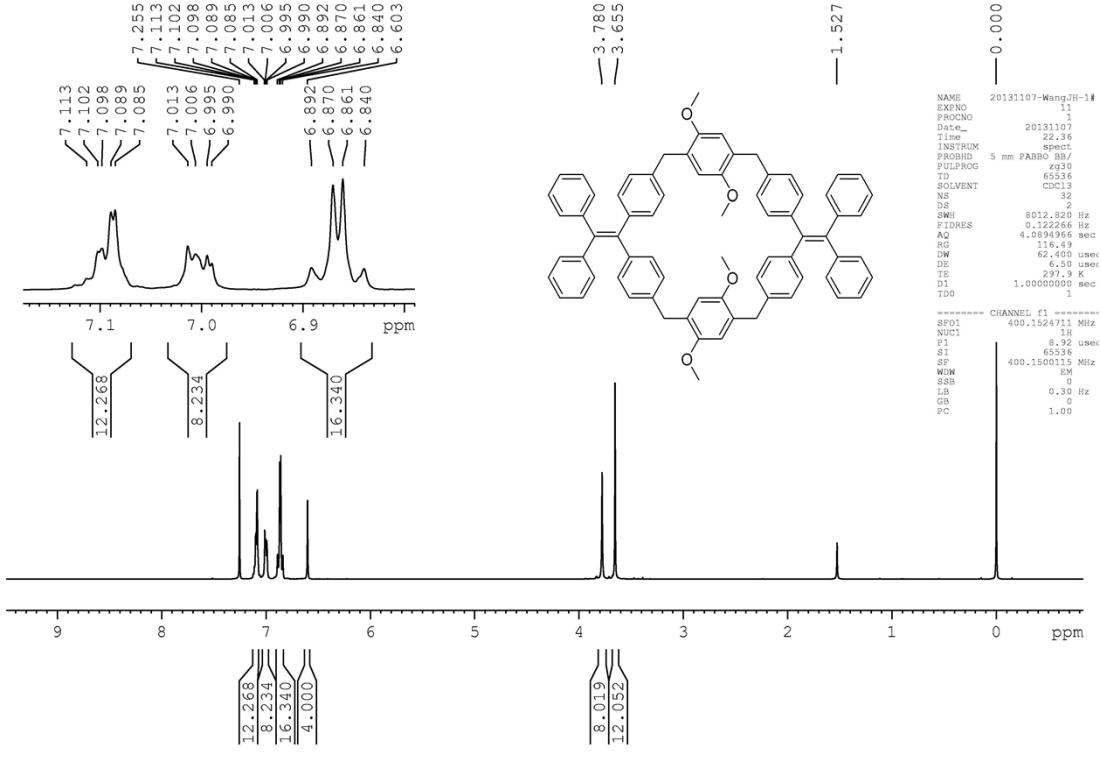


Fig. S1. ^1H NMR spectrum of **3a** in $CDCl_3$.

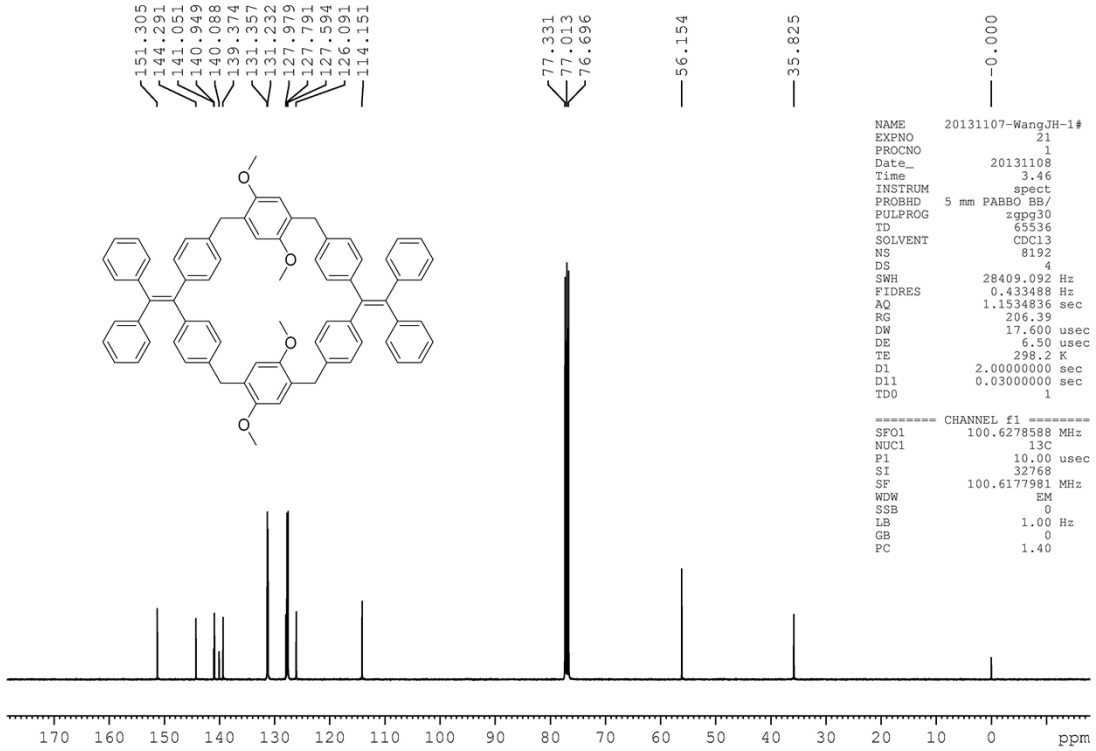


Fig. S2. ^{13}C NMR spectrum of **3a** in $CDCl_3$.

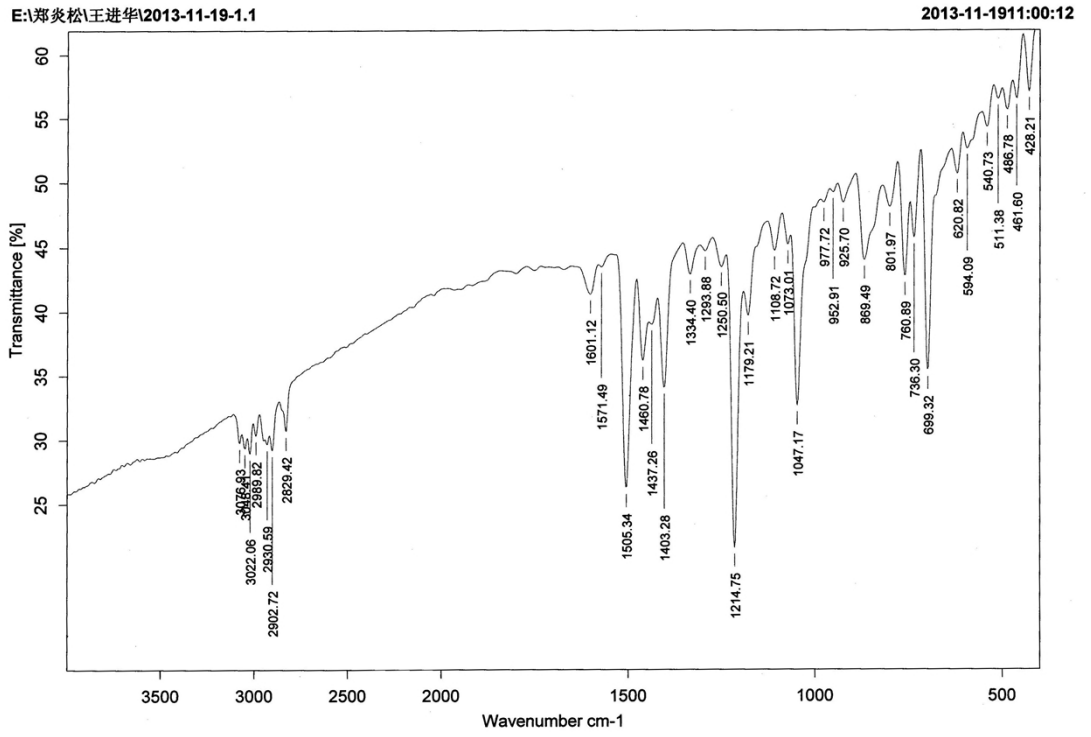
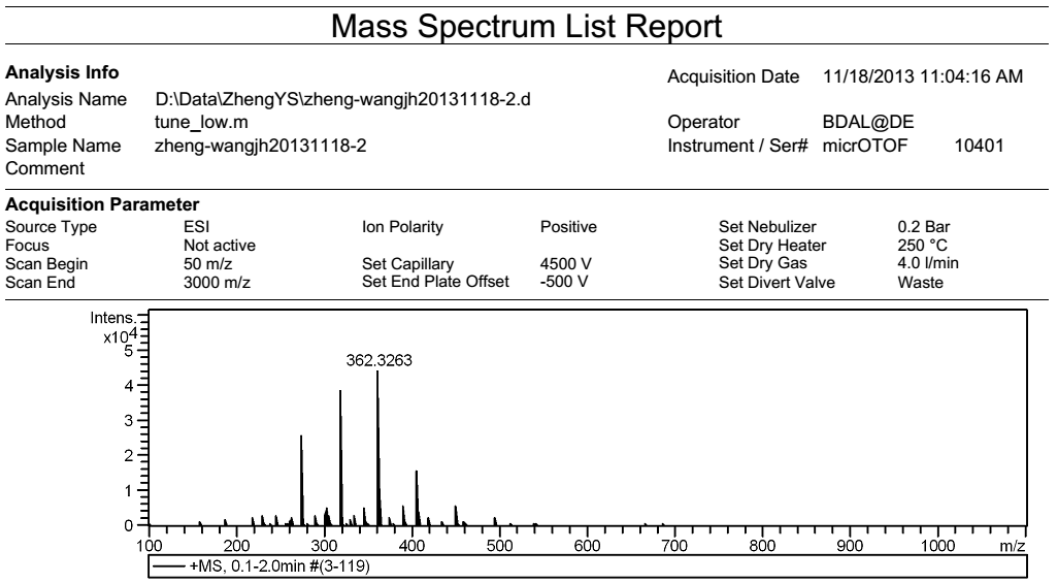


Fig. S3. IR spectrum of **3a**.



#	m/z	Res.	S/N	I	FWHM
1	274.2741	5373	2830.6	25528	0.0511
2	318.3003	5514	3415.0	38490	0.0577
3	362.3263	5677	3744.1	44356	0.0638
4	406.3523	5753	1502.0	15966	0.0706
5	406.3523	5753	1502.0	15966	0.0706
6	450.3785	5893	593.1	5583	0.0764
7	494.4041	6150	279.1	2287	0.0804
8	988.4496	6535	76.0	189	0.1513

Fig. S4. ESI$^+$-HRMS spectrum of **3a**.

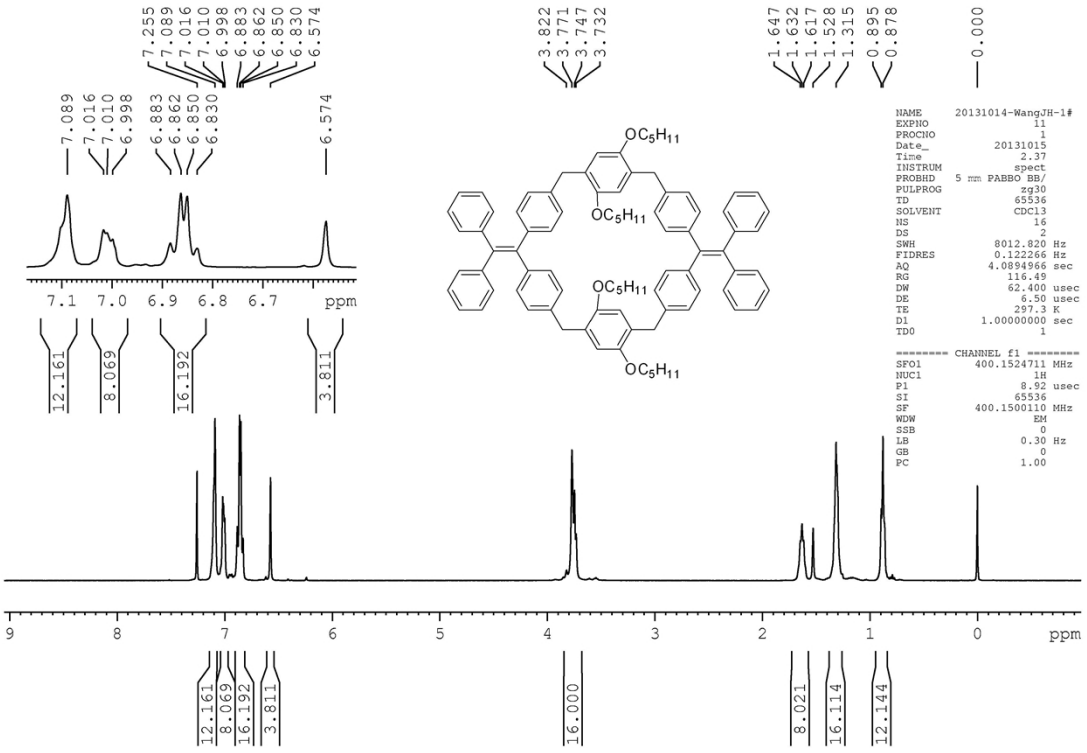


Fig. S5. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

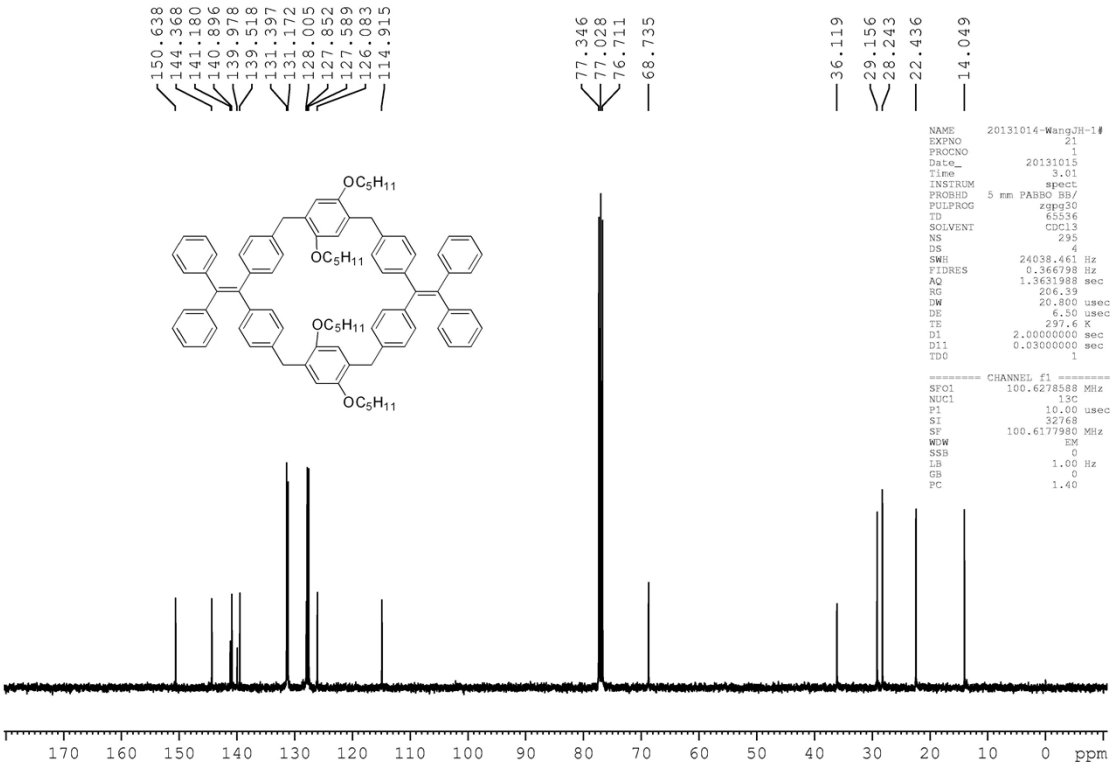


Fig. S6. ^{13}C NMR spectrum of **3b** in $CDCl_3$.

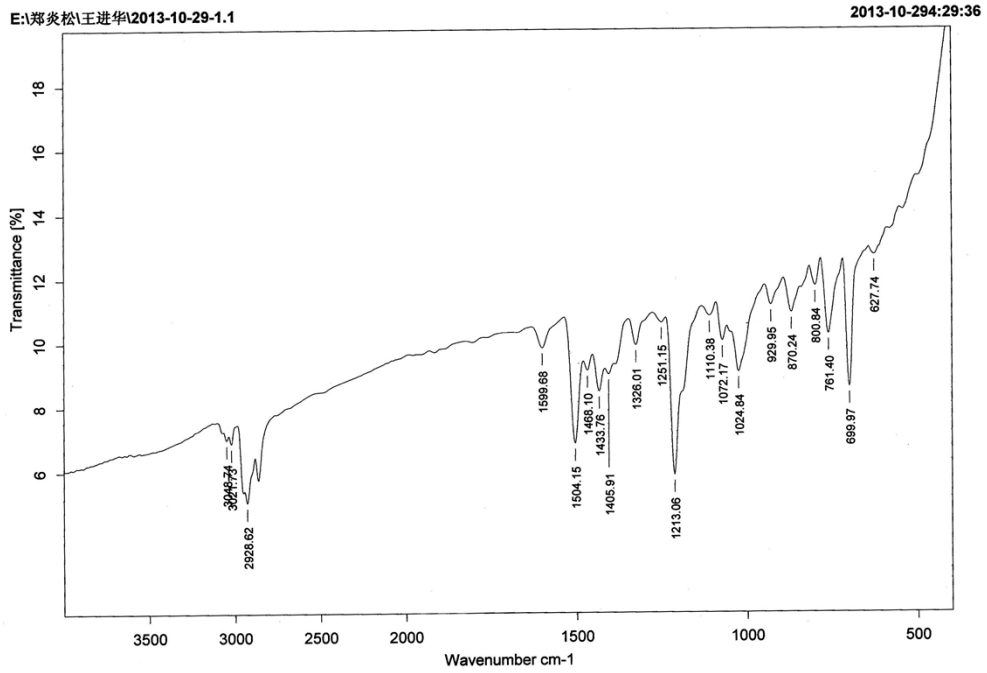


Fig. S7. IR spectrum of **3b**.

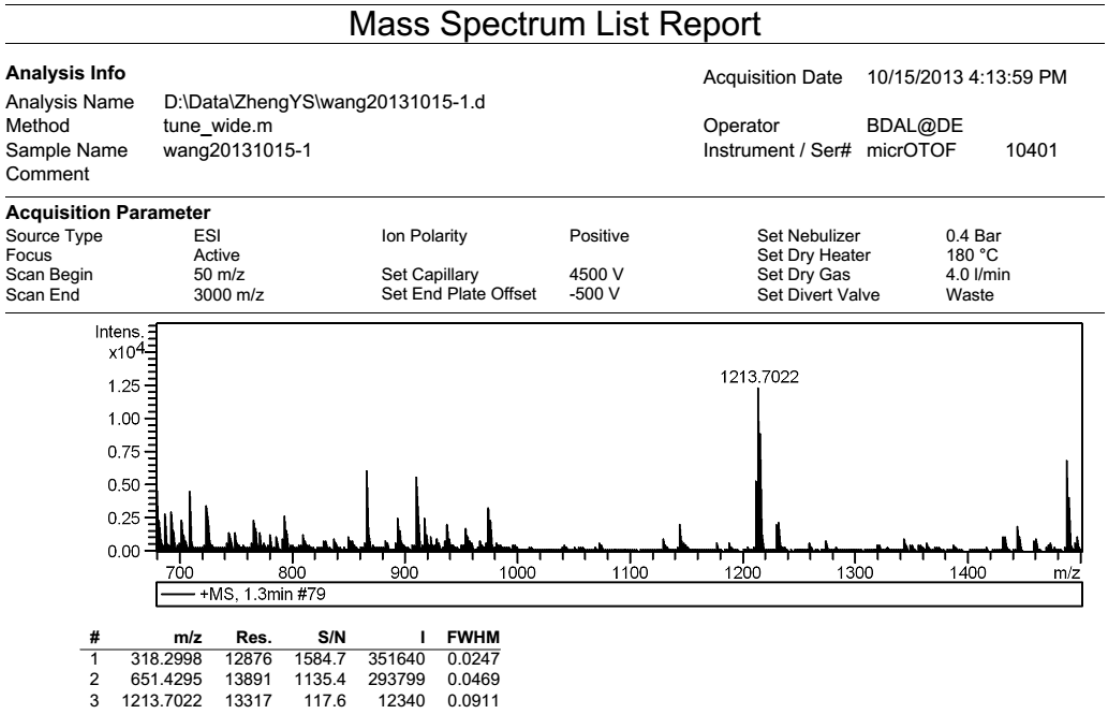


Fig. S8. ESI$^+$-HRMS spectrum of **3b**.

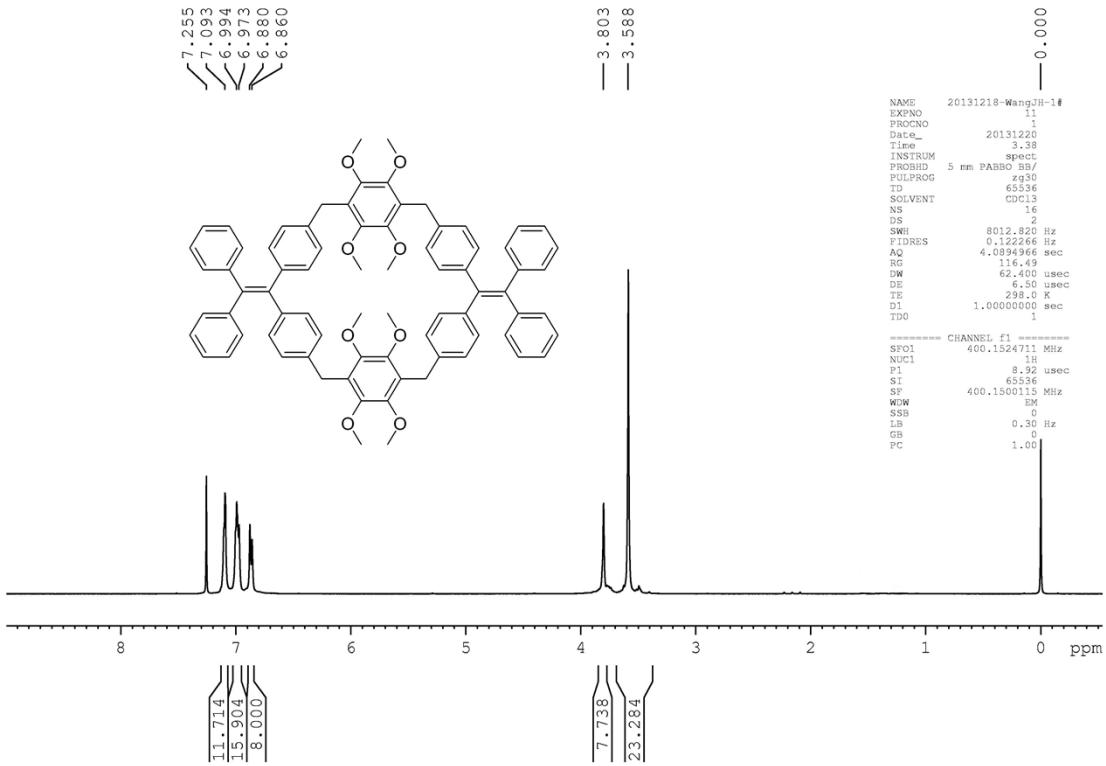


Fig. S9. ^{1}H NMR spectrum of **3c** in $CDCl_3$.

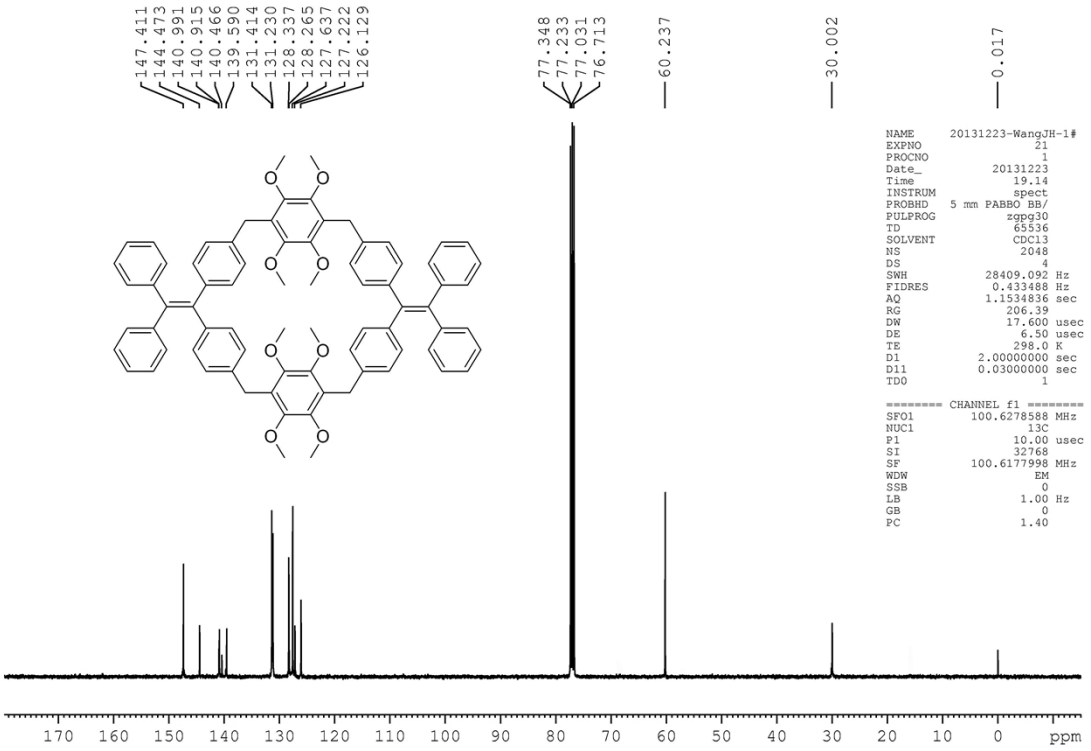


Fig. S10. ^{13}C NMR spectrum of **3c** in $CDCl_3$.

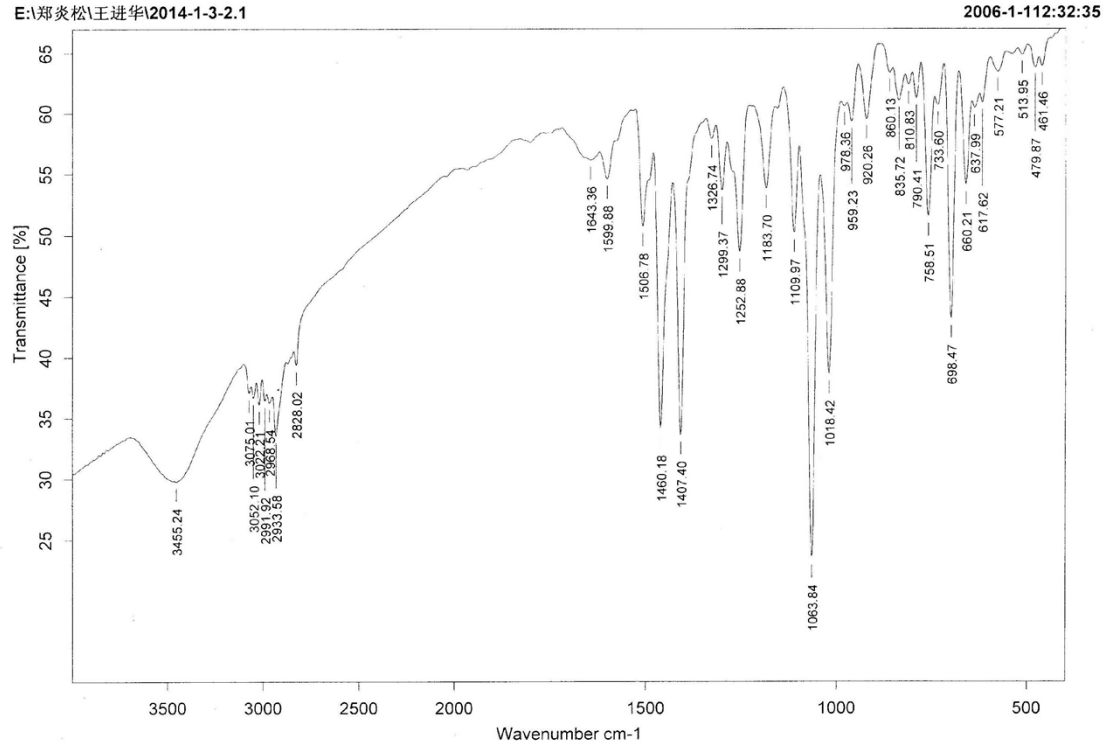


Fig. S11. IR spectrum of **3c**.

Mass Spectrum List Report

Analysis Info

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Sample Name	zheng-wang-20140114-2-3	Instrument / Ser#	micrOTOF 10401
Comment			

Acquisition Parameter

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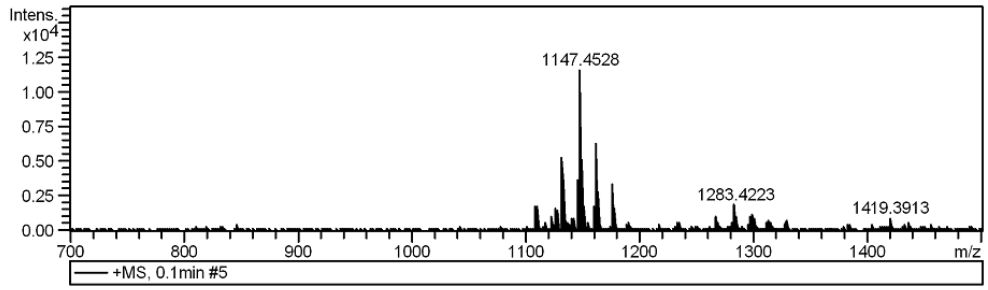

#	m/z	Res.	S/N	I	FWHM
1	1109.4919	12735	5.2	1876	0.0871
2	1131.4786	10524	13.8	5276	0.1075
3	1147.4528	10526	31.2	11620	0.1090
4	1161.4713	11682	17.3	6324	0.0994
5	1175.4823	11379	9.7	3482	0.1033
6	1283.4223	12390	6.3	1894	0.1036
7	1419.3913	36885	3.8	960	0.0385

Fig. S12. ESI$^+$-HRMS spectrum of **3c**.

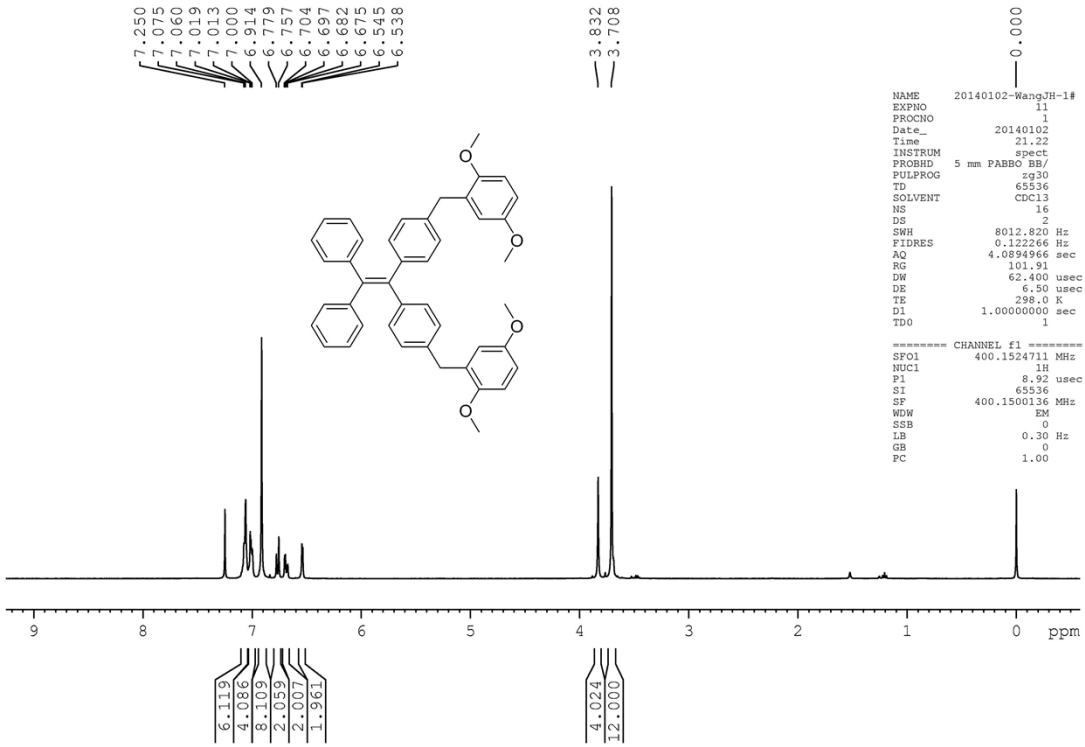

Fig. S13. ^{1}H NMR spectrum of **4** in $CDCl_3$.

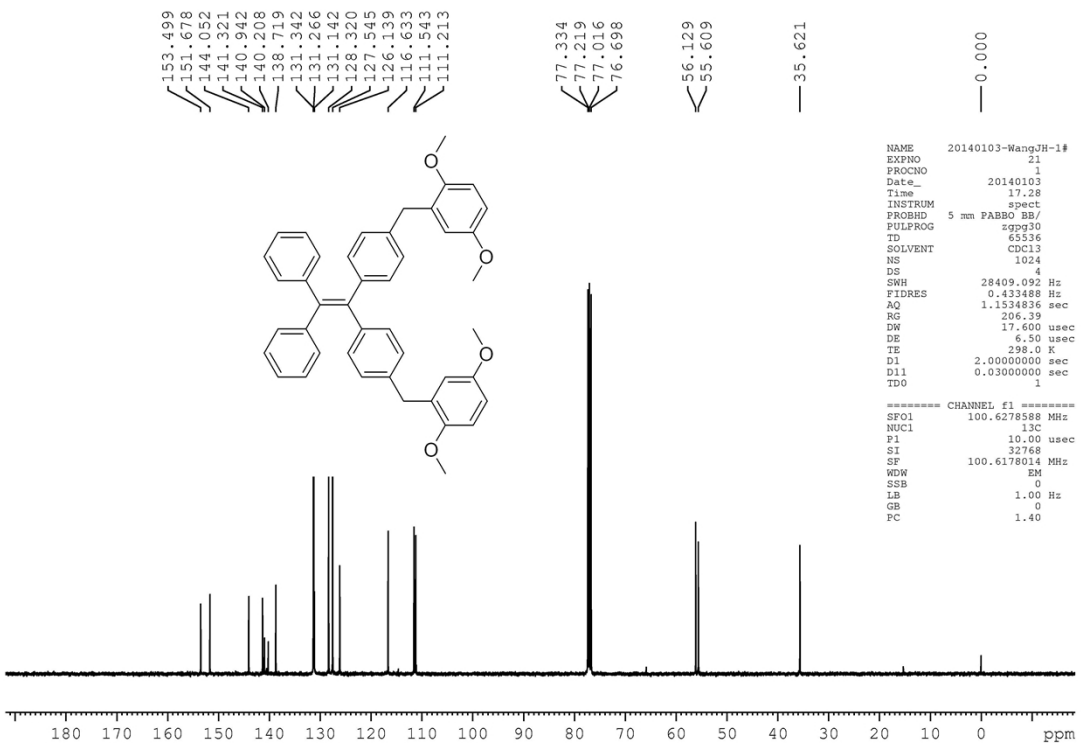

Fig. S15. ^{13}C NMR spectrum of **4** in $CDCl_3$.

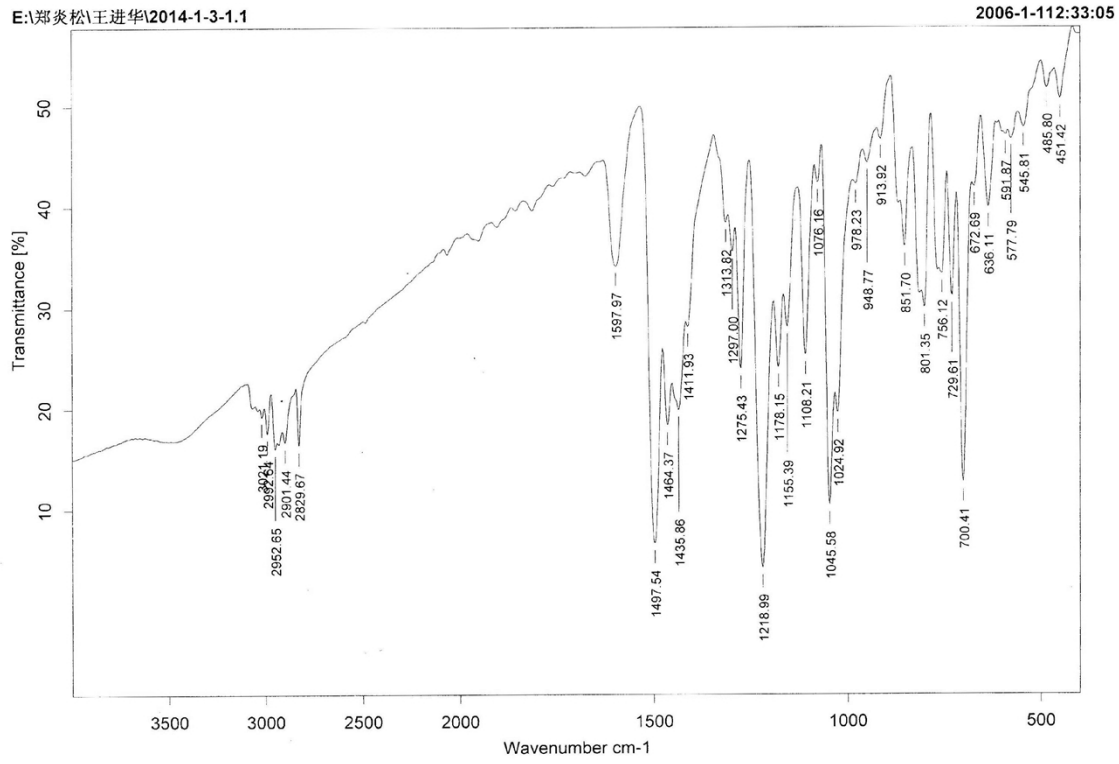

Fig. S15. IR spectrum of **4**.

Mass Spectrum List Report

Analysis Info

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Comment			

Acquisition Parameter

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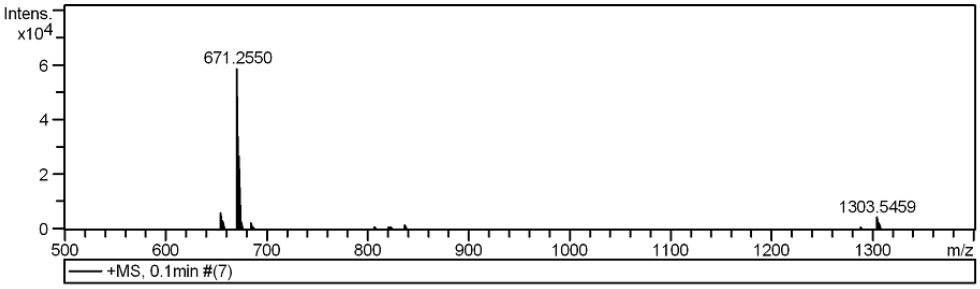

#	m/z	Res.	S/N	I	FWHM
1	633.2956	16783	2.4	390	0.0377
2	655.2804	10388	36.7	6559	0.0631
3	671.2550	12507	312.3	58994	0.0537
4	1303.5459	10994	35.6	4560	0.1186

Fig. S16. ESI$^+$-HRMS spectrum of **4**.

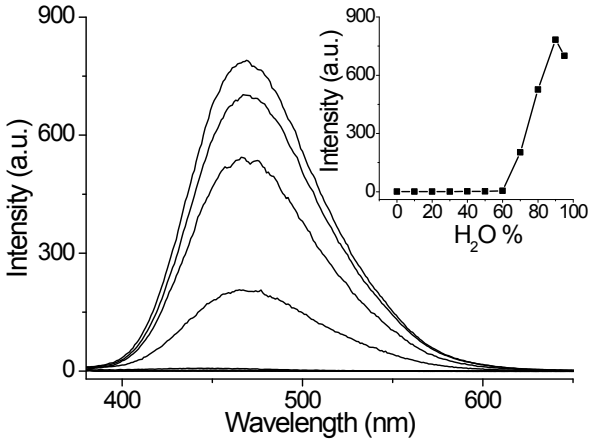

Fig. S17. Change of the fluorescence spectrum of **3a** (1.0×10^{-5} M) in THF with water fraction. Inset, the curve of the fluorescence intensity at 472 nm vs. the water fraction in THF. λ_{ex} = 342 nm, ex/em slid widths = 3/3 nm.

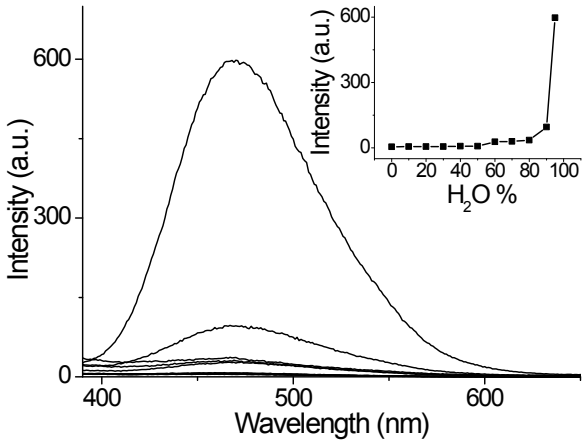

Fig. S18. Change of the fluorescence spectrum of **3b** (1.0×10^{-5} M) in THF with water fraction. Inset, the curve of the fluorescence intensity at 472 nm vs. the water fraction in THF. λ_{ex} = 339 nm, ex/em slid widths = 3/3 nm.

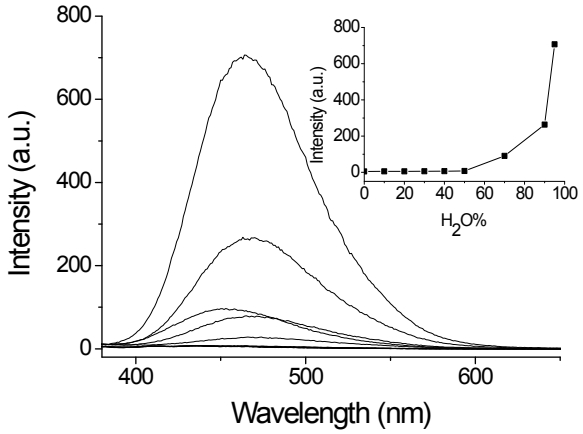

Fig. S19. Change of the fluorescence spectrum of **3c** (1.0×10^{-5} M) in THF with water fraction. Inset, the curve of the fluorescence intensity at 464 nm vs. the water fraction in THF. λ_{ex} = 343 nm, ex/em slid widths = 3/3 nm.

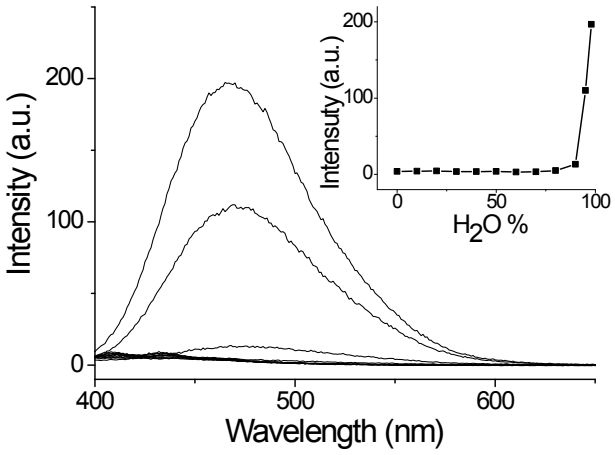

Fig. S20. Change of the fluorescence spectrum of **4** (1.0×10^{-5} M) in THF with water fraction. Inset, the curve of the fluorescence intensity at 467 nm vs. the water fraction in THF. λ_{ex} = 339 nm, ex/em slid widths = 3/3 nm.

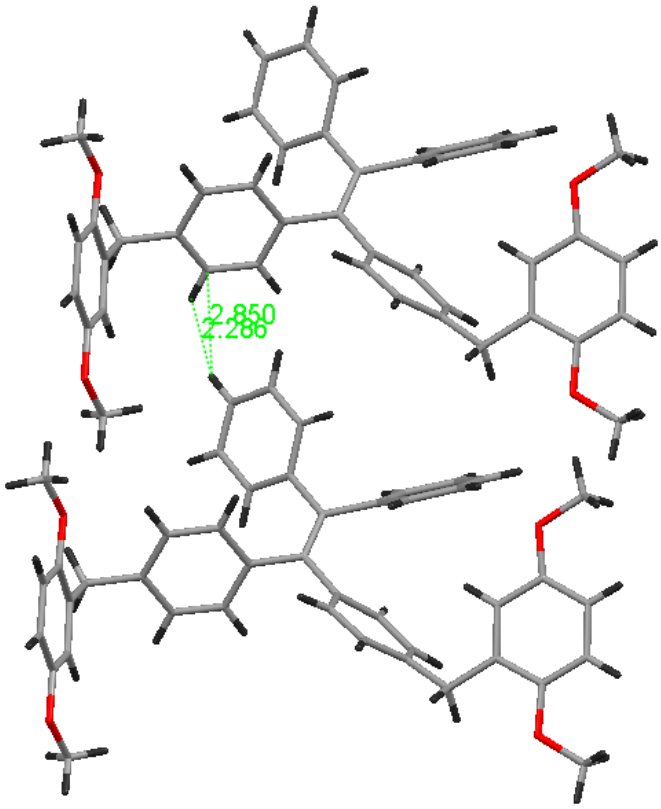

Fig. S21. Partial short contacts between molecules of **4**.