

Supporting Information

Tetraphenylethylene Imidazolium Macrocycle: Synthesis and Selective Fluorescence Turn-On Sensing of Pyrophosphate Anion

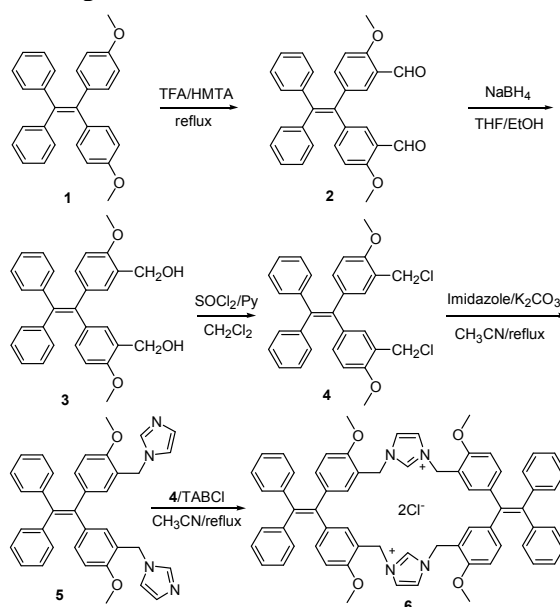
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Material and Methods

All reagents and solvents were chemical pure (CP) grade or analytical reagent (AR) grade and were used as received unless otherwise specified. ¹H NMR and ¹³C NMR spectra were measured on a Bruker AV 400 spectrometer at 298 K in CDCl₃. 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 IonSpec 4.7 Tesla FTMS instrument. Fluorescent emission spectra were collected on a Shimadzu RF-5301 fluorophotometer at 298 K. Dynamic light scattering (DLS) was measured on a Horiba LB-550 Particle Size Analyzer.

Synthesis of fluorescence probe



Scheme 1. The synthesis of tetraphenylethylene macrocycle **6**.

Synthesis of dialdehyde **2**: To a 150 mL flask was added **1** (2.5 g, 6.37 mmol),

hexamethylenetetramine (17.8 g, 127 mmol) and TFA (70 mL). The resultant mixture was refluxed for 3 h under stirring before it was cooled to room temperature. Hydrochloric acid (4 N, 45 mL) was added and stirred for additional 2 h at room temperature. The solution was extracted with dichloromethane for 3 times and the combined organic layer was washed with saturated Na₂CO₃ solution for 2 times and desiccated over anhydrous sodium sulfate. After filtration and removal of the solvent under vacuum, the slurry residue was purified with column chromatography to give a red solid (1.97 g, 69% yield). Mp: 179.5 – 181.8 °C; ¹H NMR (CDCl₃, 400 MHz) δ 10.33 (s, 2 H), 7.47 (d, *J* = 2.4 Hz, 2 H), 7.22 (d, *J* = 2.4 Hz, 1 H), 7.02 (d, *J* = 2.4 Hz, 1 H), 7.13 (m, 6 H), 7.02 (m, 4 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 3.88 (s, 6 H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 168.6, 160.5, 143.7, 141.6, 138.8, 137.8, 135.8, 131.3, 131.2, 127.9, 126.7, 124.4, 111.1, 55.7 ppm; IR (KBr) ν 3076, 3008, 2965, 2941, 2866, 2761, 1681, 1602, 1570, 1493, 1459, 1441, 1414, 1392, 1332, 1265, 1251, 1217, 1174, 1141, 1116, 1101, 1076, 1024, 949, 934, 919, 828, 756, 735, 704, 666, 648, 628, 579, 539, 515, 492 cm⁻¹.

Synthesis of dialcohol **3**: To a 100 mL of flask charged with **2** (1.76 g, 3.92 mmol), NaBH₄ (1.49 g, 39.2 mmol) and 50 mL of tetrahydrofuran and ethanol (V/V 1/1). The resultant mixture was stirred at room temperature for 3 h before it was quenched with water. The solution was extracted with ethyl acetate for 3 times and the combined organic layer was desiccated over anhydrous sodium sulfate. After filtration and removal of the solvent under vacuum, the resultant solid was purified with column chromatography to give a white solid (1.57 g, 89% yield). Mp: 178.7 – 180.1 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.09 (m, 6 H), 7.01 (m, 4 H), 6.92 (m, 4 H), 6.60 (d, *J* = 8.4 Hz, 2 H), 4.46 (s, 4 H), 3.79 (s, 6 H), 2.03 (s, 2 H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 156.0, 144.2, 139.8, 139.7, 136.0, 132.0, 131.9, 131.3, 128.2, 127.7, 126.1, 109.4, 61.9, 55.2 ppm; IR (KBr) ν 3416, 3079, 3065, 3042, 3024, 3007, 2943, 2930, 2898, 2871, 2839, 1603, 1549, 1499, 1460, 1440, 1411, 1381, 1363, 1335, 1320, 1292, 1278, 1245, 1195, 1182, 1170, 1129, 1111, 1074, 1043, 1027, 1001, 963, 932, 892, 845, 826, 814, 756, 726, 698, 668, 642, 628, 606, 586, 558, 544, 487, 460, 439 cm⁻¹.

Synthesis of dichloride **4**: To a 100 mL flask charged with **3** (1.71 g, 3.78 mmol), pyridine (freshly distilled, 380 μL) and 30 mL freshly distilled dichloromethane. A solution of thionyl dichloride (0.95 mL) in 30 mL of freshly distilled dichloromethane was slowly added. Upon finishing the addition, the resultant mixture was heated at 40 °C for 4 h before it was cooled to room temperature. The reaction was quenched by 20 mL water. The organic phase was separated and the aqueous phase was extracted with dichloromethane for 2 times. The combined organic layer was desiccated over anhydrous sodium sulfate. After filtration and removal of the solvent, the residue was recrystallized with dichloromethane and methanol to give a white solid (1.57 g, 85% yield). Mp: 149.0 – 151.8 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.08 (m, 6 H), 7.00 (m, 6 H), 6.95 (dd, *J* = 2.0, 2.0 Hz, 2 H), 6.62 (d, *J* = 8.4 Hz, 2 H), 4.42 (s, 4 H), 3.81 (s, 6 H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 156.0, 143.9, 140.2, 138.9, 135.8, 134.0, 133.2, 131.2, 127.8, 126.3, 125.0, 110.0, 55.5, 41.5 ppm; IR (KBr) ν 3052, 3026, 2994, 2965, 2929, 2838, 1607, 1501, 1459, 1442, 1304, 1292, 1267, 1247, 1176, 1162,

1124, 1112, 1075, 1028, 933, 916, 901, 821, 806, 791, 770, 755, 699, 667, 622, 597, 574, 556, 539, 514, 488 cm⁻¹.

Synthesis of diimidazole **5**: To a 100 mL flask charged with **4** (1.6 g, 3.27 mmol), imidazole (2.2 g, 32.69 mmol), K₂CO₃ (0.9 g, 6.54 mmol) and 50 mL freshly distilled acetonitrile. The resultant mixture was refluxed for 8 h under stirring before cooled to room temperature. The mixture was extracted with dichloromethane for 3 times and washed with water for 2 times. The organic phase was desiccated over anhydrous sodium sulfate. After filtration and removal of the solvent under vacuum, the residue was recrystallized with dichloromethane and acetonitrile to afford a white solid (1.05 g, 58% yield). Mp: 233.5 – 234.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.28 (s, 2 H), 7.12 (m, 6 H), 6.97 (d, *J* = 2.0 Hz, 2 H), 6.96 (m, 2 H), 6.93 (m, 3 H), 6.90 (d, *J* = 2.2 Hz, 1 H), 6.76 (d, *J* = 2.2 Hz, 2 H), 6.65 (d, *J* = 8.6 Hz, 2 H), 6.48 (s, 2 H), 4.84 (s, 4 H), 3.77 (s, 6 H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 155.8, 143.8, 140.5, 138.6, 137.0, 136.0, 133.1, 132.8, 131.2, 128.0, 127.8, 126.5, 123.2, 119.4, 110.1, 55.4, 46.3 ppm; IR (KBr) ν 3106, 3071, 3018, 2967, 2929, 2835, 1607, 1502, 1440, 1391, 1344, 1254, 1227, 1182, 1134, 1109, 1075, 1026, 946, 904, 820, 777, 762, 735, 706, 660, 627, 586, 558, 515, 452 cm⁻¹; ESI⁺ HRMS *m/z* calcd for C₃₆H₃₃N₄O₂ 553.2604 [M + H], found 553.2607 [M + H].

Synthesis of macrocycle **6**: To a 10 mL flask charged with **5** (110 mg, 0.2 mmol), **4** (98 mg, 0.2 mmol), TBACl (280 mg, 1.0 mmol) and 8 mL freshly distilled acetonitrile. The resultant mixture was refluxed for 13 h under stirring before cooled to room temperature. Then 20 mL water was added and extracted with dichloromethane for 3 times. The combined organic layer was then washed with water for 2 times before desiccated over anhydrous sodium sulfate. After filtration and removal of the solvent under vacuum, the resultant slurry was purified with column chromatography to afford a white solid (50 mg, 24% yield). Mp 291.7 – 292.9 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.91 (s, 1 H), 7.61 (d, *J* = 1.3 Hz, 4 H), 7.53 (d, *J* = 2.0 Hz, 4 H), 7.07 (m, 12 H), 7.03 (d, *J* = 2.2 Hz, 2 H), 7.01 (d, *J* = 2.2 Hz, 2 H), 6.94 (m, 8 H), 6.64 (d, *J* = 8.6 Hz, 4 H), 5.20 (s, 8 H), 3.78 (s, 12 H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 143.6, 140.2, 138.4, 136.5, 136.3, 135.6, 134.3, 131.2, 127.8, 126.4, 122.7, 120.6, 110.1, 55.6, 48.9 ppm; IR (KBr) ν 3638, 3409, 3054, 3022, 2959, 2840, 1609, 1563, 1503, 1447, 1384, 1335, 1292, 1255, 1174, 1137, 1075, 1026, 905, 876, 825, 769, 754, 725, 702, 648, 630, 580, 556, 537, 460 cm⁻¹; ESI⁺ HRMS *m/z* calcd for C₆₆H₅₈ClN₄O₄ 1005.4136 [M – Cl], found 1005.4127 [M – Cl].

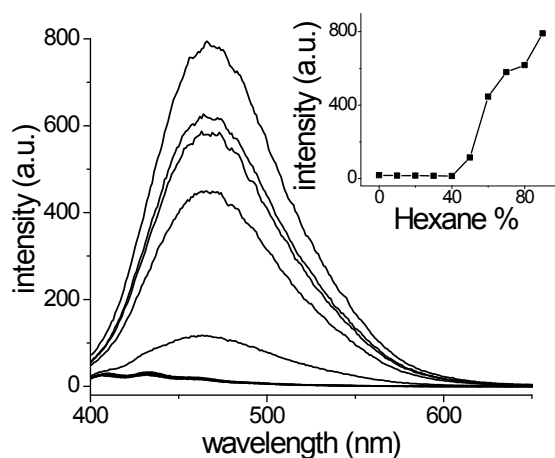


Fig. S1. Changes in fluorescence spectra of **6** in THF/hexane mixed solvent containing 0.5% acetonitrile with hexane fraction (0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, volume percentage). Inset, the curve of emission intensity at 472 nm vs. hexane fraction. $[6] = 2.5 \times 10^{-5}$ M, $\lambda_{\text{ex}} = 349$ nm, ex/em slits = 3/5 nm.

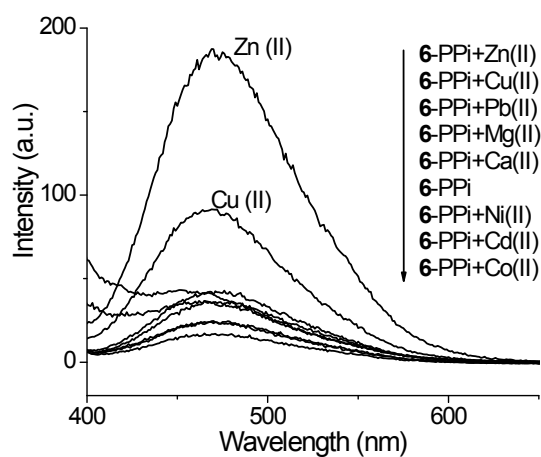


Fig. S2. The fluorescence spectra of **6** in water containing 0.5% DMSO with addition of PPI in the presence of different metal ions. $\lambda_{\text{ex}} = 347$ nm, ex/em slits = 3/5 nm. $[6] = [\text{metal ion}] = 1/2[\text{PPI}] = 5.0 \times 10^{-5}$ M. Metal ions were added in the form of acetate salt.

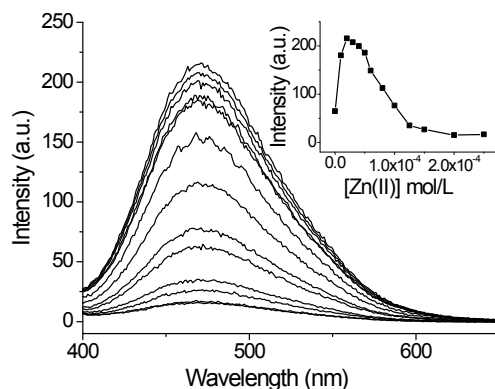


Fig. S3. The fluorescence spectra of **6** in water containing 0.5% DMSO with addition of PPI in the presence of different amount of Zn (II). Inset, curve of the intensity at 472 nm vs. the concentration of Zn (II). $\lambda_{\text{ex}} = 347 \text{ nm}$, slit width: 3/5 nm, $[\mathbf{6}] = 1/2[\text{PPI}] = 5 \times 10^{-5} \text{ M}$, inset was the intensity at 472 nm vs the $[\text{Zn (II)}]$, Zn (II) was added in the form of Zinc acetate salt.

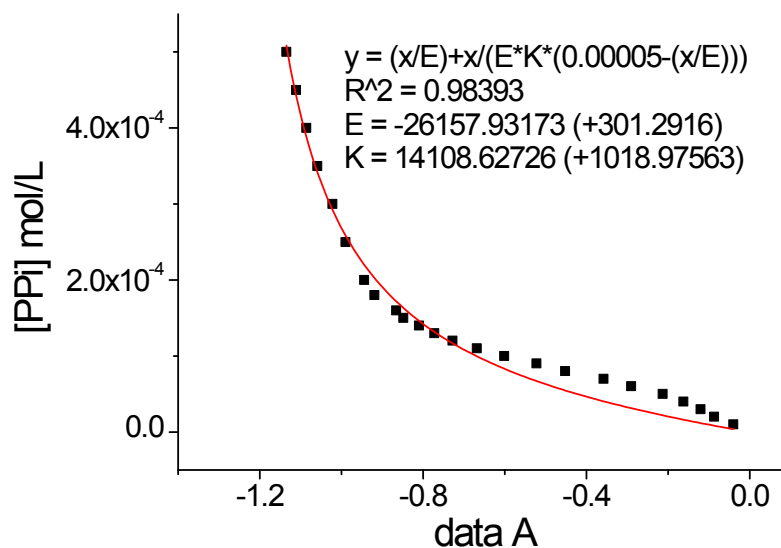
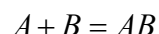


Fig. S4. Change of absorbance difference of **6** in water at 253 nm with concentration of pyrophosphate (PPI). The red curve is the result from nonlinearly curve fitting by Origin 7.5.

Association constant K was calculated by nonlinearly curve fitting according to

the following formula (Eq. 5), which was derived in a similar way to literature.^[1]

The reaction formula could be expressed as equation 1.



A denotes probe **6**; B denotes pyrophosphate anion.

The association constant K could be written as equation 1.

$$K = \frac{[AB]}{[A][B]} = \frac{[AB]}{([A]_0 - [AB])([B]_0 - [AB])} \dots\dots\dots(1)$$

$$[B]_0 - [AB] = \frac{[AB]}{K[A]_0 - [AB]}$$

$$[B]_0 = [AB] + \frac{[AB]}{K[A]_0 - [AB]} \dots\dots\dots(2)$$

Among the above equation,

[AB] denotes the molar concentration of 1:1 complex of phosphate anion with **6**;

[A] denotes the molar concentration of **6** at equilibrium;

[B] denotes the molar concentration of pyrophosphate anion at equilibrium;

[A]₀ denotes the total molar concentration of **6**;

[B]₀ denotes the total molar concentration of pyrophosphate anion.

At 253 nm, the absorbance results from [A], [B], and [AB].

$$A_{obs} = \varepsilon_A [A] + \varepsilon_{AB} [AB] + \varepsilon_B [B]$$

$$A_{obs} = \varepsilon_A ([A]_0 - [AB]) + \varepsilon_{AB} [AB] + \varepsilon_B ([B]_0 - [AB])$$

$$A_{obs} = \varepsilon_A [A]_0 + \varepsilon_B [B]_0 + (\varepsilon_{AB} - \varepsilon_A - \varepsilon_B) [AB]$$

$$\Delta A = A_{obs} - \varepsilon_A [A]_0 - \varepsilon_B [B]_0 = (\varepsilon_{AB} - \varepsilon_A - \varepsilon_B) [AB] \dots\dots\dots(3)$$

$$\text{let : } \Delta\varepsilon = \varepsilon_{AB} - \varepsilon_A - \varepsilon_B$$

$$\Delta A = \Delta\varepsilon [AB] \dots\dots\dots(4)$$

By combining equation 2 and equation 4, equation 5 is obtained, which is used to calculate the association constant.

$$[B]_0 = \frac{\Delta A}{\Delta\varepsilon} + \frac{\Delta A / \Delta\varepsilon}{K[A]_0 - \Delta A / \Delta\varepsilon} \dots\dots\dots(5)$$

In order to calculate the association constant K by Origin software without further deriving equation 5, here [B]₀ was directly acted as dependent variable and the absorbance difference ΔA as independent one to carry out the nonlinearly curve fitting (Fig. S6).

[1] a) H.-T. Feng, S. Song, Y.-C. Chen, C.-H. Shen, Y.-S. Zheng. *J. Mater. Chem. C* **2014**, 2, 2353–2359. b) Z.-Q. Guo, W.-Q. Chen, X.-M. Duan, *Org. Lett.*, **2010**, 12, 2202.

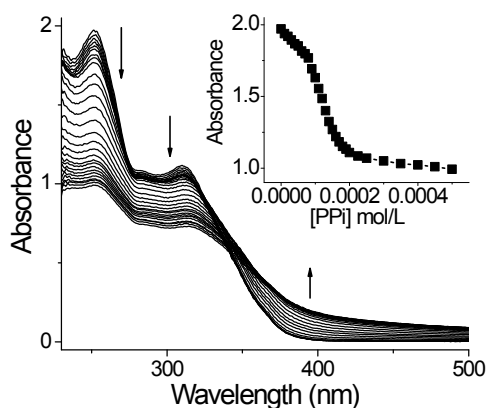


Fig. S5. Change of the absorption spectra of **6** in water containing 0.5% DMSO with PPI in the presence of Zn (II). Inset, curve of the absorbance at 253 nm vs. the concentration of PPI. $[6] = [Zn(II)] = 5.0 \times 10^{-5}$ M.

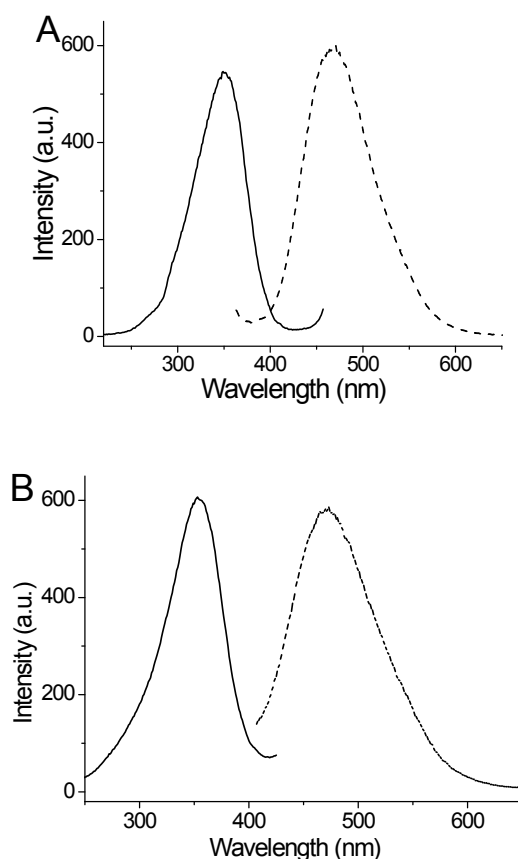


Fig. S6. (A) Excitation (solid line) and emission (dash line) spectra of **6** in THF/hexane 10:90 (v/v) containing 0.5% acetonitrile. The excitation spectrum was recorded at 467 nm, $\lambda_{ex} = 349$ nm. $[6] = 2.5 \times 10^{-5}$ M, ex/em slits = 3/5 nm. (B) Excitation (solid line) and emission (dash line) spectra of **6**/PPI/Zn(II) mixture in

water containing 0.5% DMSO. The excitation spectra was recorded at 472 nm, $\lambda_{\text{ex}} = 354$ nm. $[\mathbf{6}] = 1/2[\text{PPi}] = 2[\text{Zn(II)}] = 5 \times 10^{-5}$ M, ex/em slits = 5/5 nm.

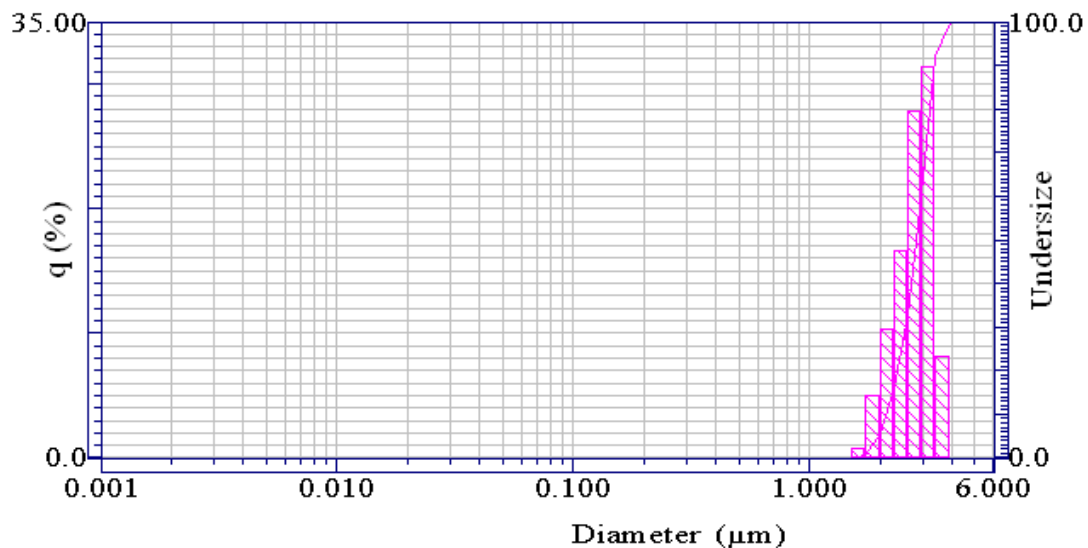


Fig. S7. Dynamic light scattering (DLS) diagram of the mixture of **6** and sodium pyrophosphate in the presence of Zn(OAc)_2 in water. $[\mathbf{6}] = 2[\text{Zn}^{2+}] = 5.0 \times 10^{-5}$ M; $[\text{PPi}] = 1.0 \times 10^{-4}$ M

Mass Spectrum List Report

Analysis Info

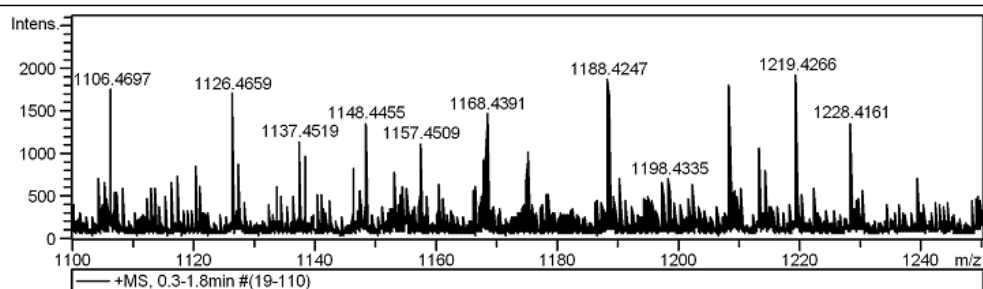
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Operator BDAL@DE
 Instrument / Ser# micrOTOF 10401

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Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	FWHM
1	1104.4605	11327	5.5	579	0.0975
2	1105.4717	15725	5.0	530	0.0703
3	1106.4697	11660	15.2	1611	0.0949
4	1117.4709	12895	5.6	598	0.0867
5	1120.4688	13173	6.7	720	0.0851
6	1126.4659	12093	14.4	1557	0.0931
7	1127.4568	12722	6.7	728	0.0886
8	1133.8049	11356	4.5	484	0.0998
9	1137.4519	12925	9.3	999	0.0880
10	1138.4448	13773	7.7	819	0.0827
11	1146.4558	11983	6.5	683	0.0957
12	1148.4455	12523	11.6	1212	0.0917
13	1153.2557	15512	6.1	634	0.0743
14	1154.4533	12508	4.5	465	0.0923
15	1157.4509	12613	9.5	977	0.0918
16	1160.4604	11711	5.0	509	0.0991
17	1166.4301	11238	4.6	464	0.1038
18	1167.7907	12278	7.7	772	0.0951
19	1168.4391	11999	13.2	1319	0.0974
20	1175.1216	12629	9.0	884	0.0931
21	1188.4247	10827	18.1	1725	0.1098
22	1190.3959	10971	5.5	526	0.1085
23	1197.4254	12549	5.6	519	0.0954
24	1198.4335	12644	6.1	564	0.0948
25	1202.4186	10862	5.3	491	0.1107
26	1208.4295	12412	18.2	1653	0.0974
27	1213.3265	15881	10.3	920	0.0764
28	1214.3465	13346	7.4	660	0.0910
29	1219.4266	13000	20.3	1785	0.0938
30	1228.4161	13265	14.2	1222	0.0926

Fig. S8. ESI⁺ HRMS spectrum of the mixture of **6** and sodium pyrophosphate in water/acetonitrile.

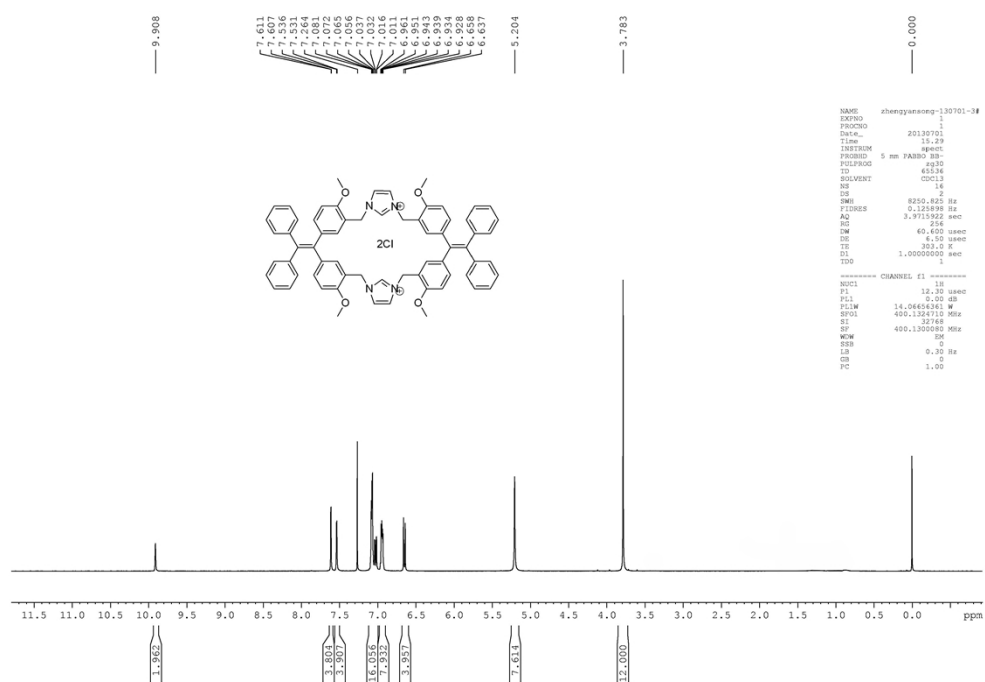


Fig. S9. ¹H NMR (400 MHz, CDCl₃) spectrum of 6.

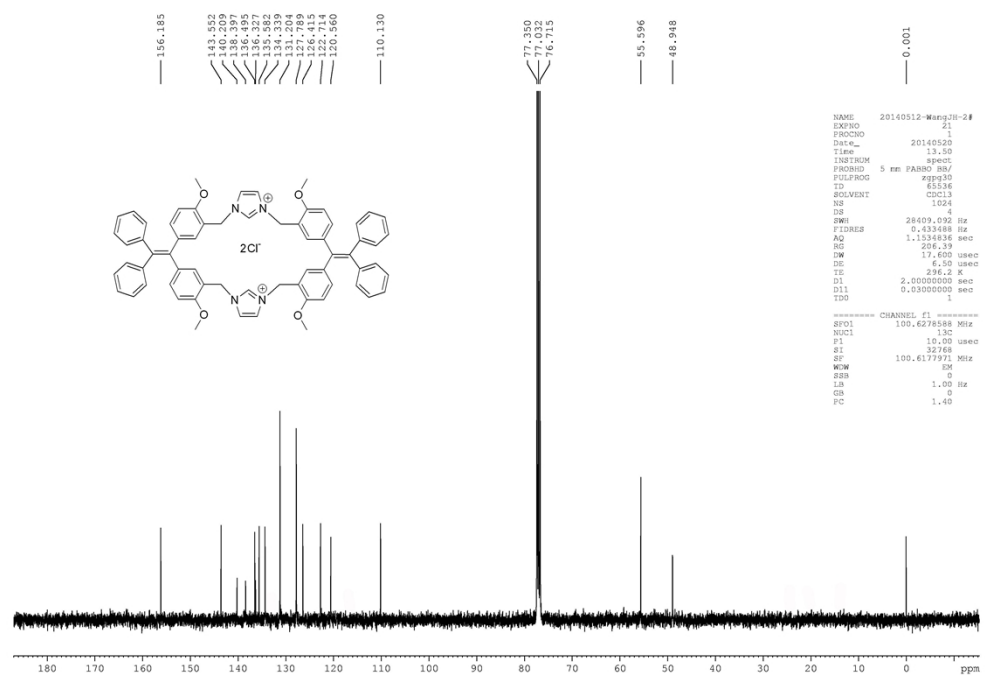
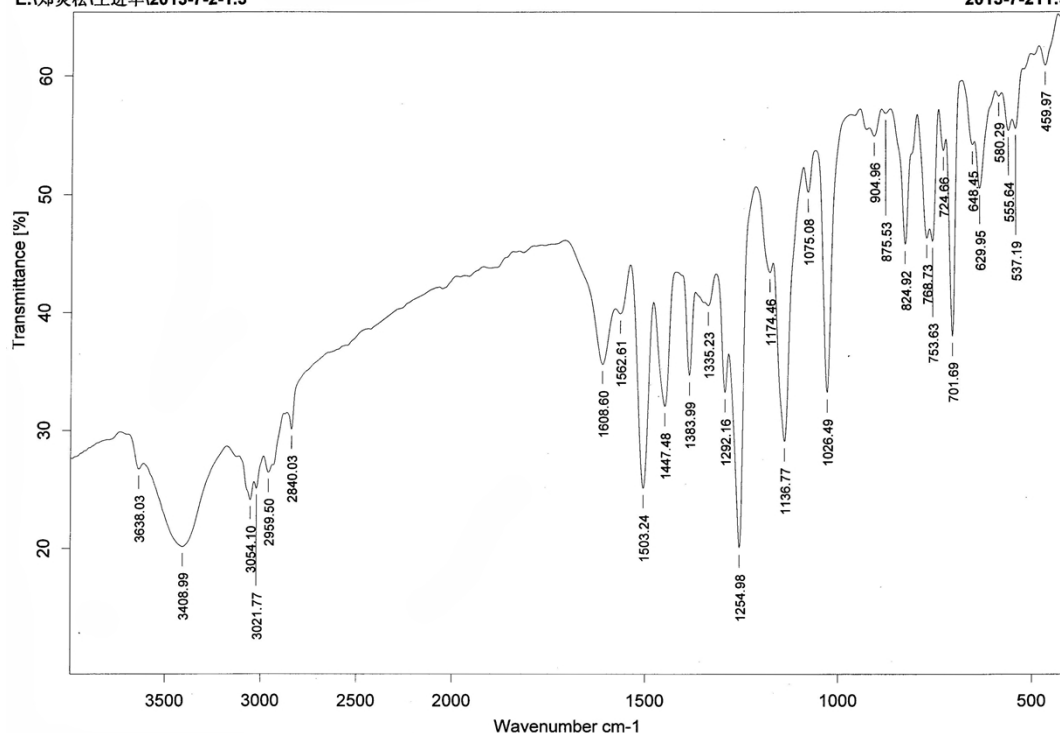


Fig. S10. ¹³C NMR (100 MHz, CDCl₃) spectrum of 6.

Fig. S11. IR spectrum of **6** in KBr.

Mass Spectrum List Report

Analysis Info

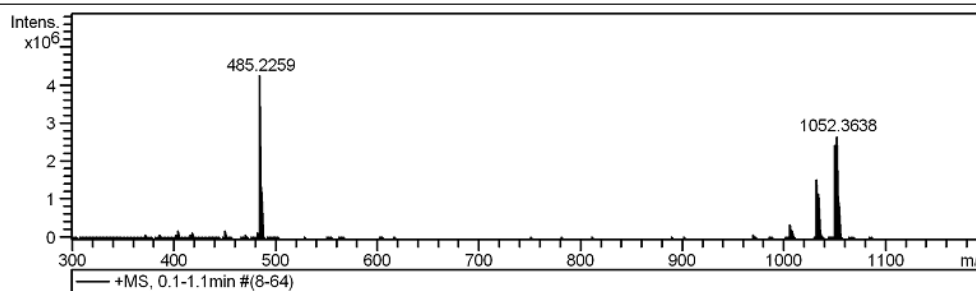
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Operator BDAL@DE
 Instrument / Ser# micrOTOF 10401

Acquisition Parameter

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Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	FWHM
1	485.2259	20908	9409.8	4259799	0.0232
2	969.4361	14211	375.9	105314	0.0682
3	1005.4127	16845	1064.5	361809	0.0597
4	1032.4307	20707	4037.8	1553318	0.0499
5	1052.3638	21785	6383.5	2666784	0.0483

Fig. S12. ESI⁺ HRMS spectrum of **6**.

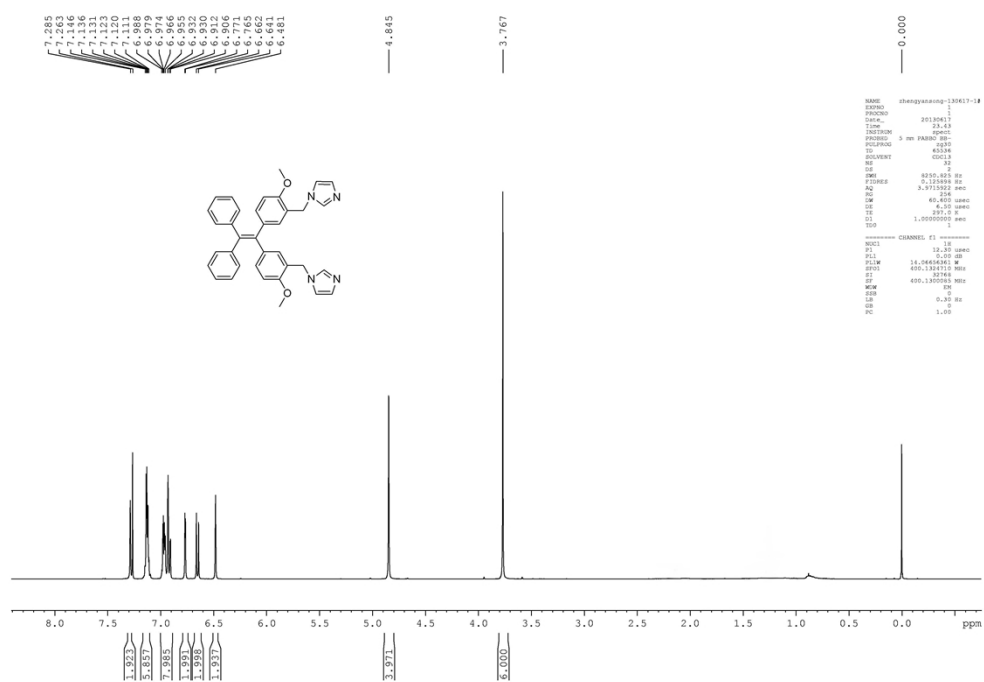


Fig. S13. ¹H NMR (400 MHz, CDCl₃) spectrum of 5.

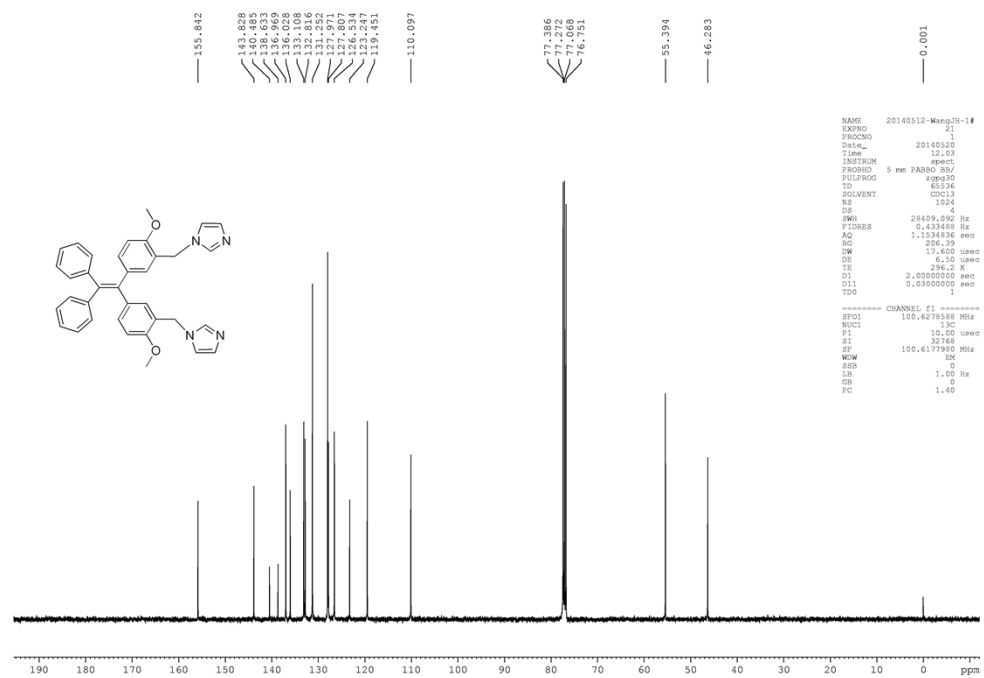


Fig. S14. ¹³C NMR (100 MHz, CDCl₃) spectrum of 5.

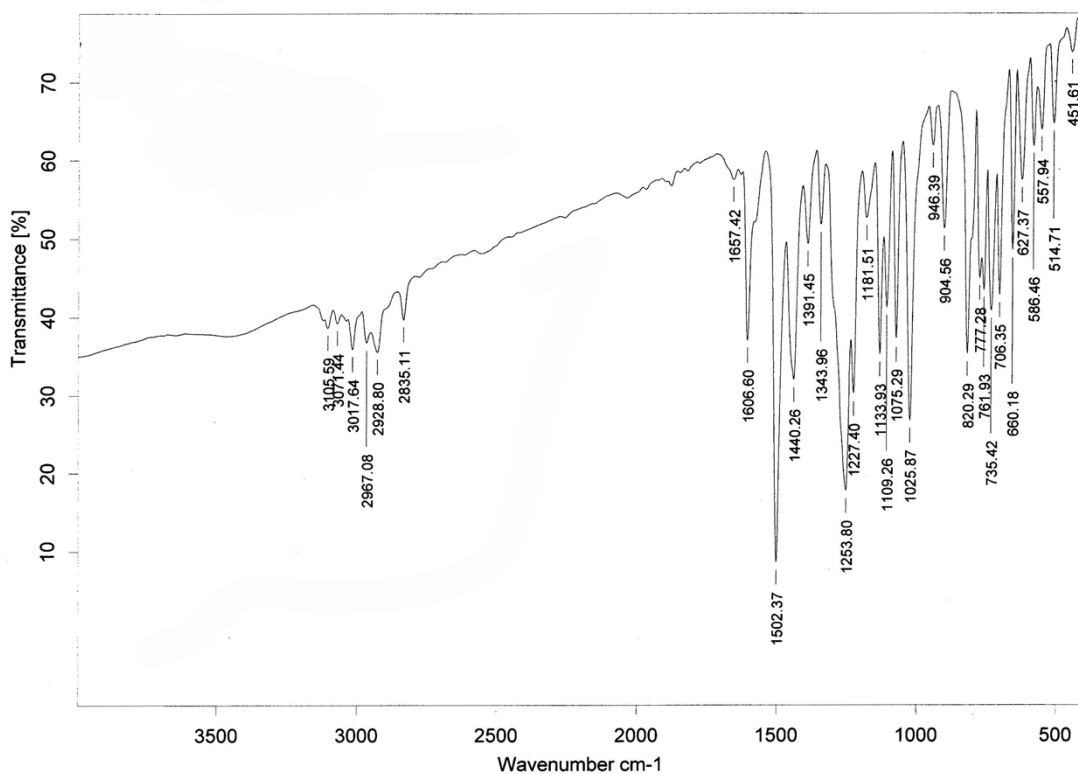
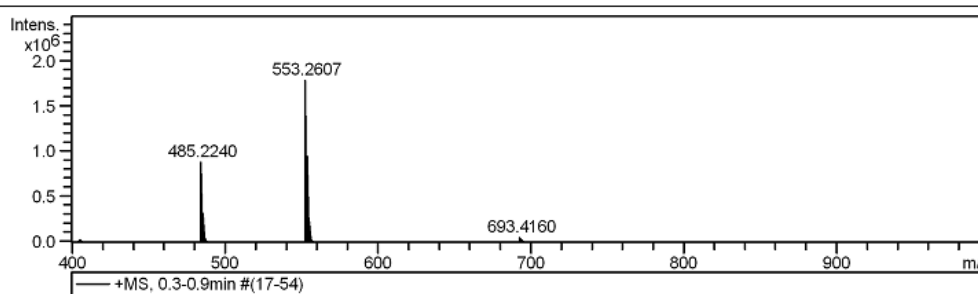


Fig. S15. IR spectrum of 5 in KBr.

Mass Spectrum List Report

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Sample Name	zheng-wang-20140509-2		
Comment			

Acquisition Parameter					
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Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	FWHM
1	405.1855	13521	339.2	36120	0.0300
2	485.2240	16999	6325.0	887269	0.0285
3	553.2607	14444	11557.7	1792117	0.0383
4	693.4160	14267	709.7	59951	0.0486

Fig. S16. ESI⁺ HRMS spectrum of 5.

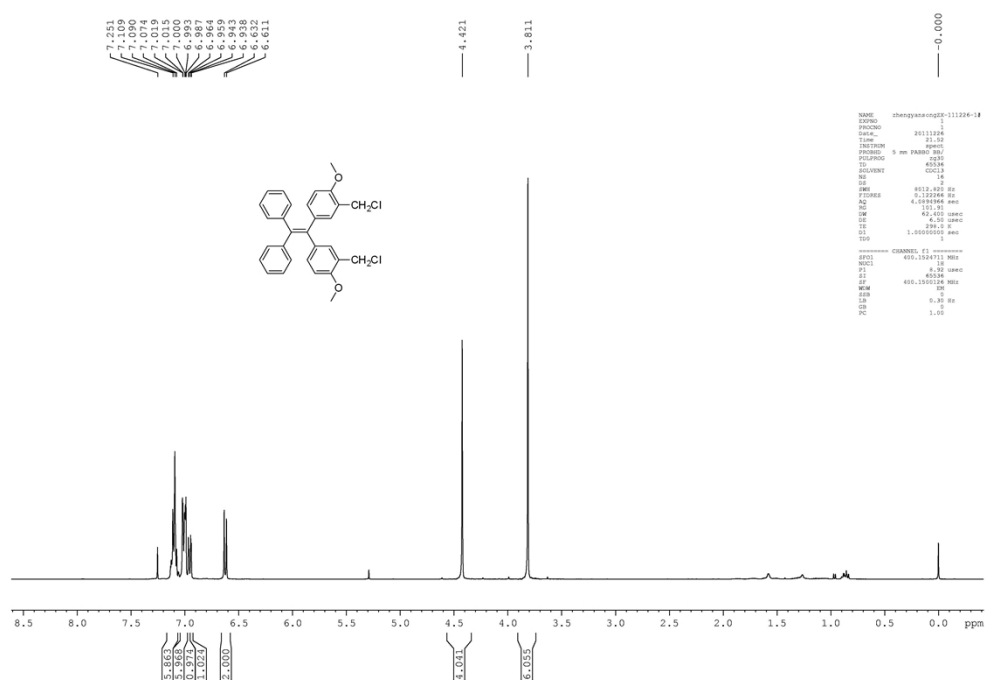


Fig. S17. ¹H NMR (400 MHz, CDCl₃) spectrum of 4.

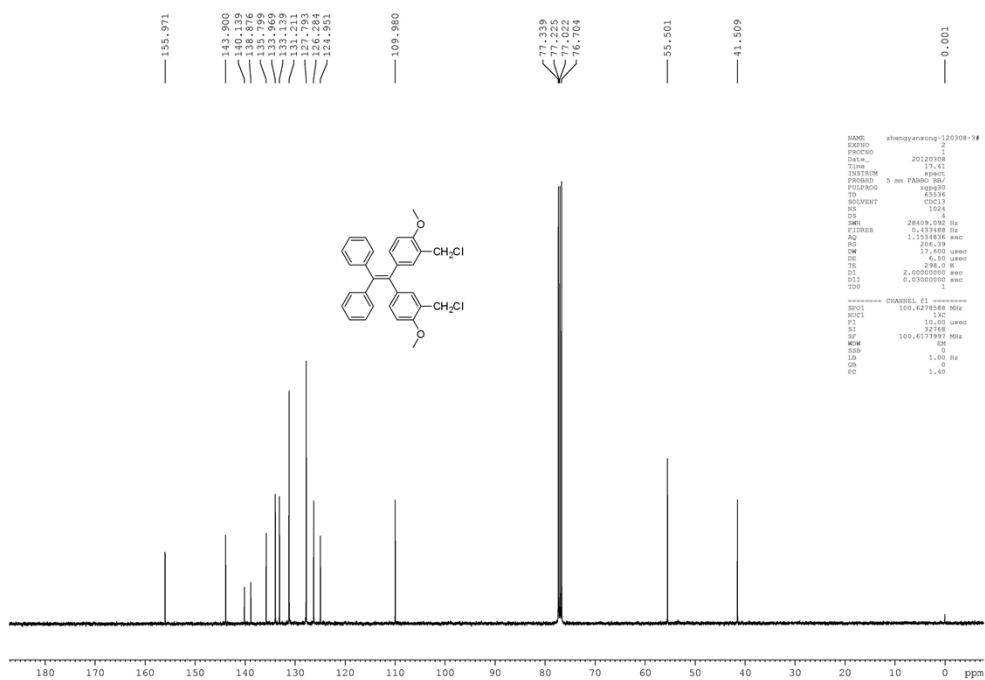


Fig. S18. ¹³C NMR (100 MHz, CDCl₃) spectrum of 4.

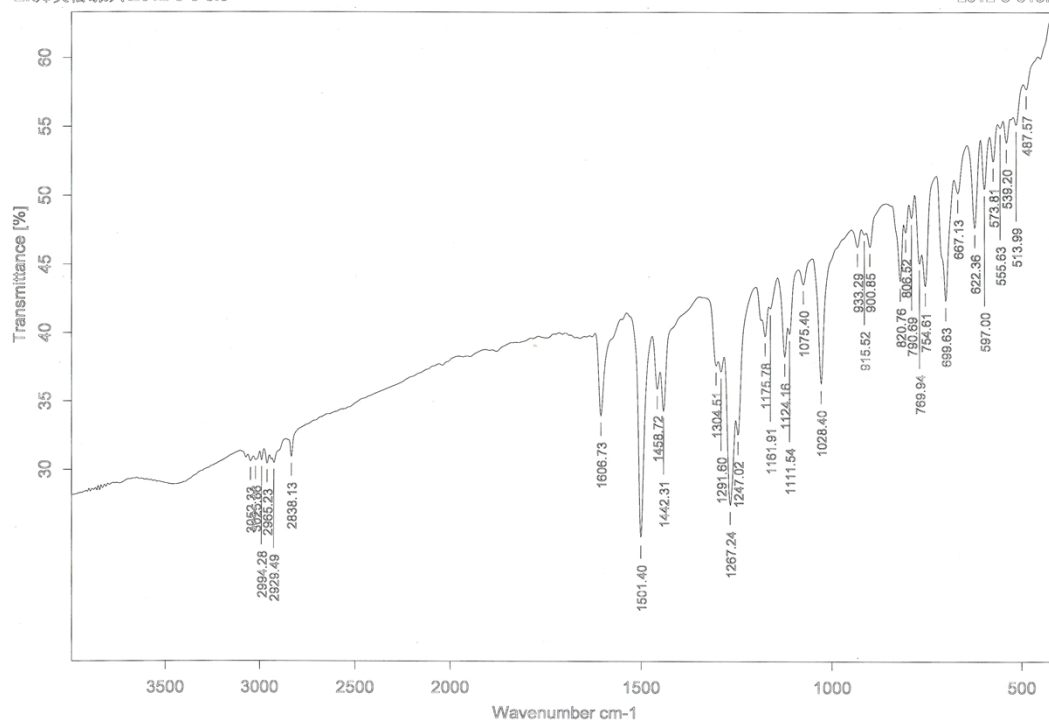


Fig. S19. IR spectrum of 4 in KBr.

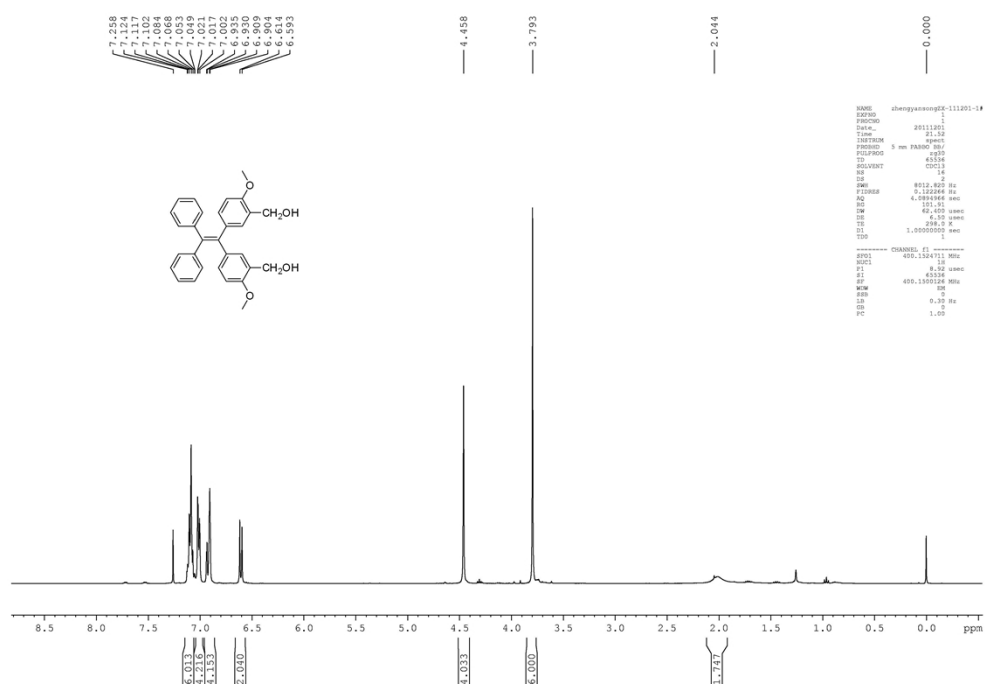


Fig. S20. ¹H NMR (400 MHz, CDCl₃) spectrum of 3.

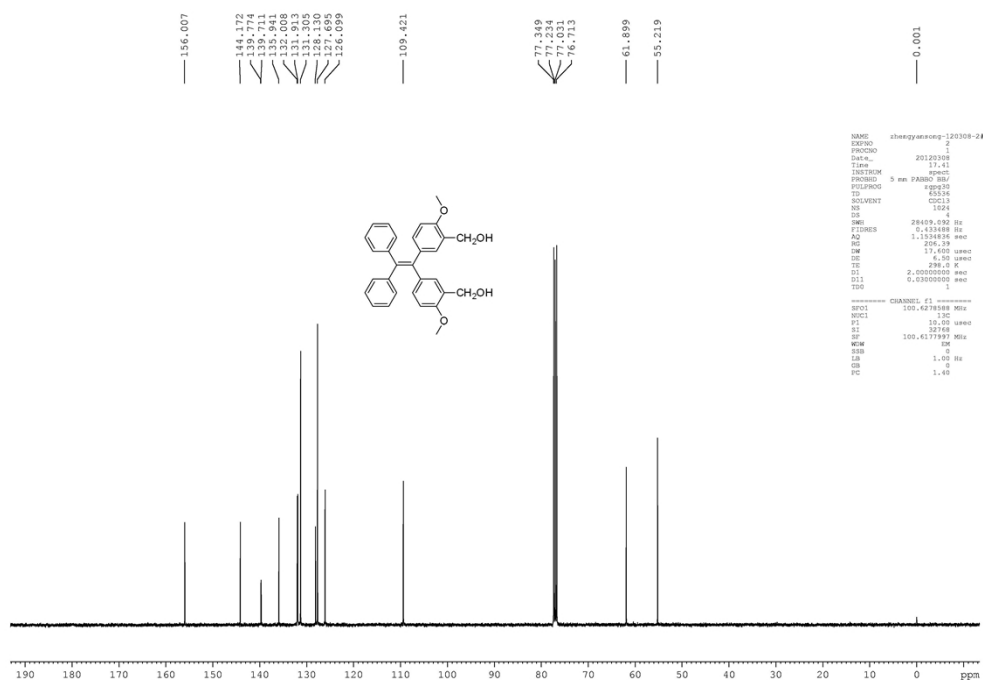


Fig. S21. ^{13}C NMR (100 MHz, CDCl_3) spectrum of 3.

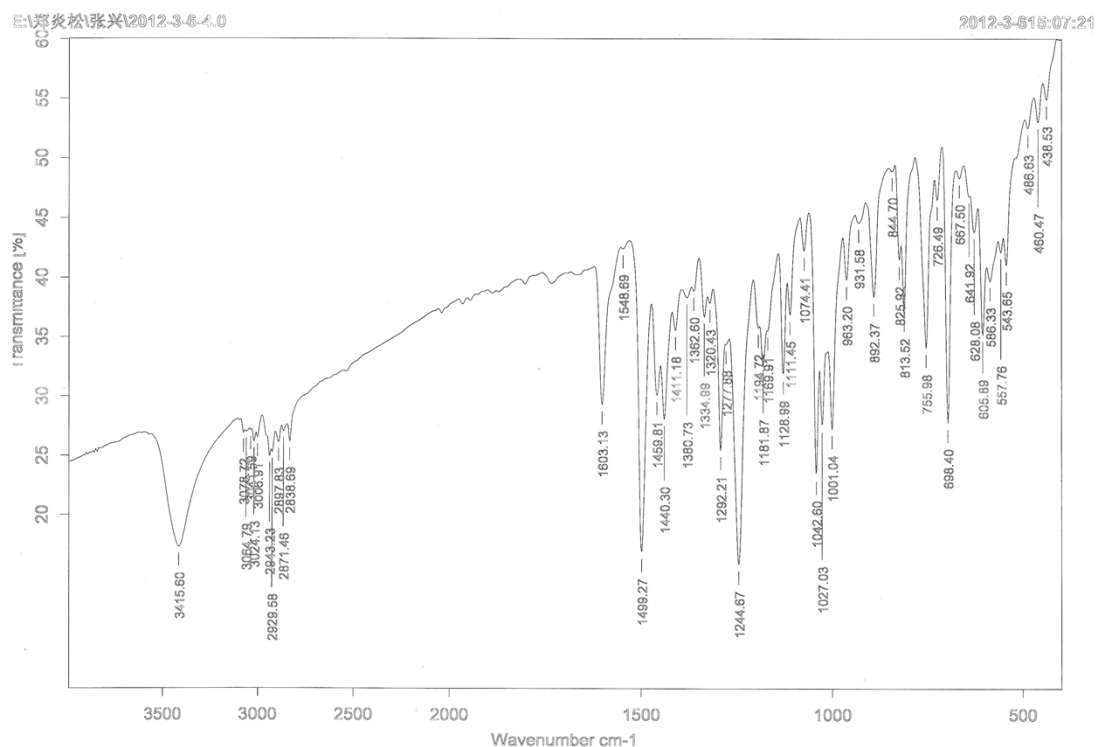


Fig. S22. IR spectrum of 3 in KBr.

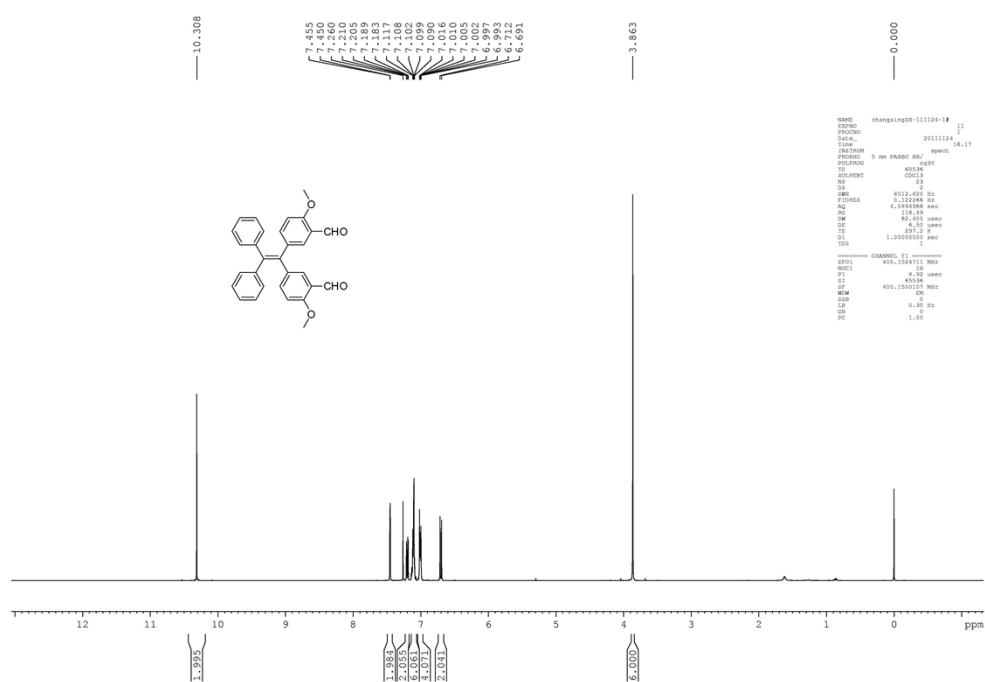


Fig. S23. ^1H NMR (400 MHz, CDCl_3) spectrum of 2.

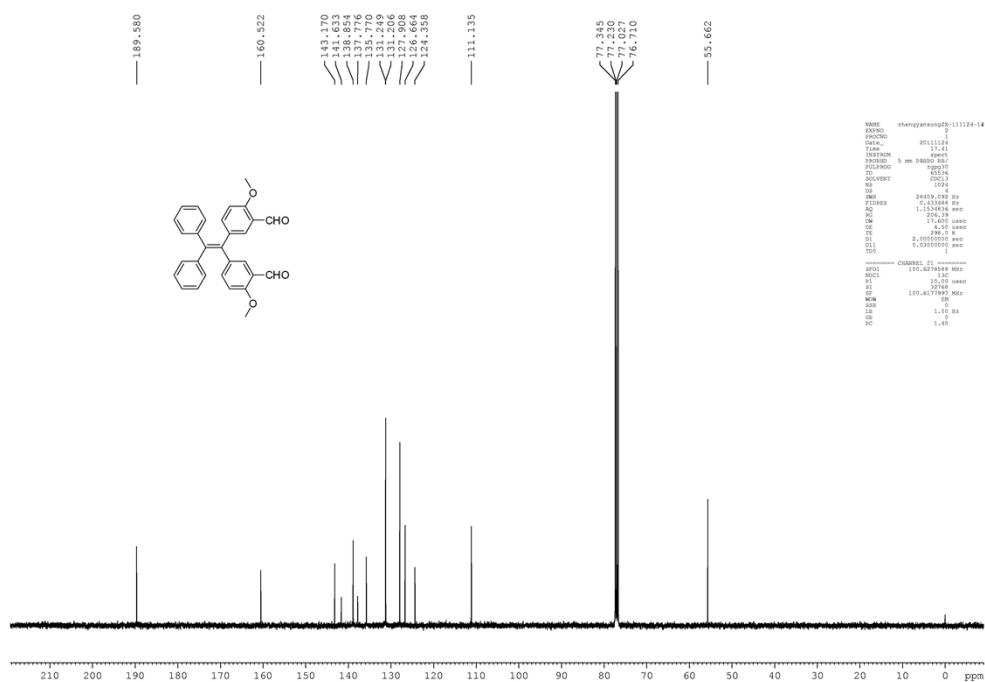


Fig. S24. ^{13}C NMR (100 MHz, CDCl_3) spectrum of 2.

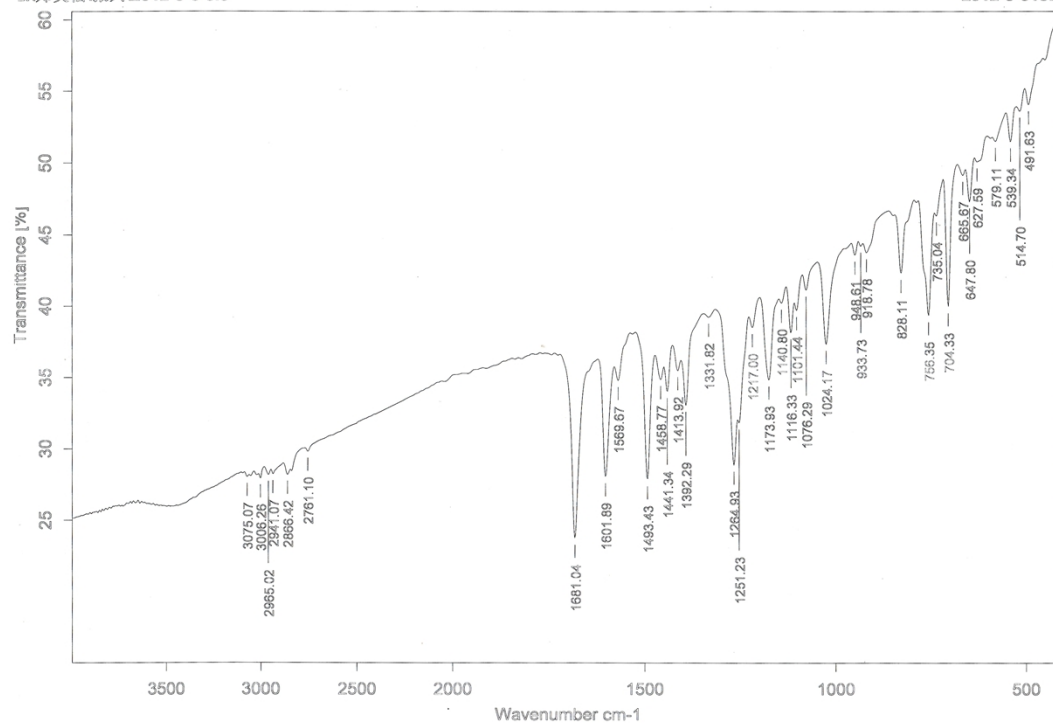


Fig. S25. IR spectrum of 2 in KBr.