

Colorimetric and Ratiometric Red Fluorescent Chemosensor for Fluoride Ion Based on Diketopyrrolopyrrole (DPP)

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Supporting information

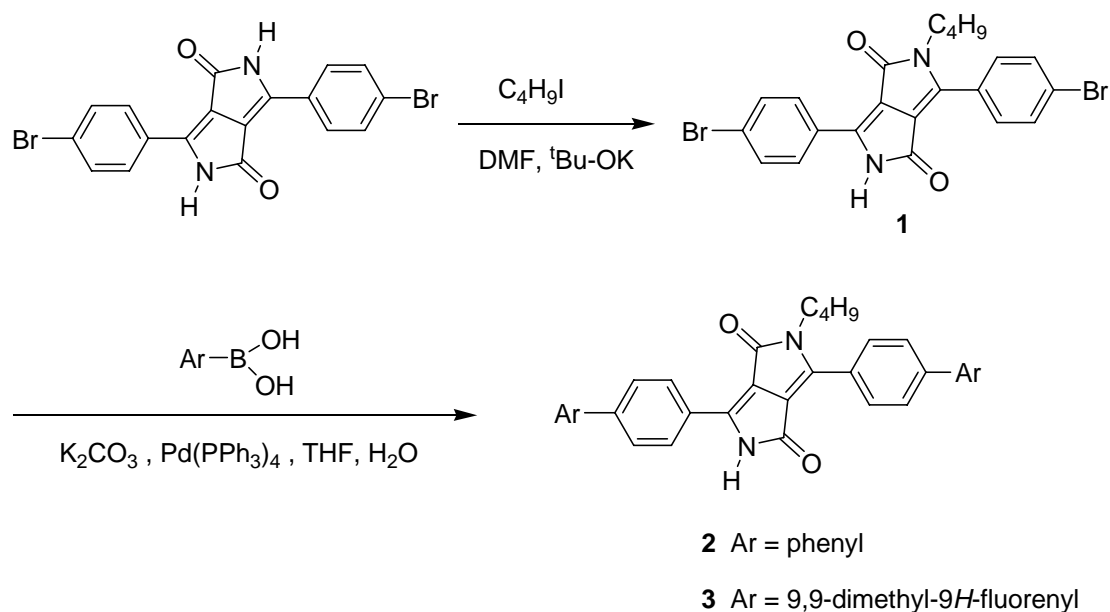
Experiment section

General procedure

¹H NMR spectra were recorded on a Bruker AM 400 spectrometer with tetramethyl silane (TMS) as internal reference. Absorption spectra were measured on a Varian Cary 500 UV-Vis spectrophotometer. Fluorescence spectra were measured on a Varian Cary Eclipse Fluorescence spectrophotometer. Mass spectra were recorded with a Waters Micromass LCT mass spectrometer.

Materials

Tetrahydrofuran (THF) was pre-dried over 4 Å molecular sieves and distilled under argon atmosphere from sodium benzophenone ketyl immediately prior to use. *N, N*-dimethyl formamide (DMF) and dichloromethane (DCM) were reflux with calcium hydride and distilled before used. Starting material 3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole-1, 4(2H,5H)-dione was synthesized and purified according to the established procedure.^[1] All other chemicals were purchased from Aldrich and used as received without further purification.



Scheme S1 Synthetic routes to the DPP-based compounds (**1–3**)

Synthesis of 3,6-bis(4-bromophenyl)-2-butylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**1**)

To a stirred solution of 3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1.14 g, 2.6 mmol) in DMF (30 mL) at room temperature under Ar was added potassium tert-butoxide (0.8 g, 7.1 mmol). The solution suddenly turned into purple and the reaction mixture was stirred for further 30 min. Then butyl iodide (0.8 g, 4.3 mmol) was gradually added. This reddish solution was stirred for 6 h at room temperature. The solution changes from back to red and reactive mixture was poured into 400 mL water and stirred for 1 h. Then, crude product was obtained by filtration and purified by flash chromatography with DCM / ethyl acetate = 10/1 as eluent. The pure **1** was obtained 0.65 g (yield: 51%). ^1H NMR (400 MHz, CDCl_3 , ppm): 9.72 (s, 1H, N-H), 8.20 (d, $J = 8.53$ Hz, 2H, Ar-H), 7.70 (m, 4H, Ar-H), 7.63 (d, $J = 8.51$ Hz, 2H, Ar-H), 3.82 (t, $J = 7.35$ Hz, 2H, -NCH₂-), 1.55 (m, 2H, -NCH₂CH₂-), 1.31 (m, 2H, -CH₂CH₃), 0.91 (t, $J = 7.35$ Hz, 3H, -CH₃). ^{13}C NMR (100 MHz, CDCl_3): δ 163.1, 162.4, 147.2, 144.0, 132.4, 132.2, 130.2, 129.3, 126.9, 126.7, 126.3, 126.0, 111.1, 110.0, 42.1, 31.5, 20.0, 13.6. HRMS: calculated for ($\text{C}_{22}\text{H}_{18}\text{Br}_2\text{N}_2\text{O}_2$) 501.9715, found: 501.9717.

Synthesis of 3,6-di(biphenyl-4-yl)-2-butylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**2**)

3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (100 mg, 0.2 mmol), tetrakis-(triphenylphosphino) palladium (0) (11 mg, 0.01 mmol), and 5 mL of 2 M aqueous potassium

carbonate solution were heated to 50 °C under a nitrogen atmosphere for 30 min. A solution of phenylboronic acid (58 mg, 0.48 mmol) in THF (26 mL) was added slowly, and the mixture was refluxed for further 36 h. After cooling to room temperature, the mixture was extracted with 30 mL of CH₂Cl₂. The organic portion was combined and removed by rotary evaporation. The residue was purified by column chromatography on silica (THF/DCM = 1/6, v/v) to give a red solid (0.89 g). Yield: 90.0 %. ¹H NMR (400 MHz , DMSO-*d*₆ , ppm) : 11.32 (s, 1H , N-H), 8.60 (d, *J* = 8.48 Hz, 2H , Ar-H), 7.98 (d, *J* = 8.47 Hz, 2H, Ar-H), 7.93 (dd, *J* = 8.51, 2.09 Hz, 4H, Ar-H), 7.82 (m, 4H, Ar-H), 7.53 (m, 4H, Ar-H), 7.45 (d, *J* = 7.29 Hz, 2H, Ar-H), 3.87 (t, *J* = 8.47 Hz, 2H, -NCH₂-), 1.51 (m, 2H, -NCH₂CH₂-), 1.30 (m, 2H, -CH₂CH₃), 0.81 (t, *J* = 7.82 Hz, 3H, -CH₃). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 162.5, 161.6, 145.4, 145.3, 143.4, 142.3, 138.9, 138.8, 129.2, 129.1, 126.9, 126.8, 110.9, 108.6, 40.9, 30.8, 19.3, 13.4. HRMS: calculated for (C₃₄H₂₈N₂O₂) 496.2151, found: 496.2147.

Synthesis of 2-butyl-3,6-bis(4-(9,9-dimethyl-9H-fluoren-2-yl)phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H, 5H)-dione (**3**)

3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (100 mg, 0.2 mmol), tetrakis(triphenylphosphino) palladium (0) (11 mg, 0.01 mmol), and 5 mL of 2 M aqueous potassium carbonate solution were heated to 50 °C under a nitrogen atmosphere for 30 min. A solution of 9,9-dimethyl-9H-fluoren-2-ylboronic acid (300 mg, 0.41 mmol) in THF (26 mL) was added slowly, and the mixture was refluxed for further 26 h. After cooling to room temperature, the mixture was extracted with 30 mL of CH₂Cl₂. The organic portion was combined and removed by rotary evaporation. The residue was purified by column chromatography on silica (THF/PE = 1/8, v/v) to give a dark red solid (0.12 g). Yield: 85.0 %. ¹H NMR (400 MHz , CDCl₃ , ppm) : 10.56 (s, 1H , N-H), 8.44-8.56 (m, 2H , Ar-H), 7.95-8.07 (m, 2 H, Ar-H), 7.61-7.85 (m, 8 H, Ar-H), 7.33-7.48 (m, 10H, Ar-H), 3.86-3.97 (m, 2H, -NCH₂-), 1.71-1.83 (m, 2H, -NH₂CH₂CH₂-), 1.55 - 1.62 (m, 2H, -CH₂CH₃), 1.40-1.53 (m, 12H, C-CH₃), 0.93-1.02 (m, 3H, -CH₂CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 162.8, 154.5, 153.9, 147.6, 145.0, 144.3, 143.9, 139.4, 138.9, 138.6, 129.4, 128.3, 127.8, 127.6, 127.5, 127.1, 126.3, 122.7, 121.4, 120.5, 120.3, 110.9, 110.1, 47.0, 42.2, 31.7, 27.2, 20.1, 13.7. HRMS: calculated for (C₅₂H₄₄N₂O₂) 728.3403, found: 728.3410.

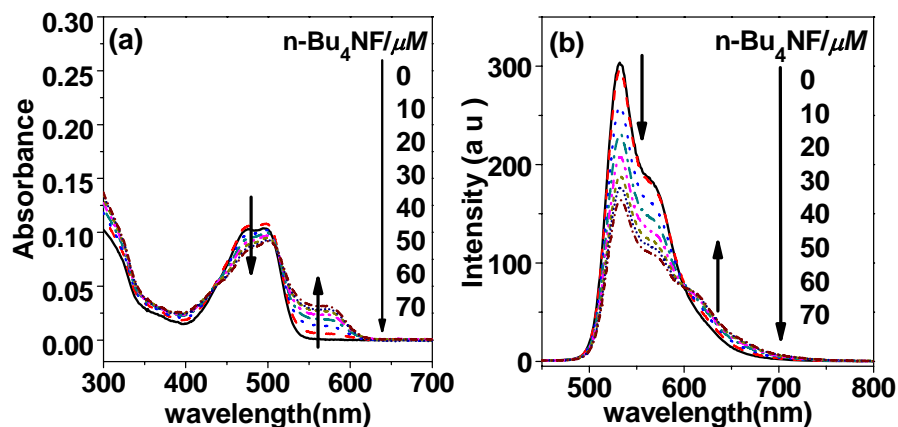


Figure S1. Changes in UV-vis absorption (a) and emission spectra (b) of **1** (5.0×10^{-6} M) in DCM upon the addition of 0-70 μM of TBAF (Excited at 435 nm).

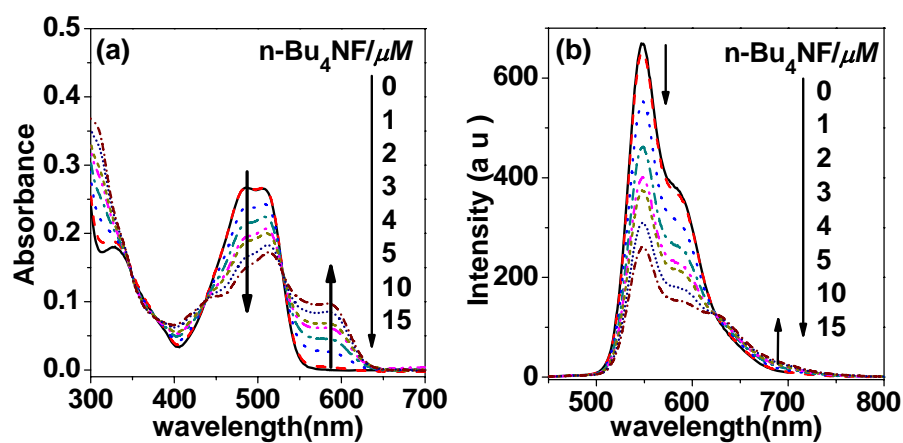


Figure S2. Changes in UV-vis absorption (a) and emission spectra (b) of **2** (5.0×10^{-6} M) in DCM upon the addition of 0-15 μM of TBAF (Excited at 435 nm).

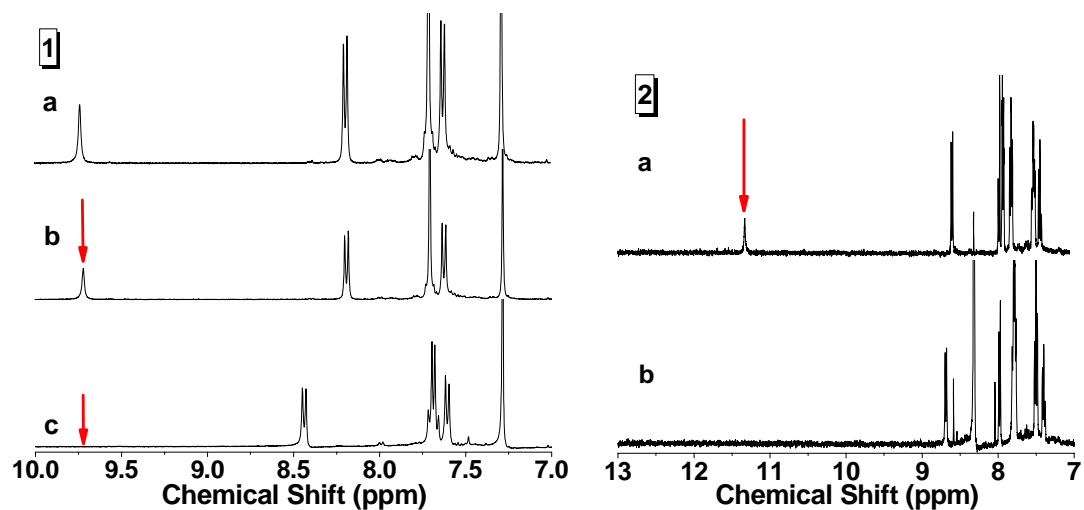


Figure S3. (a) ^1H NMR spectra of sensor **1** in CDCl_3 in the presence of (a) 0 equiv (b) 5 equiv and (c) 10 equiv of TBAF. (b) ^1H NMR spectra of sensor **2** in $\text{DMSO}-d_6$ in the presence of (a) 0 equiv and (b) 5 equiv of TBAF.

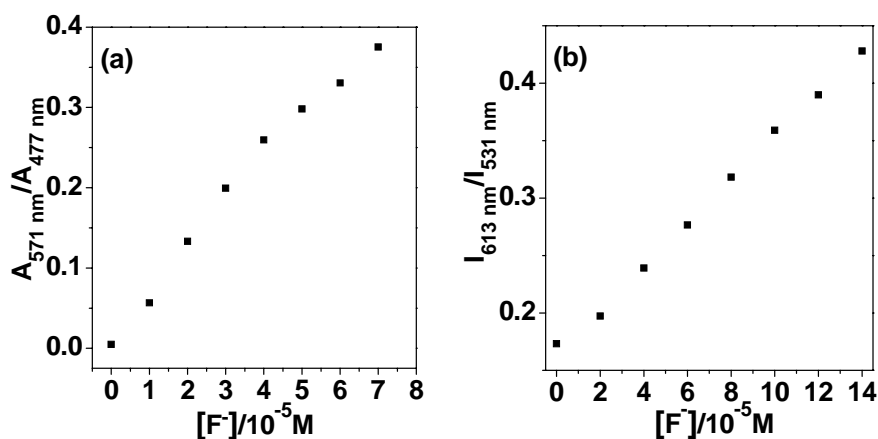


Figure S4. (a) Plot of the absorbance ratio of **1** between 571 nm and 477 nm ($A_{571 \text{ nm}}/A_{497 \text{ nm}}$) vs concentration of F^- in DCM. (b) Plot of the emission intensity ratio of **1** between 613 nm and 531 nm ($I_{613 \text{ nm}}/I_{531 \text{ nm}}$) vs concentration of F^- in DCM.

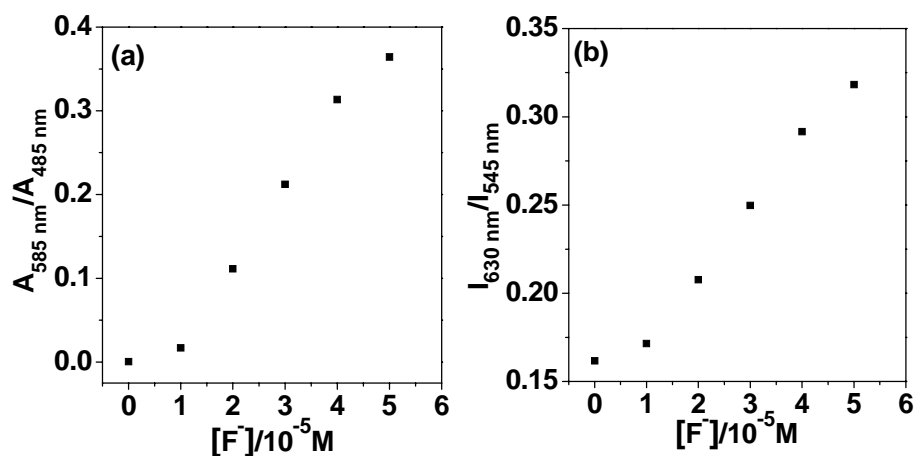


Figure S5. (a) Plot of the absorbance ratio of **2** between 585 nm and 485 nm ($A_{585 \text{ nm}}/A_{485 \text{ nm}}$) vs concentration of F^- in DCM. (b) Plot of the emission intensity ratio of **2** between 630 nm and 545 nm ($I_{630 \text{ nm}}/I_{545 \text{ nm}}$) vs concentration of F^- in DCM.

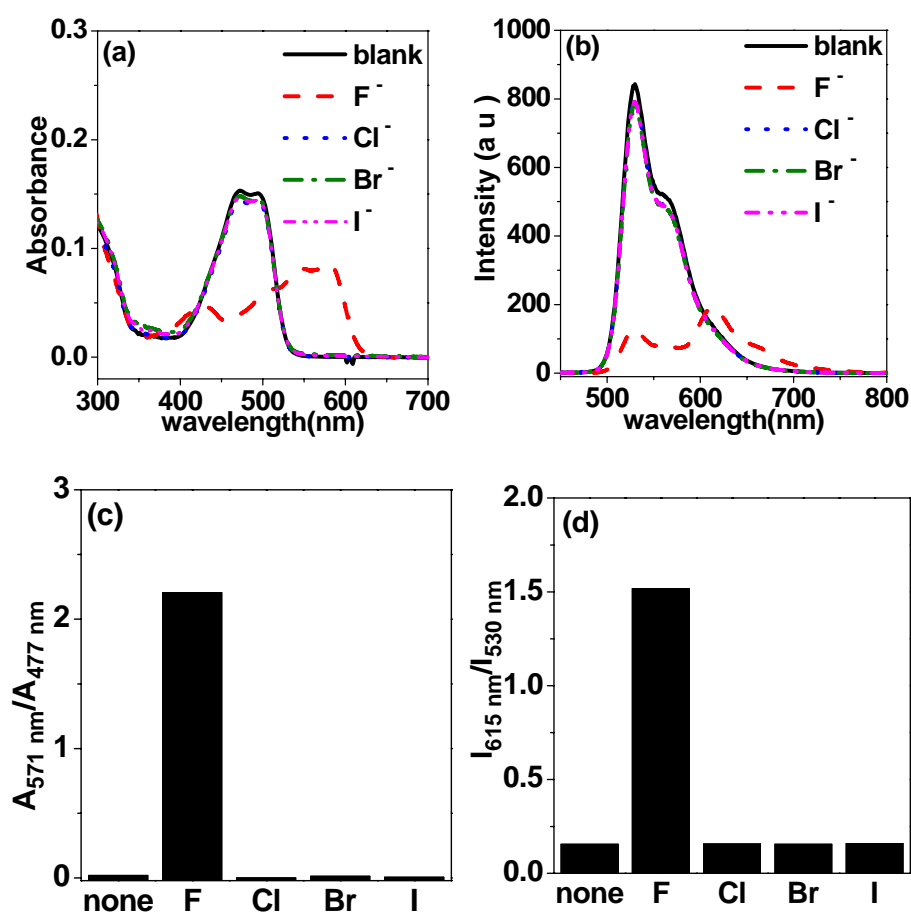


Figure S6. (Top) Absorbance (a) and fluorescence spectra (b) responses of **1** (5.0×10^{-6} M in DCM) after the addition of 30 equiv of chloride, bromide, iodide and fluoride. (Bottom) Absorbance ratiometric response of **1** between 571 and 477 nm to the halide ions (150 μ M) (c). Emission ratiometric response of sensor **1** to the halide ions (150 μ M). Excitation was at 435 nm, and emissions were at 613 and 531 nm (d).

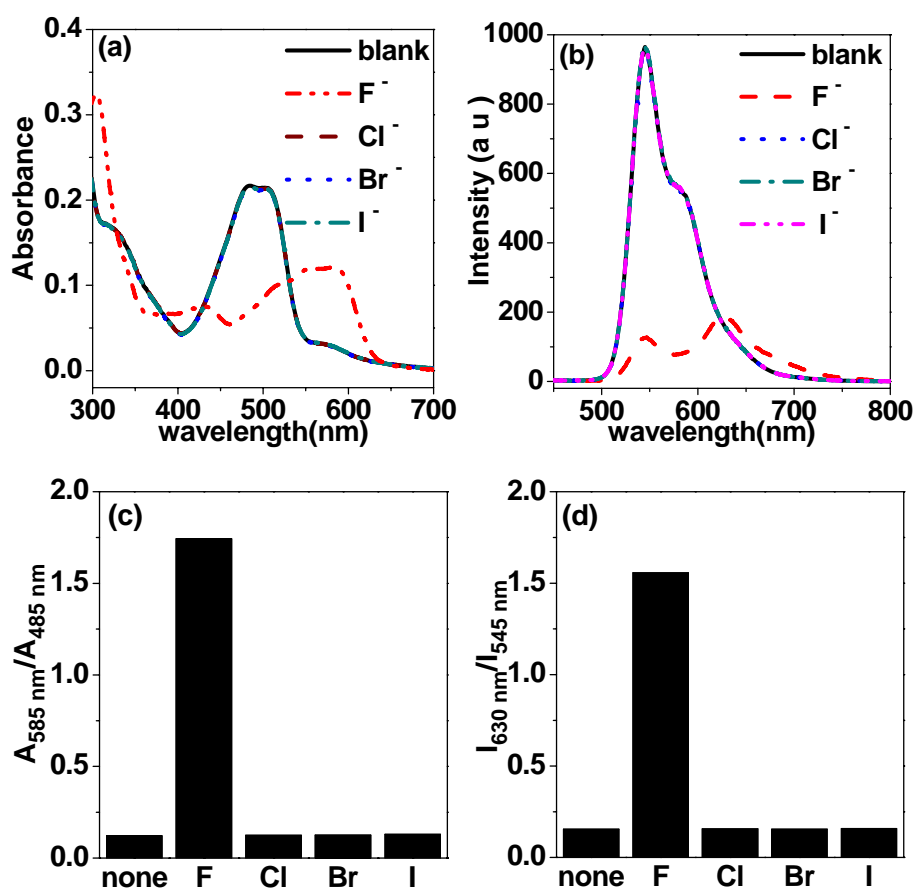


Figure S7. (Top) Absorbance (a) and fluorescence spectra (b) responses of **2** (5.0×10^{-6} M in DCM) after the addition of 30 equiv of chloride, bromide, iodide and fluoride. (Bottom) Absorbance ratiometric response of **2** between 585 and 485 nm to the halide ions (150 μ M) (c). Emission ratiometric response of sensor **2** to the halide ions (150 μ M). Excitation was at 435 nm, and emissions were at 630 and 545 nm (d).

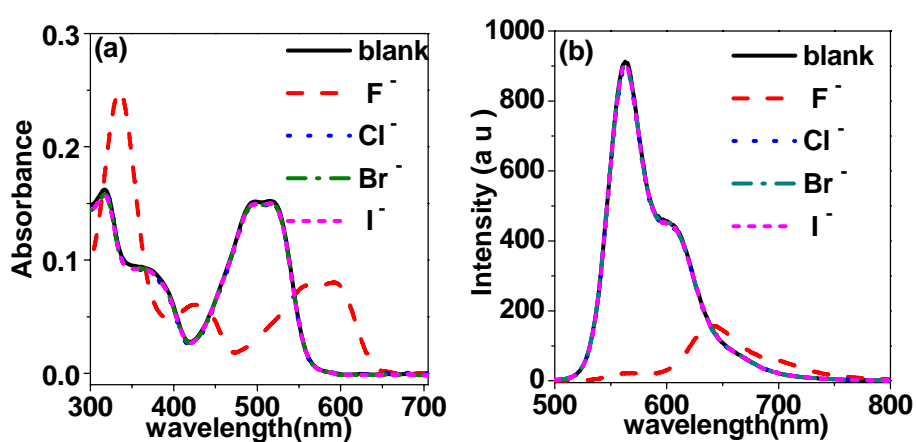


Figure S8. Absorbance (a) and fluorescence spectra (b) responses of **3** (5.0×10^{-6} M in DCM) after the addition of 30 equiv of chloride, bromide, iodide and fluoride.

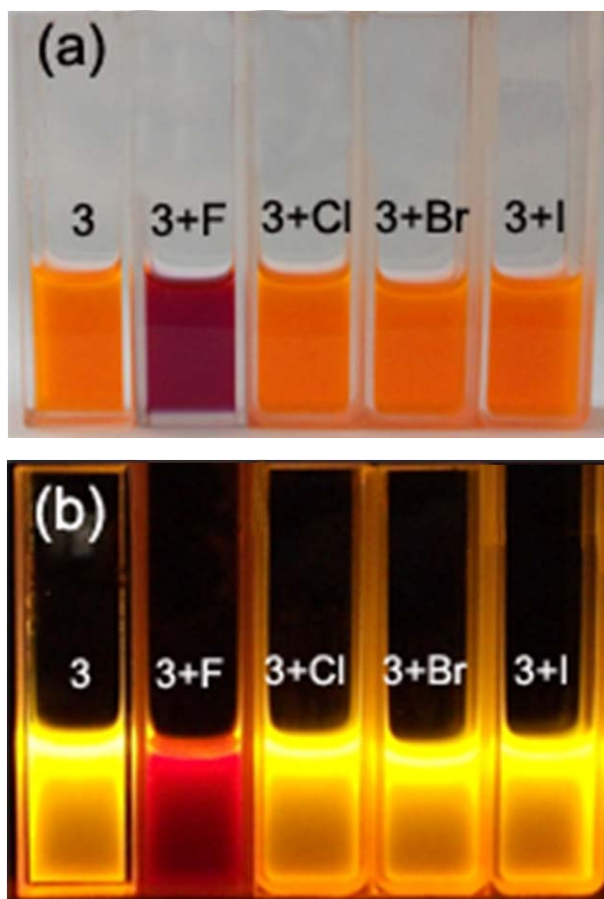


Figure S9. Color (a) and fluorescence (b) change of **3** (from left to right: **3** only; **3** + F⁻; **3** + Cl⁻; **3** + Br⁻; **3** + I⁻).

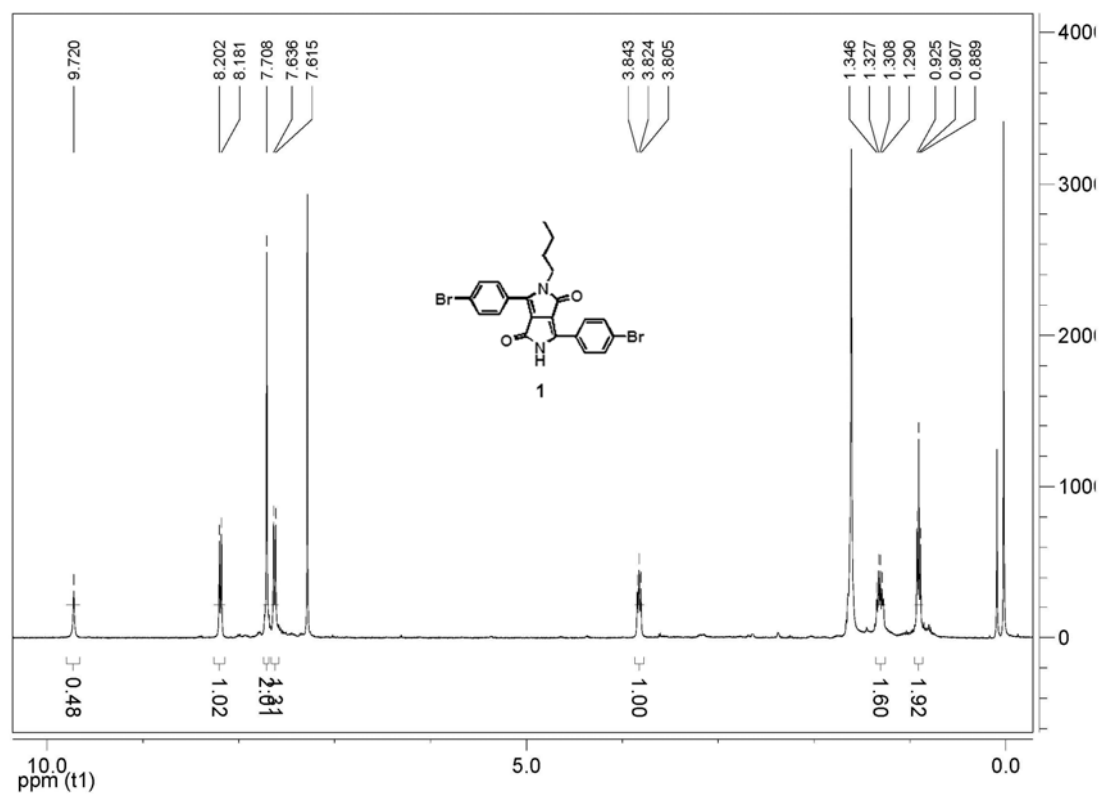


Figure S10. ^1H NMR spectrum of **1** (400 MHz, CDCl_3).

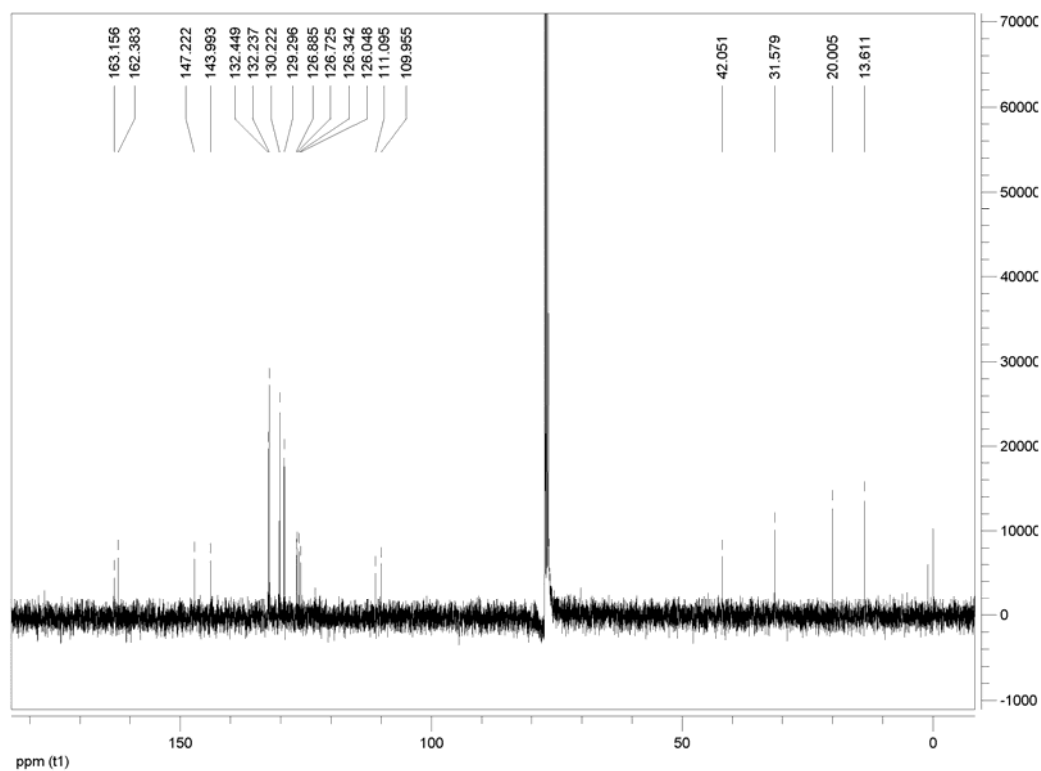


Figure S11. ^{13}C NMR spectrum of **1** (100 MHz, CDCl_3).

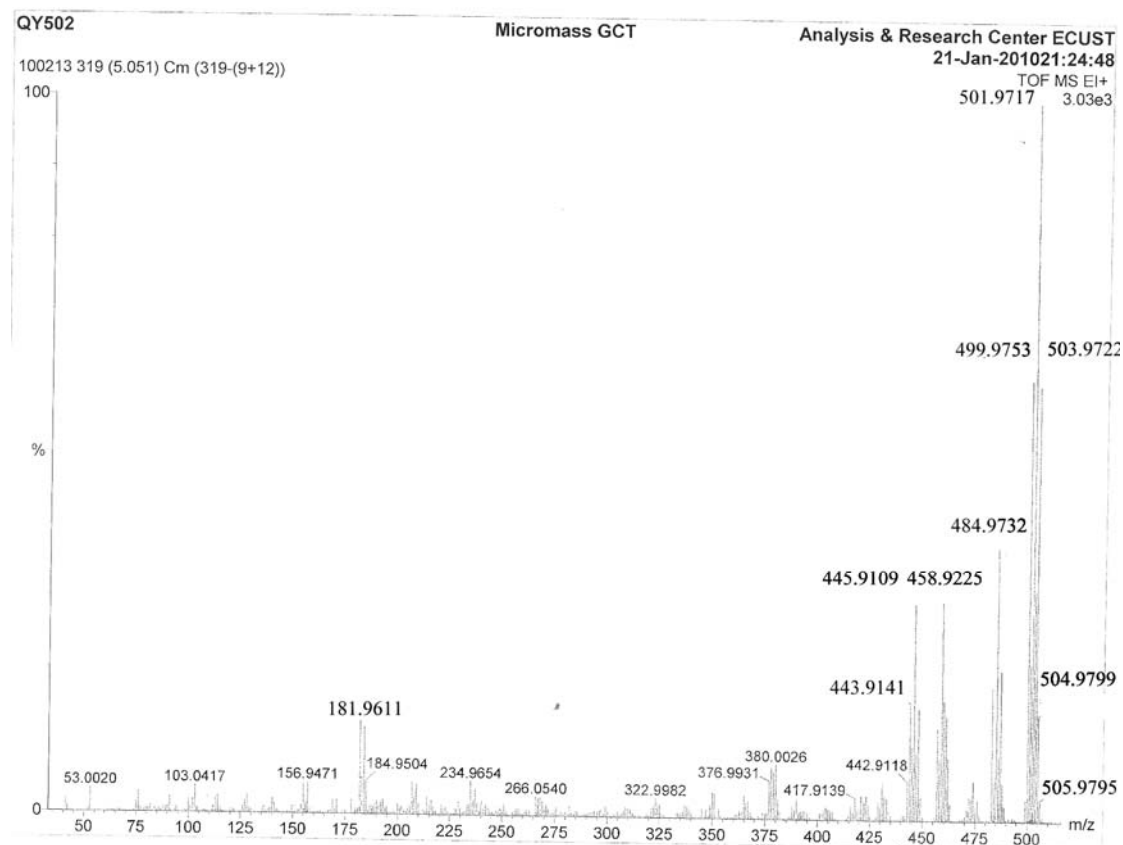


Figure S12. HRMS spectrum of **1**

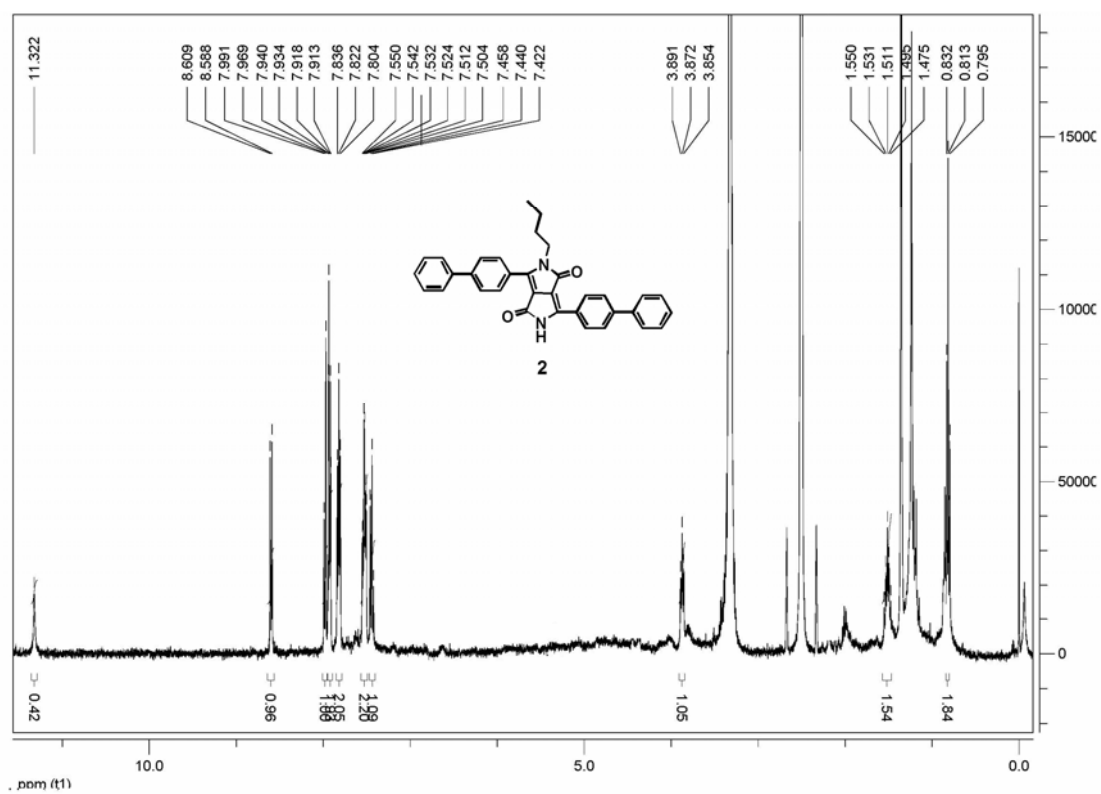


Figure S13. ^1H NMR spectrum of **2** (400 MHz, $\text{DMSO}-d_6$).

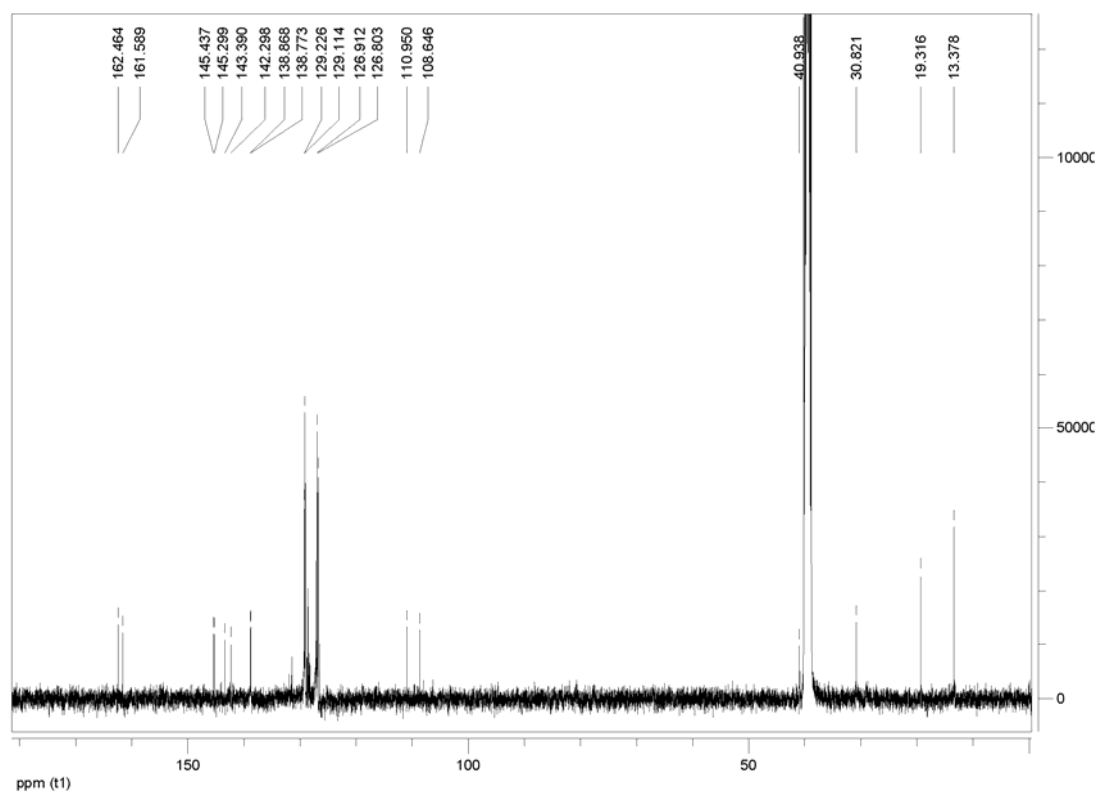


Figure S14. ¹³C NMR spectrum of **2** (100 MHz, DMSO-*d*₆).

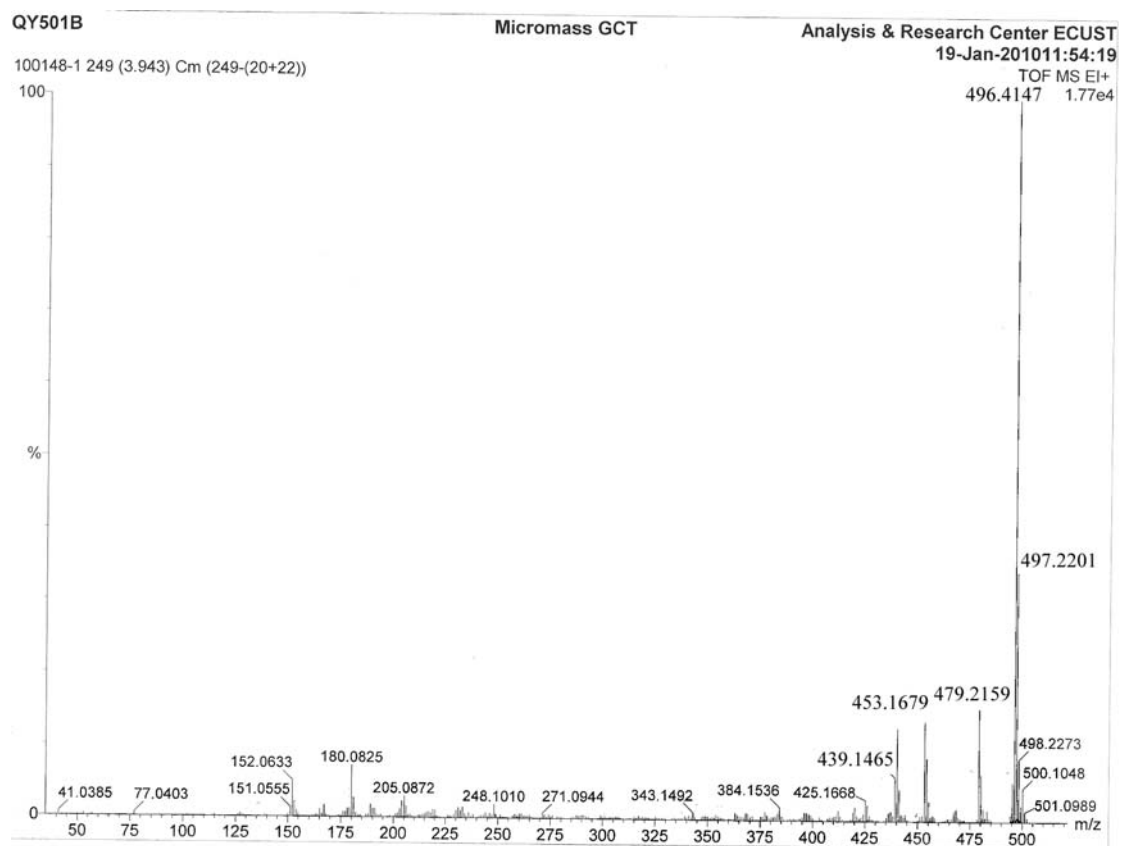


Figure S15. HRMS spectrum of **2**

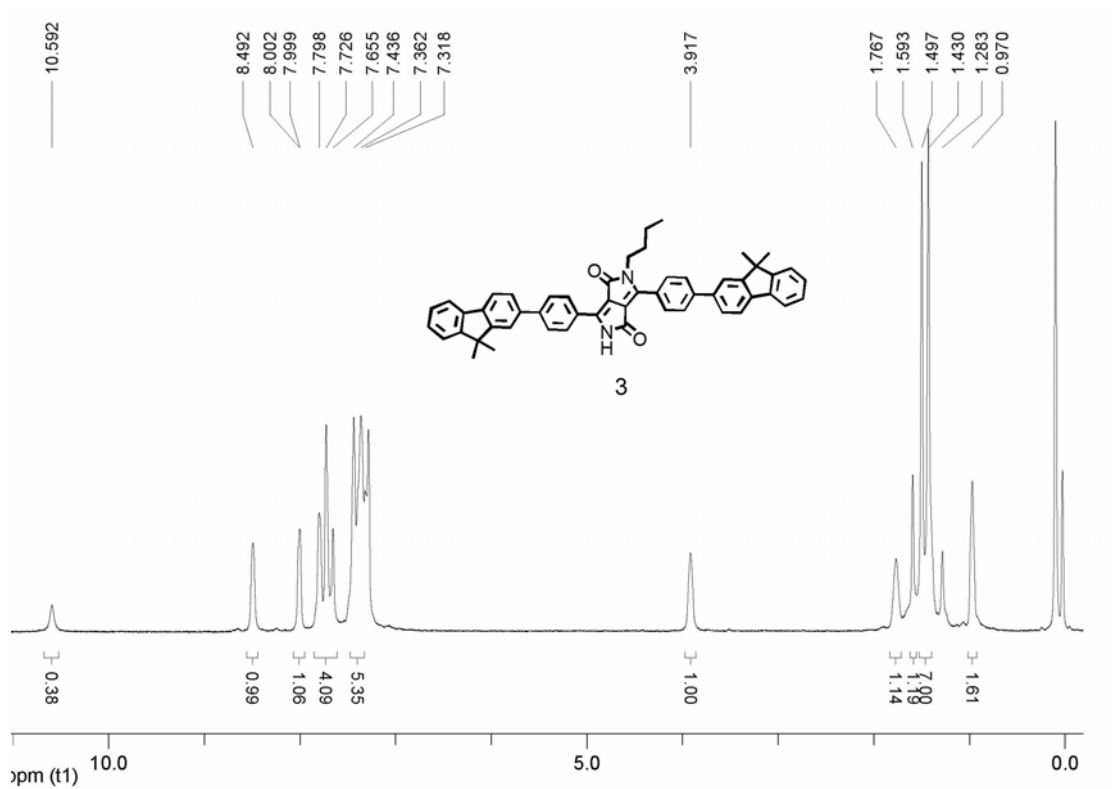


Figure S16. ^1H NMR spectrum of **3** (400 MHz, CDCl_3).

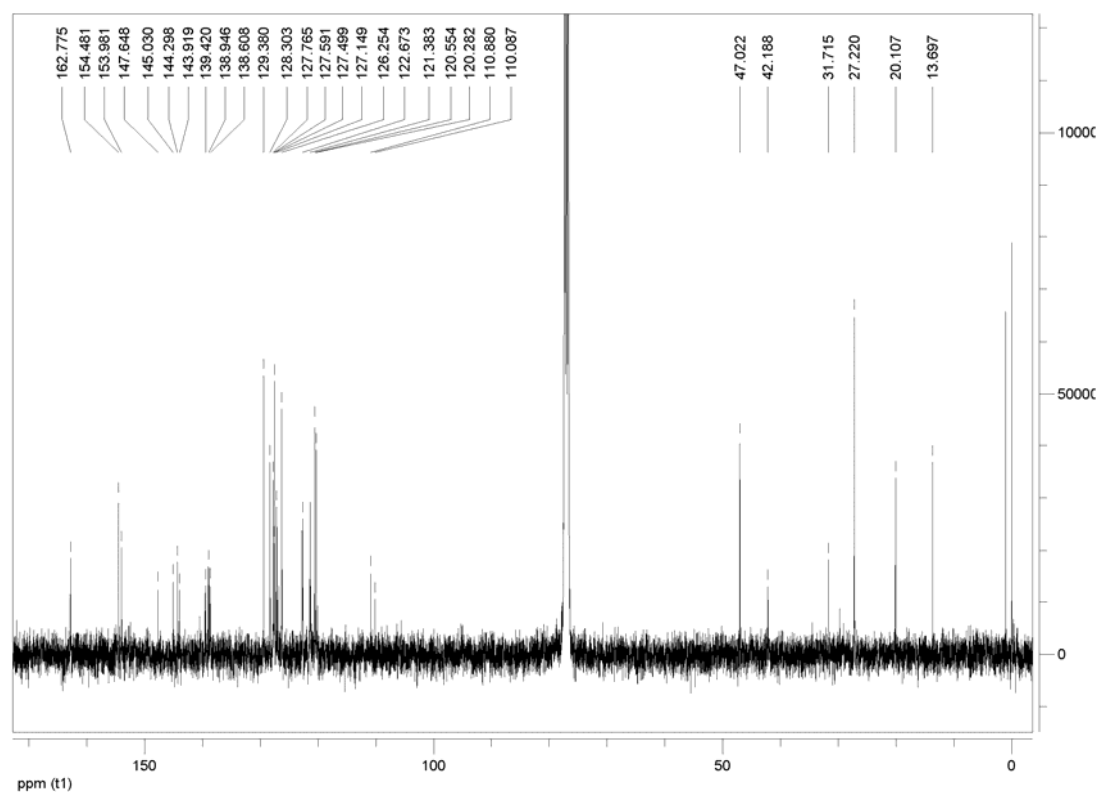


Figure S17. ^{13}C NMR spectrum of **3** (100 MHz, CDCl_3).

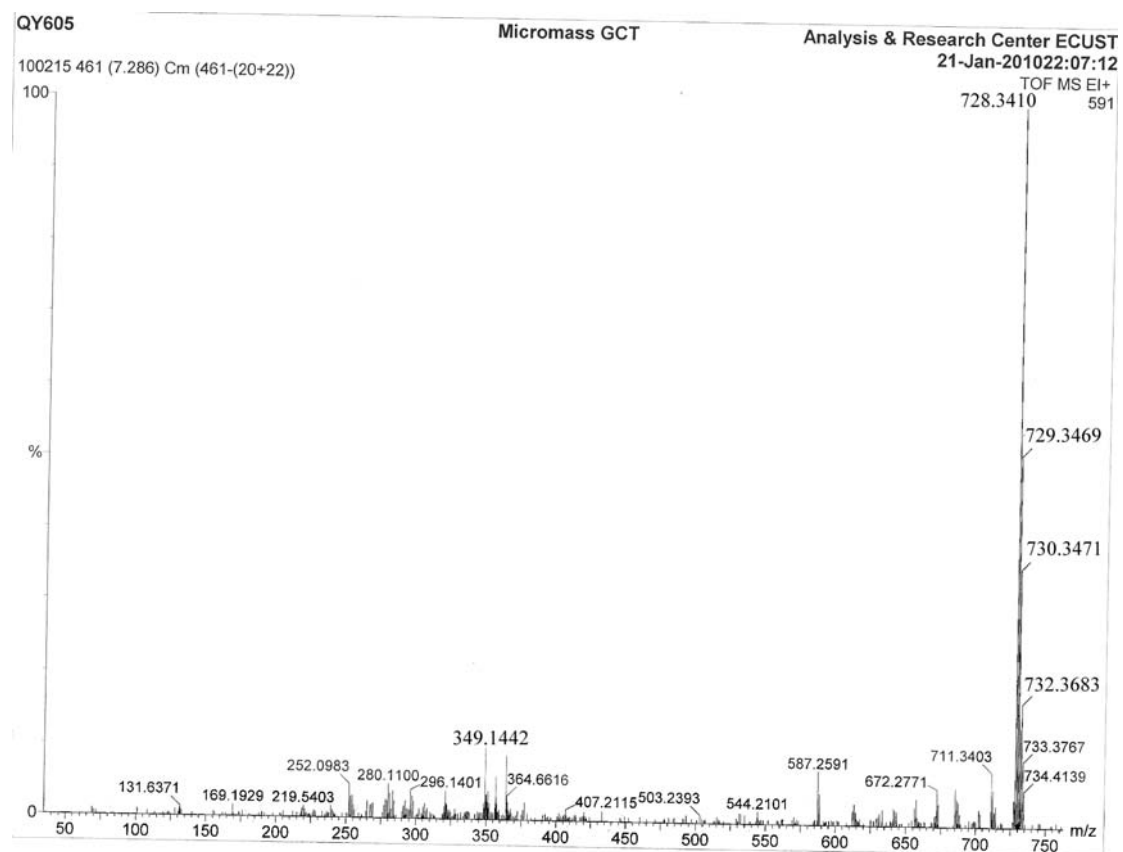


Figure S18. HRMS of **3**

Reference

[1] Jiang, Y. H.; Wang, Y. C.; Hua, J. L.; Qian, S. Q.; Tian, H. *J. Polym. Sci., Part A*. **2009**, *47*, 4400.