

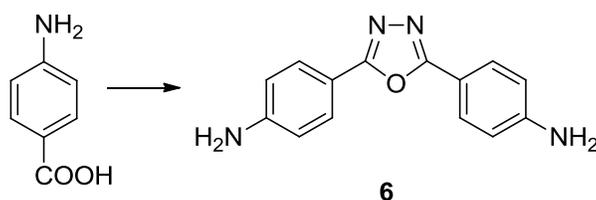
Supporting information

Polytriazole Bridged with 2,5-Diphenyl-1,3,4-Oxadiazole Moieties: A Highly Sensitive and Selective Fluorescence Chemosensor for Ag⁺

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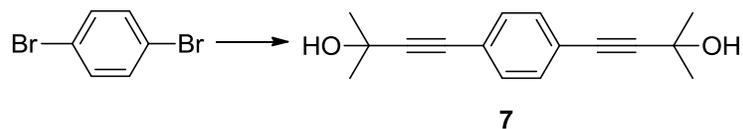
Synthesis of compounds 6~11

2,5-Bis(*p*-aminophenyl)-1,3,4-oxadiazole (**6**)¹



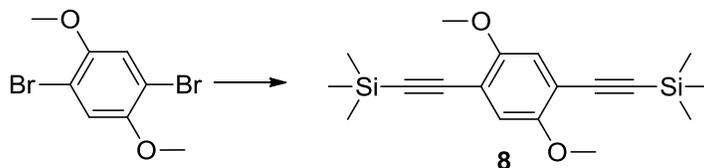
Hydrazine hydrate (1 mL, 50% in H₂O) was added to polyphosphoric acid (PPA) dropwise while maintaining the flask on the ice bath for 15 min, then 4-aminobenzoic acid (1.37 g, 10 mmol) was added into the mixture. The reaction mixture was heated to 130 °C and kept for 10 h, and poured to a mixture of ice-water with stirring. The solution was neutralized with Na₂CO₃, a powder precipitate was obtained and. The precipitate was filtered and washed with a sodium carbonate solution (400 mL).The compound was recrystallized from ethanol to give **6** as colorless solid (970 mg, 77 %). bp. 259-261 °C. ¹H NMR (CDCl₃, δ ppm): 7.73 (d, *J* = 8.8 Hz, 4H), 6.70 (d, *J* = 8.8 Hz, 4H), 5.88 (s, 4H).

*1,4-Di(2-methyl-2-hydroxy-3-butynyl)-benzene (7)*²



1,4-dibromobenzene (2.35 g, 10 mmol), CuI (95 mg, 0.50 mmol), Pd(PPh₃)₄ (351 mg, 0.5 mmol) and 2-methylbut-3-yn-2-ol (2.5 g, 30 mmol) were vigorously refluxed in dry THF (20 mL) and Et₃N (30 mL) for 8 h. The final mixture was filtered and the solvent was removed from the filtrate via a rotavap. The residue was purified by flash chromatography on a silica gel column with hexane/ethyl acetate (1 : 1) to give **7** as a light yellow solid (2.3 g, 95 %). ¹H NMR (CDCl₃, δ ppm): 1.61 (s, 12H), 2.05 (s, 2H), 7.34 – 7.35 (m, 4H).

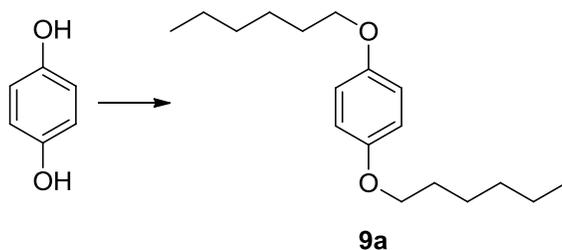
*1,4-bis(trimethylsilylethynyl)-2,5-dimethoxybenzene (8)*³



In a 25 mL flask, 1,4-dibromo-2,5-dimethoxybenzene (5 mmol), CuI (0.05 mmol) and Pd(PPh₃)₄ (0.05 mmol) were added to 10 mL triethylamine, followed by the addition of ethynyltrimethylsilane (12 mmol). The mixture was degassed by several freeze-thaw cycles, and flushed with argon. The reaction mixture was refluxed for 12 h at 70 °C under argon atmosphere. After cooling to room temperature the precipitated salt was filtered off and washed with triethylamine. The filtrate was evaporated and water were added. The mixture was extracted with diethyl ether until the aqueous phase was colorless. The combined organic phases were dried over MgSO₄, and the solvent was evaporated. The residue was recrystallized from hexane to give

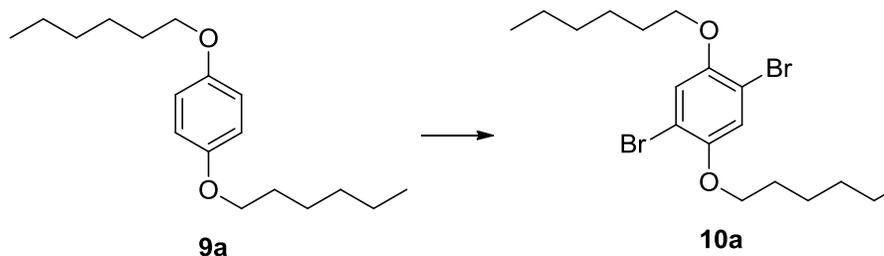
8 as a white solid (1.58 g, 93 %). $^1\text{H NMR}$ (CDCl_3 , δ ppm): 0.25 (s, 18H), 3.81 (s, 6H), 6.89(s, 2H).

*1,4-bis(hexyloxy)benzene (9a)*⁴



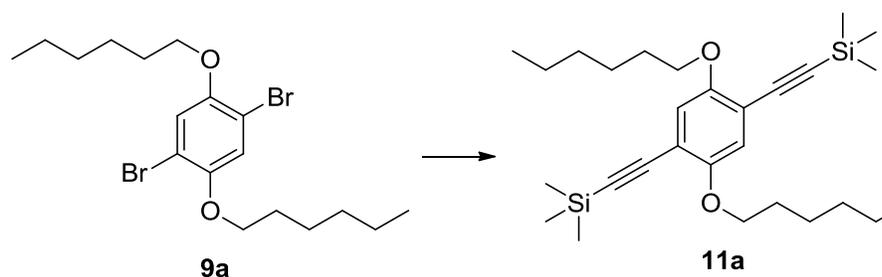
In a 100 mL flask, hydroquinone (5.50 g, 50 mmol), KOH (8.41 g, 3 mmol), NaI (1.49 g, 10 mmol), and 1-bromohexane (24.76 g, 150 mmol) were mixed in 50 mL of EtOH and refluxed for 48 h under stirring. Then, the solution was cooled to rt and the solvent was distilled off. The residue was taken up with 200 mL of 10 % NaOH/ H_2O and extracted twice with 100 mL of CH_2Cl_2 . The organic phase was combined, washed with water and dried with MgSO_4 . The solvent was distilled off. The residue was purified by flash chromatography on a silica gel column with hexane to give **9a** as colorless solid (8.4 g, 61 %). $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.82 (s, 4 H), 3.90 (t, $J = 6.5$ Hz, 4H), 1.78-1.72 (m, 4H), 1.47-1.32(m, 12H), 0.91 (t, $J = 7.0$ Hz, 6H).

*1,4-dibromo-2,5-bis(hexyloxy)benzene (10a)*⁵



In a three-neck flask was dissolved 2.78 g (10 mmol) of **9a** in a mixture of 50 mL of CH₂Cl₂/glacial CH₃COOH (1:1). Then, 3.9 g (22 mmol) N-bromosuccinimide was added. The brown orange mixture was refluxed under stirring for 24 h and was poured into 200 mL of water. The organic layer was separated, washed with 100 mL of saturated Na₂SO₃ (4 x) and dried over MgSO₄. The solvent was distilled off. The residue was purified by flash chromatography on a silica gel column with hexane to give **10a** as colorless solid (2.96 g, 68 %). ¹H NMR (CDCl₃, δ ppm): 7.08 (s, 2H), 3.94 (t, *J* = 6.5 Hz, 4H), 1.83-1.77 (m, 4H), 1.50-1.33 (m, 12H), 0.90 (t, *J* = 7.0 Hz, 6H).

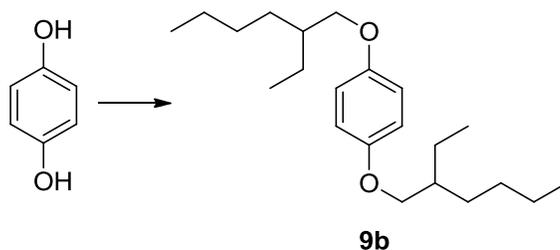
*1,4-bis(trimethylsilylethynyl)-2,5-bis(hexyloxy)benzene (11a)*⁴



In a 50 mL flask, **9a** (5 mmol), CuI (0.05 mmol) and Pd(PPh₃)₄ (0.05 mmol) were added to 10 mL triethylamine, followed by the addition of ethynyltrimethylsilane (12 mmol). The mixture was degassed by several freeze-thaw cycles, and flushed with argon. The reaction mixture was refluxed for 12 h at 70 °C under argon atmosphere. After cooling to room temperature the precipitated salt was filtered off and washed with triethylamine. The filtrate was evaporated and water were added. The mixture was extracted with diethyl ether until the aqueous phase was colorless. The combined organic phases were dried over MgSO₄, and the solvent was evaporated. The residue was recrystallized from hexane to give **11a** as crystals (1.78 g, 75 %). ¹H NMR

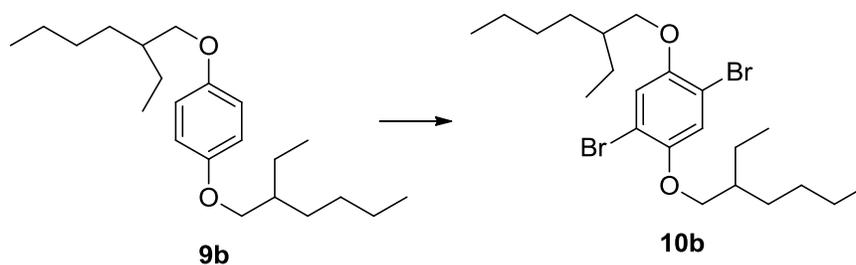
(CDCl₃, δ ppm): 6.89 (s, 2H), 3.94 (t, $J = 6.4$ Hz, 4H), 1.78 (m, 4H), 1.50 (m, 4H), 1.34 (m, 8H), 0.91 (t, $J = 7.0$ Hz, 6H), 0.25 (s, 18H).

*1,4-bis(2-ethylhexyloxy)benzene (9b)*⁶



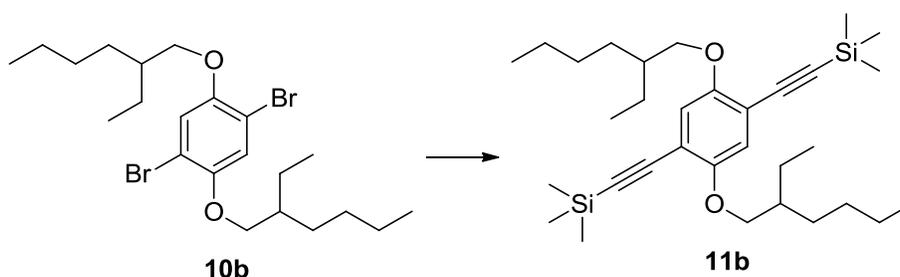
Potassium hydroxide (2.8 g, 50.9 mmol) was dissolved in DMSO (15 mL) in a 25 mL 3-neck round-bottom flask under nitrogen. Hydroquinone (2 g, 18.2 mmol) was then added, and the mixture was stirred for a half hour at room temperature, followed by addition of 2-ethylhexylbromide (8.8 g, 45.3 mmol). The reaction was stirred under nitrogen at room temperature overnight. The organic layer was separated and washed three times with 10 mL of DI water. The organic layer was dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (hexane) to afford **9b** as a yellow oil (3.6 g, 54 %). ¹H NMR (CDCl₃, δ ppm): 6.8 (s, 4H), 3.7 (m, 4H), 1.7 (m, 2H) and 1.5-0.8 (m, 28H).

*1,4-dibromo-2,5-bis((2-ethylhexyl)oxy)benzene (10b)*⁵



In a three-neck flask was dissolved 3.34 g (10 mmol) of **9b** in a mixture of 50 mL of CH₂Cl₂/glac CH₃COOH (1:1). Then, 3.9 g (22 mmol) N-bromosuccinimide was added. The brown orange mixture was refluxed with stirring for 24 h, and then poured into 200 mL of water. The organic layer was separated, washed using 100 mL of saturated Na₂SO₃ (4 x), and dried over MgSO₄. The solvent was distilled off. The residue was purified by silica gel column chromatography to afford **10b** as a yellow oil (2.4 g, 49 %). ¹H NMR (CDCl₃, δ ppm): 7.08 (s, 2H), 3.83 (d, *J* = 5.5 Hz, 4H), 1.75 (m, 2H), 1.64-1.20 (m, 16H), 1.08-0.84 (m, 12H).

*1,4-bis(trimethylsilylethynyl)-2,5-bis(2-ethylhexyloxy)benzene (11b)*⁷



In a 25 mL flask, **10b** (880 mg, 2 mmol), CuI (19 mg, 0.1 mmol) and Pd(PPh₃)₄ (115 mg, 0.1 mmol) were added to 10 mL triethylamine. The mixture was degassed by several cycles, followed by the addition of ethynyltrimethylsilane (1.2 mL, 5 mmol). The reaction mixture was degassed one more time and the reaction flask was evacuated and flushed with argon. The reaction mixture was stirring at 70 °C for 12 h. After cooling to room temperature the precipitated salt was filtered off. The filtrate was evaporated and 150 mL of water were added. The mixture was extracted with diethyl ether until the aqueous phase was colorless. The combined organic phases were dried over MgSO₄, and the solvent was evaporated. The residue was purified by flash chromatography on a silica gel column with petroleum ether to give **11b** as

a yellow oil (852 mg, 81 %). ^1H NMR (CDCl_3 , δ ppm): δ 6.88 (s, 2H), 3.83 (m, 4H), 1.71 (m, 2H), 1.64-1.16 (m, 16H), 1.02-0.80 (m, 12H), 0.24 (s, 18H).

*Fluorescence quantum yield calculation*⁸:

In the same apparatus the quantum yield of an unknown is related to that of a standard by Eqn. S1:

$$\Phi_u = \Phi_s [(A_s * F_u * n_u^2) / (A_u * F_s * n_s^2)] \quad (\text{Eqn. S1})$$

where: the u subscript refers to the unknown and s to the standard and other symbols have the following meanings: Φ is quantum yield, A is absorbance at the excitation wavelength, F the integrated emission area across the band and n 's are respectively index of refraction of the solvent containing the unknown (n_u) and the standard (n_s) at the temperature of the emission measurement.

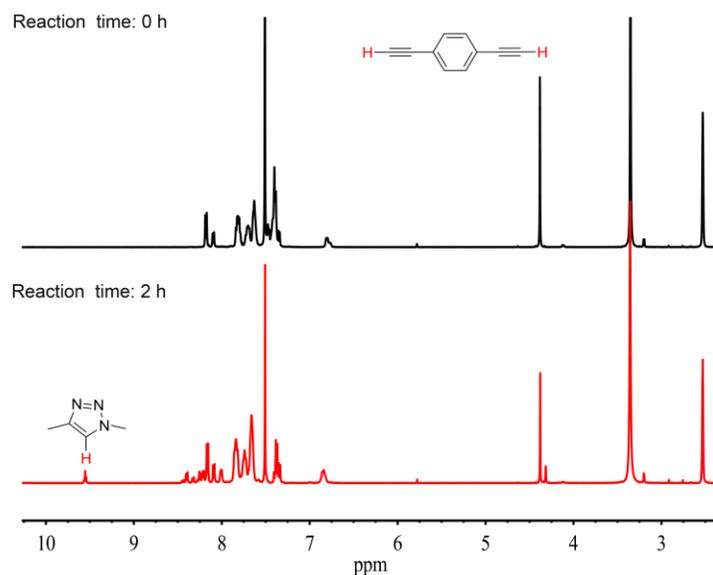


Fig. S1 The ^1H NMR spectra of the starting materials containing **1**, **2**, and $\text{Cu}(\text{PPh}_3)_3\text{Br}$ in D_6 -DMSO (black line) and the reaction mixture after 2 h at 50 °C. (red line).

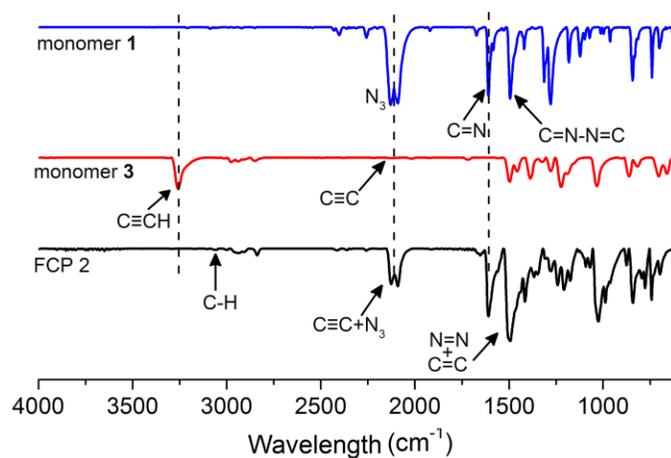


Fig. S2 FTIR spectra of **1**, **3**, and FCP **2**.

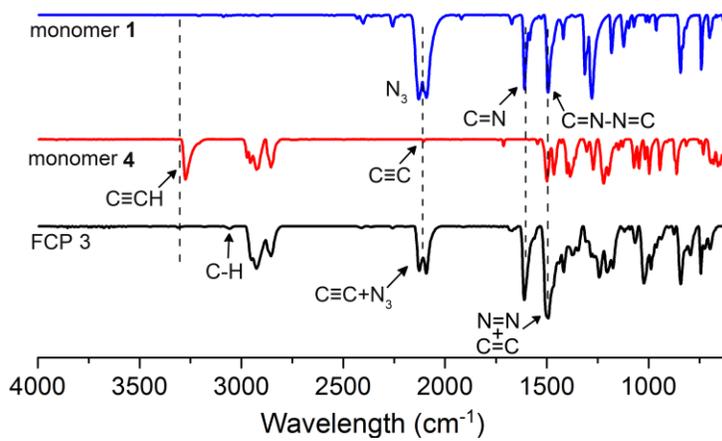


Fig. S3 FTIR spectra of **1**, **4**, and FCP **3**.

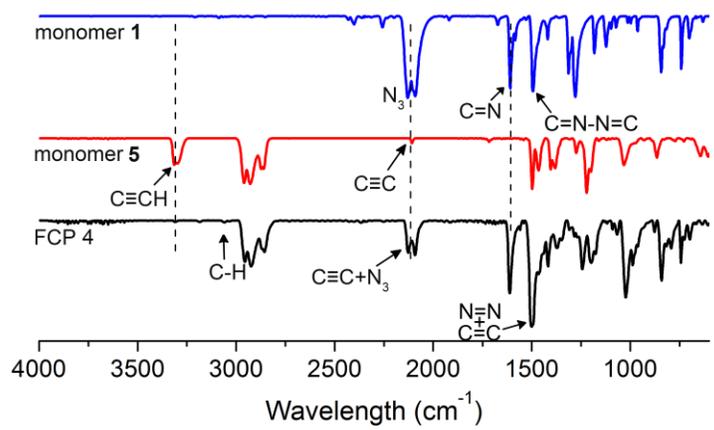


Fig. S4 FTIR spectra of **1**, **5**, and FCP **4**.

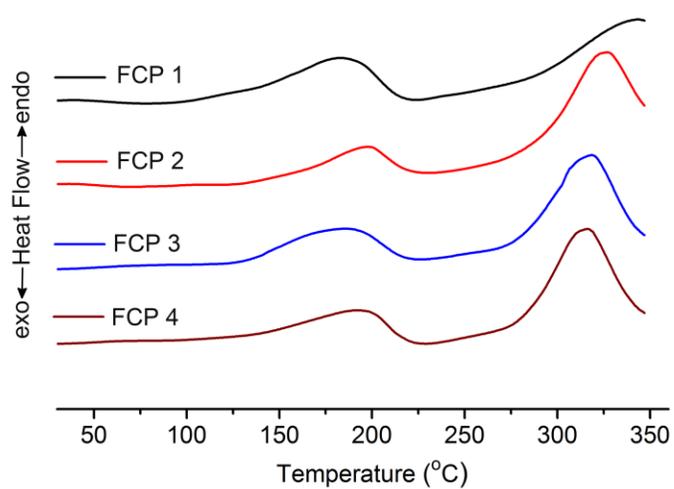


Fig. S5 DSC curves of the FCPs.

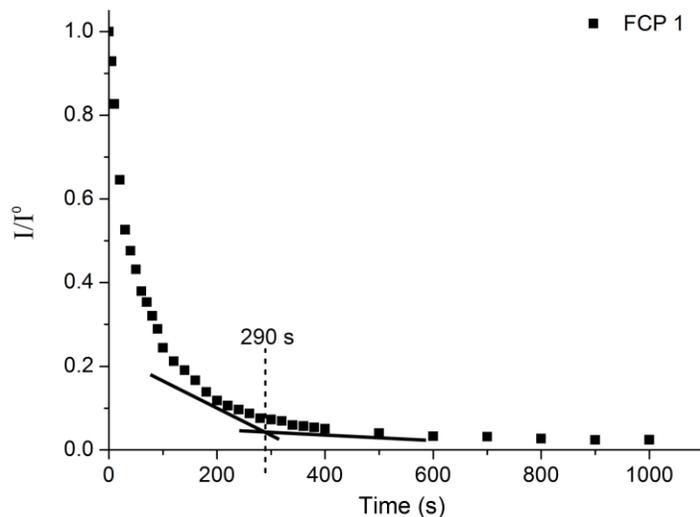


Fig. S6 The kinetics study of FCP 1 (46 μM in DMF, corresponding to the triazole unit) towards 1.0 eq. Ag^+ . The fluorescence intensities at 377 nm were used, $\lambda_{\text{ex}} = 323$ nm, room temperature.

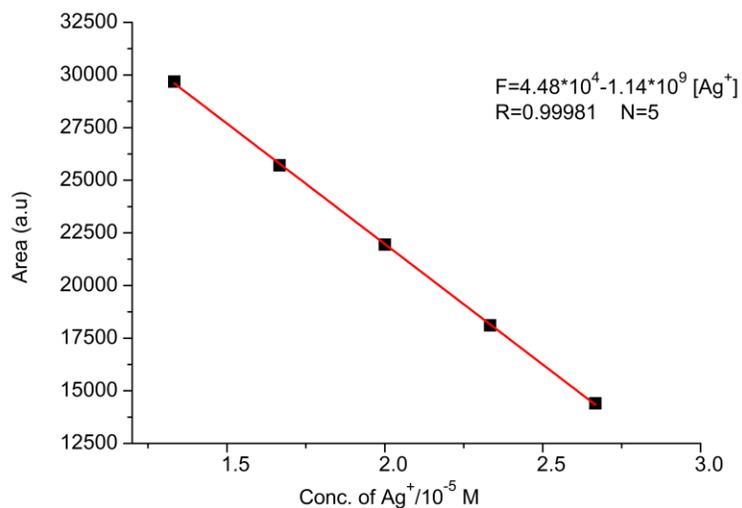


Fig. S7 Calibration curve of FCP 1 in DMF upon the addition of Ag^+ . Excitation wavelength was 323 nm. A curve equation was $F = 4.468 \times 10^4 - 1.1447 \times 10^9 [\text{Ag}^+]$, $R = 0.99981$, $N = 5$. Standard Error was 161.2423, which was got in the range of Ag^+ concentrations from 1.33×10^{-5} to 2.66×10^{-5} $\text{mol} \cdot \text{L}^{-1}$. According to the

equation and the standard deviation of the blank, $C_{DI}=(3*\text{standard error})/\text{slope}$, the lowest detection limit(C_{DI}) of the polymer sensor solution for Ag^+ was determined to be as low as $4.22 \times 10^{-7} \text{ mol L}^{-1}$.

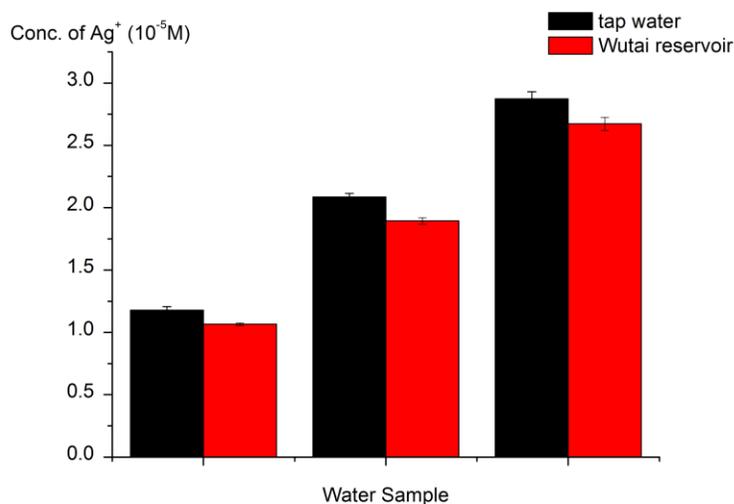


Fig. S8 The application of FCP 1 ($46 \mu\text{M}$ in DMF, corresponding to the triazole unit) in detecting the concentration of Ag^+ in real water samples.

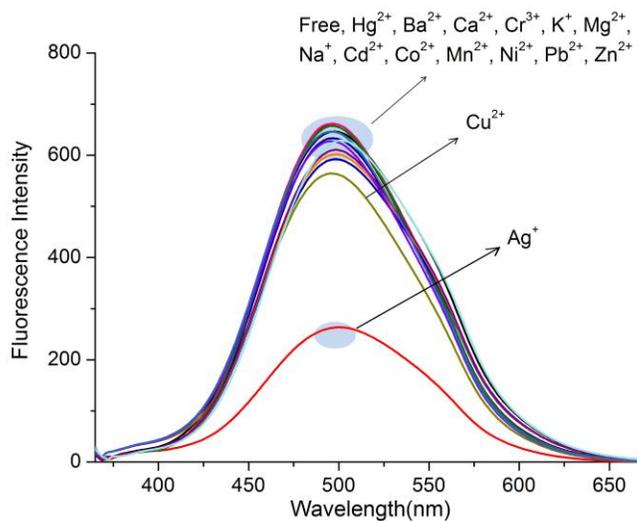


Fig. S9 The selectivity of FCP 2 ($41 \mu\text{M}$, corresponding to the triazole unit) towards Ag^+ and other metal ions. The fluorescence measurement was taken at $\lambda_{\text{ex}} = 347 \text{ nm}$ in DMF at room temperature in the presence of metal ions (10 equiv.).

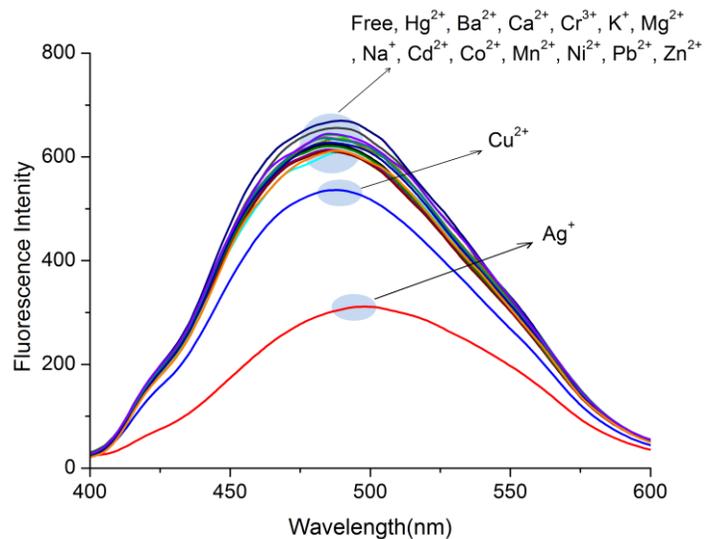


Fig. S10 The selectivity of FCP 3 (32 μ M, corresponding to the triazole unit) towards Ag⁺ and other metal ions. The fluorescence measurement was taken at $\lambda_{\text{ex}} = 365$ nm in DMF at room temperature in the presence of metal ions (10 equiv.).

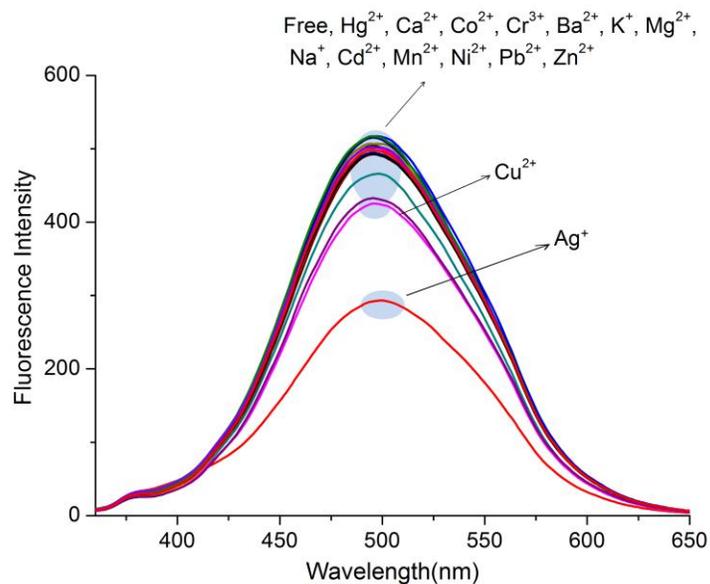


Fig. S11 The selectivity of FCP 4 (29 μ M, corresponding to the triazole unit) towards Ag⁺ and other metal ions. The fluorescence measurement was taken at $\lambda_{\text{ex}} = 340$ nm in DMF at room temperature in the presence of metal ions (10 equiv.).

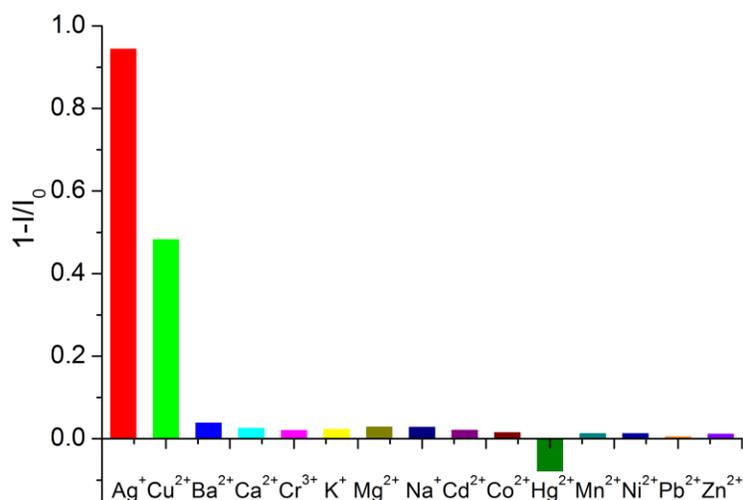


Fig. S12 Fluorescence quenching efficiencies of FCP 1 (46 μM , corresponding to the triazole unit) in DMF in the presence of various metal ions (1.0 equiv. for Ag^+ , 10 equiv for other metal ions), $\lambda_{\text{ex}}=323$ nm.

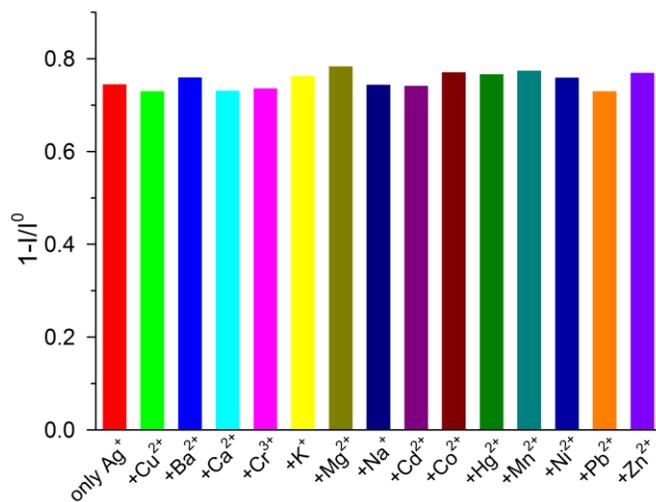


Fig. S13 Metal specificity of FCP 1 (46 μM , corresponding to the triazole) in DMF with a mixture of Ag^+ and other metal ions (Ag^+ : other metals = 1 : 5 in equiv.). The equivalent of Ag^+ was kept for 0.6 equiv., $\lambda_{\text{ex}} = 323$ nm.

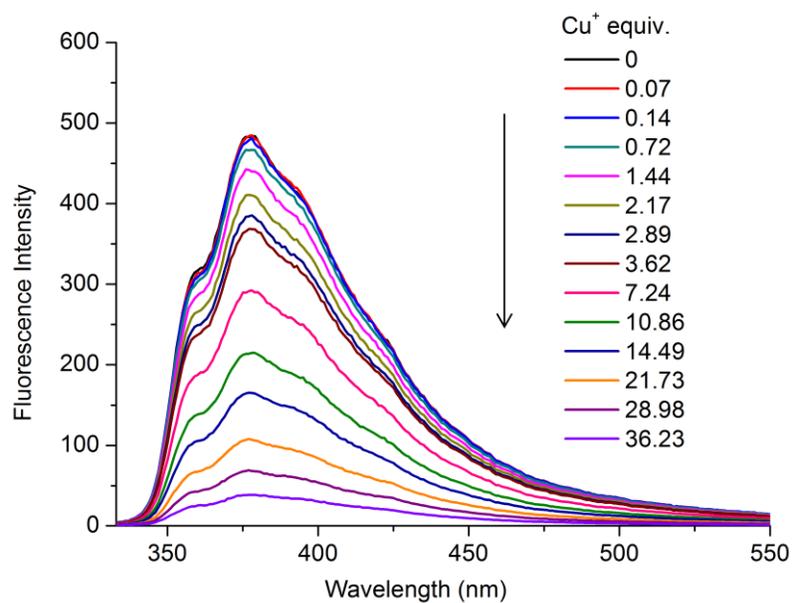


Fig. S14 Fluorescence quenching of FCP 1 (46 μM, corresponding to triazole unit) in DMF upon the addition of Cu⁺ with increasing concentrations (0 -36.23 equiv.), $\lambda_{\text{ex}} = 323 \text{ nm}$.

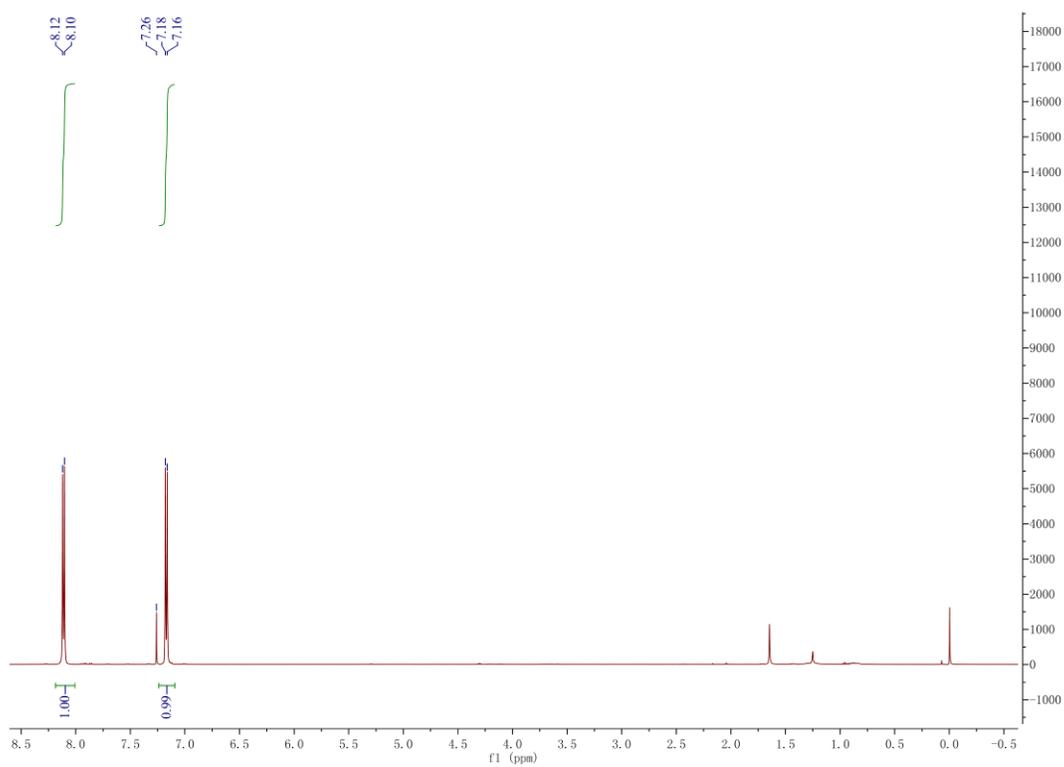


Fig. S15 ¹H NMR spectrum of monomer 1.

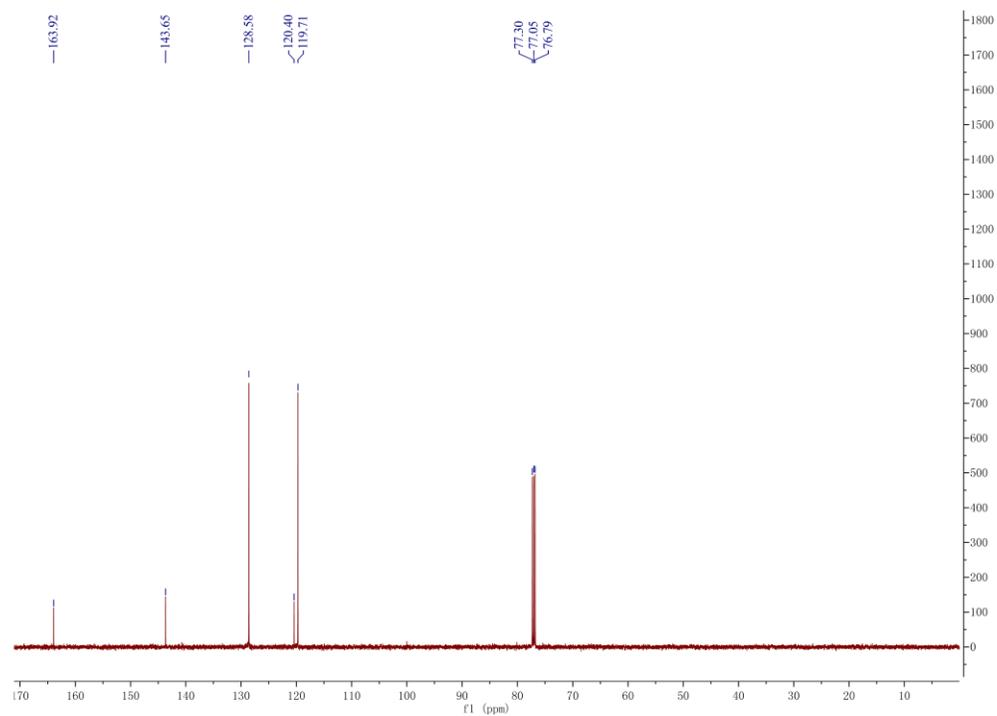


Fig. S16 ^{13}C NMR spectrum of monomer 1.

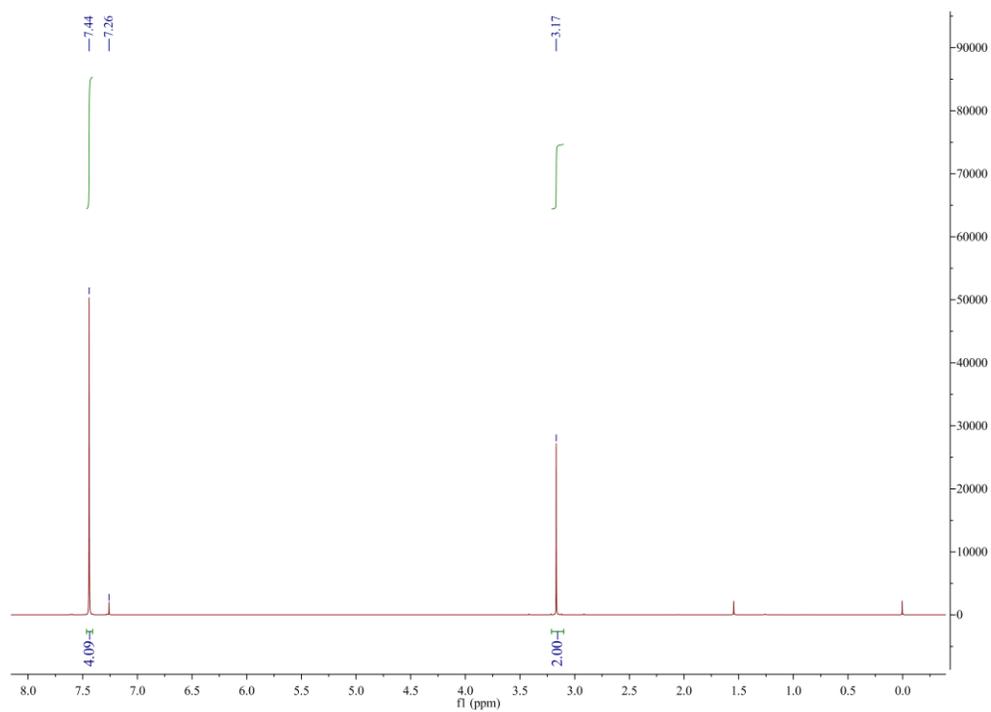


Fig. S17 ^1H NMR spectrum of monomer 2.

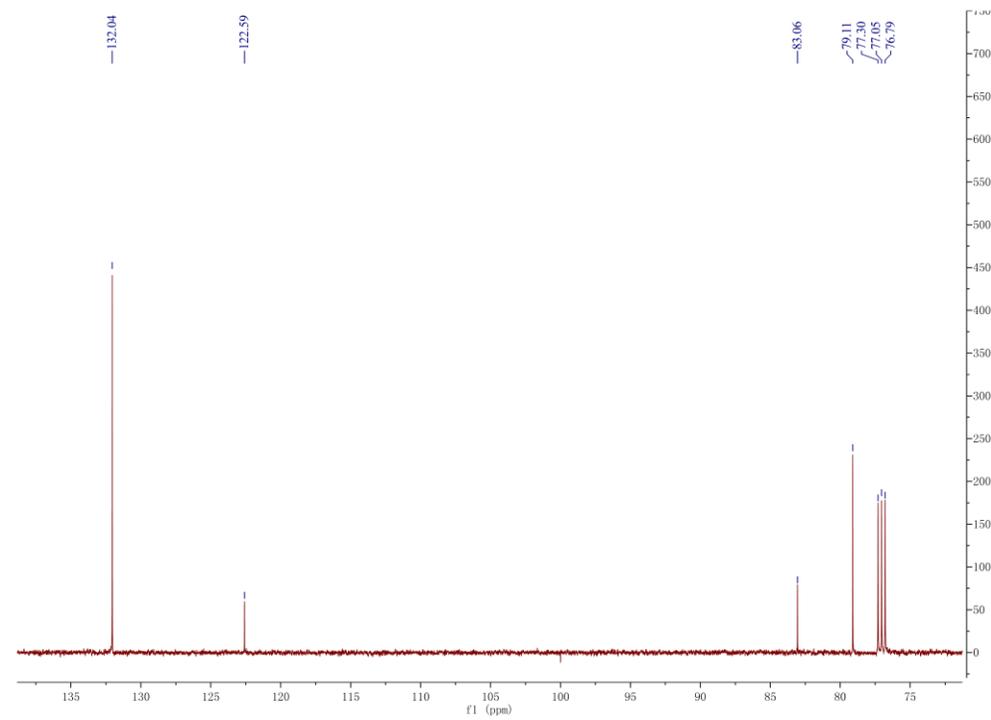


Fig. S18 ^{13}C NMR spectrum of monomer **2**

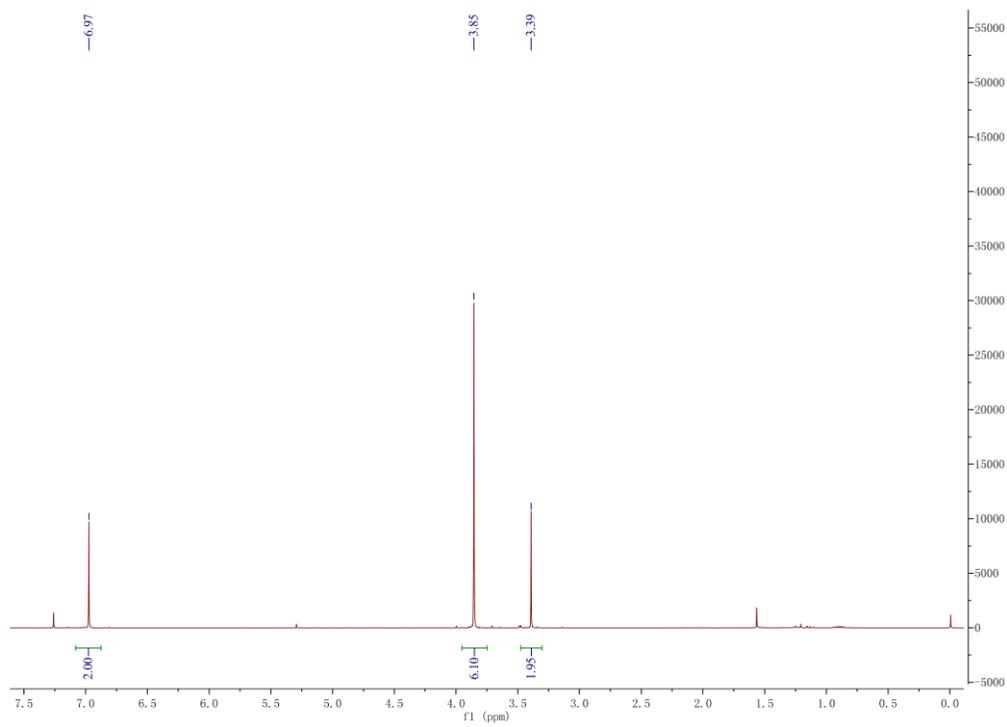


Fig. S19 ^1H NMR spectrum of monomer **3**

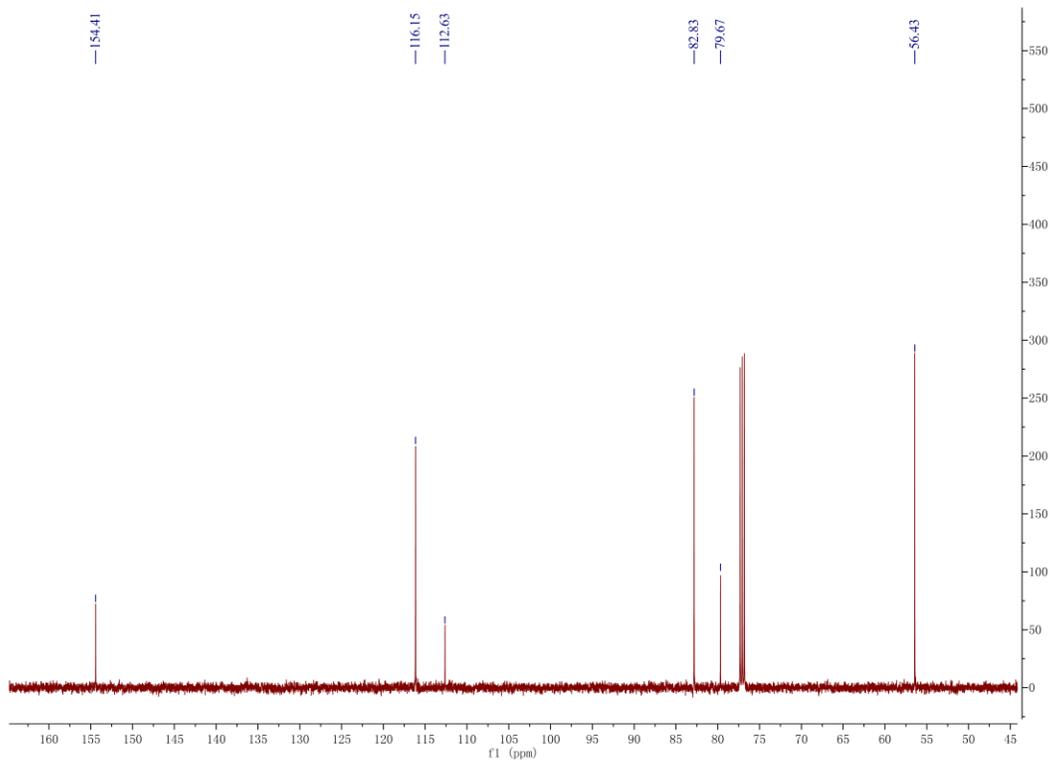


Fig. S20 ¹³C NMR spectrum of monomer 3.

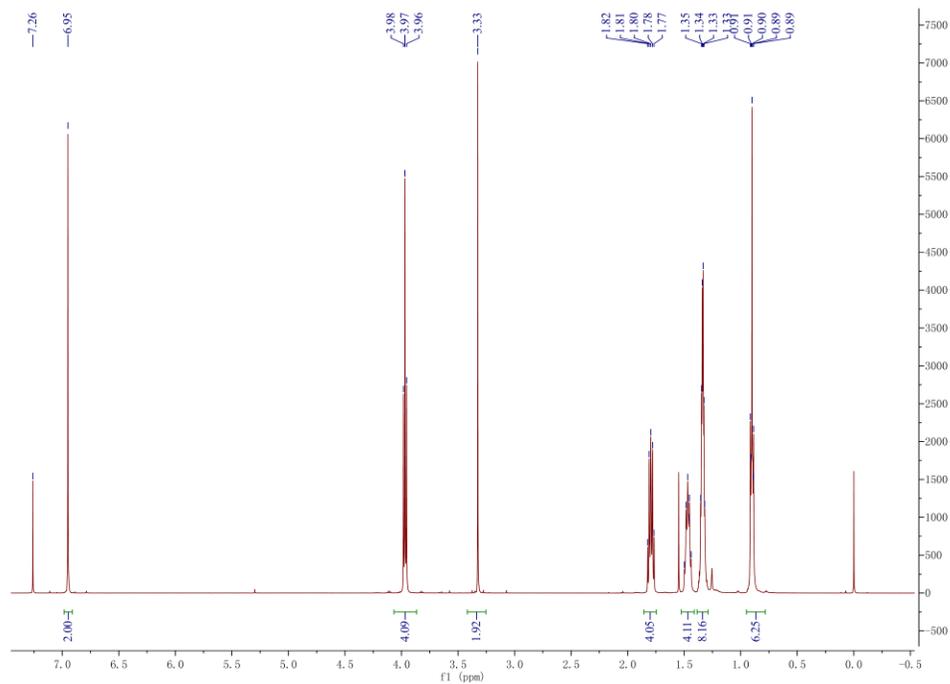


Fig. S21 ¹H NMR spectrum of monomer 4.

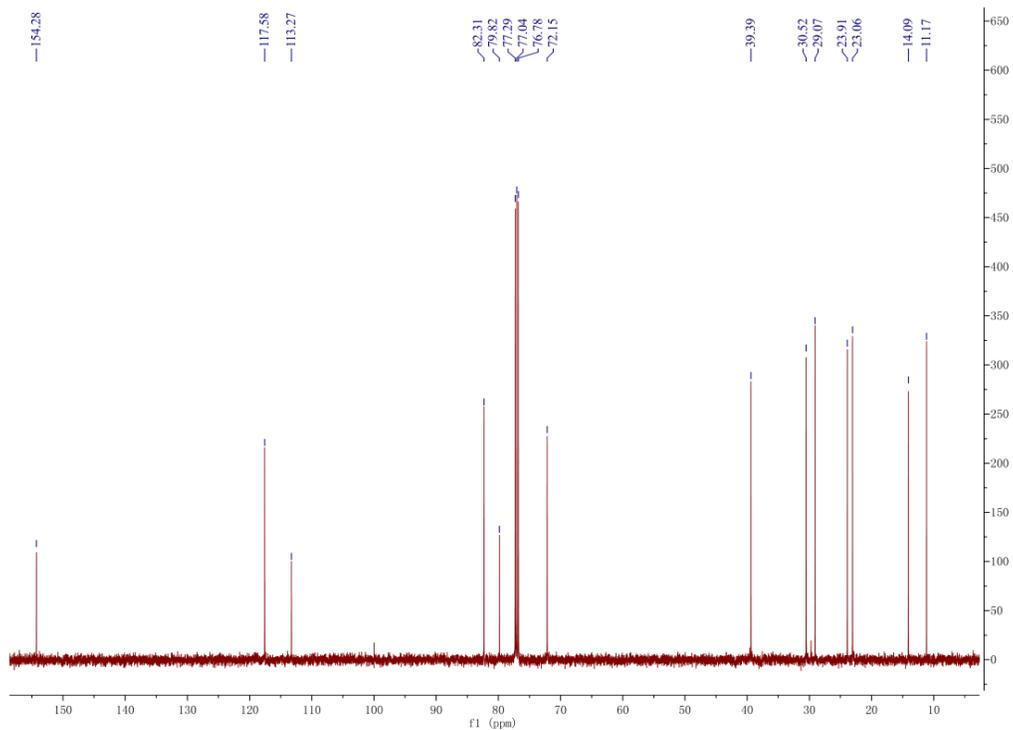


Fig. S22 ^{13}C NMR spectrum of monomer **4**.

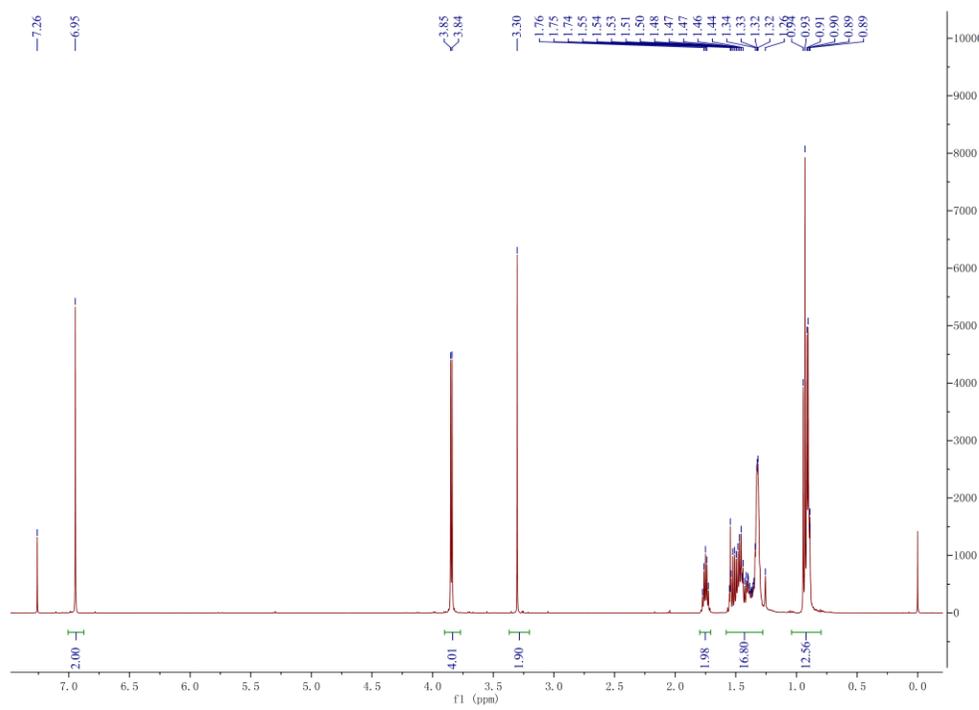


Fig. S23 ^1H NMR spectrum of monomer **5**.

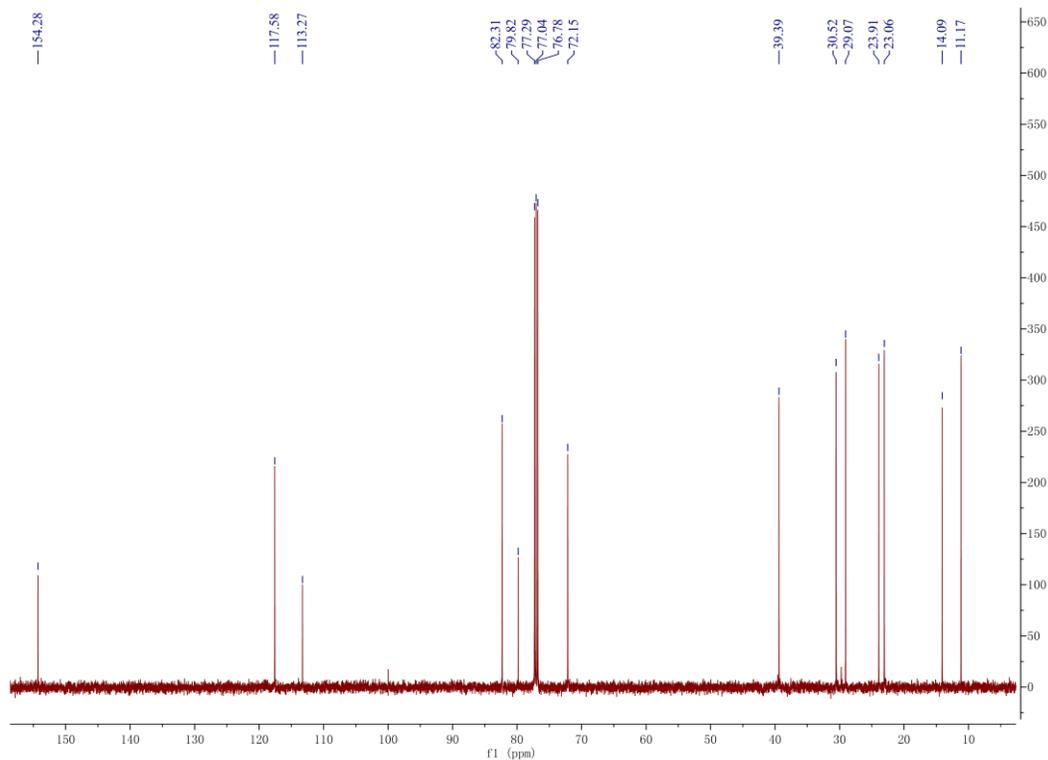


Fig. S24 ^{13}C NMR spectrum of monomer **5**.

Reference:

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