Supporting information for

A novel self-assembled platform for ratiometric fluorescent detection of spermine

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Materials and methods

Spermine, spermidine, cadaverine, putrescine and adenosine triphosphate (ATP) were purchased from Aladdin, Shanghai Mayer chem. Reagents Co. (Shanghai, China), Xiaan Wolsen Bio. Reagents Co. (Xiaan, China), and were used as received. All solvents and reagents used were reagent grade and were used without further purification unless otherwise stated. **SQ** was synthesized and purified as reported previously.[S1] Absorption and emission spectra were collected by using a Shimadzu 1750 UV-visible spectrometer and a RF-5301 fluorescence spectrometer (Japan), respectively. Water surface tension was recorded with BZY-3B surface tension measurer (China). DLS measurements were performed on a Delsa^{TM} Nano system (Beckman Coulter, U.S.A.). AFM (Nanoscope Ⅴ) was performed in the ambient air condition in the tapping mode, a frequency near resonance. The scan rate was 1 Hz with a scan field of view of 500 nm× 500 nm to 5μm× 5μm. The microstructure of the samples was analyzed by field emission scanning electron microscopy (FESEM, S-4800). All samples were dried and detected at room temperature with SE detection at 10.0 kV. HPLC was performed in Shimadzu LC-15C (Japan). Chromatographic conditions as follows: column temperature: 30 C; mobile phase: methanol/water =7:3; flow rate: 1 mL/min elution, UV detection wavelength: 254 nm; sample volume: 20 uL. Urine spermine determination was carried out using dansyl chloride dericatization with 1,7-diaminioheptane as internal standard.[S2]

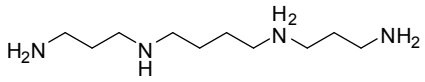
Sample preparation, data acquisition and analysis

All measurements were performed at 25 ^{0}C. Stock solution of **SQ** (5.0×10^{-4} M) was prepared in ethanol and diluted in distilled water (pH 7.0) to 5.0×10^{-6} M for titration experiments. Appropriate ratio of **POC12** was added to the above aqueous solution of **SQ** for detection of spermine. Stock solutions of polyamines and other competitive analytes were prepared in distilled water and diluted in distilled water (pH 7.0) for titration experiments. UV and emission spectra were monitored within 20 seconds. There were three measurements at each concentration for one sample. Urine was collected from different adult volunteers and filtrated with 0.4 μM filter membrane. The filtrates were diluted 3 times with distilled water for use.

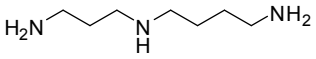
Calculation of detecting limit

Detecting limit DL = $K\times S_{b1}/S$, where K=3, S_{b1} is the standard derivation of the blank solution and S is the slope of the calibration curve. [S3]

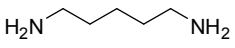
Structures of some polyamines



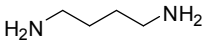
Spermine



Spermidine

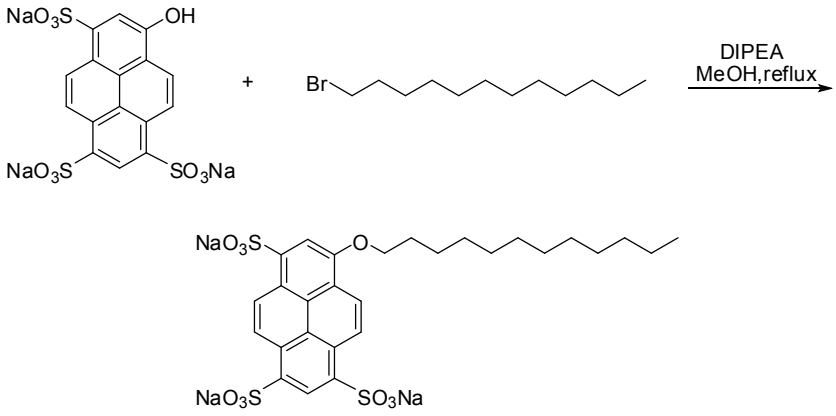


Cadaverine



Putrescine

Synthesis



POC12

To a refluxing solution of trisodium 8-hydroxypyrene-1,3,6-trisulfonate (596.5 mg,

1.14 mmol) in MeOH was added 1-bromododecane (1.00 g, 4.02 mmol) and *N*,*N*-diisopropylethylamine (0.5 mL, 2.94 mmol), and the resulting mixture was refluxed with stirring for 6 days. The solution was cooled to room temperature and then filtered and concentrated under reduced pressure. Purification on silica gel afforded **POC12** (238.0 mg, 30%) as a yellow solid. ^{1}H NMR (500 MHz, CD_3OD) δ 9.38 (s, 1H), 9.30-9.07 (m, 3H), 8.69 (d, J = 9.6 Hz, 1H), 8.42 (s, 1H), 4.48 (t, J = 6.4 Hz, 2H), 2.13-2.02 (m, 2H), 1.70 (dt, J = 15.2, 7.4 Hz, 2H), 1.54-1.25 (m, 16H), 0.91 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CD_3OD) δ 153.14, 140.75, 136.64, 129.91, 129.43, 127.06, 125.84, 125.15, 124.85, 123.14, 122.29, 121.16, 120.74, 109.09, 69.03, 53.88, 31.67, 29.40, 26.00, 22.33, 13.04.

S1 Y. Xu, Z. Li, A. Malkovskiy, S. Sun and Y. Pang, *J. Phys. Chem. B*, 2010, **114**, 8574.

S2 C. Molins-Legua, P. Campins-Falcó, A. Sevillano-Cabeza and M. Pedrón-Pons, *Analyst*, 1999, **124**, 477.

S3 A. Hakonen, *Anal. Chem.*, 2009, **81**, 4555.

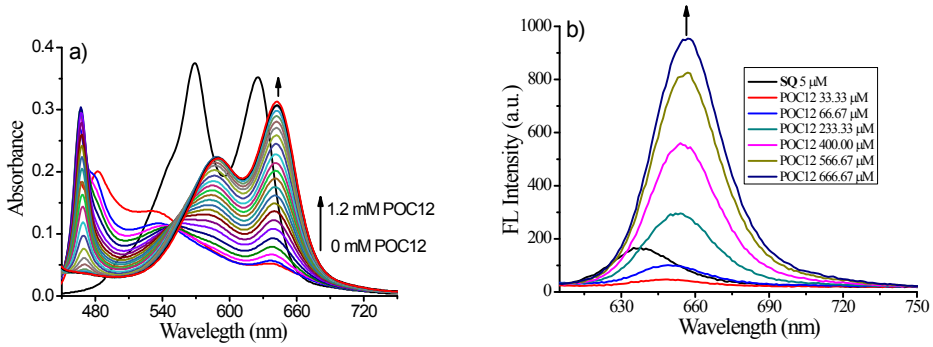


Fig. S1 UV-Vis (a) and fluorescence (b) spectra of **SQ** (5 μM) upon addition of **POC12** in distilled water (pH 7.0). (λ_{ex} = 600 nm)

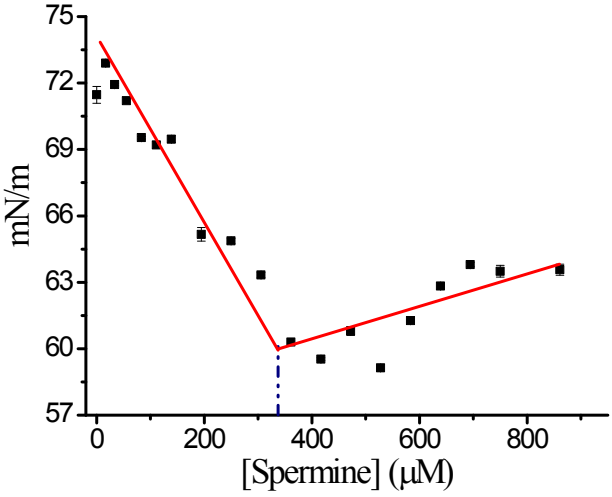


Fig. S2 The Surface tension of water as a function of **POC12** concentration in the presence of **SQ** (5 μM). There are two linear segments in the curve and a sudden decrease of the slope, implying that the CMC of **POC12** is approximately 0.33 mM in water.

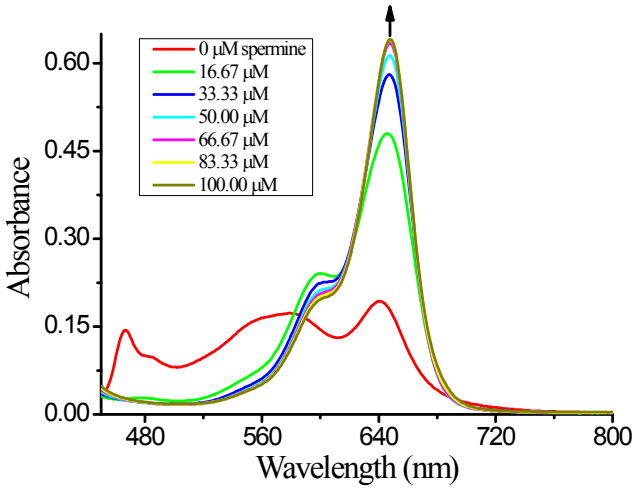


Fig. S3 The absorption spectra change of **SQ** (5 μM) in the presence of **POC12** (0.33 mM) upon addition of spermine.

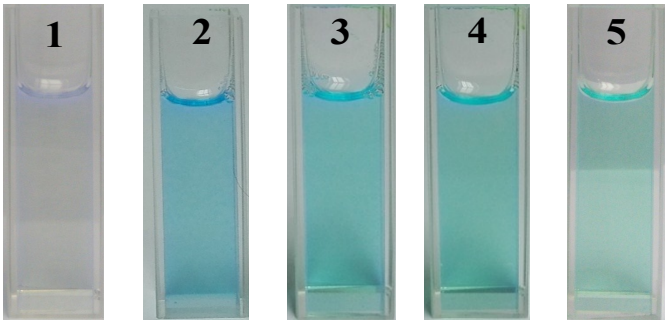


Fig. S4 The color change of **SQ** (5 μM) solution in the presence of **POC12** (0.33 mM) upon addition of spermine. 1) 0 μM; 2) 10 μM; 3) 43.3 μM; 4) 66.7 μM; 5) 100.0 μM.

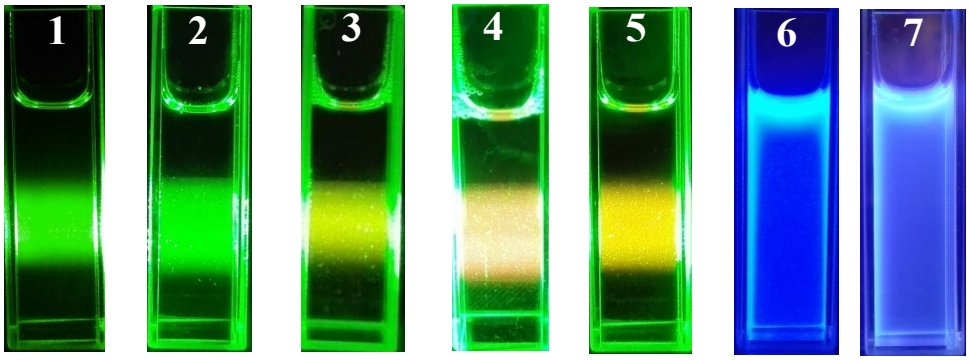


Fig. S5 The fluorescence color change of **SQ** (5 μM) solution in the presence of **POC12** (0.33 mM) upon addition of spermine as excitation at 550 nm. 1) 0 μM; 2) 10 μM; 3) 43.3 μM; 4) 66.7 μM; 5) 100.0 μM, and before (6) and after (7) addition of spermine (100.0 μM) as excited by hand-held UV lamp (365 nm)

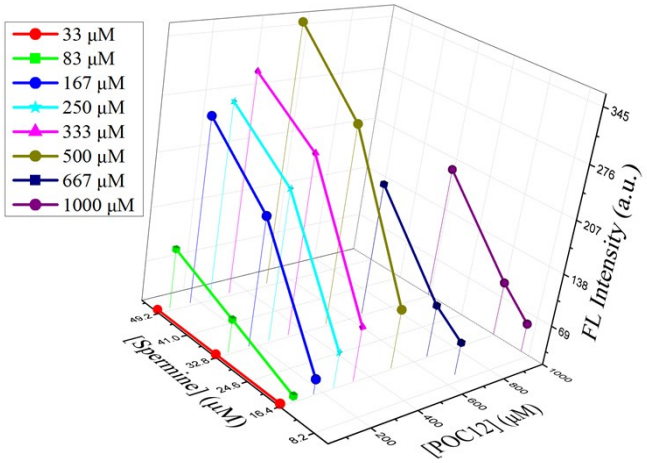


Fig. S6 The fluorescence response of **SQ** (5 μM) in the presence of different concentration of **POC12** to spermine.

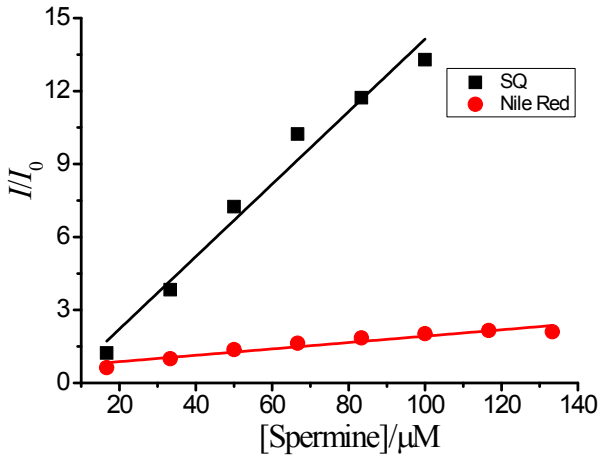


Fig. S7 The relative fluorescence change of **POC12** (0.33 mM) that encapsulated **SQ** (5 μM) at 665 nm or Nile Red (5 μM) at 646 nm upon addition of spermine.

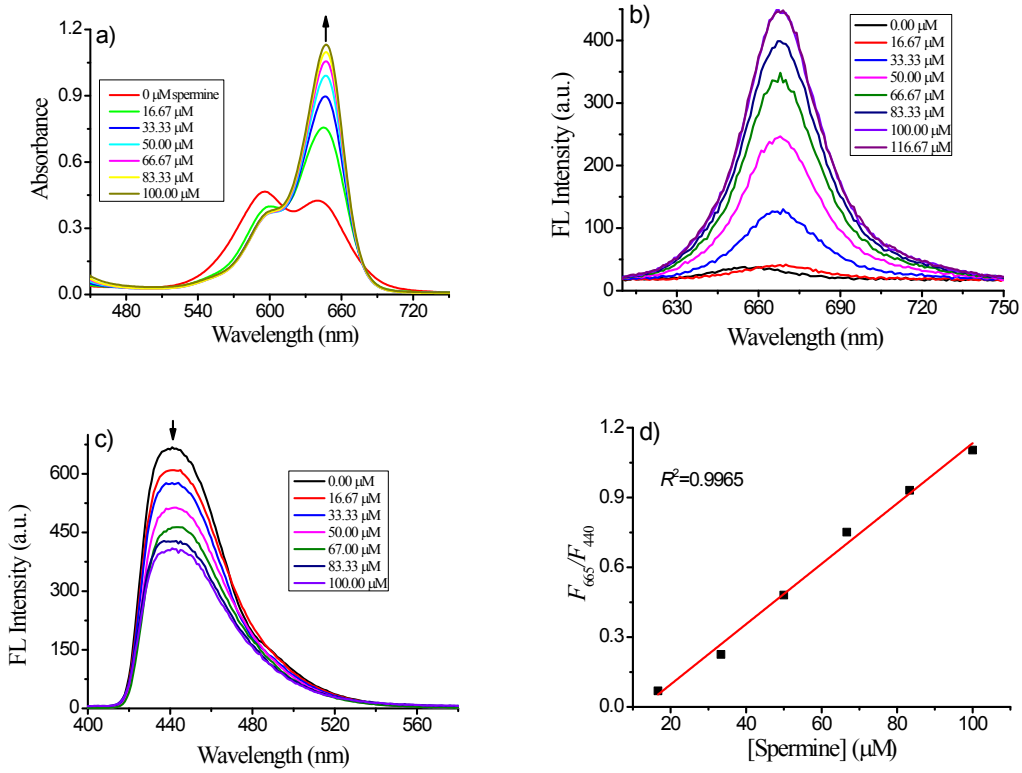


Fig. S8 Absorption (a) and fluorescence spectra change of **SQ** (5 μM) in the presence of **POC12** (0.33 mM) upon addition of spermine, excitation at 600 (b) and 350 nm (c). The relative fluorescence intensity changes (I_{665}/I_{440}) (d) to the concentration of spermine in PBS buffer (5 mM, pH=7.4).

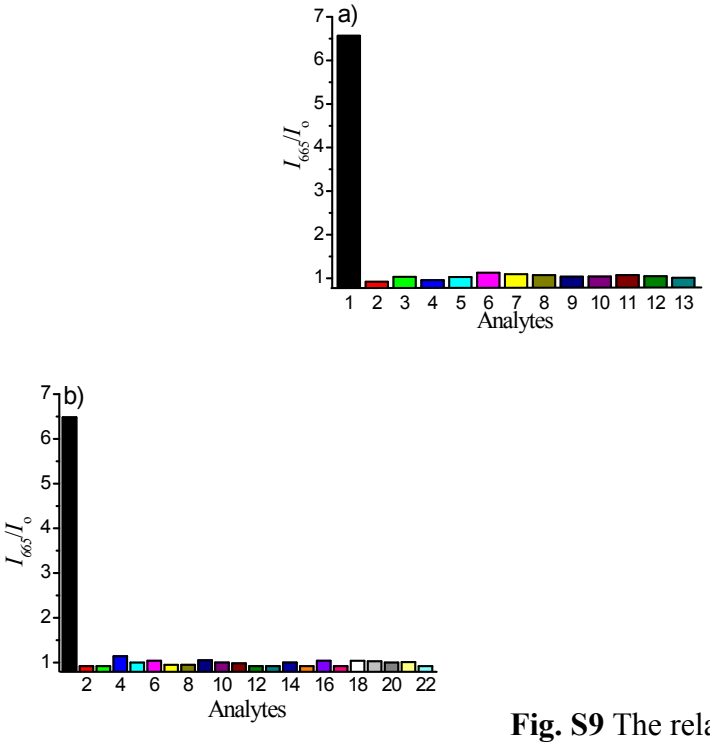
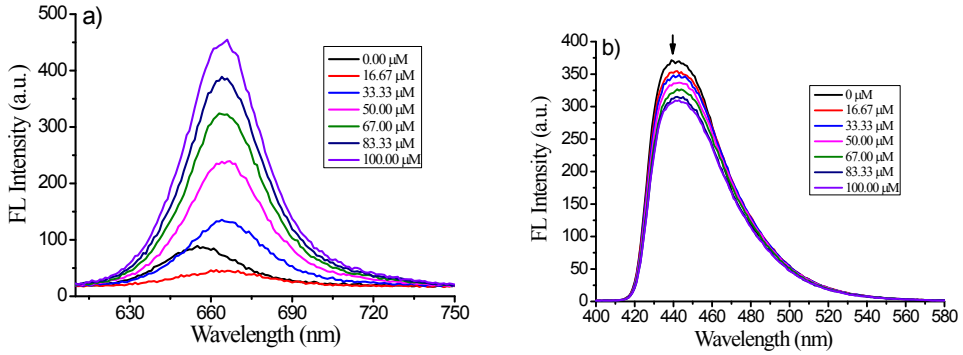


Fig. S9 The relative fluorescence changes of **SQ** (5 μM) at 665 nm in the presence of **POC12** (0.33 mM) upon addition of different analytes (66.7 μM). a). 1) Spermine, 2) $MgSO_4$, 3) $AlCl_3$, 4) $Cu(NO_3)_2$, 5) $Pb(NO_3)_2$, 6) NaCl, 7) LiCl, 8) $ZnCl_2$, 9) $CaCl_2$, 10) $MnCl_2$, 11) $CdCl_2$, 12) Ce_2CO_3, 13) glucose; b) 1) Spermide, 2) Lysine, 3) Tryptophan, 4) Tyrosine, 5) Alanine, 6) Glycine, 7) Leucine, 8) Glutamic acid, 9) Threonine, 10) Ethylenediamine, 11) 1,6-Diaminohexane, 12) n-Butylamine, 13) Diaethylamine, 14) Triethylamine, 15) Tris(2-aminoethyl)amine, 16) Aniline, 17) Benzylamine, 18 α-Phenylethylamine, 19) p-Aminobenzylamine, 20) 1,2-Diaminobenzene, 21) 1,3-Benzenediamine, 22) Adenosine triphosphate.



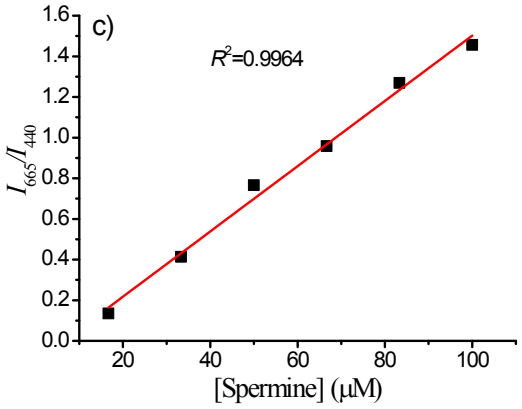


Fig. S10 Fluorescence spectra change of **SQ** (5 μM) in the presence of **POC12** (0.33 mM) upon addition of spermine, excitation at 600 (a) and 350 nm (b). The relative fluorescence intensity changes (I_{665}/I_{440}) (c) to the concentration of spermine in urine.

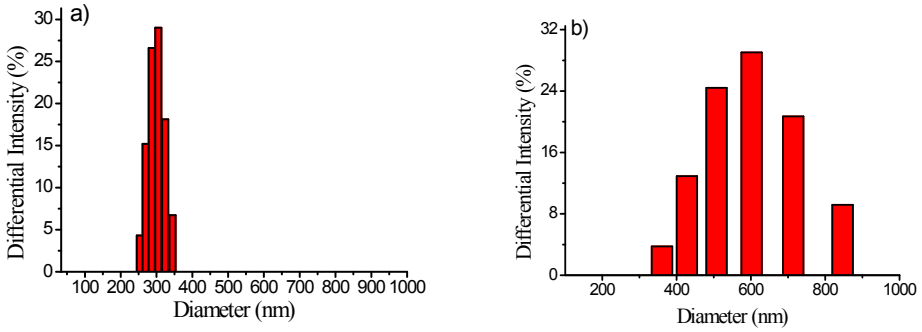


Fig. S11 DLS analysis of **SQ** (5 μM) in the presence of **POC12** (0.33 mM) before (a) and after (b) addition of spermine (50 μM).

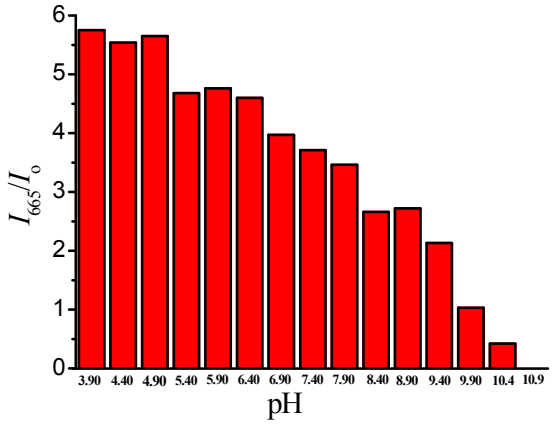


Fig. S12 The relative fluorescence response at 665 nm of **s**olution including **SQ** (5 μM), **POC12** (0.33 mM) and spermine (66.7 μM) to different pH values.

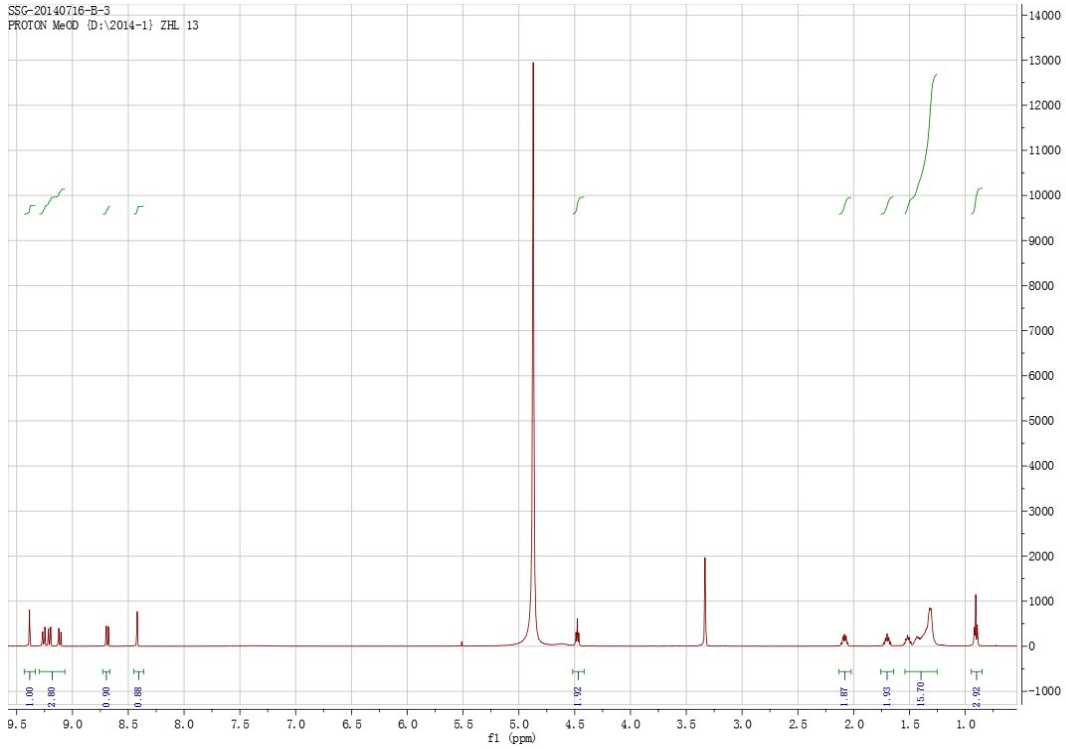


Fig. S13 ^{1}H NMR spectrum of **POC12**.

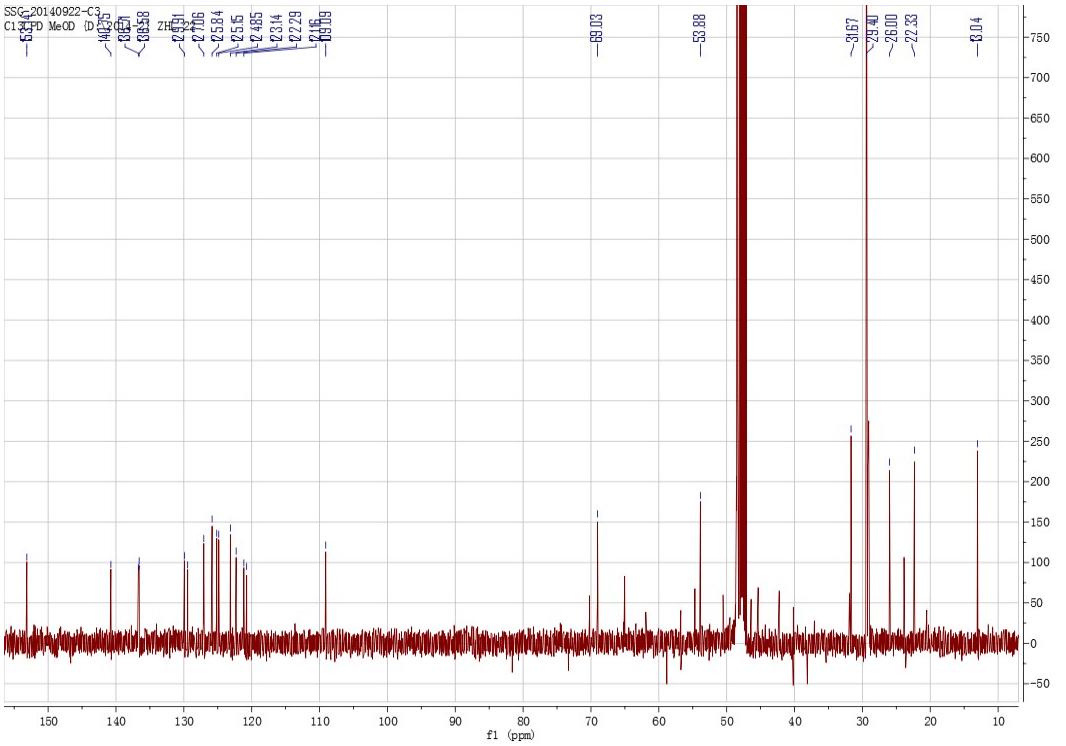


Fig. S14 ^{13}C NMR spectrum of **POC12**.