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Electronic Supplementary Information

Pillar[5]arene-functionalized paper as fluorescent sensor for cyanide ion in water

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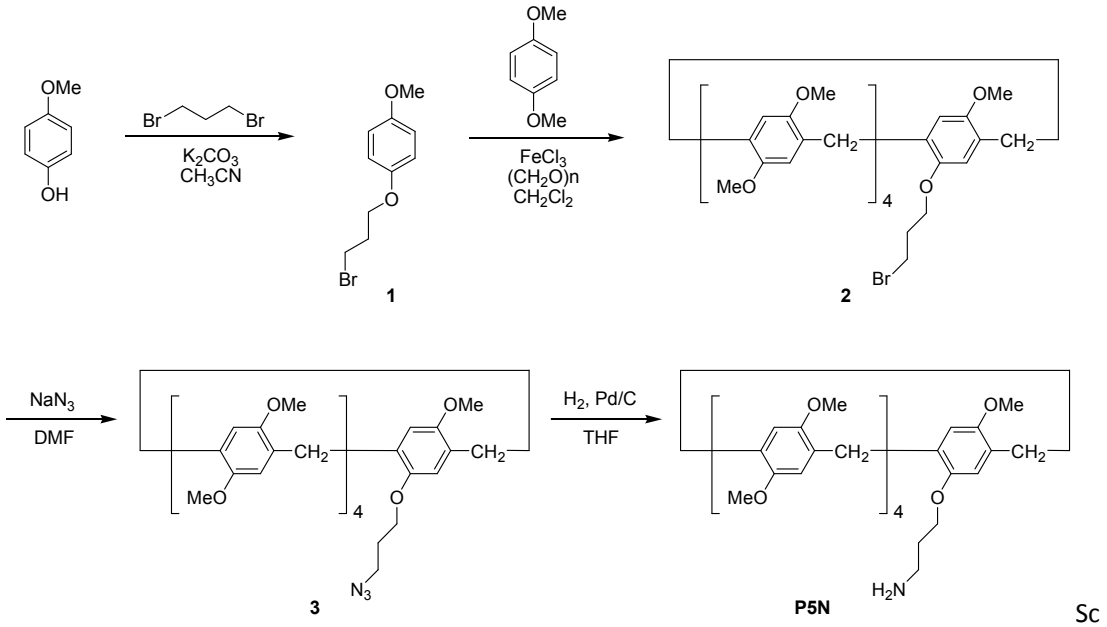
Table of Contents

Experimental Section

Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. Melting points are uncorrected. All reactions were performed under an atmosphere of dry nitrogen. NMR spectra were recorded on Bruker 400 MHz spectrometer in the indicated solvents. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards. ESI mass spectroscopy was perfomed on a Thermo Scientific LTQ XL instruments. UV-Vis experiments were performed on a Persee TU-1901 spectrometer. Fluorescent experiments were recorded on an Edinburgh FLS-980 spectrometer.

Job's method. Series of the solutions of host **P5N** and solution of guest **FI** were prepared in THF/H_2O (3:2). The volumn of the host and guest solutions varied from 1:9 to 9:1, respectively, with the total concentration of the host and guest being constant. The solutions were used without further stirring. The absorbance A of the complexation systems was measured at the maximum absorbance wavelength of the complex. The absorbance values were used to plot a diagram from which maximum the structures of the complexes were deduced.



Scheme S1 Synthetic route of host **P5N**

Compound 1. To the solution of 4-methoxyphenol (15.3 g, 0.121 mol) in acetonitrile (300 ml) was

added 1,3-dibromopropane (59.9 ml, 0.605 mol) and potassium carbonate (52.6 g, 0.363 mol) under nitrogen atmosphere. The reaction mixture was stirred under reflux for 16 h. After cooling to r.t., the mixture was evaporated under vacuum and dissolved with dichloromethane. The organic phase was washed with water and dried over anhydrous Na_2SO_4. The solution was evaporated under vacuum, and the residue was purified by column chromatography (petroleum ether: dichloromethane, 2:1) to give **1** as yellow liquid (27.0 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (d, 4H), 4.05 (t, 2H), 3.77 (s, 3H), 3.61 (t, 2H), 2.29 (t, 2H).

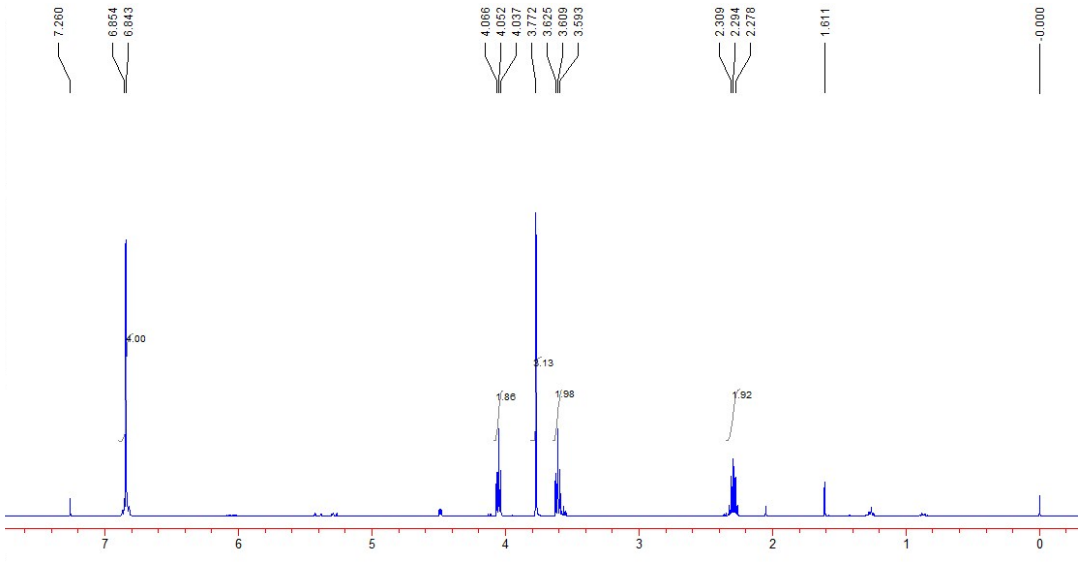


Fig. S1 ^{1}H NMR of compound 1.

Compound 2. To the solution of **1** (10.0 g, 40.8 mmol) in dichloromethane (700 ml) was added

1,4-dimethoxybenzene (34.1 g, 245 mml) and paraformaldehyde (28.9 g, 960 mmol) under nitrogen atmosphere. $FeCl_3$ (6.57 g, 40.5 mmol) was added to the solution, and the mixture was stirred at r.t. for 2 h and poured into water. After filtration, the organic phase was washed with water and dried over anhydrous Na_2SO_4. After evaporation under vacuum, the residue was purified by column chromatography (petroleum ether: dichloromethane, 2:1) to give **2** as white solid (3.5 g, 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80-6.82 (m, 9H), 6.70 (s, 1H), 3.96 (t, 2H), 3.78 (m, 10H), 3.67-3.69 (m, 27H), 3.53 (t, 2H), 2.21 (t, 2H). MS (ESI): m/z 877.3 ($M+Na^+$).

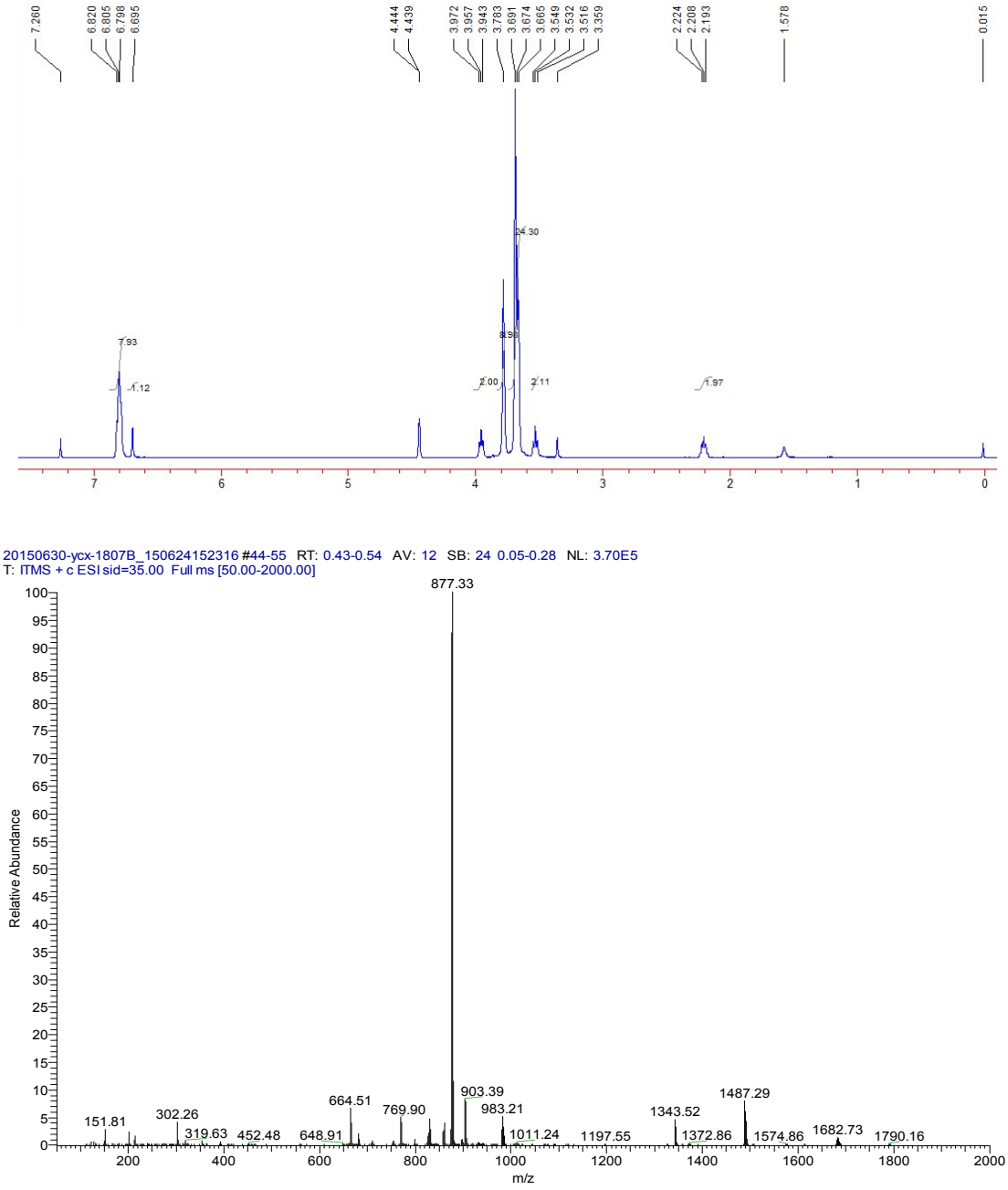


Fig. S2 ^{1}H NMR and MS of compound 2.

Compound 3. To the solution of **2** (7.5 g, 8.7 mmol) in DMF (300 ml) was added sodium azide (5.1

g, 78 mmol). The reaction mixture was stirred at 100 °C for 5 h. After cooling to r.t., the mixture was poured into water (150 ml) and extracted with dichloromethane. The organic phase was washed with water and dried over anhydrous Na_2SO_4. After evaporation under vacuum, the residue was purified by column chromatography (petroleum ether: dichloromethane, 2/1) to give **3** as white solid (7.0 g, 97.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76-6.82 (m, 9H), 6.70 (s, 1H), 3.91 (t, 2H), 3.77 (m, 10H), 3.62-3.69 (m, 27H), 3.43 (t, 2H), 1.97 (t, 2H). MS (ESI): m/z 837.7 ($M+NH_4^+$), 842.7 ($M+Na^+$).

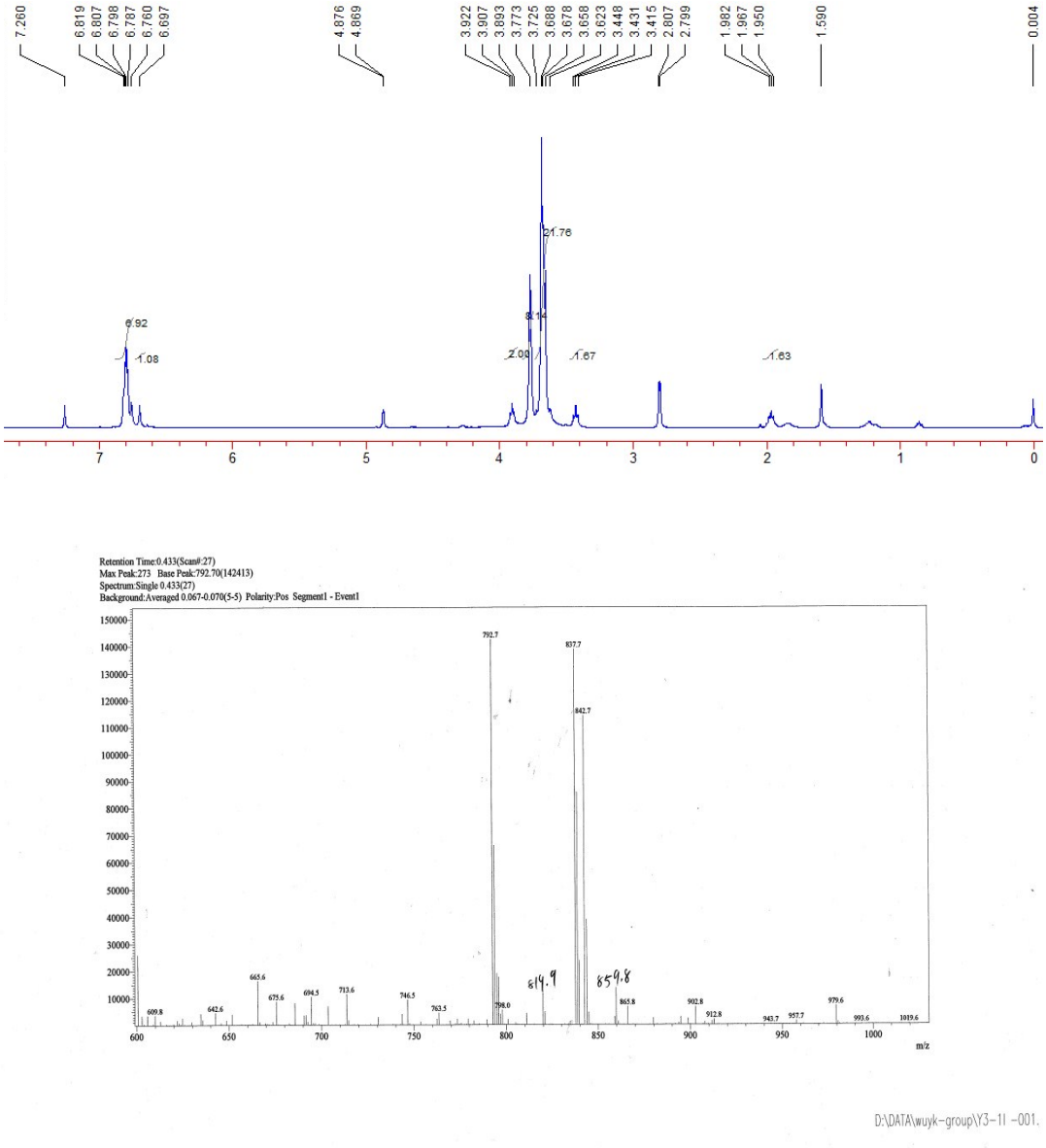
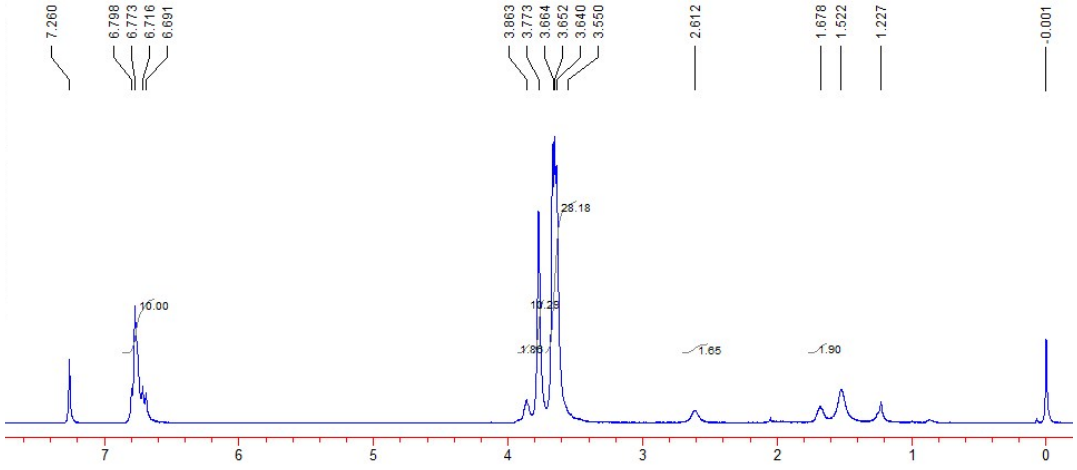
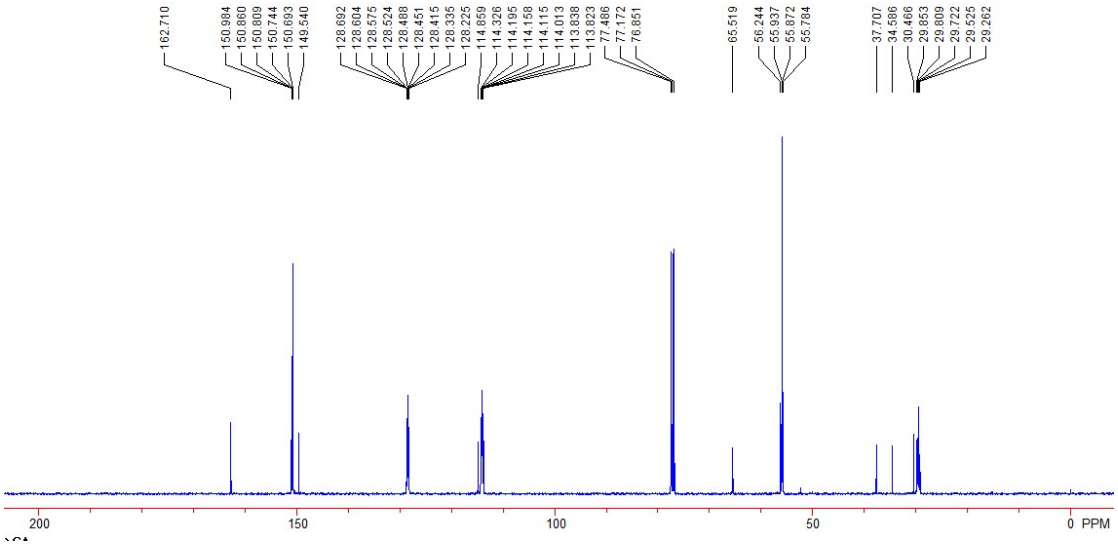


Fig. S3 ^{1}H NMR and MS of compound 3.

Host P5N. A suspension of **3** (5.0 g, 6.1 mmol) and Pd/C (10%, 1.0 g) in THF (200 ml) was stirred

at °C under hydrogen atmosphere (75 psi) for 26 h. The reaction mixture was filtered, and the filtrate was evaporated under vacuum. The residue was purified by column chromatography (dichloromethane: methane, 50/1) to give **4** as white solid (4.3 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69-6.80 (m, 10H), 3.86 (m, 2H), 3.77 (m, 10H), 3.64-3.66 (m, 27H), 2.61 (m, 2H), 1.68 (m, 2H). ^{1}H NMR (400 MHz, $CDCl_3$): δ 151, 150, 128, 115, 114, 66, 56, 38, 35, 30. MS (ESI): m/z 796.7 ($M+H^+$).





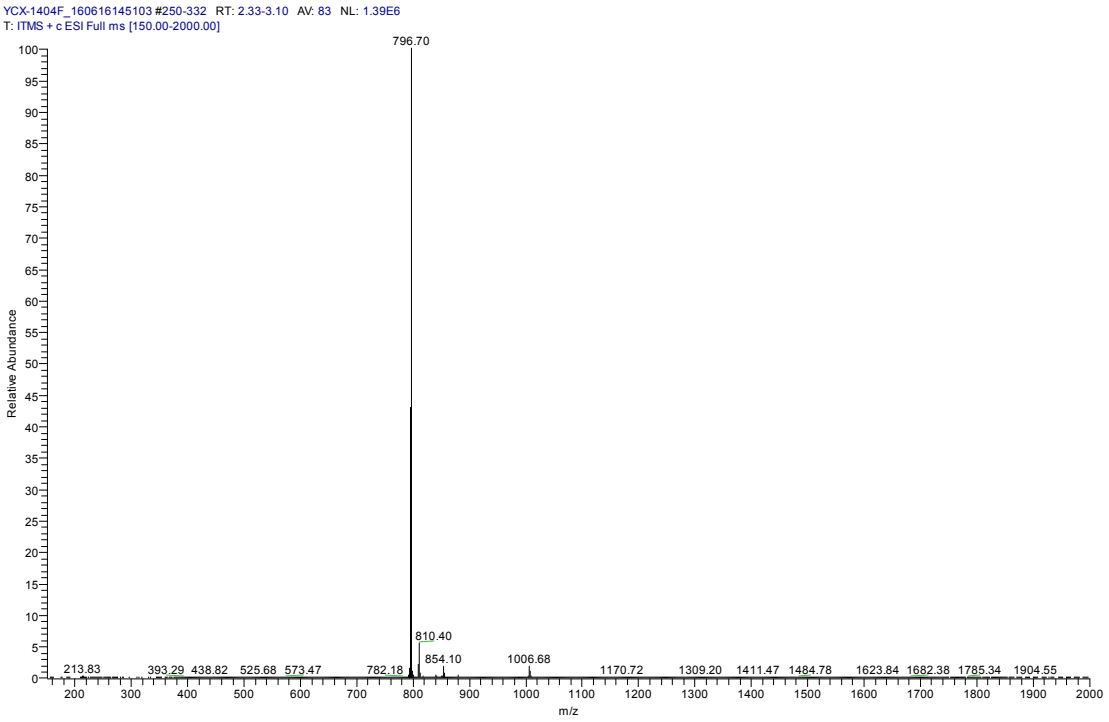
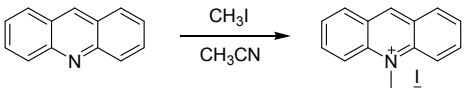


Fig. S4 ^{1}H NMR, ^{13}C NMR and MS of host P5N.



FI

Fluorescent indicator FI. To the solution of acridine (2.06 g, 11 mmol) in acetonitrile (100 ml) was added methyl iodide (5.0 g, 33 mmol). The reaction mixture was stirred under reflux for 24 h. After evaporation under vacuum, the residue was washed with THF and filtered to give **FI** as red solid (1.50 g, 70%). ^{1}H NMR (400 MHz, DMSO): δ 10.21 (s, 1H), 8.79 (d, 2H), 8.64 (d, 2H), 8.47 (t, 2H), 8.04 (t, 2H), 4.86 (s, 3H).

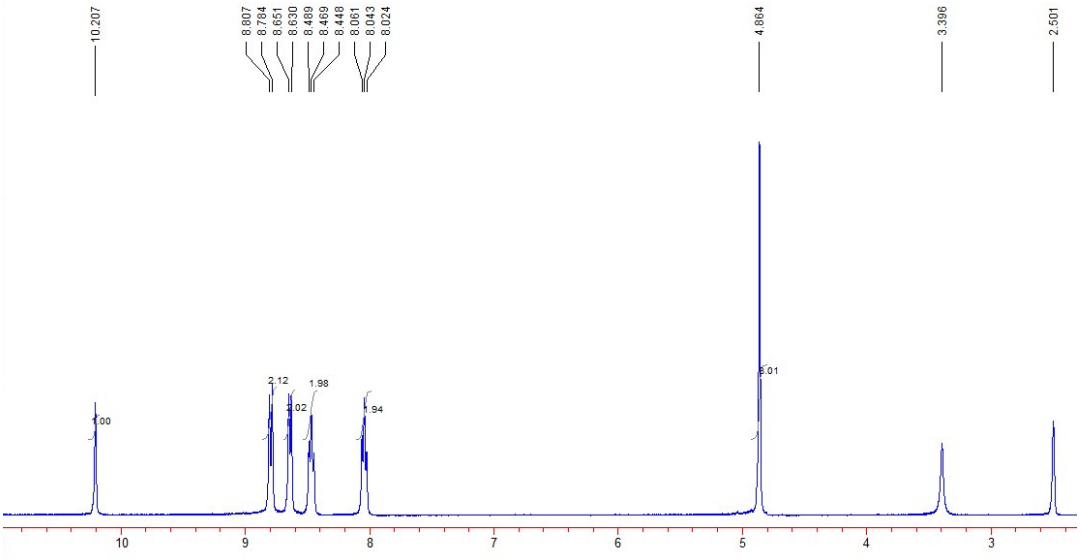
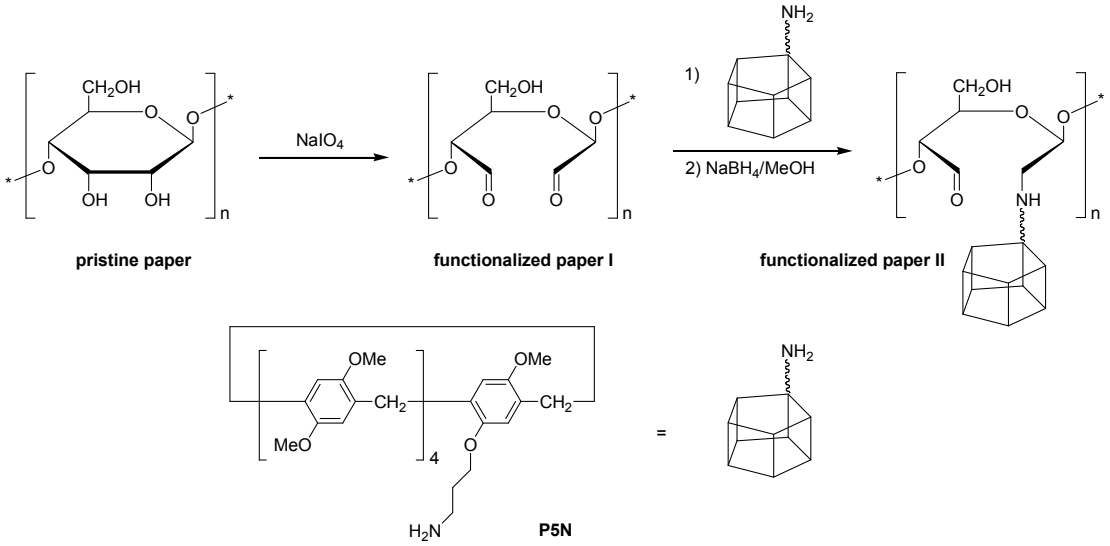


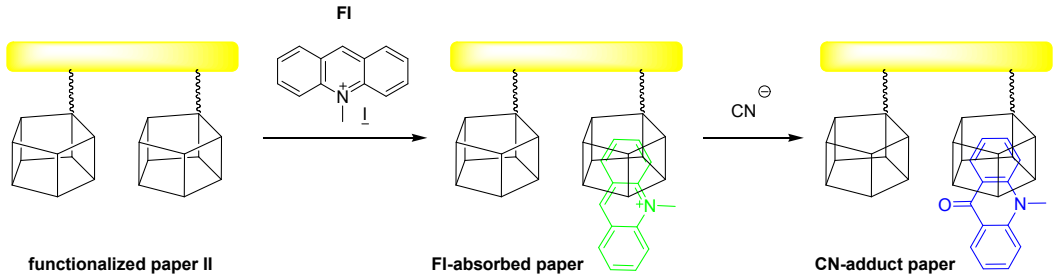
Fig. S5 ^{1}H NMR of fluorescence indicator FI.



Preparation of Pillararene-functionalized paper

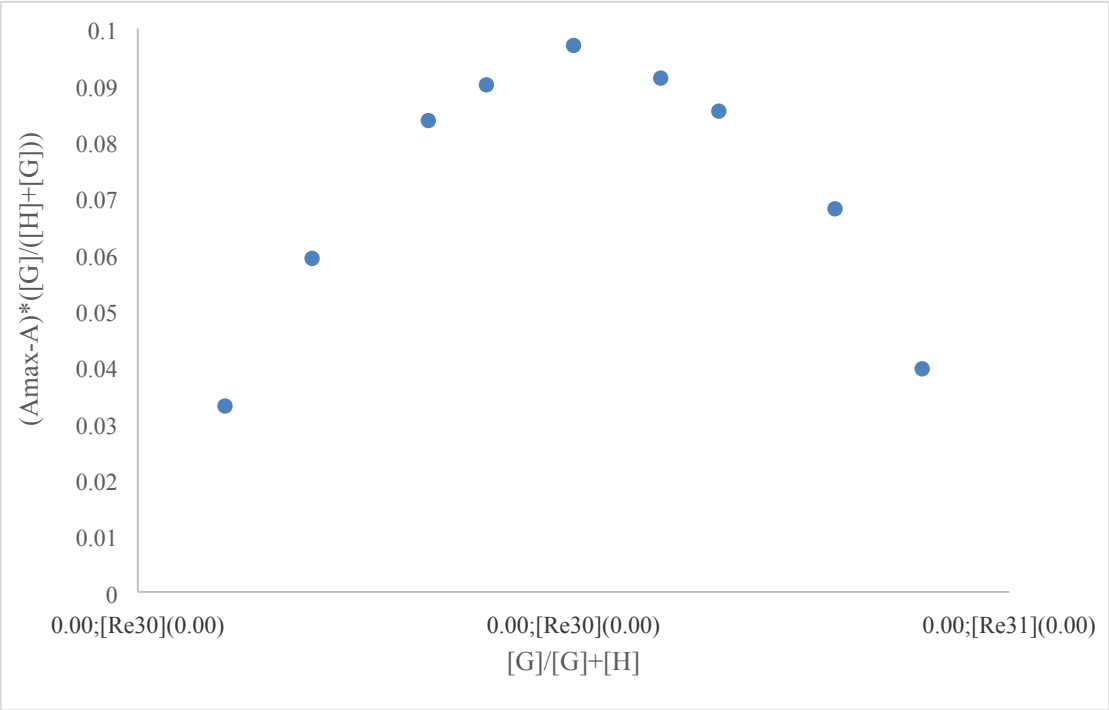
The cellulose paper (1 × 2 cm^2) was washed sequentially with THF, acetone and water, each time for 5 min by ultrasonication. The rinsed paper was immersed into the solution of sodium periodate (0.470 g) in water (20 ml). The mixture was kept in the dark at 40 °C for 5 h. Ethylene glycol (2 ml) was added and continued for 1 h. The paper was separated from the solution and washed three times with water, each time for 5 min by ultrasonication. Then the functionalized paper I was dried under vacuum and stored under argon.

The functionalized paper I was immersed into the solution of **P5N** (0.784 g) in THF (10 ml), catalyzed by 4 Å molecular sieve under argon. The mixture was kept at 50 °C for 10 h. The paper was separated from the solution and washed three times with THF, methanol, respectively, each time for 5 min by ultrasonication. The rinsed paper was immersed into the solution of sodium borohydride (0.178 g) in methanol (10 ml). The mixture was kept at r.t. for 1 h. The paper was separated from the solution and washed three times with methanol, each time for 5 min by ultrasonication. Then the functionalized paper II was dried under vacuum and stored under argon.



Preparation of FI-absorbed paper

The functionalized paper II was immersed into the solution of **FI** (0.05 M) in water. The mixture was kept at r.t. for 5 h. The paper was separated from the solution and washed three times with water, each time for 5 min by ultrasonication. Then the functionalized paper II was dried under vacuum and stored under argon.



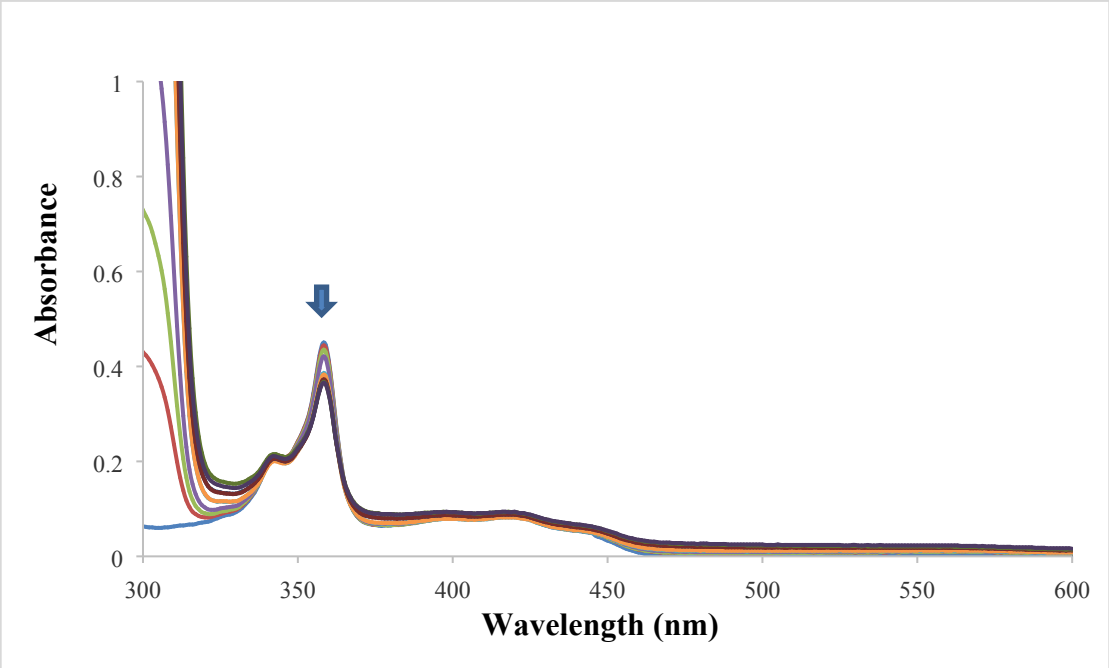


Fig. S6 Job's plot for the complexation between FI and P5N (upper) at the wavelength of 360 nm. UV-Vis titration of **FI** (0.02 mM in THF/H_2O, 2:3 at 298 K) with the increment of P5N: a) 0.0 equiv., b) 0.5 equiv., c) 1.0 equiv., d) 1.5 equiv., e) 2.0 equiv., f) 3.0 equiv., g) 4.0 equiv., h) 5.0 equiv., i) 7.0 equiv., j) 10.0 equiv. (lower).

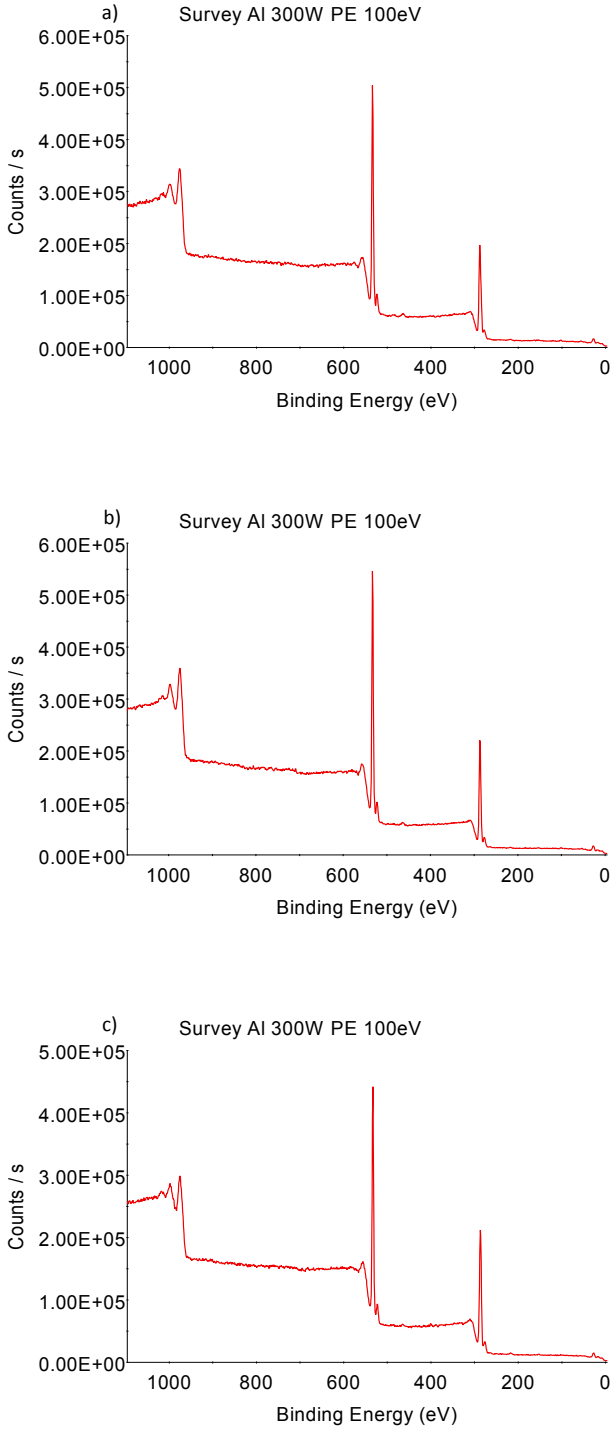


Fig. S7 XPS spectra of a) pristine paper, b) functionalized paper I, c) functionalized paper II.

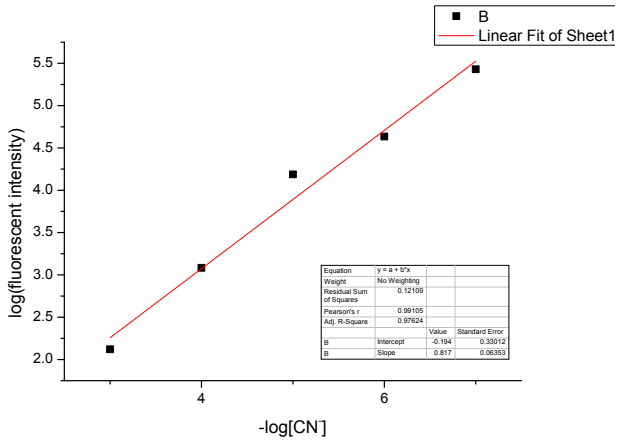


Fig. S8 Plot of the fluorescence intensities as a function of concentrations of cyanide ion.

CN^- F^- Cl^- Br^- I^- NO_3^- SCN^- SO_4^{2-} PO_4^{3-}

Fig. S9 Functionalized paper upon immersion in a series of anions (0.1 mM).

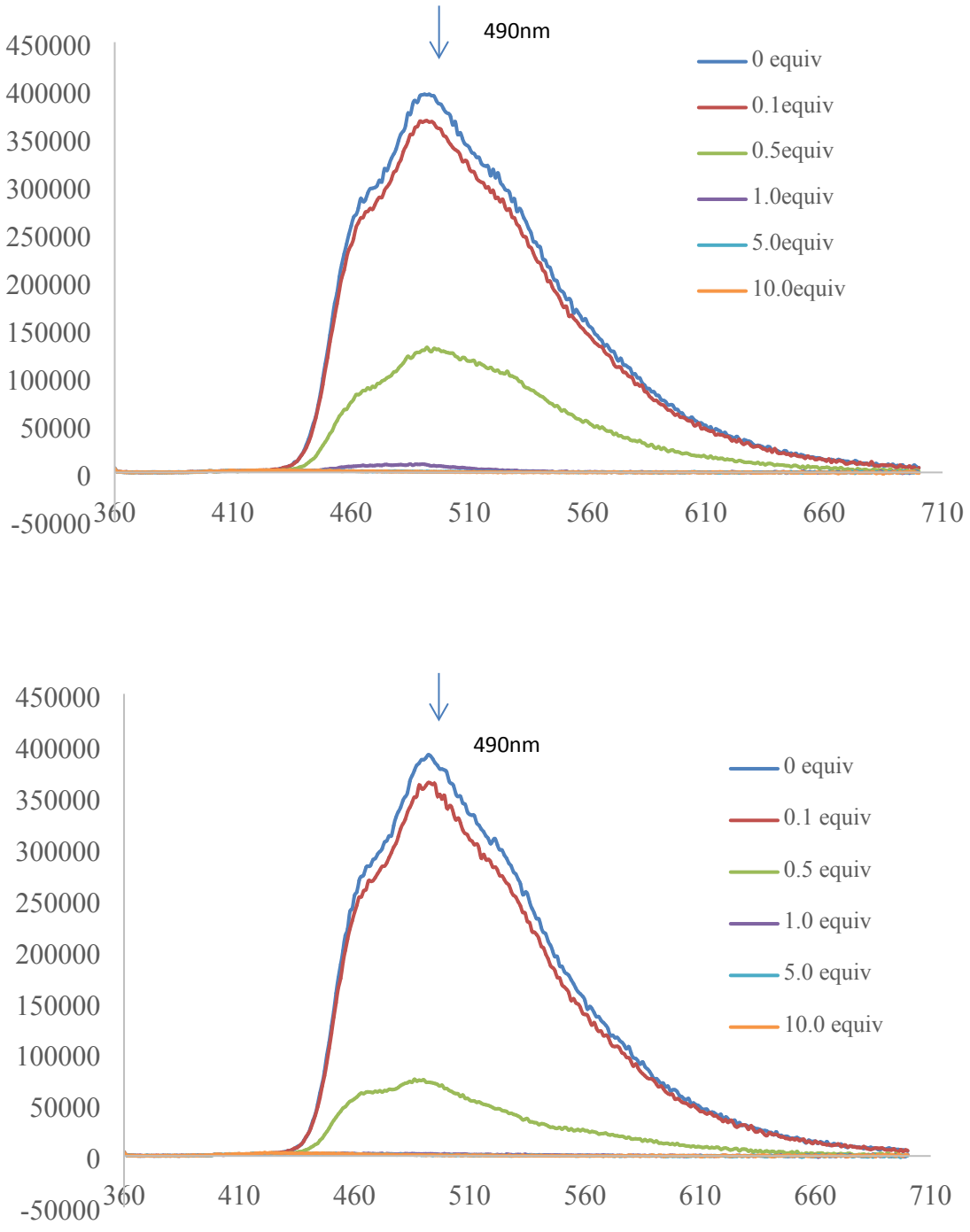


Fig. S10 Fluorescence emission of **FI** (upper) and 1:1 mixture of **P5N** and **FI** (lower) in aqueous solution with increment of cyanide ion at the wavelength of 490 nm.