

Supplementary information for

Fluorescent nanoparticles assembled from poly (ionic liquid) for selective sensor of copper ion

Kun Cui, Xuemin Lu, Wei Cui, Jun Wu, Xumeng Chen and Qinghua Lu**

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University,
Shanghai, China

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Experiment Section

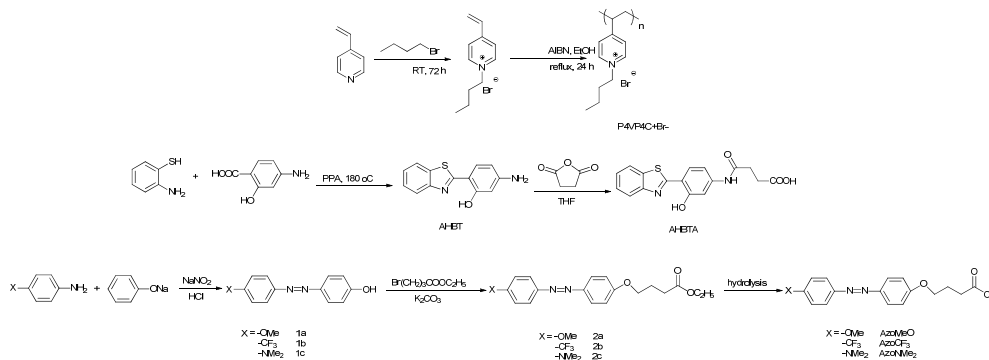
Materials. 4-Vinylpyridine (4VP) was dried over CaH_2 and distilled under reduced pressure before use. 2, 2'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. Other Chemical agents as commercial grade reagents were purchased from Aldrich Chemical Co. and Acros Co. and used directly without further purification. The water used was doubly distilled.

Instruments and Characterization.

Nuclear magnetic resonance (^1H NMR) studies were carried out with a Varian Mercury Plus 400 MHz spectrometer in $\text{DMSO}-d_6$ solvent at room temperature, with chemical shift referenced versus an internal standard (TMS) shifts at 0 ppm. Fourier transform IR (FTIR) spectra were recorded on a Perkin-Elmer Paragon1000 FTIR spectrometer on pressed thin transparent disks of the sample mixed with KBr. The fluorescent spectra measurement were performed on a Perkin-Elmer LS 50B fluorescence spectrometer. Differential scanning calorimetry (DSC) was performed on a TA DSC Q2000 instrument using a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in the temperature range of -60 to $150\text{ }^\circ\text{C}$. The heating cycles were performed twice, but only the result of the second cycle was reported, since the former was influenced by the mechanical and thermal history of the samples. Thermogravimetric analysis was performed using a TA TGA Q5000 instrument using a heated at $20\text{ }^\circ\text{C}/\text{min}$ from room temperature to $700\text{ }^\circ\text{C}$ in a flowing nitrogen atmosphere. Fluorescent nanoparticles dispersed in aqueous solution were examined using a JEOL JSM-7401F field-emission scanning electron microscope (SEM) operation at 5 kV. Samples for SEM were prepared by

freeze-drying and dispersing on a glass slide. Dynamic light scattering (DLS) measurements were carried out on a Zetasizer Nano ZS from Malvern Instruments, with a laser at 633 nm.

Synthesis of PIL, AHBTA and Azo-compounds.



Scheme S1. Synthesis of PIL, AHBTA and Azo-compounds

Preparation of poly (1-butyl-4-vinylpyridine bromide) (PIL): 4-Vinylpyridine and 1-bromide butane were stirred together for 24 h, the precipitation was formed and collected. The crude produce was dissolved in CHCl_3 and precipitated in ethyl acetic. The polymerization was occurred in ethanol and initiated by AIBN at 78 °C for 24 h. The produce was precipitated in ethyl ester. The average molecular weight was about 20000 determined by gel permeation chromatography. ^1H NMR(400MHz, DMSO-d_6 , δ (ppm)): 9.06 (pyridine-H, 2H), 8.06 (pyridine-H adjacent to main chain, 2H), 4.56 ($\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 2H), 1.95 ($\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 2H), 1.33 ($\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 2H), 0.92 (CH_3 , 3H).

Preparation of 4-((4-(benzothiazol-2-yl)-3-hydroxyphenyl) amino)-4-oxobutanoic acid (AHBTA): 2-(4-amino-2-hydroxyphenyl) benzothiazole (AHBT) was synthesis using previously report.¹ In brief, a 605 mg sample of AHBT (2.5 mmol)

and 2.5 g succinic anhydride (25 mmol) were stirring in THF for 24 h at room temperature. The yellow suspension was washed with amount of hot water several times and dried under vacuum. The pale yellow powder was obtained. Yield 80 %, ¹H NMR(400MHz, DMSO-*d*₆, δ (ppm)): 12.16 (COOH, 1H), 11.60 (OH, 1H), 10.20 (NHCO, 1H), 8.07 (ArH, 2H), 7.97 (ArH, 1H), 7.56 (ArH, 1H), 7.49 (ArH, 1H), 7.39 (ArH, 1H), 7.11 (ArH, 1H), 2.57 (CH₂CH₂COOH, 2H), 2.52 (CH₂CH₂COOH, 2H)

Preparation of 4-Hydroxy-4'-substitutedazobenzene (1a-1c): 4-substitutedaniline (0.05 mmol) was dissolved in 3 mol/L hydrochloric acid (50 mL). After complete dissolution, the solution was cooled with ice bath to a temperature below 5 °C. With vigorous stirring, to this cold solution was added slowly a solution of 3.5 g (0.05 mmol) of sodium nitrite in 10 mL of water. The resulting diazonium solution, kept below 5 °C with ice bath, was subsequently added dropwise to a cold solution of 4.7 g (0.05 mmol) of phenol in 25 mL of 10 % aqueous sodium hydroxide. The dark brown suspension was acidified and the precipitate was collected. The crude product was washed with copious amount of water and dried under vacuum.

1a: Yield 75 %. ¹H NMR(400MHz, DMSO-*d*₆, δ (ppm)): 10.17 (OH, 1H), 7.78 (ArH, 4H), 7.08 (ArH, 2H), 6.89 (ArH, 2H), 3.86 (OCH₃, 3H)

1b: Yield 80 %. ¹H NMR(400MHz, DMSO-*d*₆, δ (ppm)): 10.50 (OH, 1H), 7.86 (ArH, 4H), 7.00 (ArH, 2H), 6.98 (ArH, 2H)

1c: Yield 50 %. ¹H NMR(400MHz, DMSO-*d*₆, δ (ppm)): 9.97 (OH, 1H), 7.70 (ArH, 4H), 6.88 (ArH, 2H), 6.79 (ArH, 2H), 3.03 (NMe₂, 6H)

Preparation of Ethyl 4-(4-substitutedazobenzene-4'-oxy)butanoate (2a-2c): A

mixture of 1a-1c (0.03 mmol), ethyl 4-bromobutanoate (11.7 g, 0.06 mol), potassium carbonate (4.2 g, 0.03 mol) and acetone was refluxed with stirring for 24 h. The reaction mixture was filtered hot, and the residue was washed with acetone. The acetone was removed under reduced pressure and petroleum ether was added to the concentrated organic extracts. The resulting precipitate was collected and dried. The crude product was recrystallized with hot filtration from ethanol.

2a: Yield 65 % (calcd. **2a**). ¹H NMR(400MHz, CDCl₃, δ (ppm)): 7.87 (ArH, 4H), 6.99 (ArH, 4H), 4.09 (OCH₂CH₂CH₂COOCH₂CH₃, 4H), 3.89 (OCH₃, 3H), 2.54 (CH₂COOC₂H₅, 2H), 2.15 (OCH₂CH₂CH₂COOC₂H₅, 2H), 1.27 (COOCH₂CH₃, 3H)

2b: Yield 70 % (calcd. **2b**). ¹H NMR(400MHz, CDCl₃, δ (ppm)): 7.95 (ArH, 4H), 7.44 (ArH, 2H), 7.00 (ArH, 2H), 4.14 (OCH₂CH₂CH₂COOCH₂CH₃, 4H), 2.55 (CH₂COOC₂H₅, 2H), 2.17 (OCH₂CH₂CH₂COOC₂H₅, 2H), 1.27 (COOCH₂CH₃, 3H)

2c: Yield 87 % (calcd. **2c**). ¹H NMR(400MHz, CDCl₃, δ (ppm)): 7.83 (ArH,4H), 6.95 (ArH, 2H), 6.74 (ArH, 2H), 4.17 (OCH₂CH₂CH₂COOC₂H₅, 2H) 4.07 (COOCH₂CH₃, 2H), 3.07 (N(CH₃)₂, 6H), 2.54 (CH₂COOCH₂CH₃, 2H), 2.14 (OCH₂CH₂CH₂COOC₂H₅, 2H), 1.27 (COOCH₂CH₃, 3H)

Preparation of 4-(4-substitutedazobenzene-4'-oxy)butanoic acid (3a-3b):
2a-2b (10 mmol) was dissolved in 50 mL ethanol, and added 25 % NaOH aqueous solution 50 mL. The mixture was refluxed with stirring for 24 h. The ethanol was removed under reduced pressure. The suspending mixture was acidified, and the precipitate was collected. The crude product was washed with copious amount of water, and purified by recrystallization from ethanol.

3a (AzoMeO): Yield 95 % (calcd. **2a**). ^1H NMR(400MHz, DMSO- d_6 , δ (ppm)): 12.16 (COOH, 1H), 7.84 (ArH, 4H), 7.16 (ArH, 4H), 4.09 (OCH₂, 2H), 3.86 (OCH₃ 3H), 2.41 (CH₂COOH, 2H), 1.98 (OCH₂CH₂, 2H)

3b (AzoCF₃): Yield 97 % (calcd. **2b**). ^1H NMR(400MHz, DMSO- d_6 , δ (ppm)): 12.18 (COOH, 1H), 8.00 (ArH, 2H), 7.94 (ArH, 4H), 7.16 (ArH, 2H), 4.09 (OCH₂, 2H), 2.43 (CH₂COOH, 2H, 2H), 2.00 (OCH₂CH₂, 2H)

3c (AzoNMe₂): 3c was obtained to sodium salt without being acidified.

Yield 80 % (calcd. **2c**). ^1H NMR(400MHz, DMSO- d_6 , δ (ppm)): 7.75(ArH, 4H), 7.04 (ArH, 2H), 6.83 (ArH, 2H), 4.05 (OCH₂, 2H), 3.04 (NMe₂, 6H), 2.00 (CH₂COOH, 2H, 2H), 1.88 (OCH₂CH₂, 2H)

General Procedure for the Preparation of FNPs: The AHBTA and azo-compounds were neutralized with 1 N NaOH aqueous solution and diluted to prepare 2 mM stock solutions. The PIL was prepared with 50 mM aqueous solution. The FNPs solutions were prepared by placing the PIL solution (ca. 0.5 mL), AHBTA (ca. 1.25 mL) and azo-compound (ca. 1.25 mL) into a 10 mL volumetric flask, in this order, and then diluting the solution to 10 mL with water. The solution was stirring for 2 h at room temperature. Test solutions for UV-vis spectra and fluorescent spectra were prepared by diluting the FNPs stock solution with water to a concentration of 50 μM (showed by [AHBTA]).

General Procedure for the Metal Ion Sensing: FNPs-CF₃ aqueous solution was prepared according to the method described above to afford a stock solution of 250 μM , and metal chlorate or sulfate stock solutions (500 μM) were prepared in PBS

solution. Test solutions were prepared by placing 1 mL of FNPs-CF₃ stock solution and an appropriate aliquot of each metal stock into a 5 mL volumetric flask, and then diluting the solution to 5 mL with PBS solution. The resulting solution was shaken well before recording emission spectra of the metal ion sensor. Unless otherwise stated, for all measurements, the excitation wavelength was 389 nm, and the emission wavelength was 450 nm.

Characterization of fluorescent nanoparticles

AHBTA and azo-compound bearing different substitutes were synthesized as shown in Scheme. The molar ratio of composition was fixed to be 10:1:1 for PIL: AHBTA: Azo-complex. Firstly, FTIR spectrum was used to characterize the complex of the three ions. Some characteristic peaks in FTIR spectrum was ascribed as follows: (1) peaks at 1699 cm⁻¹ (AHBTA) and 1707 cm⁻¹ (AzoCF₃) associated with carbonyl group, (2) a peak at 1640 cm⁻¹ associated quaternization of pyridinium rings and (3) peaks at 1569 cm⁻¹ and 1515 cm⁻¹ associated with pyridinium rings. The peaks associated with carbonyl group and quaternization of pyridinium rings were relatively reduced in the complex, indicating success complex of AHBTA, Azo-complex and PIL molecules.² In addition, slight shift of *ca.* 4 cm⁻¹ in the position of pyridinium ring was occurred (from 1569 cm⁻¹ to 1565 cm⁻¹) was also found after the complex.

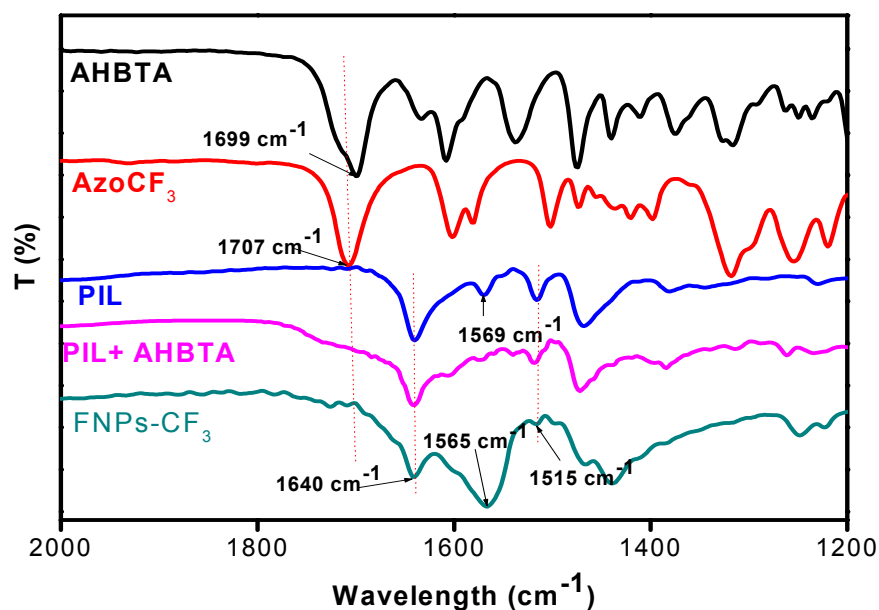


Figure S1. FTIR spectra of AHBTA, AzoCF₃, PIL, PIL+AHBTA, FNPs-CF₃

The FNPs sample were obtained by freeze-drying and subjected to thermal analysis to determine its thermal stability. Thermogravimetric analysis shows the complexes are stable up to at least 210 °C, though it was lower than the resource PIL molecules due to the introduction of AHBTA and azo-compounds. DSC was further performed to investigate the thermal behavior of the complex. The glass transition temperature (T_g) of pure PIL is 77.1 °C. The T_g s of FNPs-MeO and FNPs-CF₃ are 16.5 °C and 15.7 °C, respectively, because the incorporation of AHBTA and azo-compound break up the regularity of polymer chain.

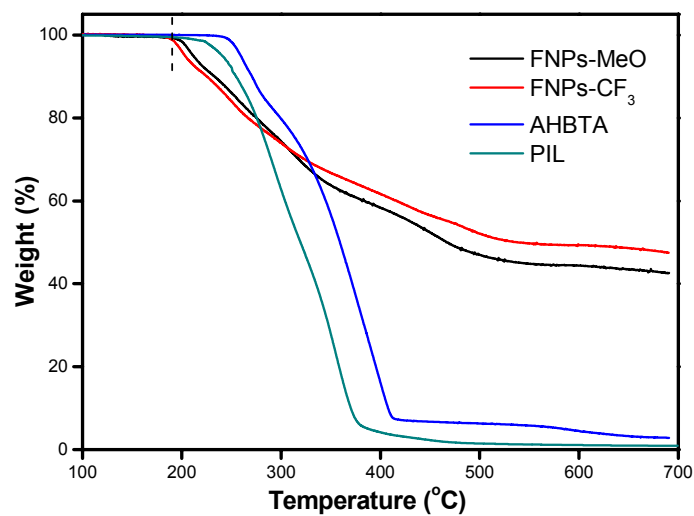


Figure S2. TGA curves of PIL, AHBTA, FNP-CF₃, and FNP-MeO

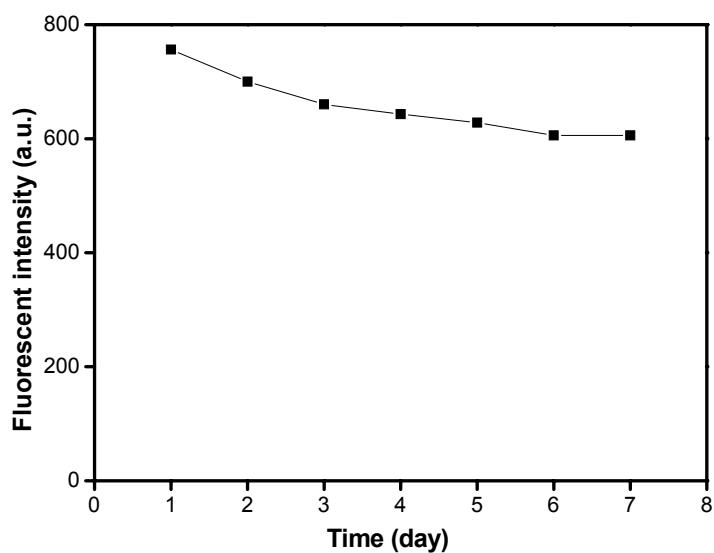


Figure S3. Plots of maximum fluorescent intensity ($\lambda_{em} = 450$ nm, $\lambda_{ex} = 389$ nm) with different days ($[FNP-CF_3] = 50$ μM)

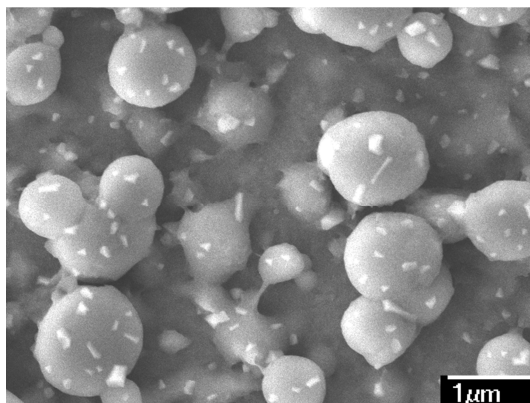


Figure S4. SEM image of FNP-CF₃ (obtained by freeze-drying, [PIL]/[AHBTA]/[AzoCF₃] = 10:1:1)

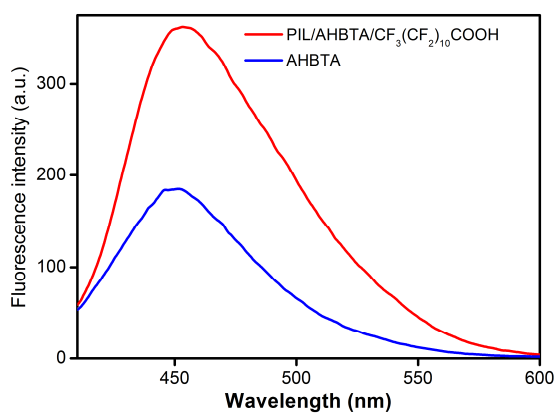


Figure S5. Fluorescent spectrum of FNP-CF₃ obtained by perfluorododecanoic acid as the secondary anion ($\lambda_{\text{ex}} = 389 \text{ nm}$, [PIL]/[AHBTA]/[CF₃(CF₂)₁₀COOH]=10:1:1)

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