Electronic Supplementary Information (ESI)

Turn-on Fluorescent Detection of Cyanide Based on the Dissolution of Gold Nanoparticles and its Application in Real Sample

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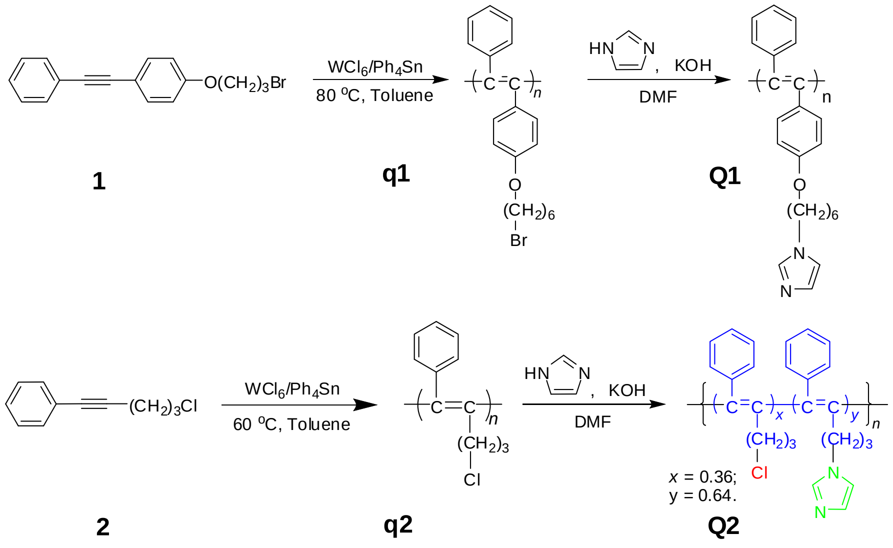

Synthesis of (5-Chloro-pent-1-ynyl)-benzene (1)

To a 250 mL flask were added 90 mg of copper (I) iodide, 180 mg of dichlorobis(triphenylphosphine)palladium and 90 mg of triphenylphosphine, in the glove box. Triethylamine (250 mL), 10.2 g of iodobenzene (50mmol) and 5.2 g of 5-chloro-1-pentyne (50mmol) were then injected. The resultant mixture was stirred at room temperature overnight. The solid was removed by filtration and the solvent was evaporated. The crude product was purified on a silica gel column using chloroform as eluent. Colorless oil of **1** was obtained in 89 % yield (7.9 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.41 (d, 2H), 7.28 (m, 3H), 3.70

(t, 2H), 2.60 (t, 2H), 2.04 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 131.7, 128.5, 127.7, 123.7, 88.1, 81.4, 43.7, 31.5, 16.9.

Synthesis of q1

Into a baked 80-mL Schlenk tube with a stopcock in the sidearm was added 1.14 g of monomer **1**. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the side arm. Freshly distilled toluene (16 ml) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 127.2 mg of tungsten (VI) chloride and 137.6 mg of tetraphenyltin in 16 mL of toluene. The two tubes were aged at 60 ^{o}C for 15 min and the monomer solution was transferred to the catalyst solution using a hypodermic syringe. The reaction mixture was stirred at 60 ^{o}C for 24 hours. The resultant solution was then cooled to room temperature, diluted with 35 mL of chloroform, and added dropwise to 2500 mL of methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight, which was then filtered. The polymer was washed with methanol and dried in a vacuum oven to a constant weight, shallow green powder (0.78 g, 68.4 %). $M_w = 15700$, $M_w/M_n = 2.27$. (GPC, polystyrene calibration). IR (thin film), υ (cm^{-1}): 3064 (Ar-H stretching), 2954, 2870 (CH_2 stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 0.8-2.6 ($-CH_2-$), 2.6-3.4 ($-CH_2-$), 6.5-7.8 (ArH). UV-Vis (Ethanol, 1.06×10^{-4} mol/L): λ_{max} (nm): 302nm.

Synthesis of Q1

q1 (89mg), imidazole (68 mg, 1.0 mmol), potassium hydroxide (140mg, 2.5mmol) were added to dry DMF (10 mL). After stirred at 80 °C for 3 days, the resultant mixture was filtered, then the filtrate was added to a dialyzer bag. The bag was immersed in distilled water (the water was changed every two hours) for several day to remove small molecules, such as imidazole (which would enter into water as its molecular weight is lower than 800). It was observed that some yellow precipitant yielded in the bag during the dialyzing process. The yellow powder was collected, and dried in a vacuum oven to a constant weight (47mg, 44.7%). ^{1}H NMR (CH_3OD) δ (ppm): 0.9-2.5 ($-CH_2-$), 2.5-4.4 ($-CH_2-$), 6.0-7.9 (ArH). EA: Found: C 73.09, H 6.620, N 9.015. UV-Vis (Ethanol, 1.06×10^{-4} mol/L): λ_{max} (nm): 302nm

Synthesis of 1-Phenyl-2-[4-(6-bromohexyloxy)phenyl]acetylene (2)

This product was synthesized by procedures similar to those described previously.[1] White solid; yield 67.6%. Mp = 71 °C. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.50 (m, 4H), 7.33 (m, 3H), 6.87 (d, 2H), 3.98 (t, 2H), 3.43 (t, 2H), 1.90 (m, 2H), 1.82 (m, 2H), 1.52 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 159.1, 133.0, 131.4, 128.3, 127.9, 123.6, 115.2, 114.5, 89.4, 88.0, 67.7, 33.8, 32.6, 29.0, 27.9, 25.3. $C_{20}H_{21}BrO$ (EA) (%, found/calcd): C, 67.19/67.23; H, 5.92/5.92.

Preparation of Poly{1-phenyl-2-[4-(6-bromohexyloxy)phenyl]acetylene} (q2)

The polymer was synthesized by WCl_6-Ph_4Sn in toluene at 100 ºC under nitrogen. The procedures could be found in our previous papers.[35] Greenish yellow solid; yield 46.8%. M_w = 13300; M_w/M_n = 3.3 (GPC, polystyrene calibration). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.22-6.44 (br, ArH), 6.36-6.00 (br, ArH), 4.10-3.60 (br, OCH_2), 3.56-3.29 (br, CH_2Br), 2.10-1.29 [br, $(CH_2)_4$]. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 156.7, 144.3, 143.6, 133.1, 130.8, 128.4, 127.2, 126.1, 125.0, 112.8, 67.7, 33.4, 32.7, 30.3, 29.1, 27.9, 25.3.

Preparation of Poly{1-phenyl-2-[4-(6-imidazolylhexyloxy)phenyl]acetylene} (Q2)

q2 (89mg), imidazole (34 mg, 0.5 mmol), potassium hydroxide (70 mg, 2.5mmol) were added to the mixture solvent of dry DMF (4 mL) and THF (2 ml). After stirred at 80 °C for 3 days, the resultant mixture was filtered, and the filtrate was dropped into water to afford yellow solid. The precipitate was washed with water for several times, then collected and dried in a vacuum to a constant weight (68 mg, 79.3%). ^{1}H NMR (CD_3Cl) δ (ppm): 1.2-2.2 ($-CH_2-$), 3.5-3.8 ($-CH_2-$), 3.8-4.0 ($-CH_2N<$), 6.0-6.3 (ArH), 6.4-7.2 (ArH), 7.4-7.6 (ArH). IR (thin film), υ (cm^{-1}): 3050 (Ar-H stretching), 2933, 2861 (CH_2 stretching).

References

1. Li, Z.; Huang, C.; Hua, J.; Qin, J.; Yang, Z.; Ye, C. Macromolecules 2004, 37, 371-376.

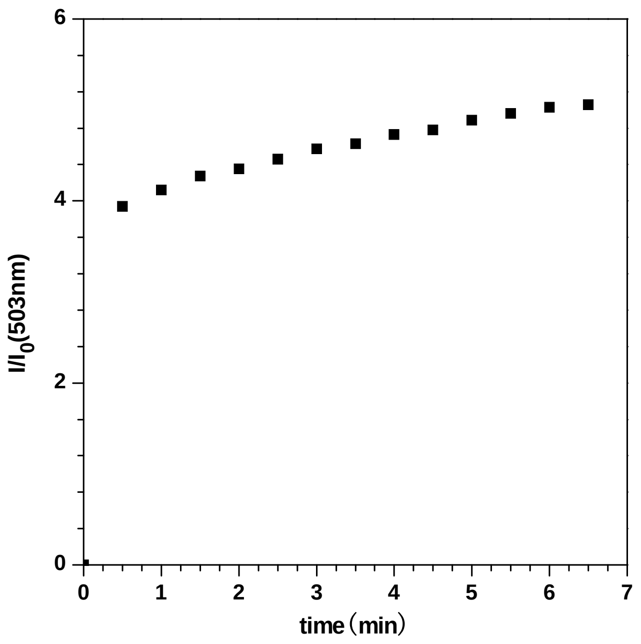

Fig. S1 Time-dependent fluorescence response of the **Q1**-Au NPs to 3×10^{-4} mol/L of CN^-.

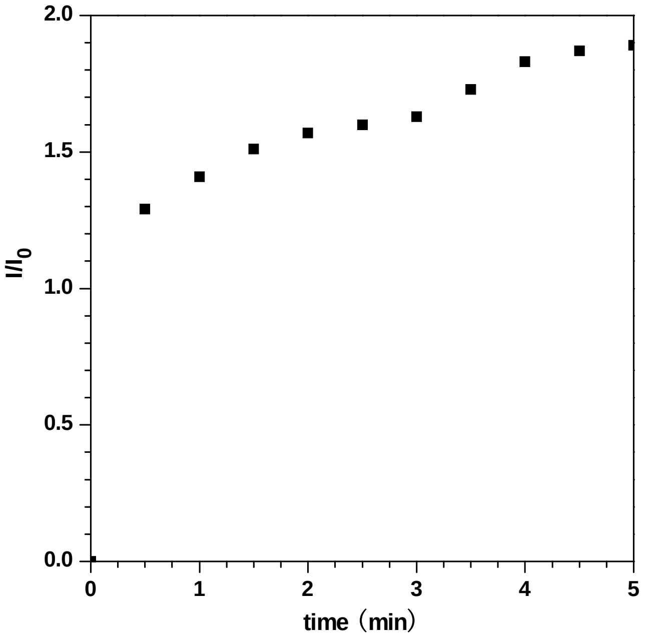

Fig. S2 Time-dependent fluorescence response of the **Q2**-Au NPs to 3×10^{-4} mol/L of CN^{-}.

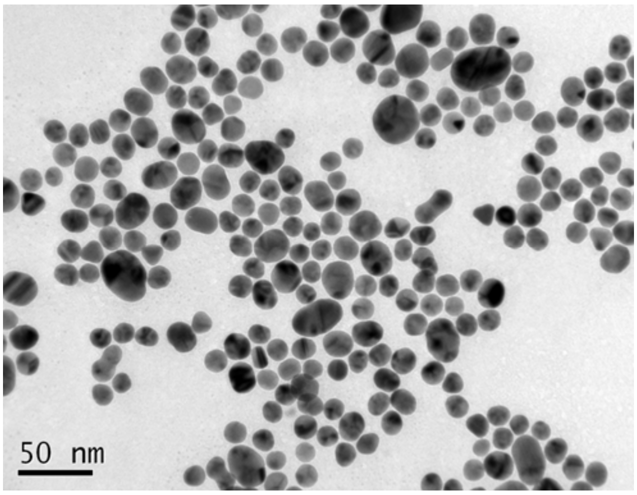

Fig. S3 TEM images of Au NPs with the average diameter of 20 nm.

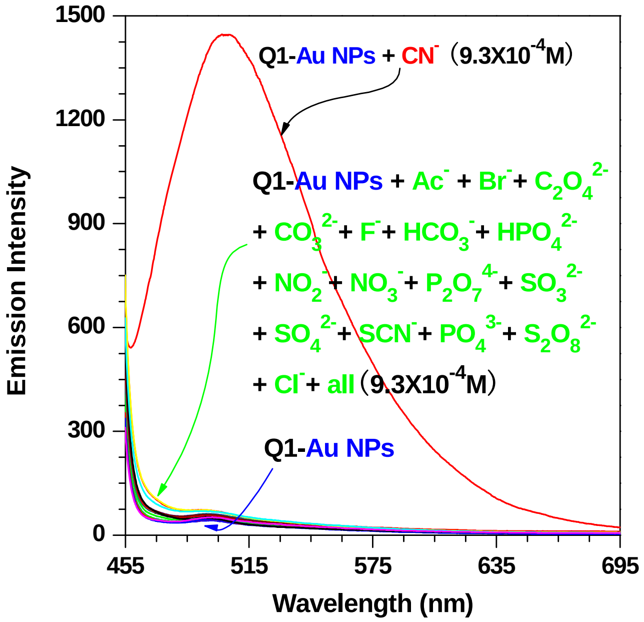

Fig. S4 Fluorescence Emission spectra of **Q1**-Au NPs in C_2H_5OH in the presence of different anions(9.3×10^{-4} mol/L). The concentration of **Q1** was 2.0×10^{-6} mol/L and Au NPs was 6.76×10^{-5} mol/L. Excitation wavelength (nm): 431.

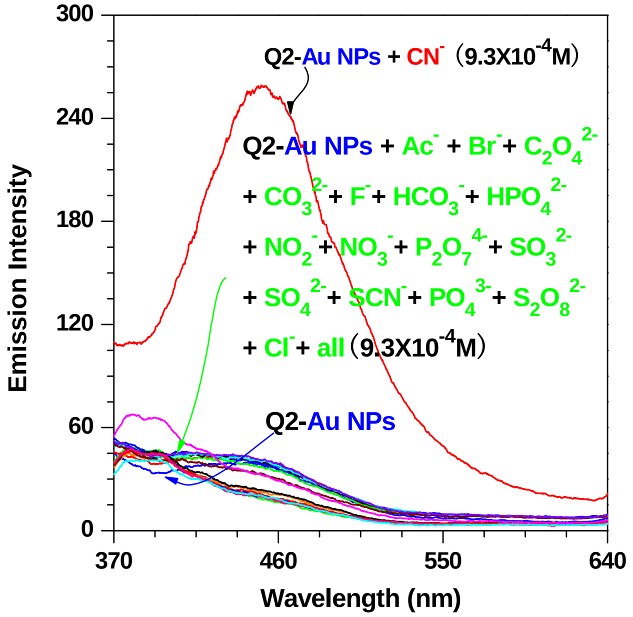

Fig. S5 Fluorescence Emission spectra of **Q2**-Au NPs in C_2H_5OH in the presence of different anions(9.3×10^{-4} mol/L). The concentration of **Q2** was 35×10^{-6} mol/L and Au NPs was 27.8×10^{-5} mol/L. Excitation wavelength (nm): 355.

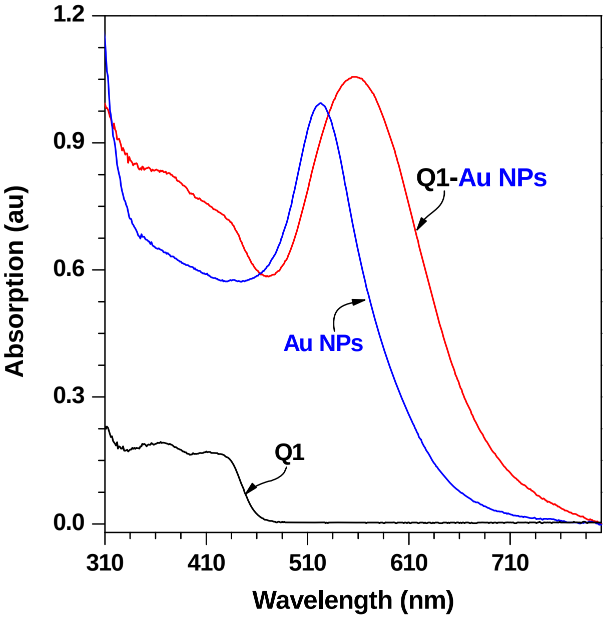

Fig. S6 Absorption spectra of Q1, Au NPs and Q1-Au NPs in C_2H_5OH.

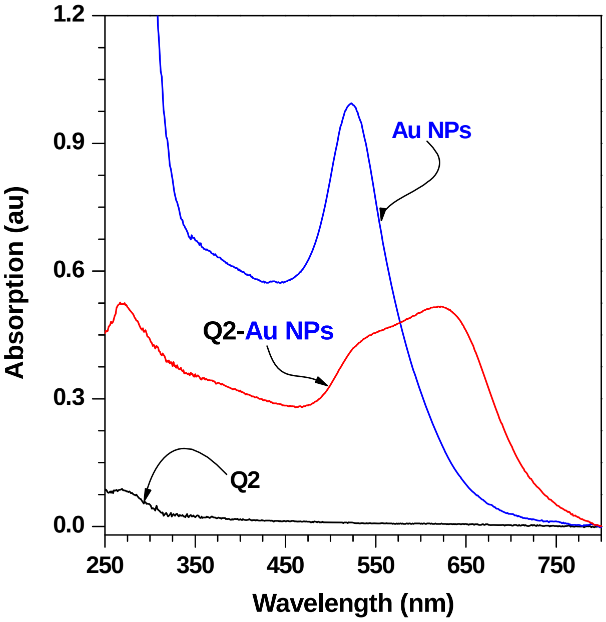

Fig. S7 Absorption spectra of Q2, Au NPs and Q2-Au NPs in C_2H_5OH.

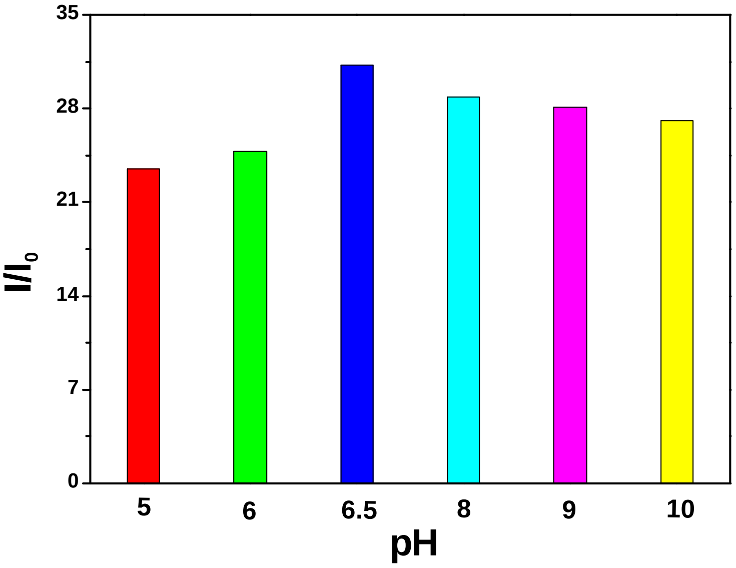

Fig. S8 The fluorescence response of the Q1-Au NPs to CN^- at different pH values.

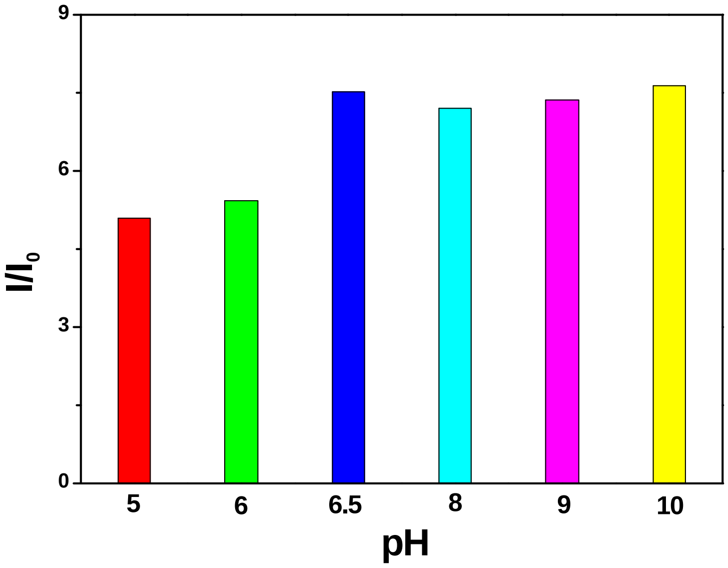

Fig. S9 The fluorescence response of the Q2-Au NPs to CN^- at different pH values.