Supporting Information

Multifunctional fluorescent material based on metallomicelles trapped in silica nanochannels

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Experimental section

Chemicals

8-hydroxyquinoline, 1,12-dibromododecane, triethylamine, dimethylsulfoxide, petroleum ether, ethyl acetate, acetonitrile, dichloromethane, methanol, tetraethoxysilane (TEOS), ammonia solution (28 %), potassium hydroxide, sodium bicarbonate, sodium chloride, and sodium sulfate were purchased from Beijing Chemical Company. All chemicals were used without further purification.

Synthesis of $QC_{12}Br(1)$

1, 12-dibromododecane (0.36 g, 1.1 mmol) was added dropwise to a mixture of 8-hydroxyquinoline (0.15 g, 1.0 mmol) and powered potassium hydroxide (0.11g, 2 mmol) in dimethylsulfoxide (10 mL) under nitrogen atmosphere. The resulting mixture was stirred at room temperature overnight. Then, the contents were poured into water, and extracted twice with ethyl acetate. The combined extracts were washed with 10% aqueous sodium bicarbonate solution, water, and saturated sodium chloride solution successively, dried with anhydrous sodium sulfate, and then filtered. The filtrate was concentrated on a rotary evaporator. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate = 20/1 (volume ratio) as an eluent to yield the desired product.

Yield: 65%; yellow solid.

¹H NMR (CDCl₃): 8.93-8.94 (d, 1H), 8.09-8.11 (d, 1H), 7.38-7.45 (m, 2H), 7.35-7.37 (d, 1H), 7.04-7.06 (d, 1H), 4.21-4.24 (t, 2H), 3.37-3.41 (t, 2H), 1.98-2.04 (m, 2H), 1.80-1.85 (m, 2H), 1.48-1.53 (m, 2H), 1.22-1.40 (m, 14H).

Synthesis of $QC_{12}Et_3Br(2)$

The obtained QC₁₂Br (1) (0.39 g, 1 mmol) was dissolved in acetonitrile (50 mL), and triethylamine (0.18 g, 1.8 mmol) was added dropwise under vigorous stirring. The resulting mixture was refluxed for 12 h, and then cooled to room temperature. The crude product was purified by silica gel column chromatography with dichloromethane/methanol = 10/1(volume ratio) as an eluent, affording the desired product.

Yield: 90%; reddish-brown solid.

¹H NMR (CDCl₃): 8.94-8.95 (d, 1H), 8.14-8.16 (d, 1H), 7.42-7.48 (m, 2H), 7.37-7.39 (d, 1H), 7.06-7.08 (d, 1H), 4.21-4.25 (t, 2H), 3.45-3.51 (q, 6H), 3.23-3.27 (t, 2H), 2.01-2.05 (m, 2H), 1.64-1.72 (m, 2H), 1.48-1.55 (m, 2H), 1.41-1.45 (m, 14H), 1.21-1.32 (t, 9H)

Synthesis of mesostructured silica with $QC_{12}Et_3Br$ as structure-directing agent The synthesis of mesostructured silica was fabricated by using TEOS as the silica source and $QC_{12}Et_3Br$ as the structure-directing agent in basic medium through hydrothermal process. In a typical synthesis, $QC_{12}Et_3Br$ was dissolved in deionized water with NH₃·H₂O under stirring to get the homogeneous mixture, and then TEOS was added dropwise at room temperature. The molar compositions of the resulting mixtures were 1 TEOS/0.12 $QC_{12}Et_3Br$ /8 NH₃·H₂O/114 H₂O. The reaction mixtures were stirred at room temperature for 2 h and then transferred into an autoclave and left standing at 80°C for 3 days. After hydrothermal treatment, the mixtures were filtered, and light pink powders were washed three times with deionized water and dried at room temperature.

Synthesis of $QC_{12}Et_3Br-Al^{3+}$ /silica with MMA

MMA (10ml) and $QC_{12}Et_3Br-Al^{3+}$ /silica (50mg) were added to a 50ml round bottom flask. Dispersed by ultrasonic for 10 min, the BPO(0.10mg, 0.0016mmol) was added into the mixture under water bath heating (80-90°C). Keep stirring constantly until the liquid into a sticky. Put the prepolymerization solution into test tubes or watch glass. The resulting mixture was polymerized into the oven under 40°C for 24h, and then cooled to room temperature. The film, rod or other shapes fluorescent polymer materials could be got.

Coordinate Process

In a typical experiment, 10 mg of $QC_{12}Et_3Br/silica$ hybrid materials were added to 10 mL of 50 mg/L Al³⁺ solution. The suspension was shaken for 15 min. The mixtures were filtered, and then $QC_{12}Et_3Br-Al^{3+}/silica$ hybrid materials were achieved.

Extraction Process

In a typical experiment, 100 mg of $QC_{12}Et_3Br/silica$ hybrid materials were dispersed in ethanol (150 mL, 95%) containing 30 mg of NH_4NO_3 , and the mixture was stirred at 60 °C for 20 min. Solids were recovered by filtration and washed with cold ethanol, and the above treatment could be repeated twice.

Preparation of the fluorometric anion titration solution

Stock water solutions $(1 \times 10^{-2} \text{ M})$ of PPi, ATP, Cl⁻, Br⁻, I⁻, NO₃⁻, NO₂⁻, SO₄²⁻, HSO₃⁻, S₂O₃²⁻, SCN-, ClO₄⁻, ClO₃⁻ were prepared. The suspension solution of the resultant silica hybrid materials (0.02 g L⁻¹) was prepared in water solution. Each time, a 2 mL suspension solution was added to a quartz cuvette of 1 cm optical path length, and different stock solutions of anions were gradually added into the quartz cuvette by micro-syringe addition.

Characterization

X-Ray diffraction (XRD) patterns of the as-synthesized magnetic mesoporous silica were obtained at room temperature on a Rigaku D/MAX-2400 X-ray powder diffraction (Japan) using Cu K α radiation (λ =1.5405 Å) at 40 kV and 10 mA. Small angle X-ray diffraction was obtained in the 2 θ range from 1.5° to 10°, employing a scanning rate 0.02° s⁻¹. The nitrogen adsorption and desorption isotherms were measured at 77 K using an ASAP 2010 analyzer (Micromeritics Co. Ltd.). Before measurement, samples were degassed under vacuum at 373 K for 4 h. Surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, and the pore volume and pore size distributions were calculated using the Barret-Joyner-Halenda (BJH) model. FT-IR spectra (4000-500 cm⁻¹) in KBr were collected on a Nicolet Avatar 360 FT-IR spectrometer, accumulating 32 scans at a resolution of 4 cm⁻¹. The samples were pressed to a thin disc with KBr before measurements. Element contents (C, N) were performed on 0.0001mg/vario EL III. The concentrations of dye solutions were measured by UV-visible absorption spectroscopy (Perkin-Elmer Lamda 35 spectrometer). The fluorescence emission measurements were carried out using a fluorescence spectrometer (Perkin-Elmer, LS55). Both excitation and emission slit widths were fixed at 5 nm and 10 nm. The emission data were collected in the region of 390 to 700 nm. Related ion concentration was collected by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). ¹H-NMR spectra was measured on a Varian INOVA 400M spectrometer with chemical shifts reported as ppm (CDCl₃ as internal standard). All the spectroscopic measurements were performed in at least triplicate.



Scheme. S1 Schematic representation of 8-hydroxyquinoline containing cationic surfactant $QC_{12}Et_3Br$.



Figure. S1 Nitrogen adsorption-desorption isotherms (inset: pore size distribution) of $HQC_{12}Et_3Br/silica$ hybrid materials after extraction with ammonium nitrate. Isotherm parameters of $HQC_{12}Et_3Br-Al^{3+}/silica$ hybrid materials, surface area (1069 m² g⁻¹); pore volume (0.87 mL g⁻¹); pore diameter (2.43 nm).



Figure. S2 FT-IR spectra of $HQC_{12}Et_3Br$ (A), $HQC_{12}Et_3Br/silica$ hybrid materials (B) and $HQC_{12}Et_3Br-Al^{3+}/silica$ hybrid materials (C).



Figure. S3 UV-Vis titration profiles of $QC_{12}Et_3Br$ (10⁻⁴ M) in water solution when titrated by Al^{3+} based on F_{365} .



Figure. S4 Fluorescence titration profiles of $QC_{12}Et_3Br/silica$ hybrid materials (0.02 g/L) in water solution when titrated by Al^{3+} based on F_{493} , $\lambda_{ex} = 365$ nm.



Figure. S5 Leaching rate of the functionalities out of the respective composites in aqueous buffer solution (pH 7.0).



Figure. S6 Fluorescence titration profiles of $QC_{12}Et_3Br/silica-Al^{3+}$ hybrid materials (10g/L) in water solution when titrated by PPi based on F_{493} , $\lambda_{ex} = 365$ nm.