Supporting Information

Fluorescent amphiphilic cellulose nanoaggregates for sensing trace explosives in aqueous solution

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1. Experimental Details

Materials and instruments: Hydroxyethyl cellulose (HEC) (Mw: 250,000 Dalton) and 1-bromododecane (BD) were purchased from Aladdin chemistry Co. DNT and picric acid were purchased from Aldrich and were handled in small quantities. A blue light-emitting conjugated polymer poly (9, 9-dioctylfluorene) (PFO) (Mw: 35000 Dalton, polydispersity 2.3) was synthesized following literature methods. [1] All of the other chemicals, including isopropanol, tetrahydrofuran (THF), acetone, and hexane were of analytical purity and used as received.

The Fourier transform infrared (FT-IR) spectra of hydrophobic modified hydroxyethyl cellulose (HMHEC) samples were conducted with a Nicolet-750 infrared spectrometer of USA. All of the samples were made into KBr pellets containing 1% finely ground samples and the range of spectra was from 4000 cm^{-1} to 400 cm^{-1}. The ^{1}H-NMR spectra were obtained on a Bruker AVIII 400 MHz spectrometer in D_2O. Solution viscosities were measured with a NDJ-7 rotator viscometer under the following conditions: temperature, 25°C, shear rate, 6 s^{-1}, concentration, 3 g/L. Photoluminescence (PL) spectra were recorded with the use of a Jobin–Yvon spectrometer with 90° detection for solution samples. The UV-vis sbsorption spectra were obtained with the use of a HP 8453 spectrophotometer.

Synthesis of HMHEC: HMHEC was prepared according to following procedure: 5 g HEC and 30 ml isopropanol (IPA) were added into a three-necked flask, and vigorously stirred for thirty minutes. Subsequently, 30 ml NaOH (5%, w/v) aqueous solution was added drop wise to the flask with strong stirring and nitrogen gas protection. After the NaOH solution was added, the stirring speed was reduced and HEC was sufficiently swelled in this system for 24 h. The mixture was then heated to 80 °C, and a definite amount of BD's IPA solution at a molar ratio of 0.25mol BD per mol anhydroglucose unit (AGU) was added into it slowly. The reaction was kept for about 5 h with the protection of nitrogen gas. After cooled down to room temperature, the product was neutralized with HCl, filtrated, washed and soaked with hexane and acetone. Finally, the product was dried under reduced pressure at 80 °C for 24 h. Yield

(64.3%). IR (KBr): v = 3430 (s; ν_s(OH)); 2920(s; ν_{as}(C-H)), 2875 (s; ν_s(C-H)); 1580(m); 1457 (m; δ_s(C-H)); 1050 (m; ν_s(C-O-C)); 875 cm^{-1} (w). ^{1}H-NMR (400 MHz, D_2O, δ): 3.0-5.5 (AGU H), 1.81 (m, 20H; CH_2 alkyl chain); 1.20 (q, 2H; CH_2); 0.78 (t, J = 7.2 Hz, 3H; CH_3).

In the FT-IR spectrum of modified HEC, enhanced adsorption can be observed at 2980-2850 cm^{-1}, 1457 cm^{-1} and 1210-1000 cm^{-1}, which represent the stretching vibration of C-H, deformation vibration of C-H and asymmetric C-O-C stretching vibration, respectively. These results suggest the successful introduction of alkyl chain to the HEC molecule. The occurrence of alkylation is also confirmed by the 1H-NMR spectrum of modified HEC, in which new signals representing methyl and methylene protons appear at 0.78, 1.20 and 1.81 ppm, respectively.

After modification, the HMHEC derivatives show good solubility both in water and in organic solvent, e.g. dimethyl sulfoxide (DMSO), dimethylformamide, etc, while the unmodified HEC can only be dissolved in water. Moreover, the solution viscosity was dramatically increased from 1.5 mPa·s to 51.5 mPa·s, which is an evidence for the associative behaviors of HMHEC.[2]

Preparation and characterization of HMHEC nanoaggregates: The obtained HMHEC (20mg) was firstly dissolved in 2 ml DMSO under gentle shaking at room temperature for 24 h, and then the solution was slowly added to 20 ml pure water under vigorous stirring to initiate the self-assembly process. After stirring overnight, the solution was dialyzed (MWCO 3.0 kDa) against deionized water for 72 h with a water change of about every 8 h to completely remove DMSO. The solution inside the dialysis bag was collected and diluted to a certain concentration with pure water. The final solutions were then stored in stock for a subsequent sample characterization.

The CPs encapsulated HMHEC nanoaggregates were prepared by slowly adding the PFO THF solution (2 g/l) into the HMHEC nanoaggregates aqueous solution under vigorous stirring, and then the THF solvent was removed by rotary evaporation. The solution was then filtered through a 0.25 μm microfilter to eliminate nonincorporated PFO. The concentration of PFO in the HMHEC nanoaggregates solution was determined by UV-vis spectrometer at 380 nm. The encapsulation efficiency (EE, %) of PFO in the HMHEC nanoaggregates was determined by the following equation:

EE (%) = (weight of loaded CPs/weight in feed)×100%

Based on the above calculation, the EE (%) of PFO in the HMHEC nanoaggegates was found to be over 80%. The resulted solution was then diluted with a certain volume of water to make the concentration of PFO being around 0.01g/L.

The average hydrodynamic diameter and size distribution of the as prepared nanoparticles were determined using a Malvern 90 Plus particle size analyzer equipped with a 30 mW semiconductor laser diode (659 nm) with an output at a scattering angle of 90°. All measurements were made at 25 °C. The morphology of the HMHEC nanoparticles was observed by a JEM-100CXII Transition Electron Microscopy (TEM) instrument operating at an accelerator voltage of 120kV. The samples were prepared by casting the micellar solution (0.1 g/l) onto a carbon-coated copper grid after negative staining with 2% (w:v) phosphotungstic acid.

Fluorescence quenching studies with nitroaromatics analytes: For the Stern-Volmer measurements, 2.5 mL of PFO encapsulated nanoaggregates solution were placed in a covered quartz cuvette. Fluorescence quenching of PFO was obtained by successive addition of aliquots of analyte solution. Fluorescence spectra of the solution were measured immediately after each addition with excitation at 385 nm. Slit widths were optimized for signal strength within the limits where the detector response was linear. The concentration of PFO for the fluorescence quenching measurements was kept constant at 0.01 g/l.

2. Sensing properties of PFO-containing cellulose nanoaggregates towards PA in aqueous solution

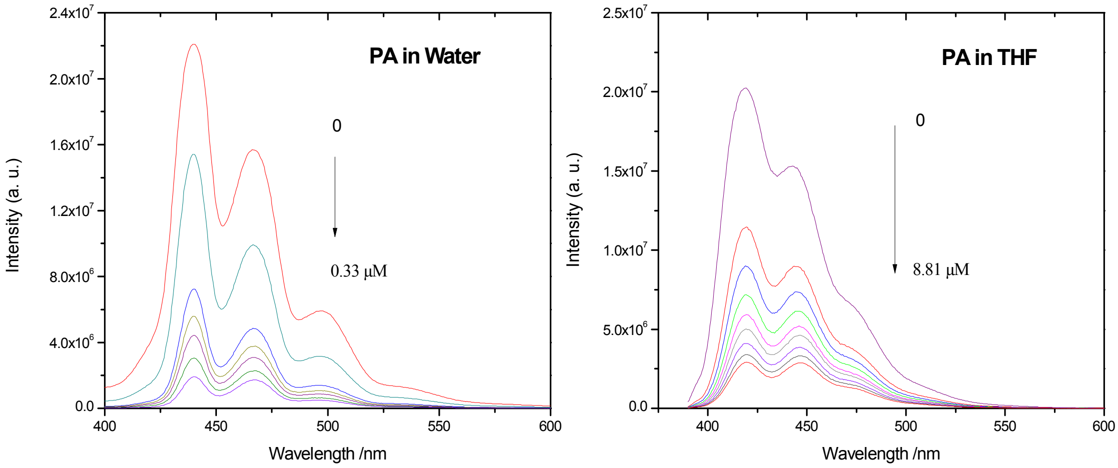

Fig. 1. Fluorescence emission spectra of PFO in water (left) and in THF solution (right) in the presence of different concentrations of PA (λ_{ex} = 335nm).

The figure above shows the PL spectra of PFO and PFO-containing nanocarriers upon exposure to PA in THF solution (a) and in aqueous solution (b), according to which the PL intensity of PFO in THF solution was significantly quenched when 1.1

μmol of PA was added, while only 0.033 μmol PA could significantly quench the PL intensity of PFO in nanocarriers aqueous solution. When 0.066 μmol PA was added to the aqueous solution of PFO-containing nanocarriers, the PL intensity of PFO was mostly quenched.

3. Summary of quenching efficiencies

The PL quenching efficiencies, which were determined from the slopes of steady-state Stern-volmer plots and indicated by the values of K_{SV} are summarized in follow table.

Table 1. Summary of Stern-Volmer constants (Ksv) for the fluorescence quenching of PFO by DNT and PA.

Samples	**DNT** **M^{-1}**	**PA** **M^{-1}**
PFO in THF	221	1486
PFO in Water	11103	102260

Reference:

1 Q. Hou, Y. Xu, W. Yang, M. Yuan, J. Peng, Y. Cao, *J. Mater. Chem.*, 2002, **12**, 2887.

2 L. M. Zhang, *Carbohy. Polym.*, 2001, **45**, 1.