Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for:

Photoluminescent Eu-containing Polyoxometalate/Gemini Surfactant Hybrid Nanoparticles for biological applications

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Materials

Europoum nitrate hexanydrate (99%) and sodium tungstate dehydrate (99%) were all purchased from J&K Chemical Technology, China. 1-bromododecane (98%), 1-bromohexadecane (98%), n-alkylimidazole (99%), bromoacetic acid (99%), acrylonitrile (99%) and isopropanol (99%) were purchased from Aladdin Chemistry Co., Ltd. of China. Benzophenone and sodium hydroxide was obtained from Sinopharm Chemical Reagent Co., Ltd. of China. Hexadecyl trimethyl ammonium Bromide was purchased from J&K Chemical Technology, China. All above reagents were used without further purification.

Synthesis of ionic liquid-type Gemini imidazolium surfactants

According to the literature[1], this class of ionic liquid-type Gemini imidazolium surfactants was synthesized by mixing 0.15 mol of imidazole and 0.24 mol of acrylonitrile in methanol (16 ml) and stirring for 8 h at 55-60 °C under nitrogen. Methanol and unreacted acrylonitrile were subsequently removed. After that, alkyl bromide (0.12 mol of 1-bromododecane, or 1-bromohexadecane) was added with isopropanol (20 ml) and the mixture was refluxed at 60-65 °C for 24 h under nitrogen. After the reaction finished, the residue was dissolved in 35 ml of chloroform followed by addition of aqueous sodium hydroxide solution (60 ml, 15%, w/w) and then was stirred at room temperature for 3 h. Subsequently, the aqueous layer was removed and the resulting chloroform layer was washed several times with deionized water. Residual solvent was removed under vacuum for 2 h at 50 °C followed by addition of isopropanol (20 ml). Then 0.05 mol of 1, 2-dibromoethane was added dropwise and the mixture was stirred at 60-65 °C for 24 h under nitrogen. After removal of isopropanol, the product was purified five times by recrystallization in acetone and then dried under vacuum for 2 days. For $[C_{12}\text{-}2\text{-}C_{12}im]Br_2$, ^{1}HNMR(400MHz, $CDCl_3$): δ(ppm) 10.35(s, 2H), 8.85(s, 2H), 7.16(s, 2H), 5.32(t, 4H), 4.15(t, 4H), 1.92(m, 4H), 1.30(m, 36H), 0.88(t, 6H)

Synthesis of ionic liquid-type imidazolium surfactant

1-methylimidazole (0.1 mol) and 1- bromohexadecane (0.12 mol) were dissolved in acetonitrile, and the mixture was stirred at 75-80 ℃ under nitrogen atmosphere for 48 h. The solvent was removed by evaporation under reduced pressure. The product was purified by recrystallization from ethyl acetate at least four times and then dried in vacuo for 48 h.

For C_{16}mimBr, ^{1}H NMR ($CDCl_3$, δ/ppm): 0.88 (t, 3H), 1.25-1.33 (d, 26H), 1.92 (t, 2H), 4.13 (s, 3H), 4.31 (t, 2H), 7.21 (d, 2H), 10.95 (s, 1H)

Preparation of surfactant/Eu-POM hybrids

$Na_9EuW_{10}O_{36}\cdot 32H_2O$ was prepared as described by Sugesta and Yamase.[2] Aqueous solutions of Eu-POM (5 mL, 0.5 mM) and [C_{16}-2-C_{16}im]Br_2 (45 mL, 0.5 mM) were mixed in a 250 mL flask. After 30 min, the products were collected by filtration, and washed three times with water to remove salts and possible precursors. The final products were dried under vacuum at 55 °C for 24 h.

Characterization of hybrid materials

The ^{1}H NMR spectra were recorded using a Bruker AV-300 NMR spectrometer with a pulse field gradient module (Z-axis) and a 5 mm sample tube. The instrument was operated at a frequency of 300.13 MHz at 25 ^{o}C with tetramethylsilane as an internal reference. Deuterated dimethylsulfoxide (DMSO) was selected as the solvent. The nanostructures were characterized by transmission electron microscopy (TEM) (JEM-100CX II (JEOL)). Steady state fluorescence spectra, time correlated fluorescence spectra, and fluorescence lifetimes were recorded on a FLS920 (Edinburgh) fluorometer with the excitation at 280 nm. Fourier transform IR (FTIR) spectra were recorded between 4000 and 400 cm^{-1} by using a VERTEX-70/70v FTIR spectrometer (Bruker Optics, Germany) on pressed thin KBr sample disks. Small angle X-ray scattering (SAXS) measurements were performed using an Anton-paar SAX Sess mc2 system with a Ni-filtered Cu Kα radiation (1.5406 Å) operated at 50 kV and 40 mA.

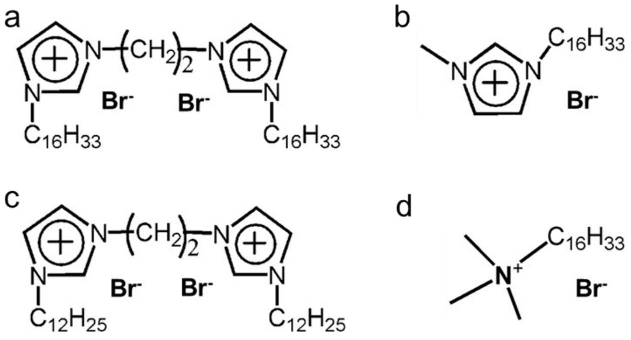

Fig. S1 The chemical structures of (a) [C_{16}-2-C_{16}im]Br_2, (b) [C_{16}im]Br, (c) [C_{12}-2-C_{12}im]Br_2 and (d) CTAB.

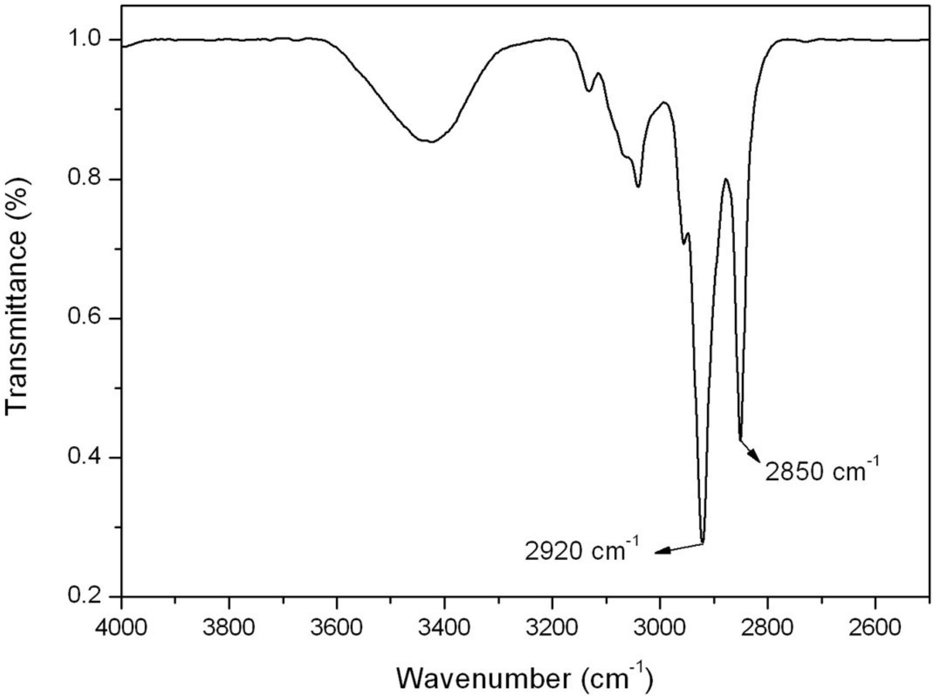

Fig. S2 FTIR spectrum of the [C_{16}-2-C_{16}im]Br_2/Eu-POMs hybrids.

References

1 M Ao, G Xu, Y Zhu, Y Bai. J. *Colloid. Interf. Sci*. 2008, **326**, 490-495.
2 M. Sugeta; T. Yamase, Bull. *Chem. Soc. of Jpn.* 1993, **66**, 444-449.