Electronic Supplementary Information

Sulfonated Ethylenediamine-Acetone-Formaldehyde Condensate: Preparation, Highly Efficient Photoluminescence and Unconvertional Aggregation-Enhanced Emission

Wei Yu,[ab] Ying Wu,[ab] Jiachun Chen,[ab] Xiangyan Duan,[c] Xiaofang Jiang,[c]
Xueqing Qiu[ab] and Yuan Li*[ab]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, China.

[b] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China.

[c] Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China

Corresponding Author

* Yuan Li, Email: celiy@scut.edu.cn, Tel/Fax: +86-20-87114033.

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1. Experimental section

1.1 Materials

Ethylenediamine, acetone and formaldehyde aqueous solution (37wt%) and all other reagents were of analytical grade which purchased from Energy Chemical Co. Ltd. (Shanghai, China). Water used throughout the experiments was deionized water which produced by LTDAXLK1830 (ASURA, Chongqing, China).

1.2 Preparation of AF, SAF and SEAF

AF can be readily synthesized by the polymerization of acetone and formaldehyde in aqueous NaOH solution. Acetone (3.0mL) and formaldehyde (6.0mL, 37wt%) were mixed in reaction flask at pH of 10 adjusted by NaOH. The reaction was quenched after stirring for 5 hours at the temperature of 85℃. The solid product of AF was filtered and purifed by washing with deionized water to remove salt and raw materials for several times. The faint yellow product was obtained after drying at 80℃under vacuum for 24 hours. AF can be dissolved in ethanol and THF, however, it is not soluble in water.

We introduced sulfonic groups to the structure of AF to prepare water soluble SAF by using a one-pot method as following procedure. Formaldehyde (6.0mL, 37wt%) and acetone (3.0mL) were mixed in aqueous solution with pH of 10. The mixture was kept at 50℃ for one hour, and 2.5g of Na_2SO_3 was added. The polymerization was stopped after 5 hours of reflux at 85℃. The residue raw materials were removed by vacuum rotary evaporation, and then the the pH of water soluble product solution was adjusted to 2~3 by addition of hydrochloric acid. Subsequently, the acidic products were dialyzed by a dialysis membrane and freeze-dried under vacuum for 24 hours. The brown solid product showed excellent water solubility (solubility: higher than 400mg/mL) and obvious photoluminescence in aqueous solution. The solubility of SAF in DMSO is about 50 mg/mL.

With the similar method for the synthesis of SAF, SEAF was prepared under the following detailed conditions. Ethylenediamine (5.6mL), acetone (6.0mL) and formaldehyde (12.5mL, 37wt%) were mixed in reaction flask at the pH of 10. 5g of Na_2SO_3 was added after the reaction solution was kept at 50℃ for 1 hour. Then the reaction was stopped after 5 hours of reflux at 85℃.With the same purification procedure, SEAF was collected as brown powder and it is very soluble in water (solubility: higher than 400mg/mL). The solubility of SEAF in DMSO is around

50mg/mL. It is interesting that SEAF displayed bright yellow photoluminescence under UV lamp in both aqueous solution and powder state.

1.3 Characterization of AF, SAF and SEAF

The molecular weight distributions of the samples were respectively determined by aqueous GPC (SAF, SEAF) of Waters 1515 Isocratic HPLP pump/Waters 2487 UV and organic GPC (AF) of Waters 515 Isocratic HPLP pump/Waters 2414 RI (Waters Co, Milford, MA, USA). The calibration standard was polystyrenesulfonate and the eluent was 0.10mol/L $NaNO_3$ solution of 0.50mL/min for aqueous GPC. The other calibration standard and eluent of organic GPC were polystyrene and THF. The samples were respectively dissolved and diluted into 0.3wt% in deionized water and THF, and filtered by a 0.22μm filter.

^{1}H-NMR spectra of samples were measured by DRX-400 spectrometer (Bruker Co., Ettlingen, Germany) with 30mg of each sample dissolved in 0.5mL of deuterated DMSO at room temperature. FTIR spectra of samples were performed using KBr pellets in the 4000-400cm^{-1} region by Fourier Transform infrared spectrometry of Auto system XL/I-series/Spectrum 2000 spectrometry (Thermo Nicolet Co., Madison, WI, USA). The contents of elements (C/H/N/S) were rationed with about 5.0mg packed in aluminized paper by Vario EL cube (Elementar, Germany). The particle sizes distributions were monitored with the concentration of 0.5mg/mL using Dynamic light scattering (DLS) on a Zeta PALS instrument (Brookhaven, USA). The Atomic force microscopy (AFM) image was recorded by Park XE-100 instrument in tapping mode to observe the nanoparticle of SAF. The sample was spread out on the mica plate with the concentration of 0.5g/L.

UV-Vis absorption spectra of the samples were obtained by a UV-3600 UV-Vis spectrophotometer (Shimadzu, Japan). The photoluminescence (PL) spectra were obtained on F-4500 fluorescence spectrometer (Hitachi, Japan) with photomultiplier tube voltage of 400V and scanning speed of 1200nm/min. Fluorescence lifetimes were determined with a Hamamatsu C11367-11 Quantaurus-Tau time-resolved spectrometer. The quantum yield of each sample was calculated using a formula shown below.

$$\emptyset_x = \emptyset_{ST}\left(\frac{I_x/A_x}{I_{ST}/A_{ST}}\right)\left(\frac{{\eta_x}^2}{{\eta_{ST}}^2}\right)$$

Using quinine sulfate as the fluorescence standard and controlling the UV absorbance of samples less than 0.06 in the excitation wavelength of photoluminescence. *I* is the integral area of PL spectra. η is the refractive index (RI) of the solvent. The QY of quinine sulfate ($Ø_{ST}$) is 0.54 dissolved in 0.1M H_2SO_4. AF was dissolved in ethanol which RI is 1.362. SAF and SEAF both dissolved in water which RI is 1.333.

2. Supplemental figures

Figure S1 ^{1}H-NMR spectra of AF (30mg, DMSO), SAF and SEAF (30mg, D_2O).

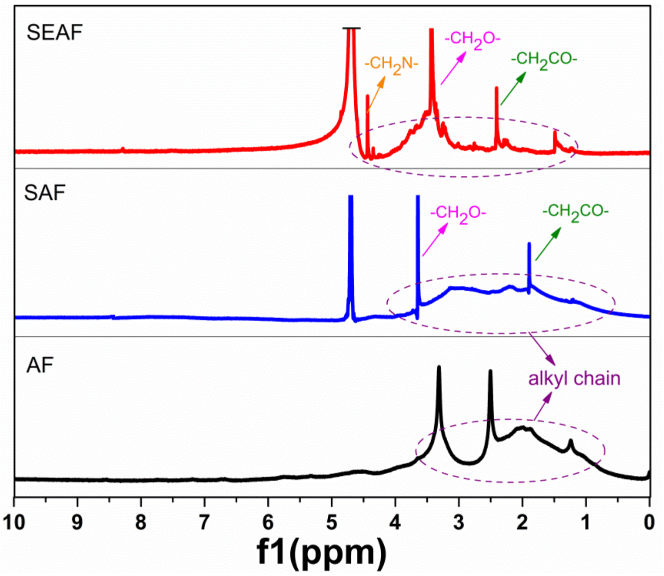
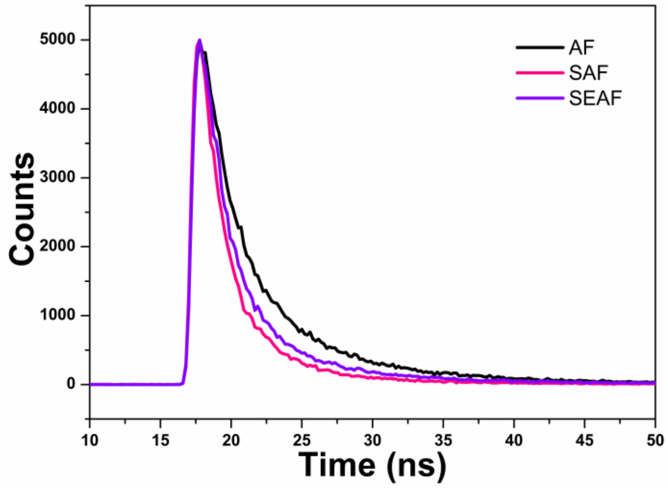


Figure S2 The fluorescence decay of AF, SAF and SEAF in solution and powder state, (a) in the solution state, AF in ethanol, SAF and SEAF in water; (b) in the powder state.

(a) Solution state



(b) Powder state

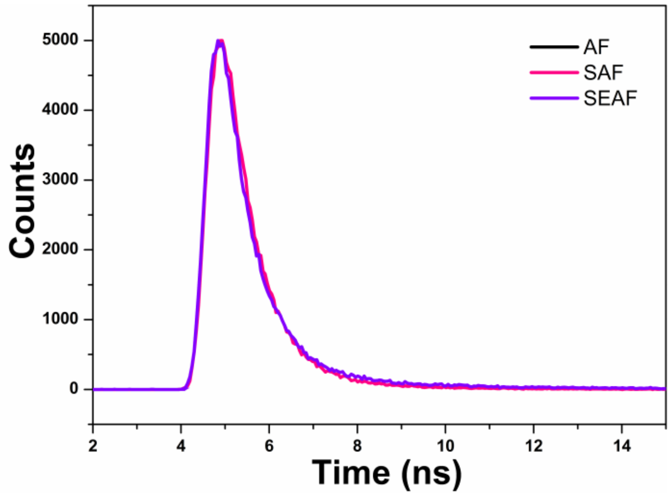
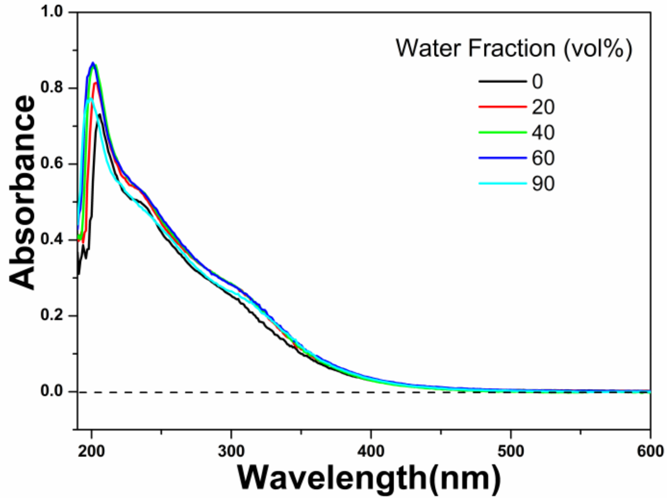
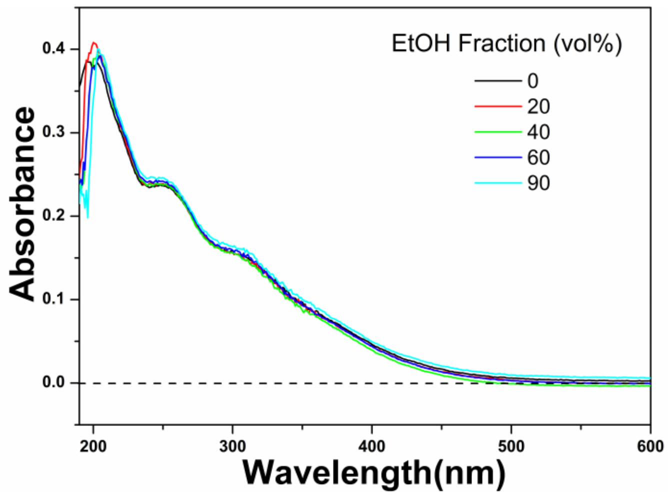


Figure S3 UV absorption spectra of AF, SAF and SEAF in water/ethanol mixtures with different poor solvent fractions, (a) AF, (b) SAF, (c) SEAF, [c] = 1.0 × 10^{-3} g/L.

(a) AF



(b) SAF



(c) SEAF