

Electronic Supplementary Information

**Nonconventional photoluminescence from sulfonated acetone-formaldehyde
condensate with aggregation-enhanced emission†**

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1. Materials

The phenol materials, including Nonyl phenol and P-tert-butylphenol, were purchased from Energy Chemical Co. Ltd. (Shanghai, China). 37% mass fraction of formaldehyde aqueous solution, acetone and all other reagents were of analytical grade. The water used throughout the experiments was deionized water.

2. Experiment sections

2.1 Synthesis of sulfonated phenol-acetone-formaldehyde (SPAF) polymers

Polymerization processes for sulfonated phenol-acetone-formaldehyde polymers (NSPAF, t-SPAF) and sulfonated acetone-formaldehyde polymer (SAF) were shown in Figure S1. Using a one-pot method, 5 g of nonyl phenol or *p*-tert-butylphenol was mixed with 25 mL of 10% sodium hydroxide aqueous solution in a round-bottom flask, respectively. After heating at 50°C for 30 min to melt the phenol material, 2.0 mL of formaldehyde aqueous solution (37% mass fraction) was slowly injected and the temperature was maintained at 75°C for 30 minutes. The rest 2.5 mL of formaldehyde aqueous solution and 3.0 mL of acetone were added together, and 5.0 g of sodium sulfite was added 1 hour later, the reaction was stopped after stirring for 4 hours at 90°C. Remained formaldehyde and acetone were removed the by vacuum rotary evaporation, and a certain amount of hydrochloric acid (20% mass fraction) was added to adjust the pH of the value to 2~3. The acidic products were dialyzed by a dialysis membrane (Special products laboratory, USA, MWCO of 1,000 Da) to remove inorganic salts and excessive starting materials and the purified products were then freeze-dried to obtain brown solid powder samples. The two samples, which were obtained using Nonyl phenol or P-tert-butylphenol as raw material, were named as NSPAF and t-SPAF, respectively.

2.2 Synthesis of sulfonated acetone-formaldehyde (SAF)

With a similar method, SAF was readily prepared as follows. 6.0 mL of formaldehyde aqueous solution (37% mass fraction) and 3.0 mL acetone were mixed with 25 mL of NaOH aqueous solution (10% mass fraction) in flask, and 5 g of

Na₂SO₃ was added after heating reflux at 75°C for 1 hour. The temperature was kept at 90°C and the reaction was finished after stirring for 4 hours. The tawny product that we named as SAF was purified through a same method by vacuum rotary evaporation and dialysis membrane after being adjusted to acidic solution.

2.3 Characterization and measurements

The molecular weights distributions of samples were determined by Waters 1515 Isocratic HPLP pump/Waters 2487 GPC (Waters Co, Milford, MA, USA) which the calibration standard was polystyrene sulfonate with Mw range from 2 to 100 kDa. The eluent was 0.10 mol/L NaNO₃ solution of 0.50 mL/min, all samples were dissolved and diluted into 0.3 wt% in deionized water and filtered by a 0.22 µm aqueous filter.

The ¹H-NMR and ¹³C-NMR spectrum of samples were recorded with 200 mg of each sample dissolved in 0.5 mL of deuterium oxide (D₂O) at room temperature by DRX-400 spectrometer (Bruker Co., Ettlingen, Germany).

The FTIR spectrum of samples were performed using KBr pellets in the 4000-400 cm⁻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 5.0 mg packed in aluminized paper by Vario EL cube (Elementar, Germany).

UV-Vis absorption spectra of the samples were obtained by a UV-2450 UV-Vis spectrophotometer (Shimadzu, Germany). The photoluminescence (PL) spectra of samples were obtained on F-4500 fluorescence spectrometer (Hitachi, Japan) with photomultiplier tube voltage of 400 V and scanning speed of 1200 nm/min, and all samples were recorded using excitation wavelength of 320 nm.

Particle sizes distributions were monitored with the concentration of 0.5 g/L 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 0.5 g/L.

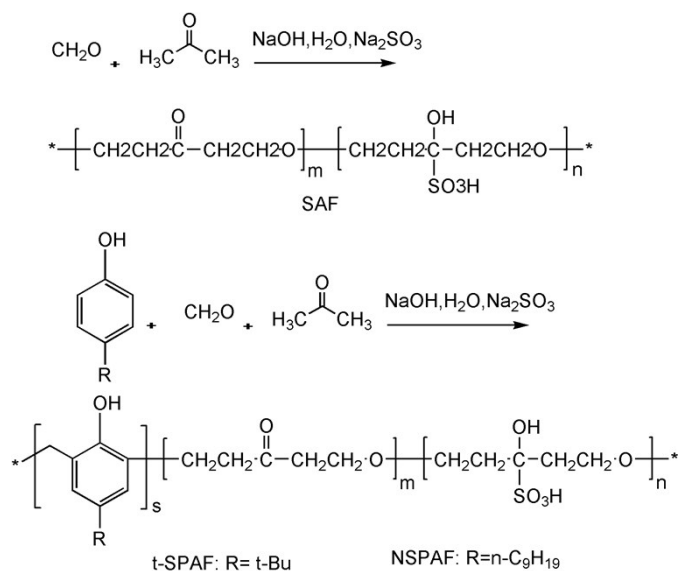
The quantum yield of each sample was calculated using a formula shown below.

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

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 (Φ_{ST}) is 0.54 dissolved in 0.1M H₂SO₄. AF was dissolved in ethanol which RI is 1.362. SAF and SEAF both dissolved in water which RI is 1.333.

3. Synthesis route and chemical structure

Scheme S1 Synthesis route and chemical structure of SAF and SPAFs; s, m and n in the structures respectively indicate the polymerization degree of different elements; R indicates different substituent groups of the phenols.



4. Partial characterization results

Figure S1 Molecular weights distributions of SAF, NSPAF and t-SPAF.

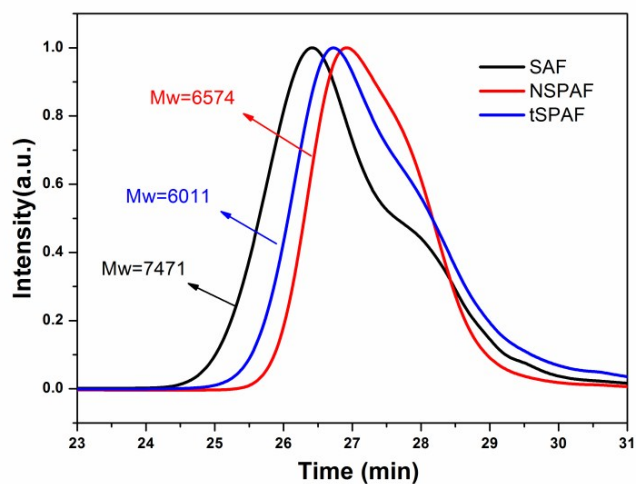


Figure S2 ¹H-NMR and FTIR spectra of SAF, NSPAF and t-SPAF.

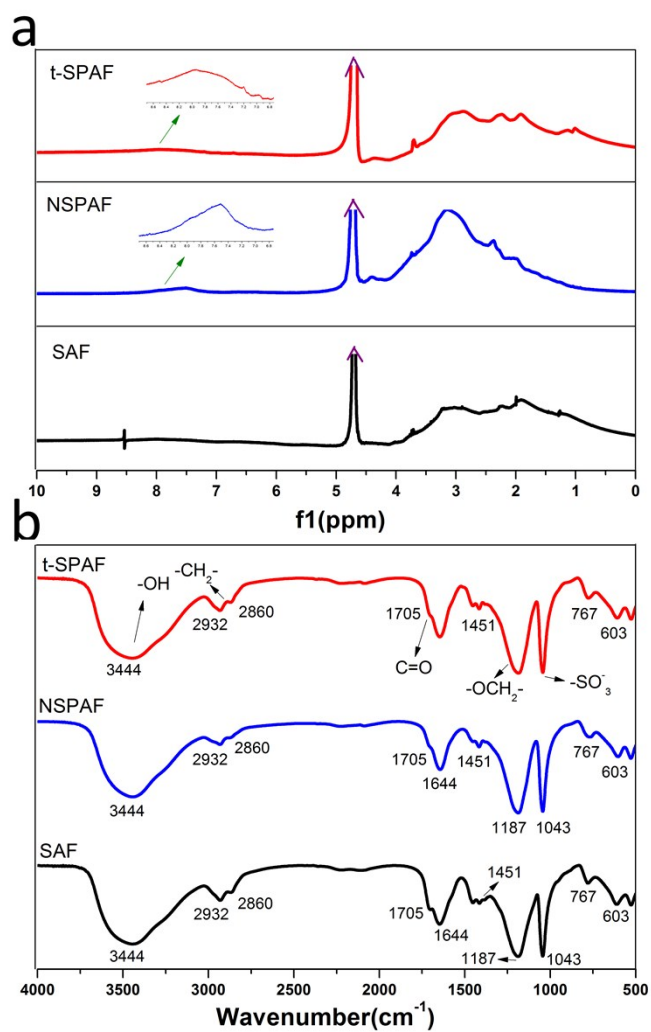


Figure S3 a1), b1) PL spectra of the samples with different concentrations; a2), b2) Plot of PL intensity and fluorescence wavelength versus different concentrations of samples; (a) SAF, (b) NSPAF

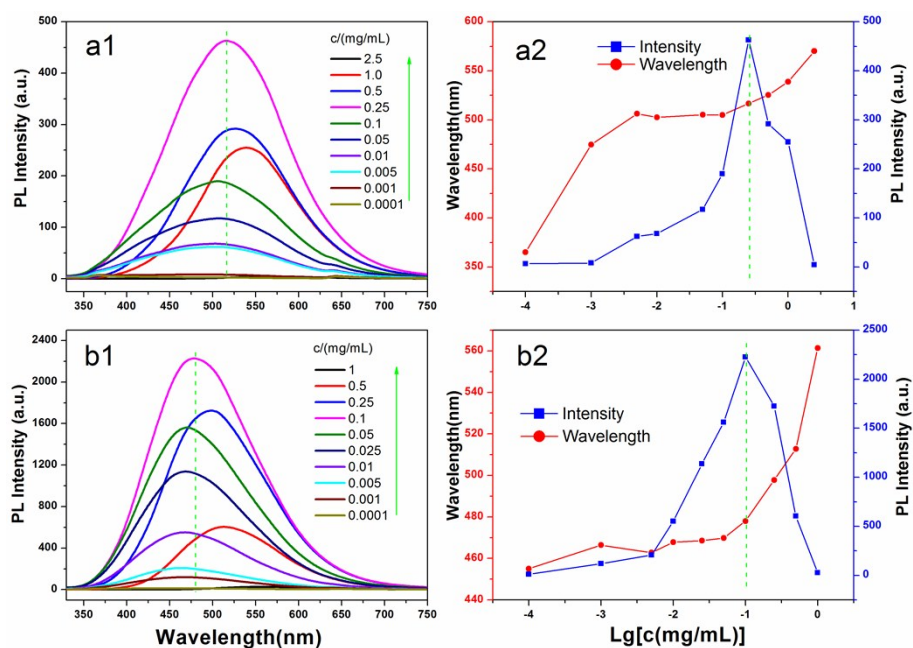
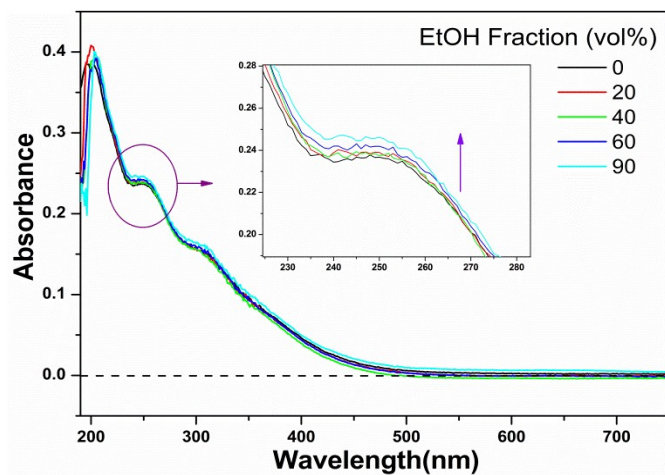
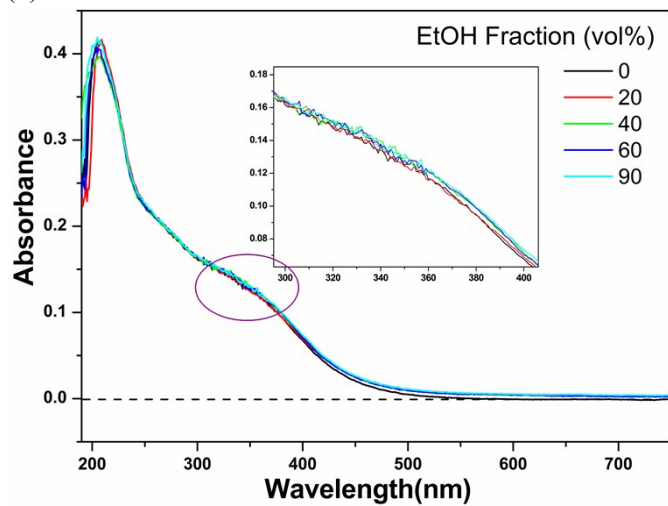


Figure S4 UV-Vis spectra of SAF and SPAFs in water/ethanol mixtures with different ethanol fractions (f_w), (a) SAF, (b) NSPAF, (c) t-SPAF, $[c] = 1.0 \times 10^{-3}$ g/L.

(a) SAF



(b) NSPAF



(c) t-SPAF

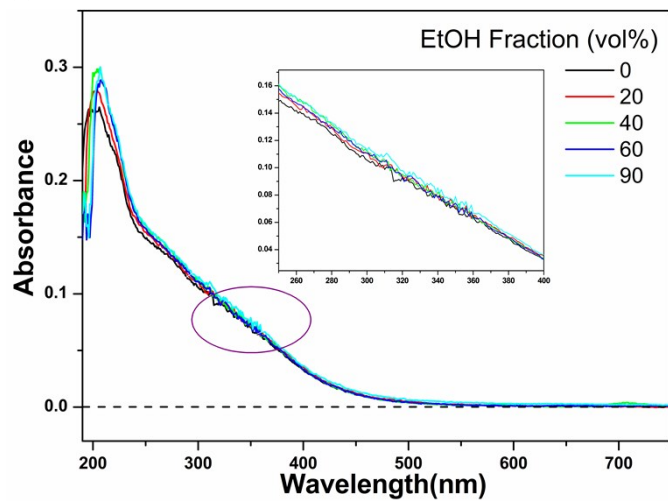


Figure S5 The variation trends for PL intensity of SPAFs in water/glycerol mixtures with glycerin fractions from 0 to 90%. $\lambda_{\text{ex}} = 320\text{nm}$, $[c] = 1.0 \times 10^{-3}\text{g/L}$.

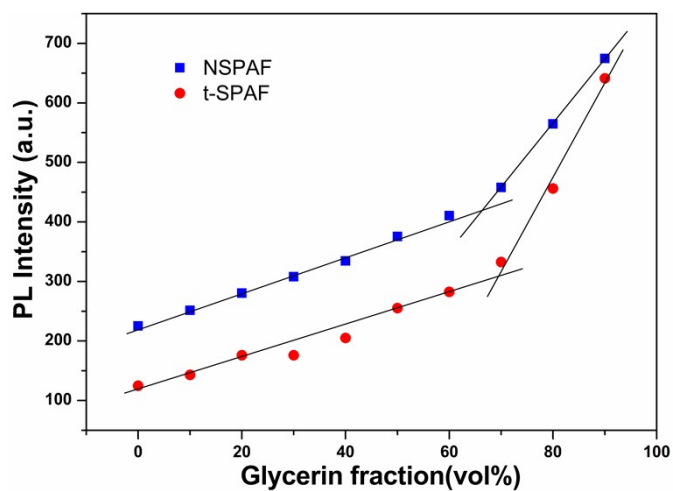


Table S1 Element contents (C, H, N, S) and quantum yields of SAF, NSPAF and t-SPAF

Samples	Element contents (%)				Quantum yields (%)
	C	H	N	S	
SAF	32.98	4.561	0.096	9.911	1.8
NSPAF	28.77	4.179	0.140	12.55	8.3
t-SPAF	32.67	4.434	0.114	15.31	4.3