

Electronic Supplementary Information

Translating efficient fluorescence into persistent room-temperature phosphorescence by doping bipolar fluorophore into polar polymer matrix

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Content

- 1. Materials**
- 2. Experimental section**
- 3. Measurements and methods**
- 4. Supplementary figures and tables**

1. Materials

Coumarin (**Cum**), 7-amino-4-methylcoumarin (**7-AMCum**), 7-hydroxy-4-methylcoumarin (**7-HMCum**) and 7-diethylamino-4-methylcoumarin (**7-DEAMCum**) were purchased from Adamas. Polyacrylic acid (PAA, $M_w = 2000$ g/mol), polyacrylonitrile (PAN, $M_w = 150000$ g/mol), polymethyl methacrylate (PMMA) and polystyrene (PS, $M_w = 104.14$ g/mol) were purchased from Adamas. Polyvinyl alcohol (PVA) with the alcoholysis degree of 87-89% was purchased from General-reagent. All the guests were used with recrystallization for three times and all the hosts were used directly without further purification.

2. Experimental section

Preparation of polymer solutions

PAA (1.2 g) was added in deionized water (40 mL) and stirred at room temperature for 30 min, the PAA solution (15 mg/mL) was obtained. Similarly, PVA (0.6 g) was dissolved in H₂O (40 mL) at 95 °C for 2 h, PAN (0.6 g) was dissolved in N, N-dimethylformamide (DMF) (40 mL) at room temperature for 1 h, PMMA (0.6 g) was dissolved in acetone (40 mL) at 65 °C for 2 h and PS (0.6 g) was dissolved in tetrahydrofuran (THF) (40 mL) at room temperature for 1 h, the PVA, PAN, PMMA, PS solutions (15 mg/mL) were obtained. All the solutions were used for the following experiments.

Preparation of doped polymer films

Cum, **7-HMCum**, **7-AMCum** and **7-DEAMCum** (0.1 mg/mL for each chromophore) were dispersed in the aqueous PAA solution (15 mg/mL), respectively, and each solution was ultrasonicated for 1 h. Then, the films were produced with the drop-casting approach on a 20 mm × 20 mm piezoid substrate. After drying at 100 °C for 2 h, transparent films were obtained.

3. Measurements and methods

Instruments

The UV-Vis absorption spectra were determined on a Perkin Elmer Lambda35 UV-vis spectrometer. The photoluminescence spectra, phosphorescence spectra, the lifetimes of phosphorescence spectra and the photoluminescence quantum efficiency were performed at room temperature on a FLS980 Series of Fluorescence Spectrometers. All the photos were taken by Apple 12 camera.

Computational details

Time-dependent density functional theory (TD-DFT) calculations were performed using Gaussian 16 based on b3lyp6-311g (d,p) level, the excited state energy level, oscillator strength (f), and spin-orbit coupling constant (ξ) of **7-AMCum** were provided.

Phosphorescence quantum yields

The phosphorescence quantum yields of all the doped films were obtained following the equation

$$\Phi_P = \frac{B}{A} \times \Phi_{PL}$$

where A and B represent the integral areas of total photoluminescence and phosphorescence spectra, respectively. The ϕ_{PL} represent the total quantum efficiency of photoluminescence. This method has been reported in previous literature (Jiang, J. Zhi, Y. Wang, H. Yang, W. Zhu, Z. An, *Angew. Chem. Int. Ed.* **2021**, 60, 20058).

The detail for the security protection application

The information encryption pattern is processed into the desired shape with the aid of silicone rubber mold. The ink based on ground **7-HMCum@PVA**, **7-AMCum@PVA** and **7-DEAMCum@PVA** solutions were firstly added into silicone rubber mold. Then the pattern with ρ RTP was obtained after drying at 100 °C for 2 h.

4. Supporting figures and tables

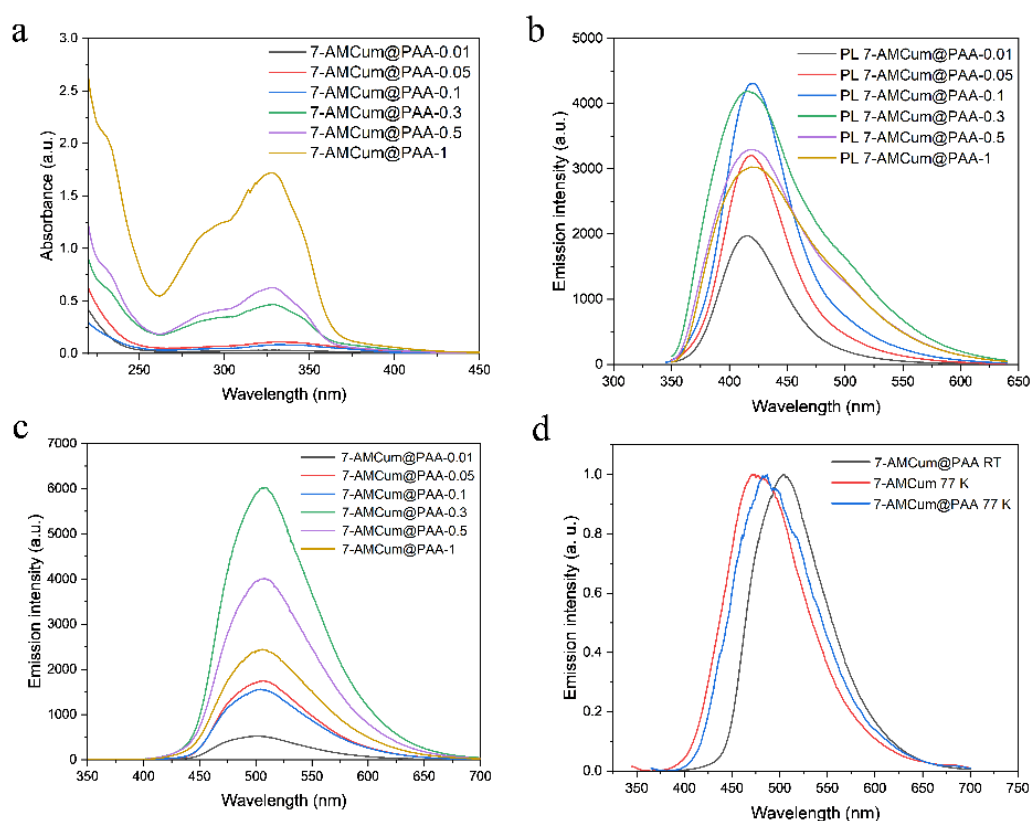


Fig. S1 (a) UV-Vis absorption spectra of **7-AMCum@PAA** at different concentrations under ambient conditions. (b) Normalized PL spectra of **7-AMCum@PAA** at different concentrations under ambient conditions ($\lambda_{ex} = 350$ nm). (c) Delayed spectra of **7-AMCum@PAA** at different concentrations under ambient conditions (delayed time = 8 ms; $\lambda_{ex} = 350$ nm). (d) Delayed spectra of **7-AMCum@PAA** at ambient conditions, **7-AMCum** in EtOH (concentration = 1.0×10^{-5} M) at 77 K and **7-AMCum@PAA** at 77 K ($\lambda_{ex} = 350$ nm).

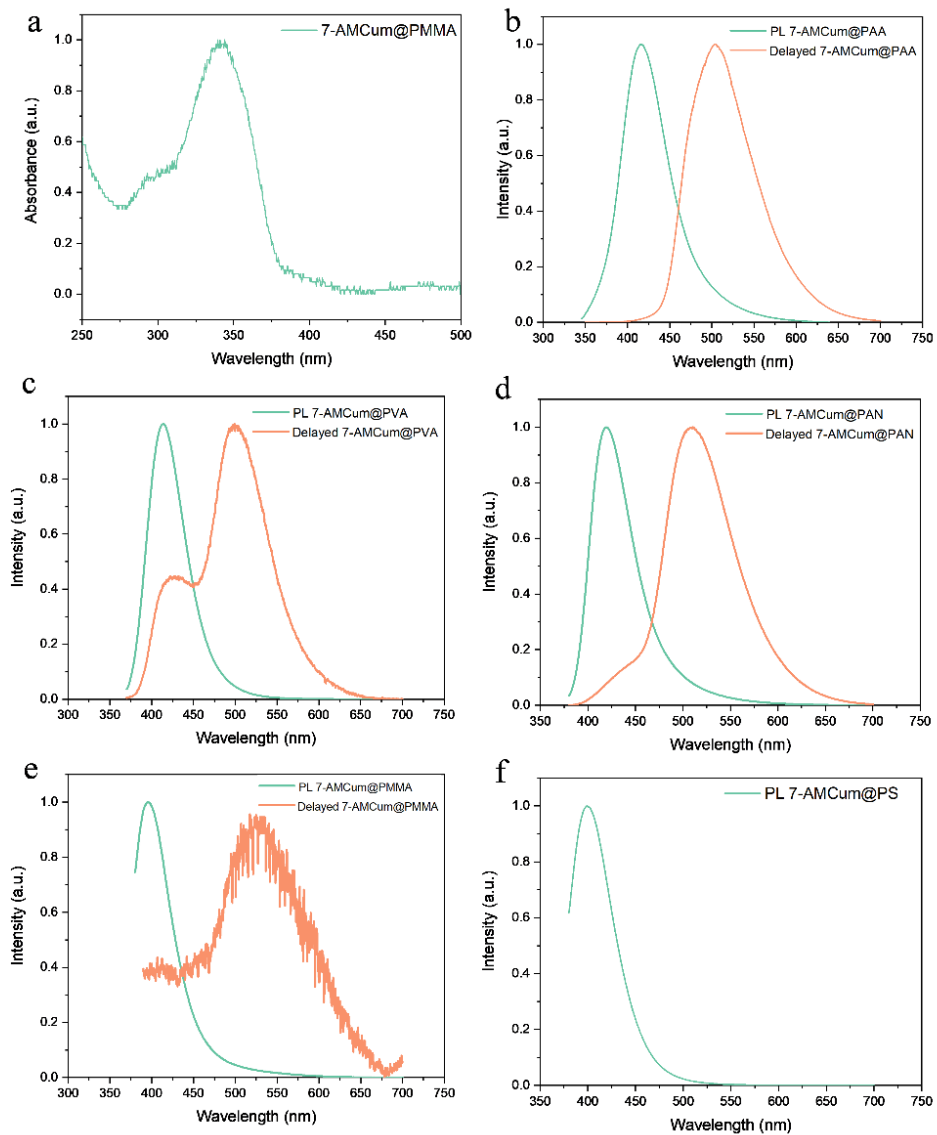


Fig. S2 (a) UV-Vis absorption spectra of **7-AMCum@PMMA** under ambient conditions. Normalized PL and delayed spectra of (b) **7-AMCum@PAA** (c) **7-AMCum@PVA** (d) **7-AMCum@PAN** (e) **7-AMCum@PMMA** under ambient conditions (delayed time = 8 ms; $\lambda_{\text{ex}} = 350$ nm). (f) Normalized PL spectra of **7-AMCum@PS** under ambient conditions ($\lambda_{\text{ex}} = 350$ nm).

Table S1 Photophysical parameters of **7-AMCum** doped in different hosts at 0.1mg/mL doping concentration.

Doped films ^a	λ_F (nm) ^b	λ_P (nm) ^c	ΔE_{ST} (eV) ^d
7-AMCum@PAA	415	504	0.53
7-AMCum@PVA	413	504	0.54
7-AMCum@PAN	419	506	0.51
7-AMCum@PMMA	395	506	0.69

^a The concentration of guests and polymer matrices were 0.1 mg/mL and 15 mg/mL, respectively. To prepare films, the guest and polymer matrix were doped by 1:1. ^b Fluorescence emission maxima of steady-state photoluminescence spectra. ^c pRTP maxima of delayed emission spectra. ^d The difference value of energy level between singlet state and triplet state.

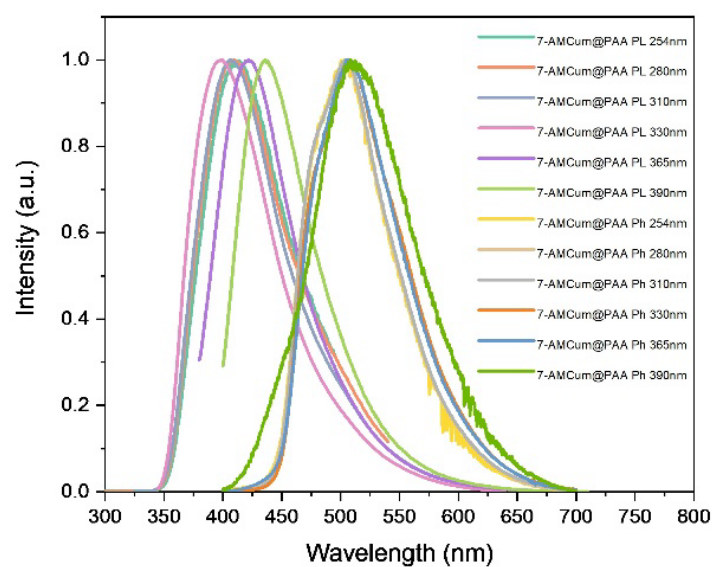


Fig. S3 PL and phosphorescence spectra of **7-AMCum@PAA** under different excitation wavelength.

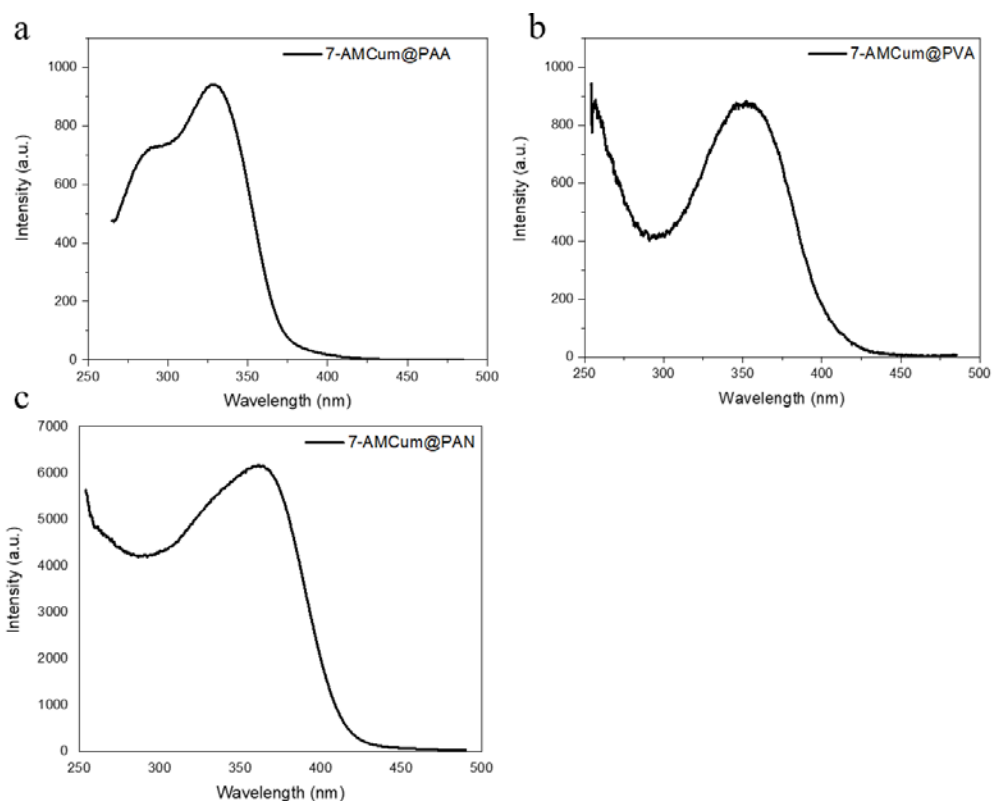


Fig. S4 Excitation spectra of **7-AMCum@PAA** (a), **7-AMCum@PVA**(b) and **7-AMCum@PAN** (c) at 0.1 mg/mL under ambient conditions ($\lambda_{ex} = 500$ nm).

Table S2 Photophysical parameters of **7-AMCum** doped in different hosts at 0.1mg/mL doping concentration.

Doped films ^a	ϕ_{PL} (%) ^b	ϕ_p (%) ^c	τ_p (ms) ^d	k_p (s ⁻¹) ^e	k_{nr} (s ⁻¹) ^f
7-AMCum@PAA	8.00	4.48	1000	4.48×10^{-2}	9.55×10^{-1}
7-AMCum@PVA	74.52	12.44	294	4.23×10^{-1}	2.98
7-AMCum@PAN	31.63	5.54	178	3.11×10^{-1}	5.31

^a The concentration of guests and polymer matrices were 0.1 mg/mL and 15 mg/mL, respectively. To prepare films, the guest and polymer matrix were doped by 1:1. ^b Fluorescence and phosphorescence emission maxima of steady-state photoluminescence spectra and phosphorescence spectra. ^c Fluorescence quantum yield. ^d Phosphorescence quantum yield. ^e Phosphorescence lifetime at room temperature. ^f k_p and ^g k_{nr} are the radiative rate constant and nonradiative rate constant of T_1 state, respectively. $k_p = \phi_p / \tau_p$; $k_{nr} = (1 - \phi_p) / \tau_p$.

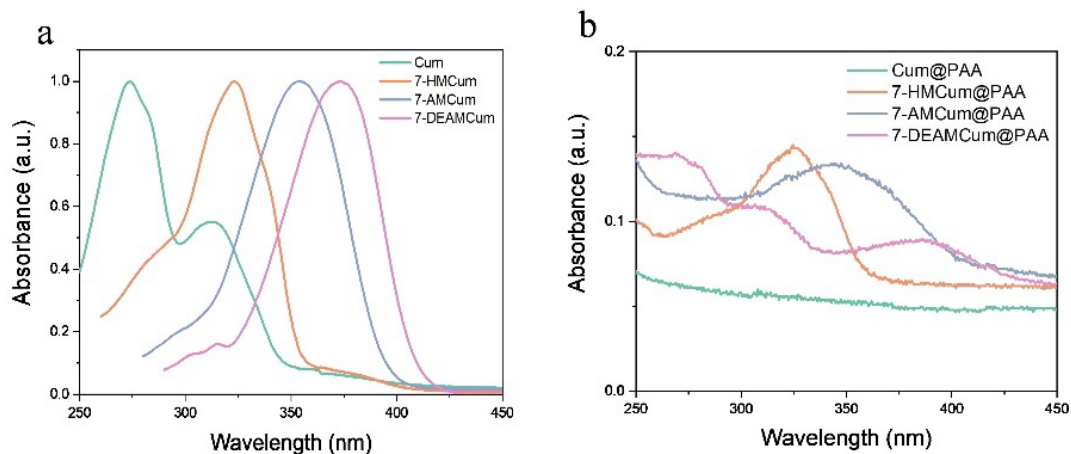


Fig. S5 (a) UV-Vis absorption spectra of guests in EtOH under ambient conditions (concentration = 1.0×10^{-5} M). (b) UV-Vis absorption spectra of **Cum@PAA**, **7-HMCum@PAA**, **7-AMCum@PAA** and **7-DEAMCum@PAA** under ambient conditions (0.1 mg/mL).

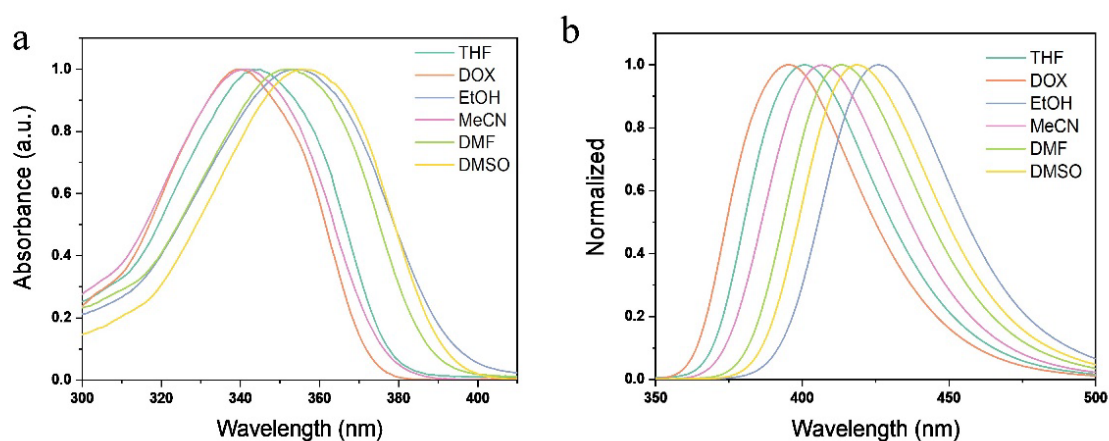


Fig. S6 (a) UV-Vis absorption spectra of **7-AMCum** in different solvents (concentration = 1.0×10^{-5} M) under ambient conditions. (b) PL spectra of **7-AMCum** in different solvents (concentration = 1.0×10^{-5} M) under ambient conditions ($\lambda_{\text{ex}} = 350$ nm).

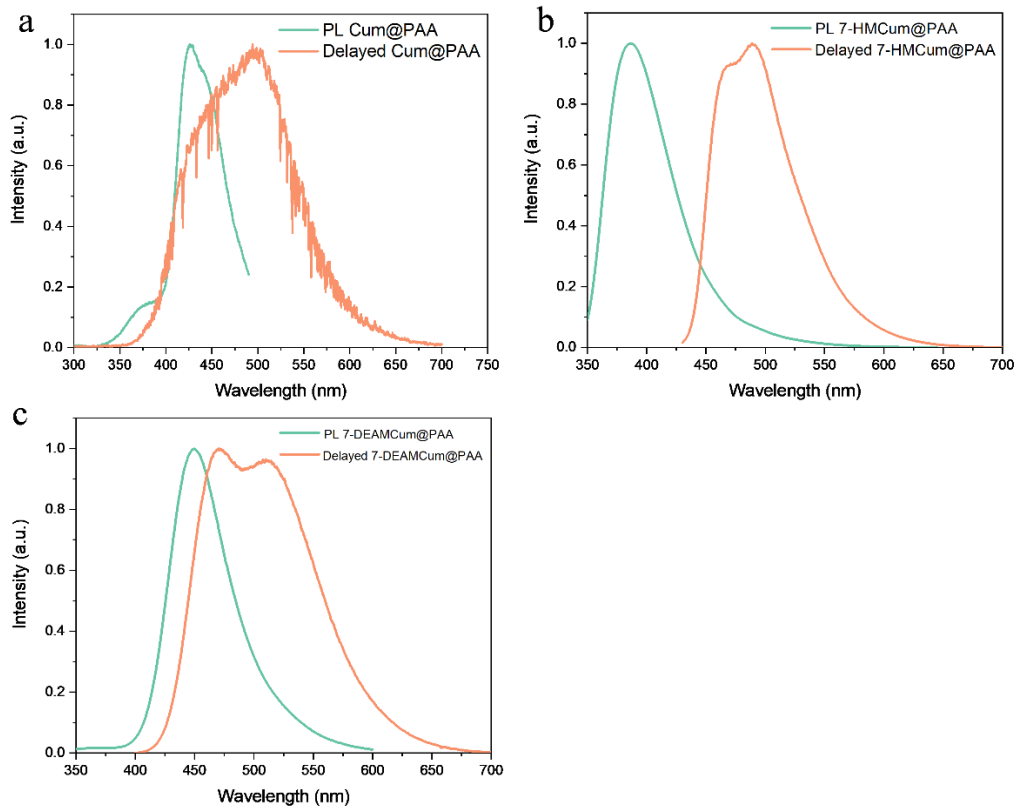


Fig. S7 Normalized PL and delayed spectra of (a) **Cum@PAA** (b) **7-HMCum@PAA** (c) **7-DEAMCum@PAA** at room temperature ($\lambda_{ex} = 280, 330, 300$ nm, respectively).

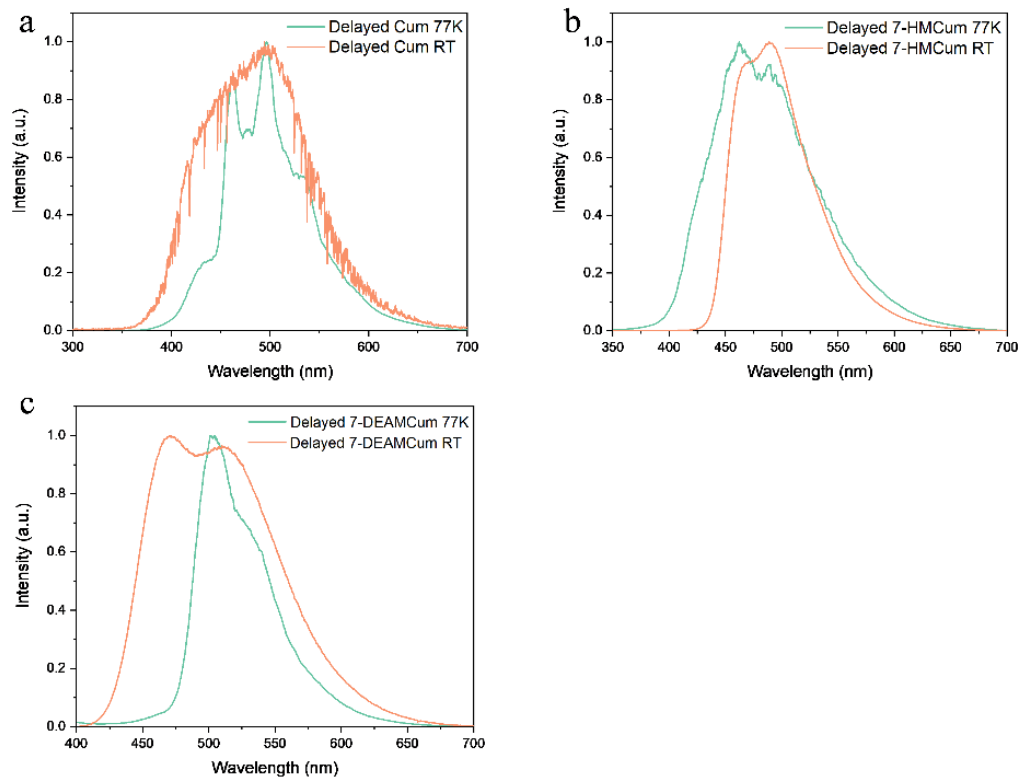


Fig. S8 Delayed spectra of (a) **Cum** (b) **7-HMCum** (c) **7-DEAMCum** in EtOH (concentration = 1.0×10^{-5} M) at 77 K (λ_{ex} = 280, 365, 365 nm, respectively) and in films under ambient conditions.

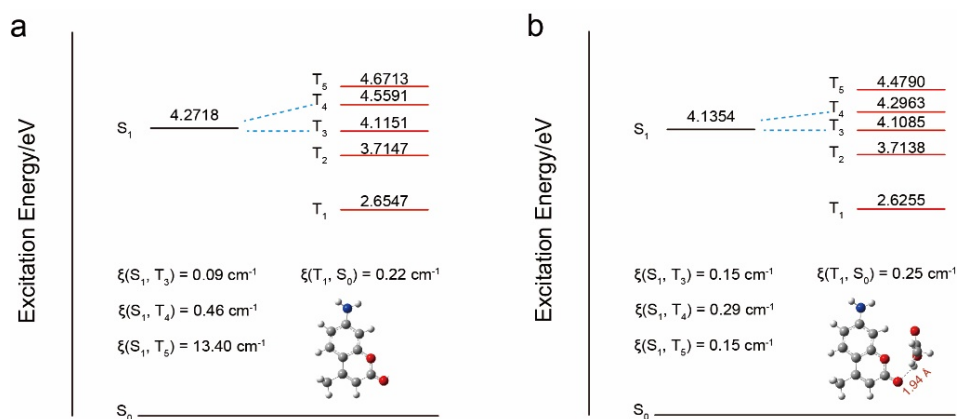














Fig. S9 Calculated S_1 and T_n energy levels and SOC matrix element values between S_1 and T_n states of (a) **7-AMCum**, (b) **7-AMCum** in acetic acid.

Table S3 Calculated NTO pairs and energy levels of the excited singlet and triplet states of **7-AMCum** (b3lyp 6-311g (d, p) basis set).

State	Hole	Particle	Excitation energy
S_1			4.27 eV
T_1			2.65 eV
T_2			3.71 eV
T_3			4.12 eV
T_4			4.56 eV
T_5			4.67 eV

Table S4 Calculated NTO pairs and energy levels of the excited singlet and triplet states of **7-AMCum** (b3lyp 6-311g (d, p) basis set, in acetic acid).

State	Hole	Particle	Excitation energy
S ₁			4.14 eV
T ₁			2.63 eV
T ₂			3.71 eV
T ₃			4.11 eV
T ₄			4.30 eV
T ₅			4.48 eV

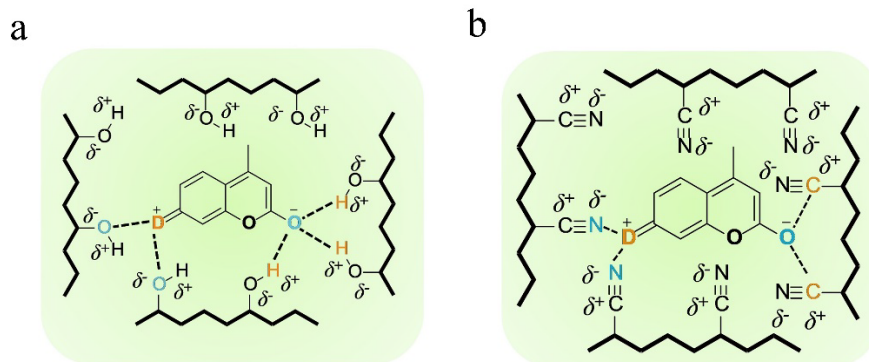


Fig. S10 Stabilizing the charge separated state of polar coumarin by polar (a) PVA, (b) PAN host under first excited singlet state (S₁).