Boosting Room-Temperature Phosphorescence via Polarity-Induced Through-space conjugation in a Host-Guest Doping System

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1. Experimental part

1.1 Reagents and Materials

All the chemical reagents used were purchased from Adamas Company. Unless otherwise stated, all the reagents used in the experiments were obtained from commercial sources and purified through three rounds of recrystallization.

1.2 Preparation of the doping material Cums/Ar-COOH

0.3 g of PA, IPA and TMA were respectively taken into vials, 6 mL of methanol was added, and then certain amounts of 5 mg/mL guest-methanol mixed solutions were added at different molar ratios. The solutions were thoroughly stirred and dissolved until they became clear and transparent. The materials with different doping concentrations were obtained by vacuum rotary evaporation.

1.3 Measurements

Steady-state photoluminescence spectra, phosphorescence spectra, and phosphorescence decay curves under ambient conditions were measured with an FL-7100 spectrometer. Phosphorescence

spectra were acquired with a delay time of 8 ms. Phosphorescence spectra were measured using Edinburgh FLS1000 at 77 K. Photoluminescence quantum yields were collected for all materials under ambient conditions using an Edinburgh FLS 1000 equipped with an integrating sphere. Photoluminescence photos were taken with an iPhone 16 Pro max under room temperature with handheld UV lamp (365 nm) illumination.

Powder X-ray diffraction (P-XRD) spectra were measured using a Shimadzu-6100 X-ray diffractometer with Cu-Kα radiation at a wavelength of 1.542 Å. Diffraction was measured over a 2θ angle range of 5-60° and recorded at a scan rate of 1 degree per minute.

Solid-state ultraviolet-visible absorption (UV-vis) spectra were obtained using the Shimadzu UV-2600 i. Liquid-state UV-visible absorption spectra were obtained using UV-9000 s.

1.4 Calculation of optical physical parameters

The phosphorescence quantum yield of the compounds is given by Eq:

$$\emptyset_{Ph} = \frac{A_{Ph}}{A_{PL}} \times \emptyset_{PL}$$

Where A_{PL} and A_{Ph} represent the integration regions of the total photoluminescence and phosphorescence spectra, respectively.

The energy gap between T_1 and S_1 (ΔE_{ST}), as reported in the literature, is calculated as follows:

$$\Delta E_{ST} = hk\left(\frac{c}{\lambda_1} - \frac{c}{\lambda_2}\right)$$

Where h is Planck's constant (4.14×10^{-15} eV·s), c is the speed of light (3×10^{17} nm/s), k is the conversion constant (1.6×10^{-19} J/eV), and λ_1 and λ_2 are the fluorescence and phosphorescence emission wavelengths, respectively.

1.5 Theoretical calculation

In this study, all simulations of ground- and excited-state geometries and electronic structures were performed using the Gaussian 16 package The ground-state (S_0) geometries of all molecules were

optimized at the B3LYP/def2-SVP level of density functional theory (DFT), ensuring that each structure reached the minimum-energy configuration. Based on these optimized geometries, time-dependent density functional theory (TD-DFT) calculations were subsequently carried out at the PBE0/6-31G(d,p) level to optimize the triplet excited-state (T_1) geometries, thereby obtaining the stable molecular conformations in the excited state for further investigation of their photophysical properties.

2. Other properties

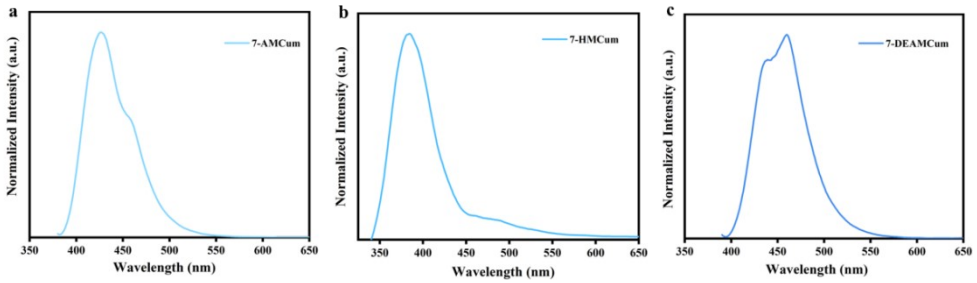

Figure S1. Steady-state PL Spectra of a) 7-AMCum, b) 7-HMCum, c) 7-DEAMCum in ethanol solution (1×10^{-5} M) at 298 K (λ_{ex} = 318/360/330 nm).

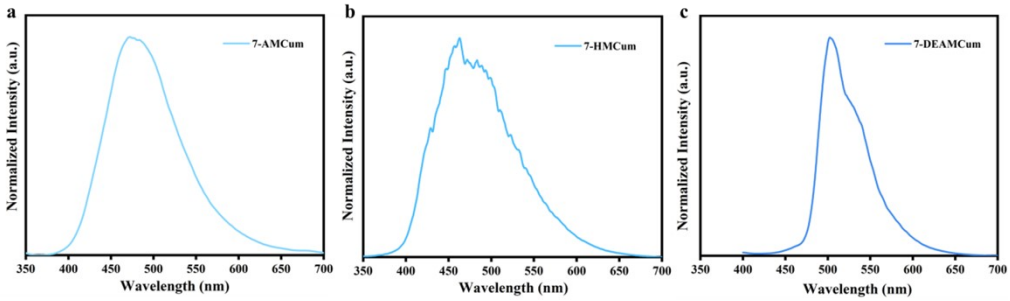

Figure S2. Delay Spectra of a) 7-AMCum, b) 7-HMCum c) 7-DEAMCum in ethanol solution (1×10^{-5} M) at 77 K (λ_{ex} = 350/365/365 nm).

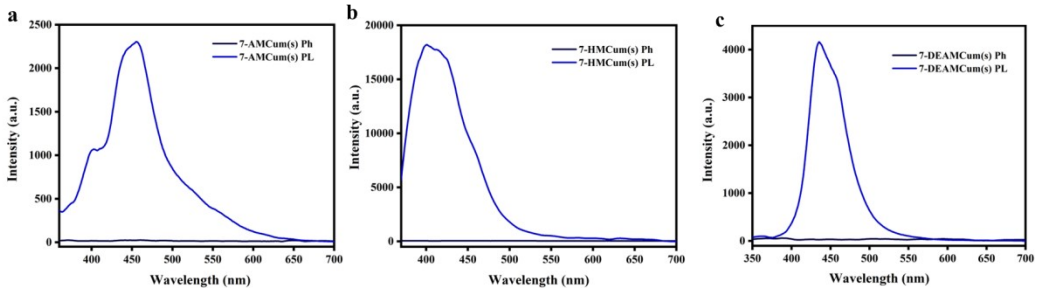

Figure S3. Steady-state PL spectra and delay spectra of a) 7-AMCum, b) 7-HMCum c) 7-DEAMCum in solid state at 298 K (λ_{ex} = 318/360/330 nm, delay time = 8 ms).

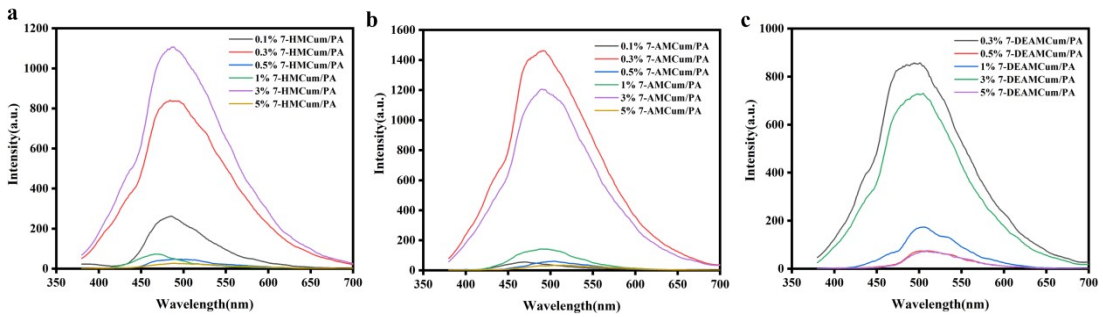

Figure S4. Delay spectra of a) 7-HMCum, b) 7-HMCum c) 7-DEAMCum at 298 K with different doping concentrations (λ_{ex} = 290 nm, delay time = 8 ms).

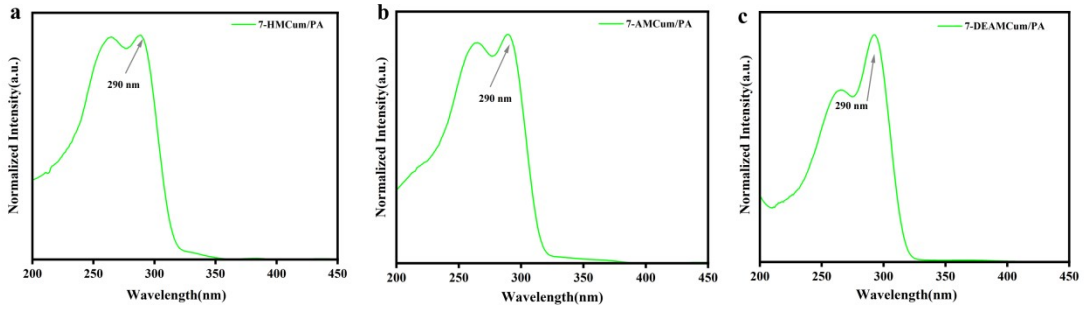

Figure S5. Phosphorescent Excitation spectra of a) 7-HMCum/PA, b) 7-AMCum/PA c) 7-DEAMCum/PA at 298 K (λ_{em} = 480/490/500 nm, delay time = 8 ms).

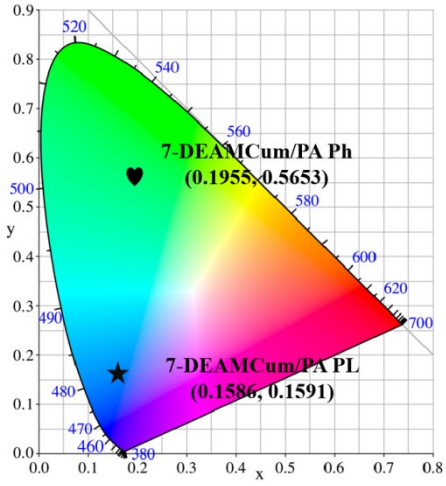

Figure S6. The fluorescence and phosphorescence CIE coordinates of 7-DEAMCum/PA

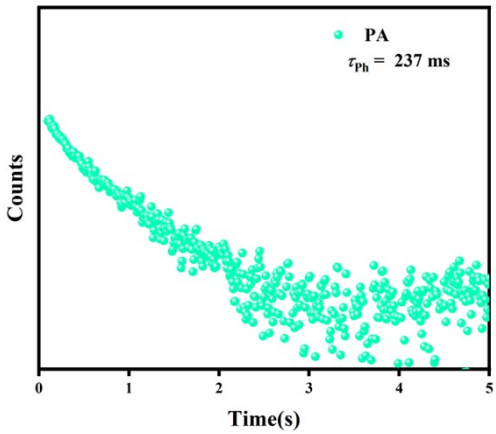

Figure S7. Phosphorescence decay curves of PA at 298 K

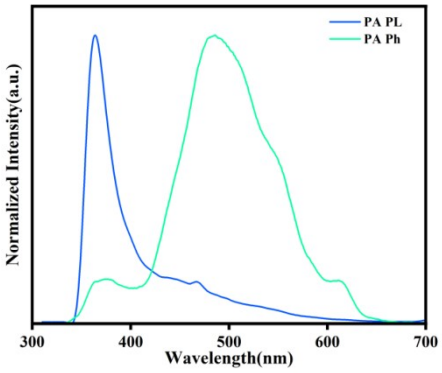

Figure S8. Normalized steady-state PL spectra and delayed spectra of PA at 298 K (λ_{ex} = 290 nm, delayed time = 8 ms)

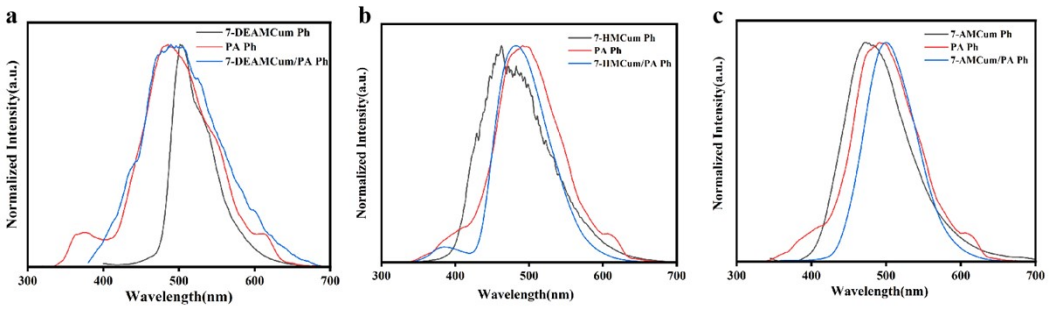

Figure S9. Normalized delayed spectra of a) PA, 7-DEAMCum/PA and 7-DEAMCum b) PA, 7-HMCum/PA and 7-HMCum c) PA, 7-AMCum/PA and 7-AMCumin. (PA, 7-DEAMCum/PA, 7-HMCum/PA and 7-AMCum/PA are in the solid state at 298K; 7-DEAMCum, 7-HMCum and 7-AMCum in ethanol solution (1×10^{-5} M) at 77 K).

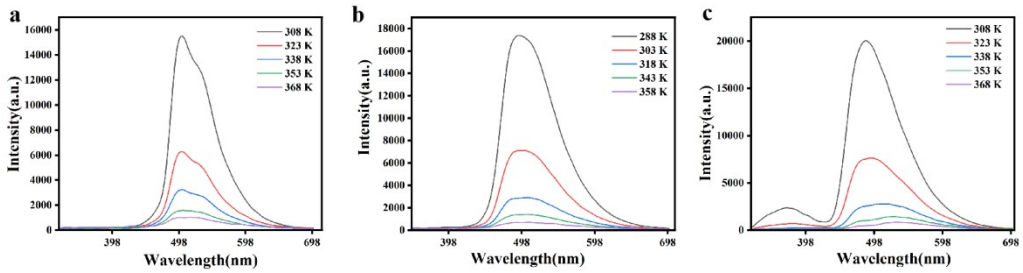

Figure S10. Phosphorescence spectra of a) 7-DEAMCum/PA b) 7-AMCum/PA and c) 7-HMCum/PA at different temperatures

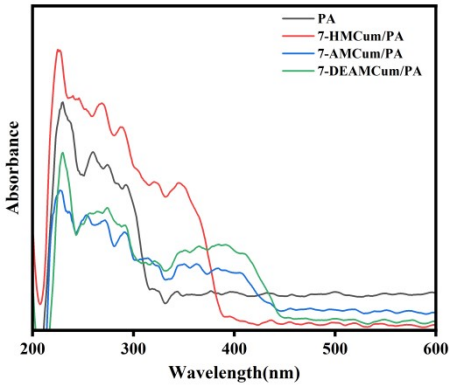

Figure S11. a) Solid-state UV-vis absorption spectra of PA, 7-HMCum/PA, 7-AMCum/PA, and 7-DEAMCum/PA at ambient conditions

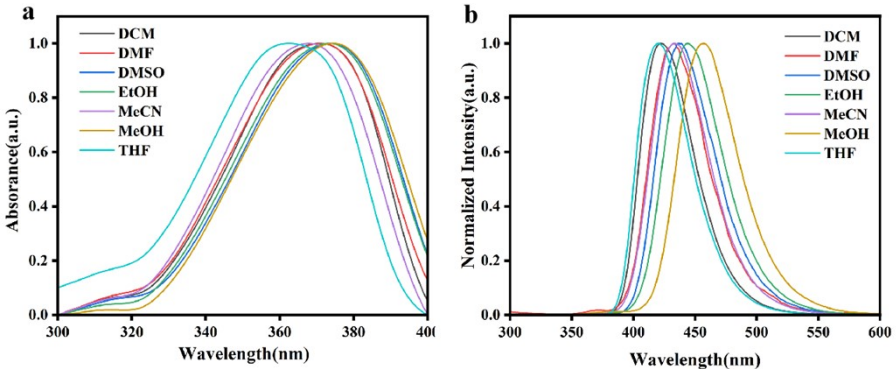

Figure S12. a) UV-Vis absorption spectra of 7-DEAMCum in different solvents (concentration = 1.0×10^{-5}M) under ambient conditions b) PL spectra of 7-DEAMCum in different solvents (concentration = 1.0×10^{-5} M) under ambient conditions.

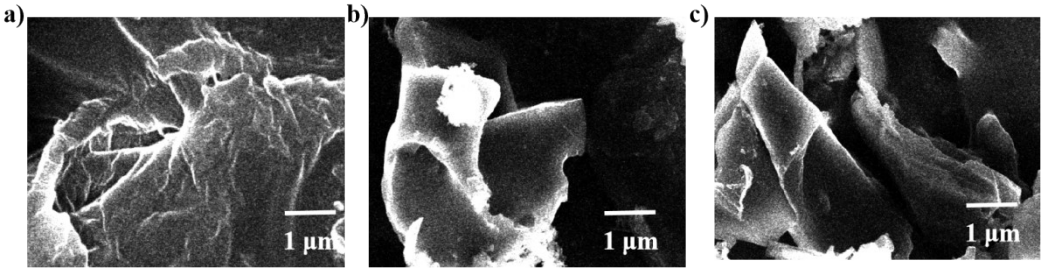

Figure S13. a) SEM image of PA b) SEM image of 7-AMCum/PA c) SEM image of 7-HMCum/PA.

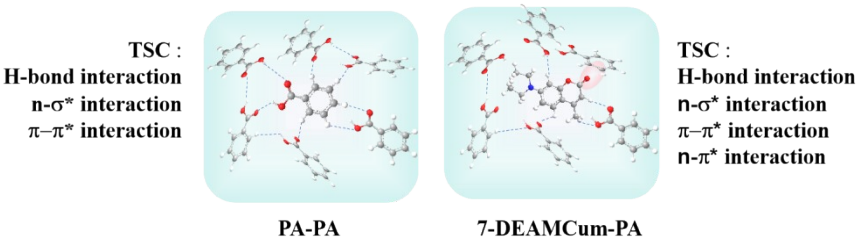

Figure S14. The changes in through-space conjugation (TSC) before and after the mixing of the host and guest.

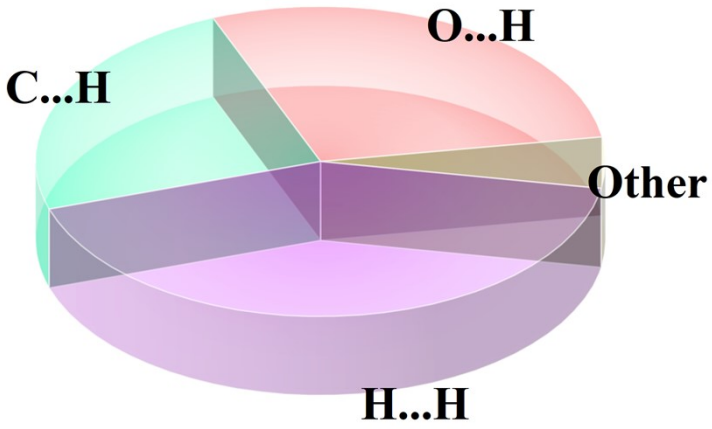

Figure S15. Pie chart (PA-PA) of the relative contribution of the Surface area of Hirshfeld Surface.

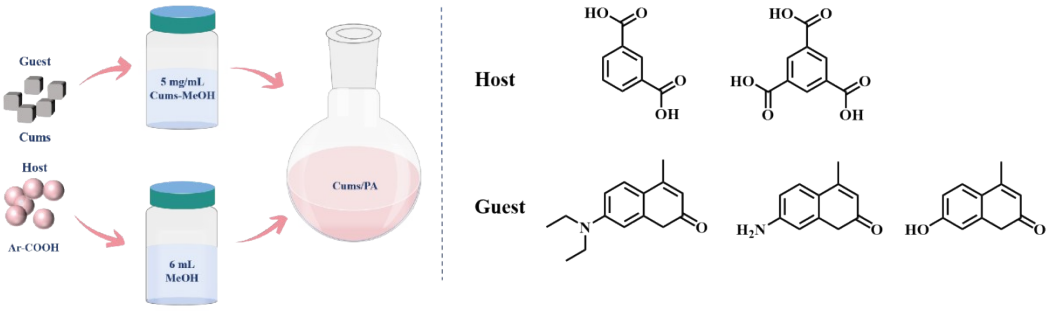

Figure S16. Flowchart of the general applicability experiment and chemical structures of the host-guest materials.

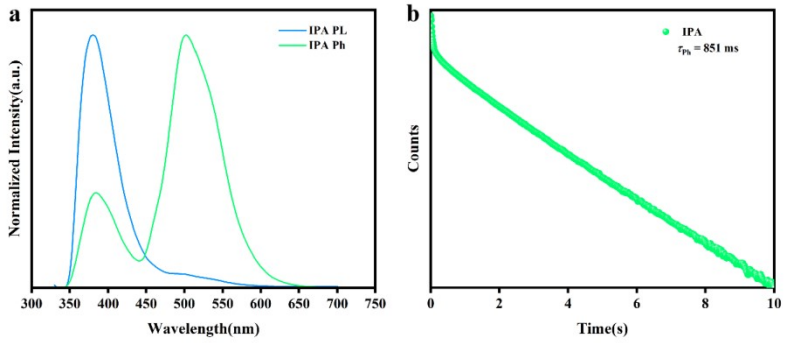

Figure S17. a) Normalized steady-state PL spectra and delayed spectra of IPA at 298 K (λ_{ex} = 275 nm, delayed time = 8 ms) b) Phosphorescence decay curves of IPA at 298 K

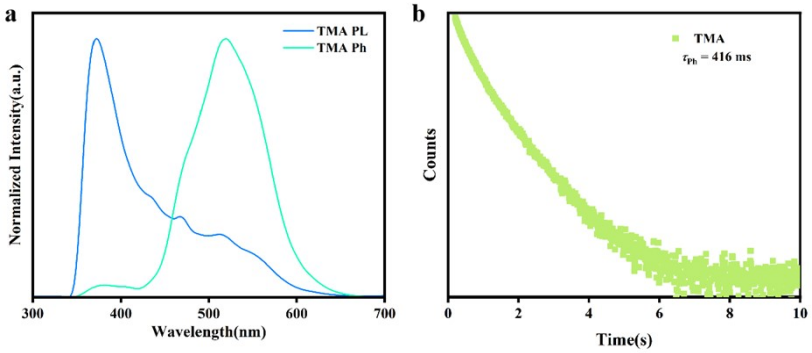

Figure S18. a) Normalized steady-state PL spectra and delayed spectra of TMA at 298 K (λ_{ex} = 275 nm, delayed time = 8 ms) b) Phosphorescence decay curves of TMA at 298 K

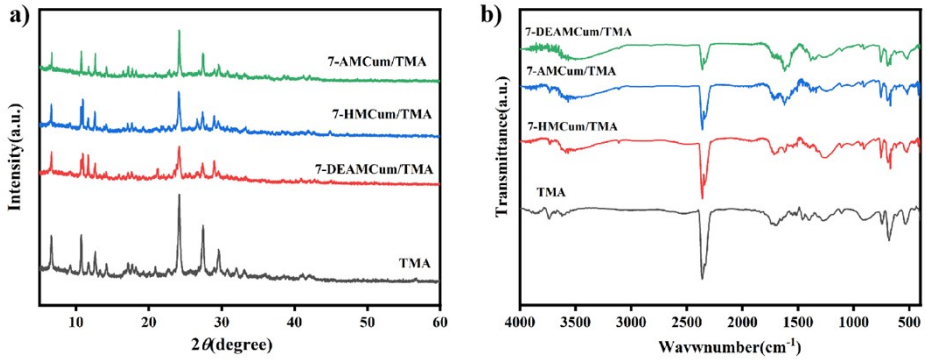

Figure 19. a) P-XRD patterns of TMA, 7-HMCum/TMA, 7-AMCum/TMA and 7-DEAMCum/TMA b) FT-IR spectra of TMA, 7-HMCum/TMA, 7-AMCum/TMA and 7-DEAMCum/TMA

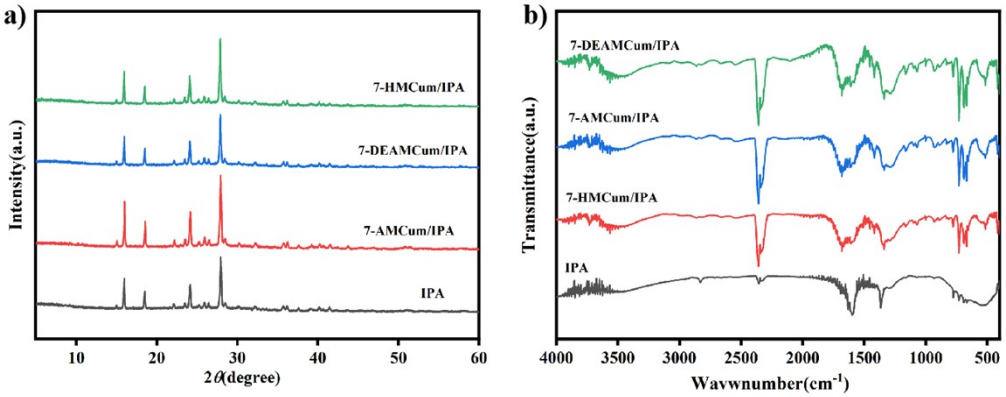

Figure 20. a) P-XRD patterns of IPA, 7-HMCum/IPA, 7-AMCum/IPA and 7-DEAMCum/IPA b) FT-IR spectra of IPA, 7-HMCum/IPA, 7-AMCum/IPA and 7-DEAMCum/IPA

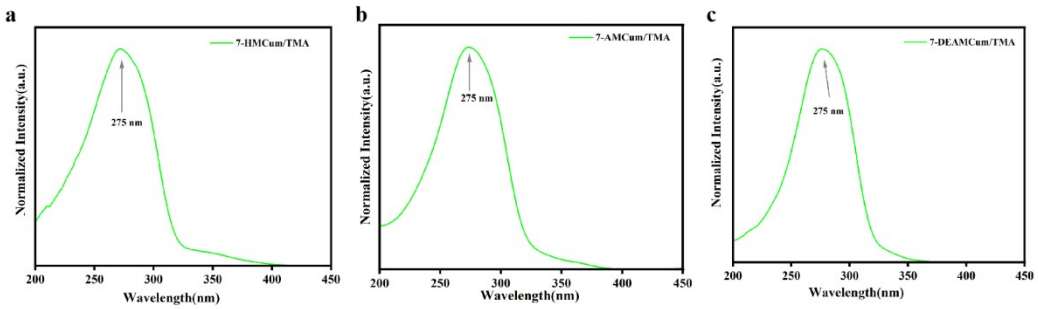

Figure S21. Phosphorescent Excitation spectra of a) 7-HMCum/TMA, b) 7-AMCum/TMA c) 7-DEAMCum/TMA at 298 K (λ_{em} = 540/537/540 nm, delay time = 8 ms).

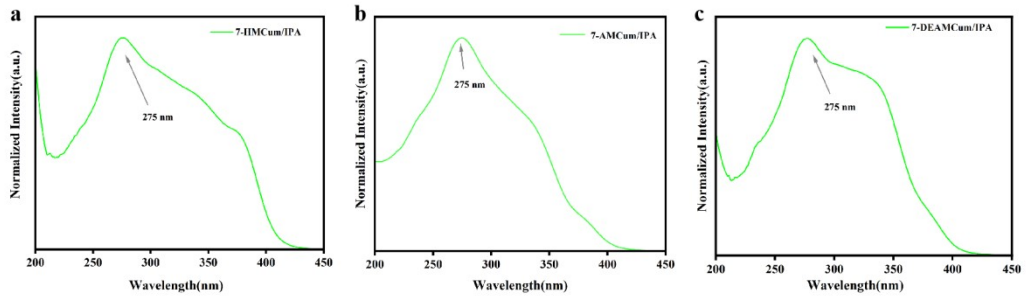

Figure S22. Phosphorescent Excitation spectra of a) 7-HMCum/IPA, b) 7-AMCum/IPA c) 7-DEAMCum/IPA at 298 K (λ_{em} = 506/506/506 nm, delay time = 8 ms).

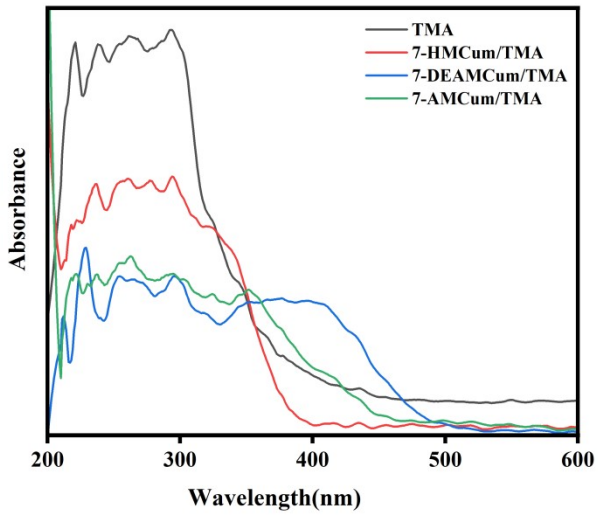

Figure S23. a) Solid-state UV-vis absorption spectra of TMA, 7-HMCum/TMA, 7-AMCum/TMA, and 7-DEAMCum/TMA at ambient conditions

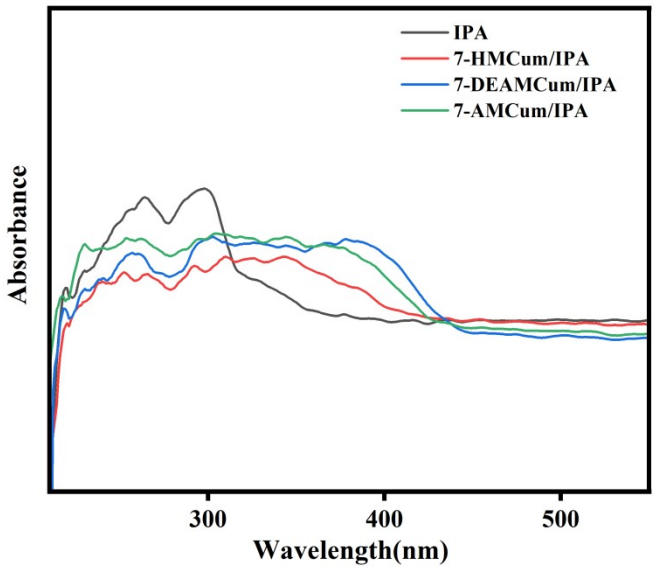

Figure S24. a) Solid-state UV-vis absorption spectra of IPA, 7-HMCum/IPA, 7-AMCum/IPA, and 7-DEAMCum/IPA at ambient conditions

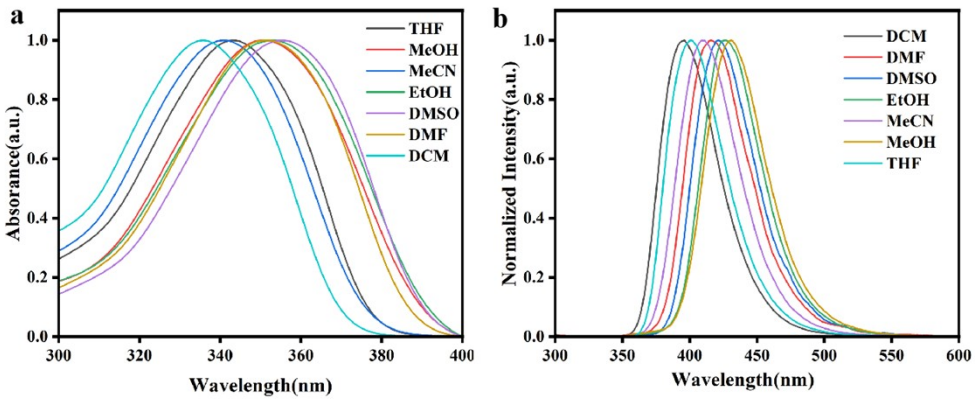

Fig. S25 a) UV-Vis absorption spectra of 7-AMCum in different solvents (concentration = 1.0×10^{-5}M) under ambient conditions b) PL spectra of 7-AMCum in different solvents (concentration = 1.0×10^{-5} M) under ambient conditions.

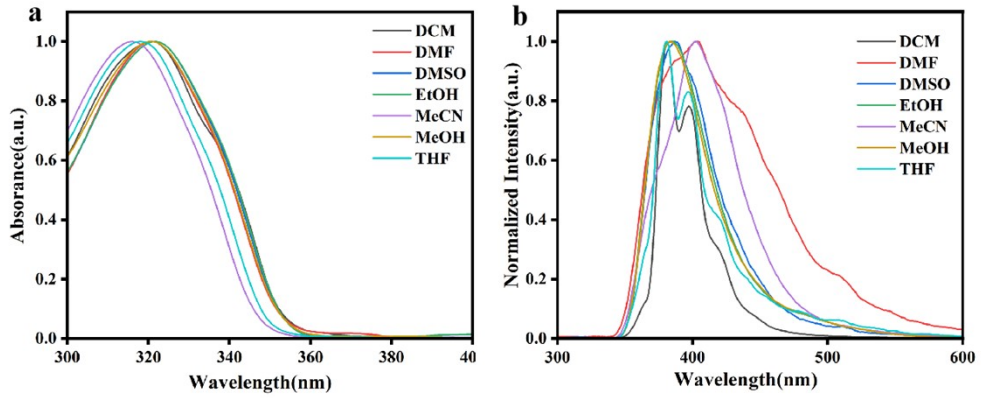

Fig. S26 a) UV-Vis absorption spectra of 7-HMCum in different solvents (concentration = 1.0×10^{-5}M) under ambient conditions b) PL spectra of 7-HMCum in different solvents (concentration = 1.0×10^{-5} M) under ambient conditions.

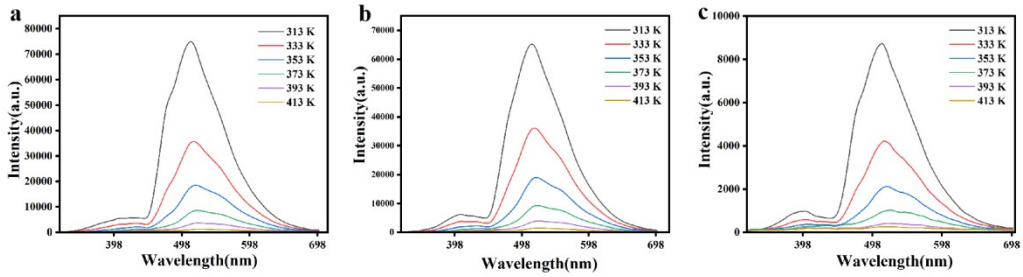

Figure S27. Phosphorescence spectra of a) 7-DEAMCum/IPA b) 7-AMCum/IPA and c) 7-HMCum/IPA at different temperatures

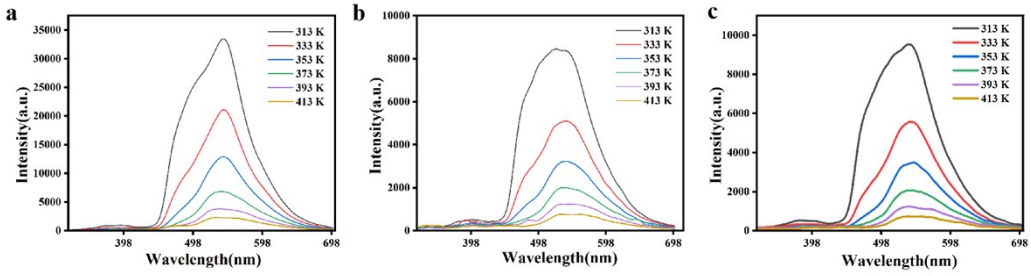

Figure S28. Phosphorescence spectra of a) 7-DEAMCum/TMA b) 7-AMCum/TMA and c) 7-HMCum/TMA at different temperatures

Table S1. Dipole moment values of coumarin derivatives in the ground and excited states.

Sample	The ground state dipole moment	The excited state dipole moment
7-HMCum	4.31	4.05
7-AMCum	6.80	6.72
7-DEAMCum	7.06	7.09

Table S2. Transition dipole moments of coumarin derivatives.

Sample	$\mu_{T_1 \to S_0}{}^1$	$\mu_{T_1 \to S_0}{}^2$	$\mu_{T_1 \to S_0}{}^3$	$\mu_{T_1 \to S_0}$
7-HMCum	2.00×10^{-5}	2.24×10^{-5}	1.00×10^{-5}	1.75×10^{-5}
7-AMCum	2.00×10^{-5}	2.24×10^{-5}	3.00×10^{-5}	2.41×10^{-5}
7-DEAMCum	2.45×10^{-5}	2.37×10^{-5}	4.12×10^{-5}	2.98×10^{-5}

Table S3. Intermolecular interaction energy.

	E_{com1}[a] (au)	E_{com2}[b] (au)	$E_{7\text{-DEAMCum}}$[c] (au)	E_{PA}[d] (au)	E_{mt1}[e] (au)	E_{mt2}[f] (au)
1	-420.8550871	-420.8550438	-591.9770708	-421.0209149	592.1428986	421.1867860
2	-420.8549571	-420.8550162	-591.9770708	-421.0209149	592.1430286	421.1868136
3	-420.8549267	-420.8551430	-591.9770708	-421.0209149	592.1430590	421.1866868
4	-420.8549571	-420.8549190	-591.9770708	-421.0209149	592.1430286	421.1869108
5	-420.8550375	-420.8550040	-591.9770708	-421.0209149	592.1429482	421.1868258

[a] The energy of the 7-DEAMCum/PA composite system.

[b] The energy of the PA/PA composite system.

[c] The energy of 7-DEAMCum.

[d] The energy of PA.

[e] 7-DEAM Cum/PA interaction energy.

[f] PA/PA interaction energy.

Table S4. Photophysical data of host (PA, IPA and TMA), guest (C,CCA and CE), and doped materials.

Sample [a]	λ_F [b](nm)	ϕ_F [c] (%)	λ_P [d] (nm)	τ_p [e] (ms)	ϕ_p [f] (%)	ϕ_{PL} [g](%)	k_p [i] (s^{-1})	k_{nr} [j] (s^{-1})
PA	364	1.31	484	237	3.56	5.94	1.50×10^{-1}	4.07×10^{0}
IPA	378	1.38	501	851	5.52	6.90	6.49×10^{-2}	1.11×10^{0}
TMA	374	0.30	524	416	0.20	0.10	4.81×10^{-3}	2.4×10^{0}
7-HMCum/PA	385	0.32	482	246	0.13	0.55	5.28×10^{-3}	4.06×10^{0}
7-AMCum/PA	365	1.31	493	473	0.46	1.77	9.73×10^{-3}	2.10×10^{0}
7-DEAMCum/PA	391	1.02	502	732	0.46	1.48	6.28×10^{-3}	1.30×10^{0}
7-HMCum/IPA	389	4.06	506	883	1.38	5.42	5.61×10^{-2}	4.01×10^{0}
7-AMCum/IPA	391	2.11	506	912	1.08	3.19	1.18×10^{-2}	1.18×10^{-2}
7-DEAMCum/IPA	377	2.65	507	969	1.08	3.73	1.11×10^{-2}	1.11×10^{-2}
7-HMCum/TMA	355	0.20	540	438	0.22	0.42	5.02×10^{-3}	2.28×10^{0}
7-AMCum/TMA	378	0.07	537	458	0.05	0.12	1.09×10^{-3}	2.18×10^{0}
7-DEAMCum/TMA	340	0.02	540	466	0.08	0.10	1.72×10^{-3}	2.14×10^{0}

[a] Doping concentrations of different materials were PA, IPA, TMA and optimal concentration of Cums/Ar-COOH doped material.

[b] Excitation wavelength.

[c] Fluorescence emission wavelength.

[d] Fluorescence quantum yield.

[e] Phosphorescence emission wavelength.

[f] Phosphorescence lifetime at room temperature.

[g] Phosphorescence quantum yield.

[h] Photoluminescence quantum yield.

[i] k_p is the radiative rate constant, $k_p = \phi_p/\tau_p$.

[j] k_{nr} is the nonradiative rate constant of the T_1 state, $k_{nr} = (1-\phi_p)/\tau_p$.a