

SUPPORTING INFORMATION

An anti-freeze fluorescent organogel with rapid shape-forming for constructing artificial light harvesting systems used in extremely cold environments

Xinxian Ma,^{#*} Jiahong Tang,[#] Tianqi Ren, Jiali Zhang, Jiuzhi Wei, Yuchua Liang, Juan Zhang, Enke Feng, Xinning Han

Key Laboratory of Green Catalytic Materials and Technology of Ningxia, Ningxia Normal University, Guyuan 756000, China. E-mail: maxinxian@163.com

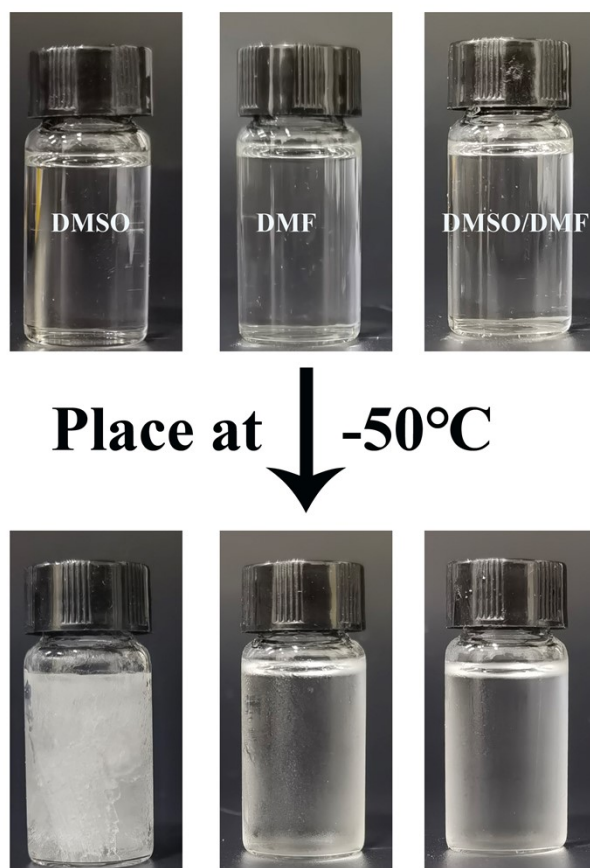


Fig. S1. Various solvent systems are placed at -50 °C for a period of time

Preparation method of dry gel

The obtained gel sample was soaked in anhydrous ethanol for a while and placed in a constant temperature oven at 70 °C for seven days, and the xerogel required for SEM was successfully prepared.

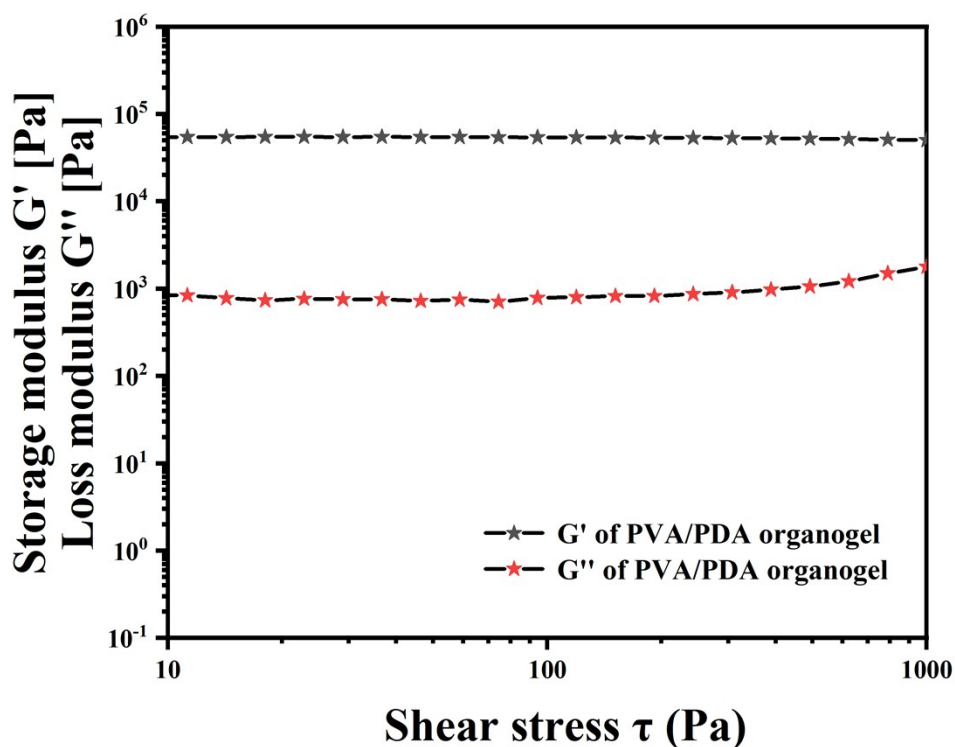


Fig. S2. Frequency dependence of G' (storage modulus) and G'' (loss modulus) for PVA/PDA organogel at different Shear stress. Condition: 68 rad s⁻¹ frequency, 10Hz constant frequency.

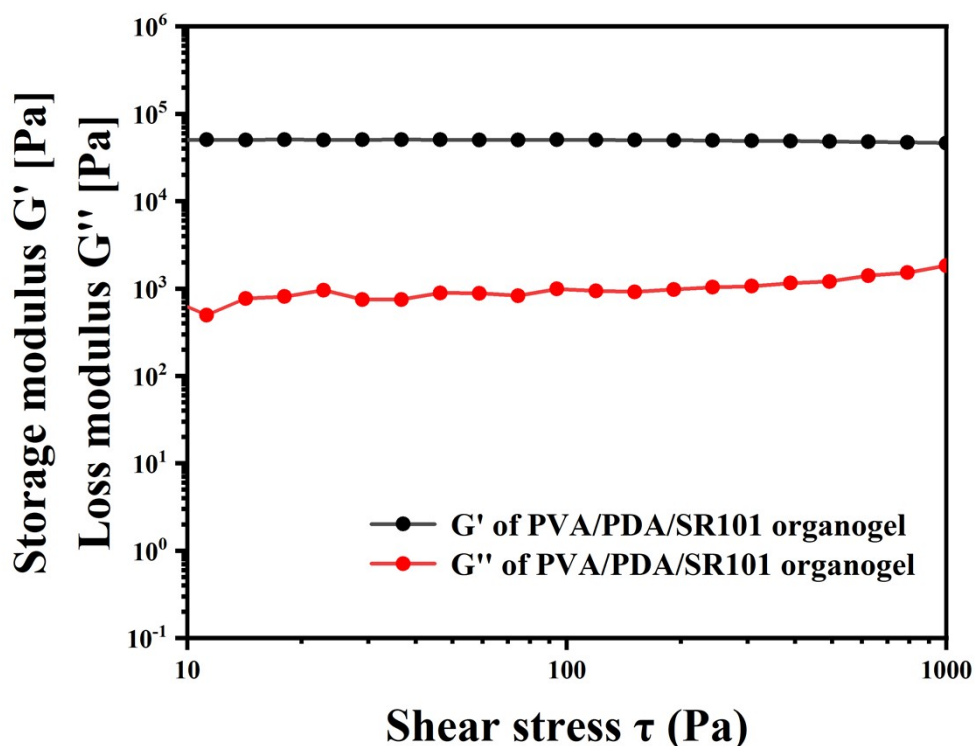


Fig. S3. Frequency dependence of G' (storage modulus) and G'' (loss modulus) for PVA/PDA/SR101 organogel at different Shear stress. Condition: 68 rad s⁻¹ frequency, 10Hz constant frequency.

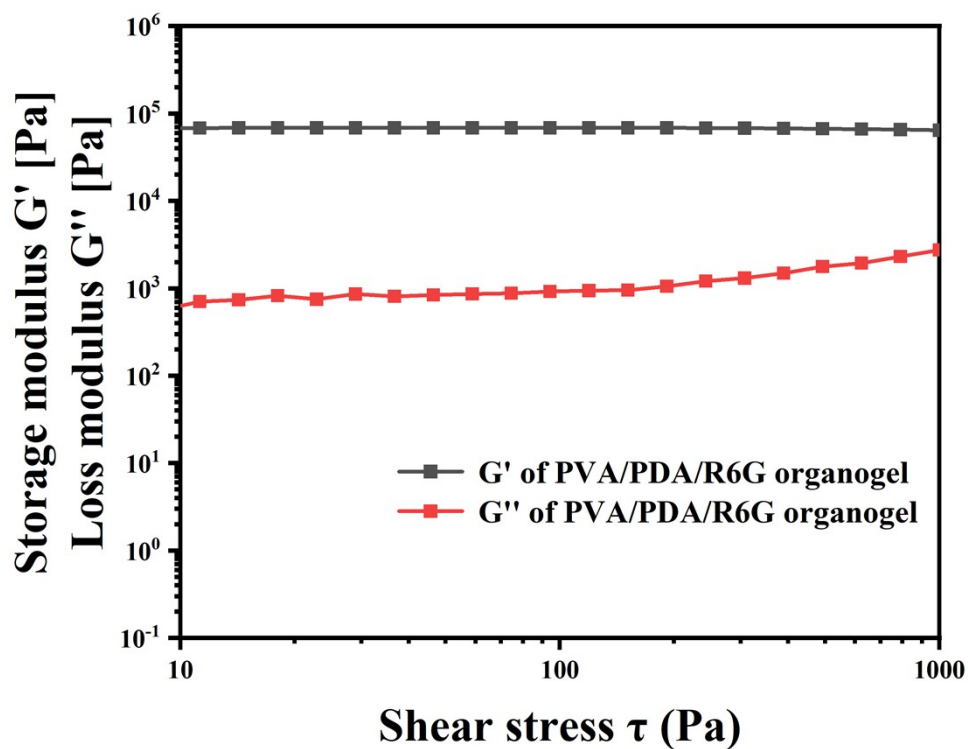


Fig. S4. Frequency dependence of G' (storage modulus) and G'' (loss modulus) for PVA/PDA/R6G organogel at different Shear stress. Condition: 68 rad s⁻¹ frequency, 10Hz constant frequency.

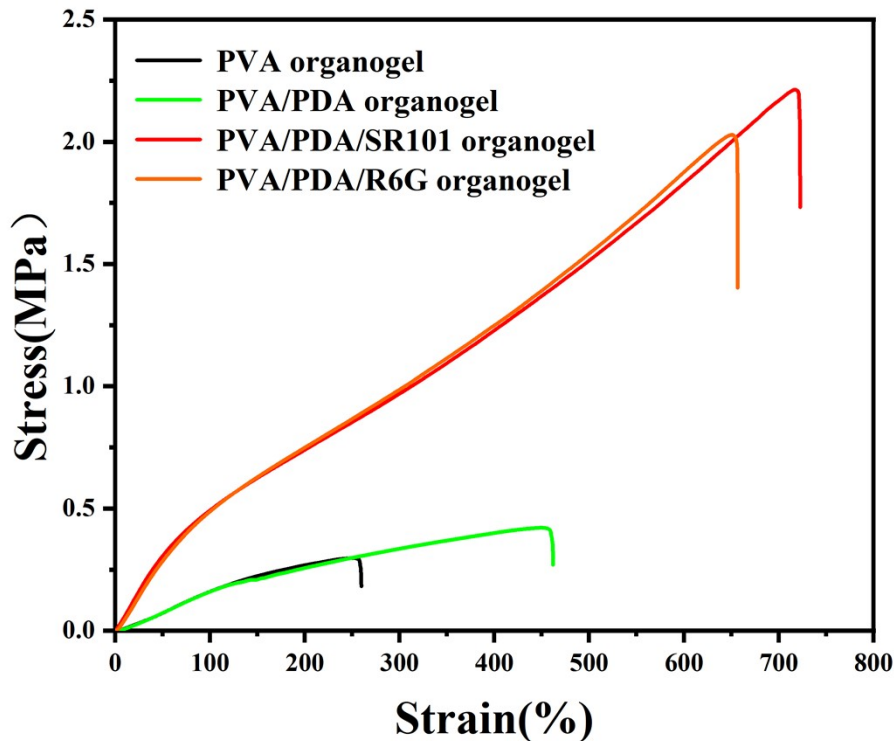


Fig. S5. Tensile stress–strain curves of four organogels at room temperature.

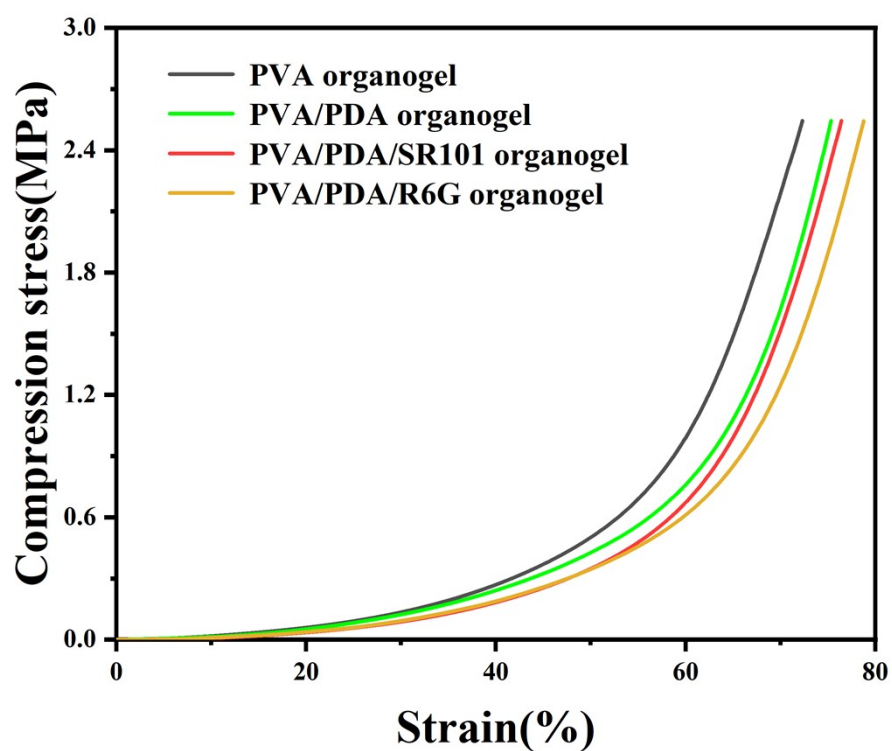


Fig. S6 Compression stress–strain curves of two organogels at room temperature.

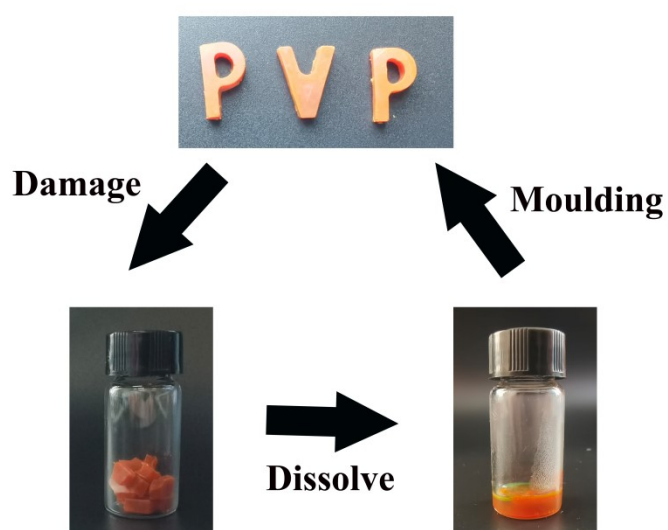


Fig. S7. Photos of the recyclability of PVA/PDA organogel

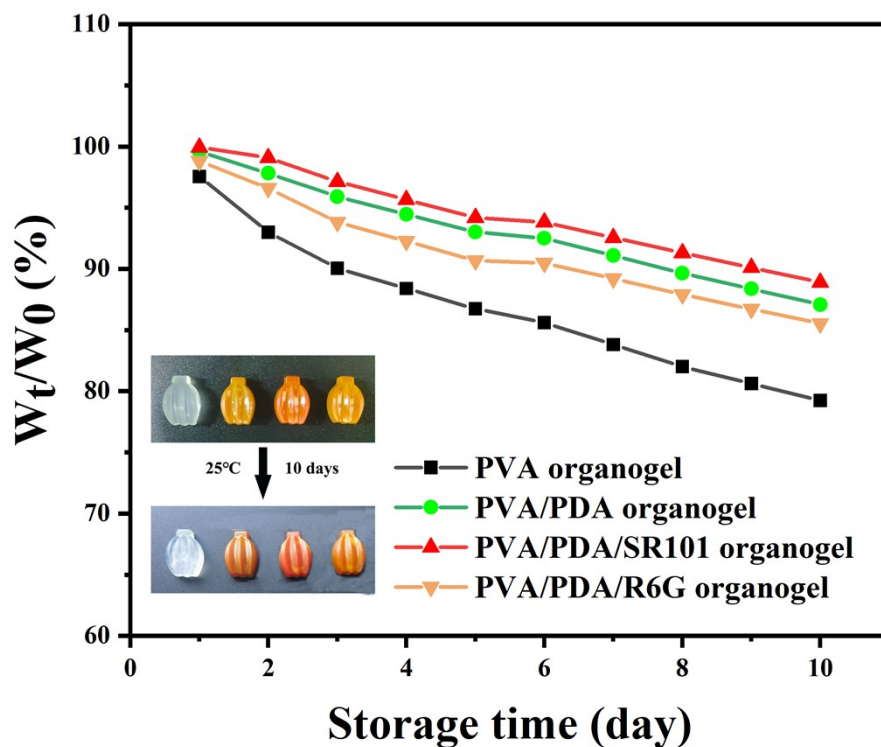


Fig. S8. Line chart of residual weight of organogels over time. Inset: Photographs of the organogels was placed at 25 °C for the first and tenth day.

The water retention ratio was calculated by the following equation:

$$\text{Water retention ratio (\%)} = W_t/W_0 \times 100\%;$$

Where W_0 is the initial quality of the organogels and W_t is the quality of the organogels after various storage days.

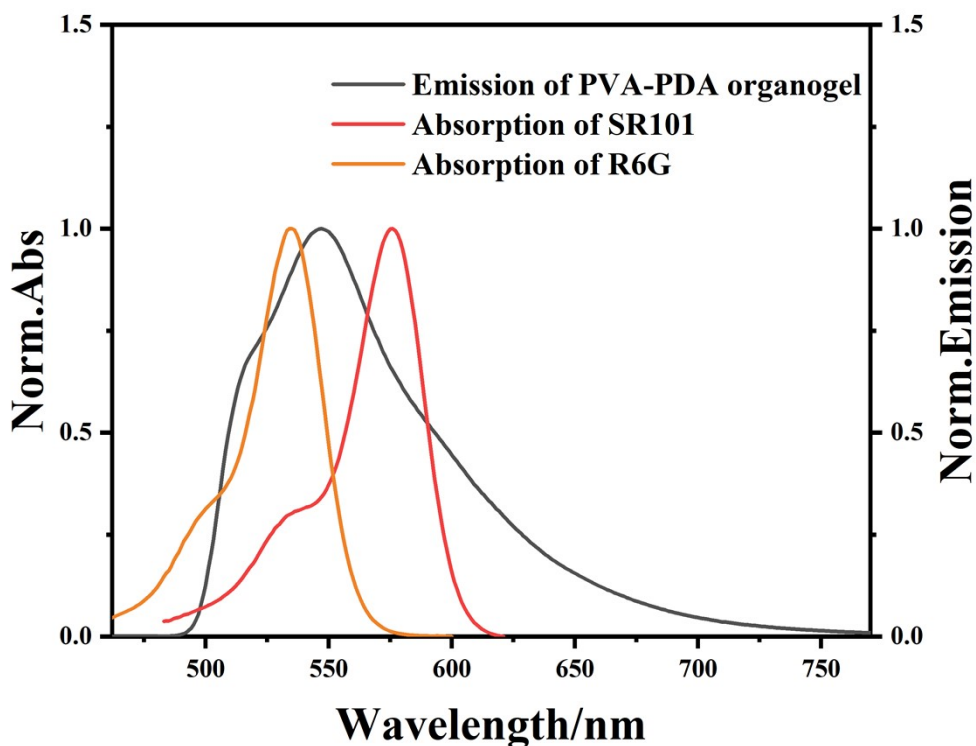


Fig. S9. Normalised emission spectrum of PVA/PDA organogel ($\lambda_{\text{ex}} = 357 \text{ nm}$), absorption spectrum of SR101 ($[\text{SR101}] = 1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) and the absorption spectrum of R6G ($[\text{R6G}] = 1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$).

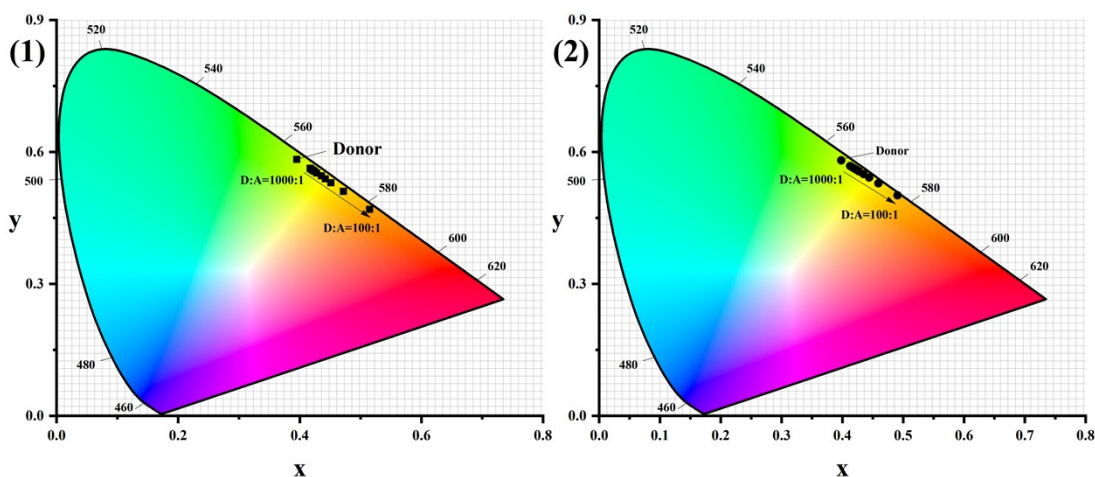


Fig. S10. The CIE diagram corresponding to the spectrum of (1) different PVA/PDA organogel/SR101 ratios (left) and (2) different PVA/PDA organogel/R6G ratios (right).

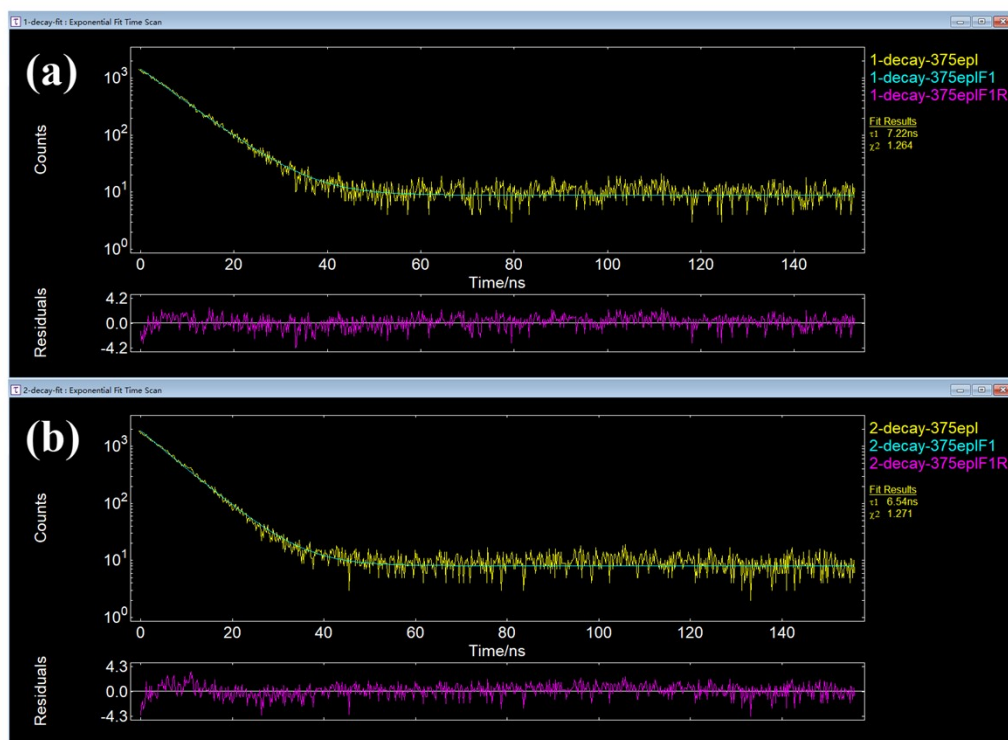


Fig. S11. (a) Fluorescence lifetime of PVA/PDA organogel ($[PDA] = 1.5 \times 10^{-6}$ mol. Monitored at 547 nm upon excitation at 357 nm.). (b) Fluorescence lifetime of PVA/Tmt/AYG organogel ($[PDA] = 1.5 \times 10^{-6}$ mol, $[SR101] = 1.5 \times 10^{-8}$ mol. Monitored at 547 nm upon excitation at 357 nm.).

Table S1. Fluorescence lifetimes of PVA/PDA organogel, PVA/PDA/SR101 organogel ($[PDA] = 1.5 \times 10^{-6}$ mol, $[SR101] = 1.5 \times 10^{-8}$ mol, respectively).

Sample	τ_1/ns	$RW_1[\%]$	τ/ns	χ^2
PVA/PDA organogel	7.2	100	7.2	1.264
PVA/PDA/SR101 organogel	6.5	100	6.5	1.271

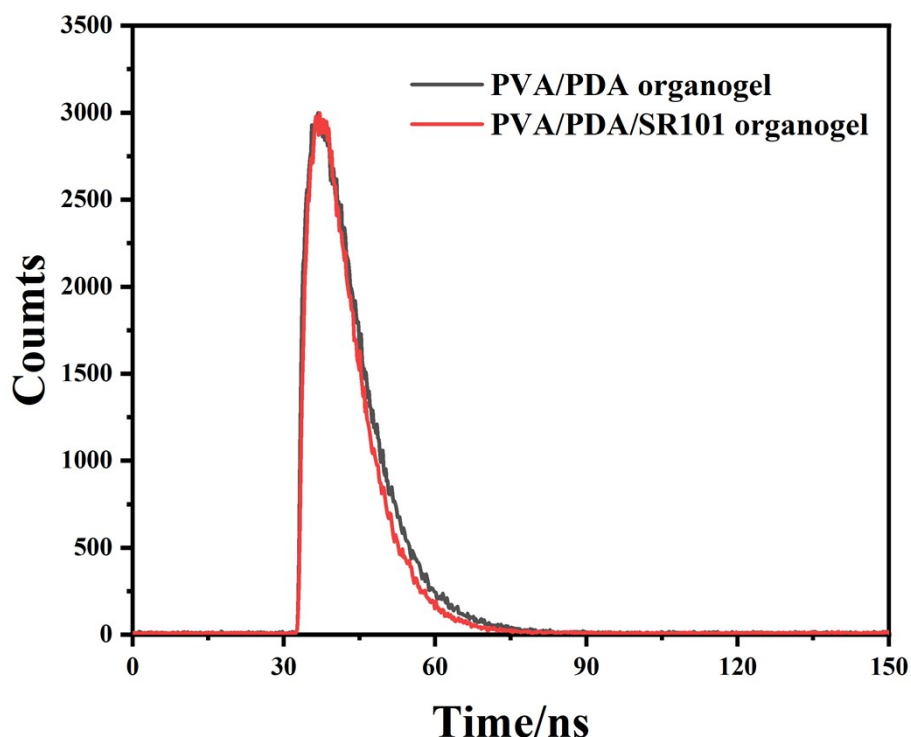


Fig. S12. Fluorescence decay profiles of PVA/PDA organogel (black line, [PDA] = 1.5×10^{-6} mol, Monitored at 547 nm upon excitation at 357 nm.) and PVA/PDA/SR101 organogel assembly (red line, [PDA] = 1.5×10^{-6} mol, [SR101] = 1.5×10^{-8} mol, Monitored at 547 nm upon excitation at 357 nm.).

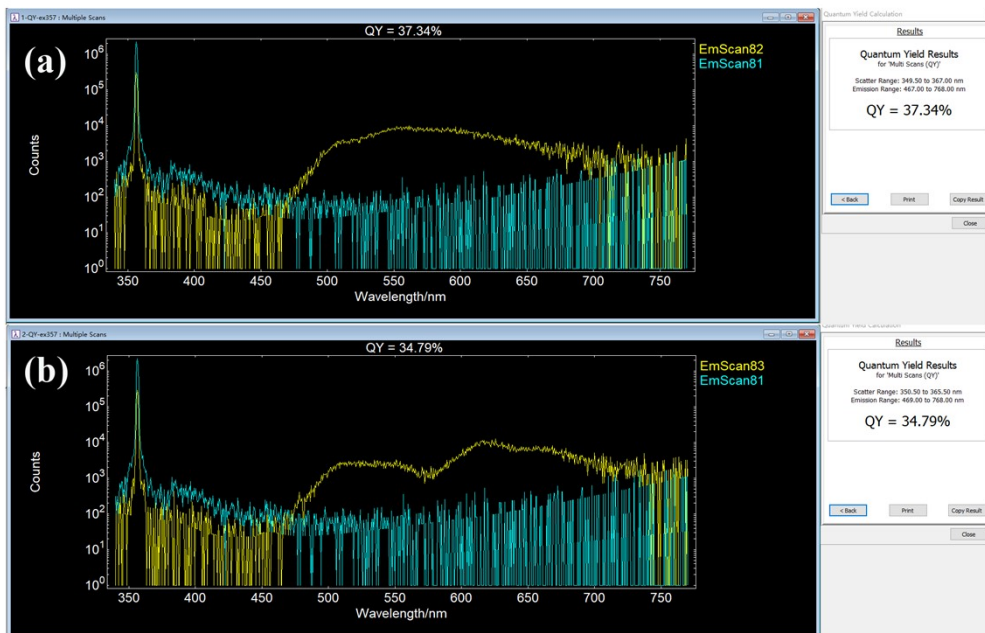


Fig. S13. (a) Quantum yield diagram of PVA/PDA organogel with luminescence range of 450–770 nm; (b) Quantum yield diagram of PVA/PDA/SR101 organogel with luminescence range of 574–770 nm ([PDA] = 1.5×10^{-6} mol, [SR101] = 1.5×10^{-8} mol).

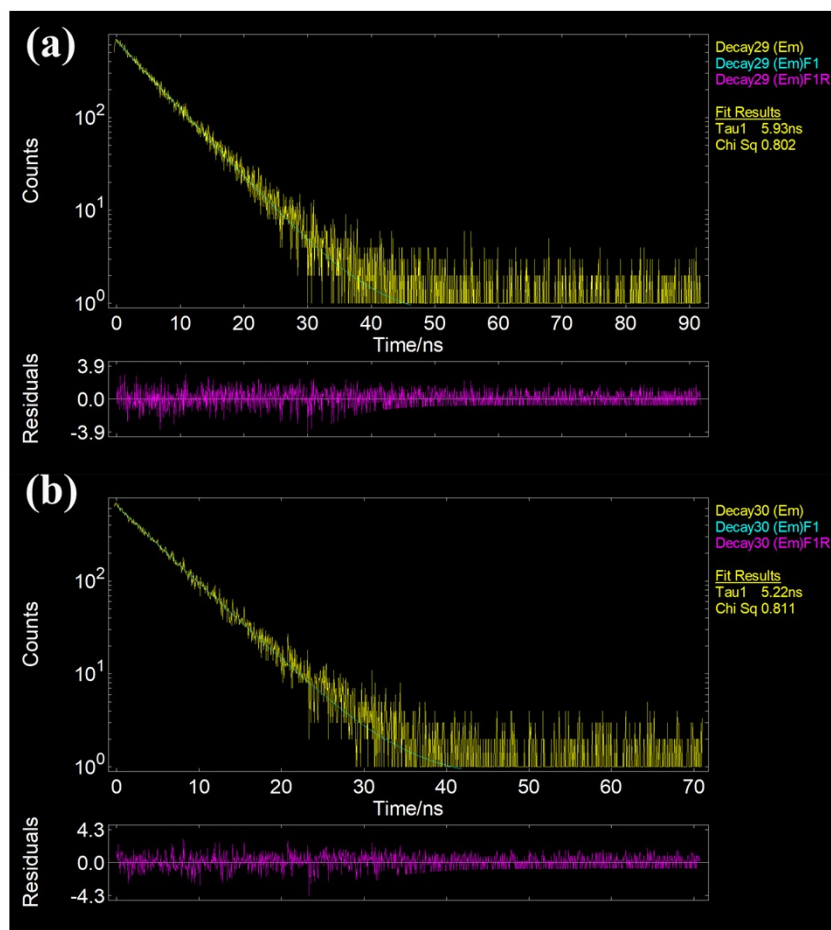


Fig. S14. (a) Fluorescence lifetime of PVA/PDA organogel ($[PDA] = 1.5 \times 10^{-6}$ mol. Monitored at 547 nm upon excitation at 357 nm.). (b) Fluorescence lifetime of PVA/Tmt/R6G organogel ($[PDA] = 1.5 \times 10^{-6}$ mol, $[R6G] = 1.5 \times 10^{-8}$ mol. Monitored at 547 nm upon excitation at 357 nm.).

Table S2. Fluorescence lifetimes of PVA/PDA organogel, PVA/PDA/R6G organogel ($[PDA] = 1.5 \times 10^{-6}$ mol, $[R6G] = 1.5 \times 10^{-8}$ mol, respectively).

Sample	τ_1/ns	$RW_1[\%]$	τ/ns	χ^2
PVA/PDA organogel	5.9	100	5.9	0.802
PVA/PDA/R6G organogel	5.2	100	5.2	0.811

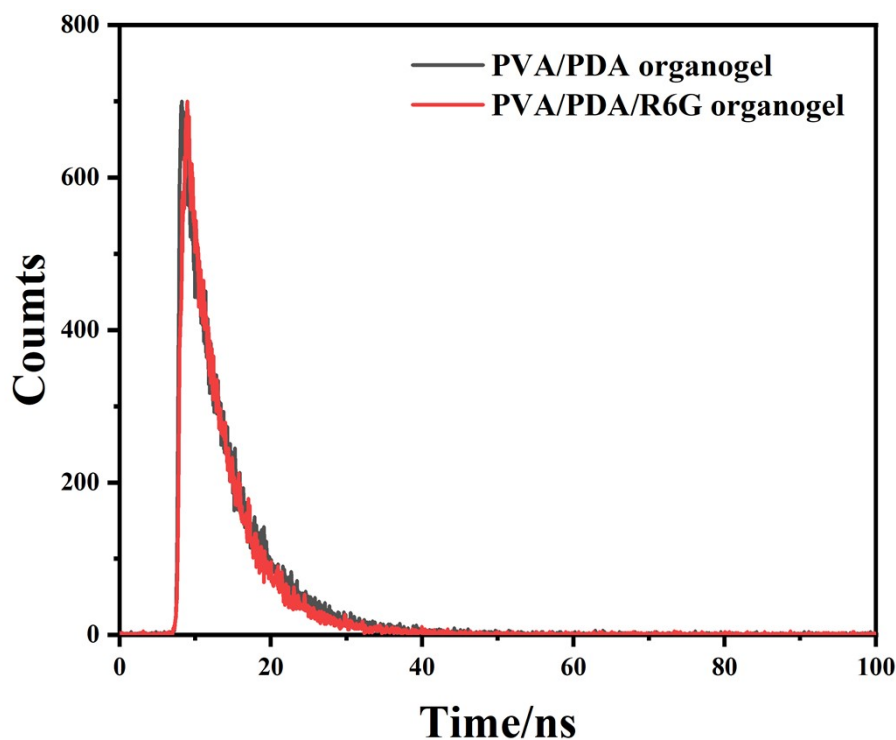


Fig. S15. Fluorescence decay profiles of PVA/PDA organogel (black line, [PDA] = 1.5×10^{-6} mol, Monitored at 547 nm upon excitation at 357 nm.) and PVA/PDA/R6G organogel assembly (red line, [PDA] = 1.5×10^{-6} mol, [R6G] = 1.5×10^{-8} mol, Monitored at 547 nm upon excitation at 357 nm.).

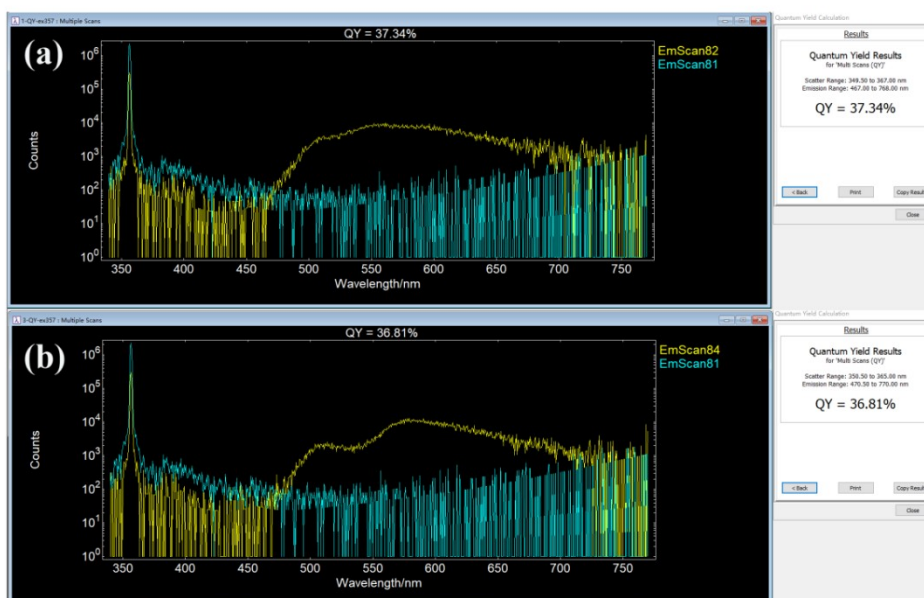


Fig. S16. (a) Quantum yield diagram of PVA/PDA organogel with luminescence range of 450–770 nm; (b) Quantum yield diagram of PVA/PDA/R6G organogel with luminescence range of 532–770 nm. ([PDA] = 1.5×10^{-6} mol, [R6G] = 1.5×10^{-8} mol.)

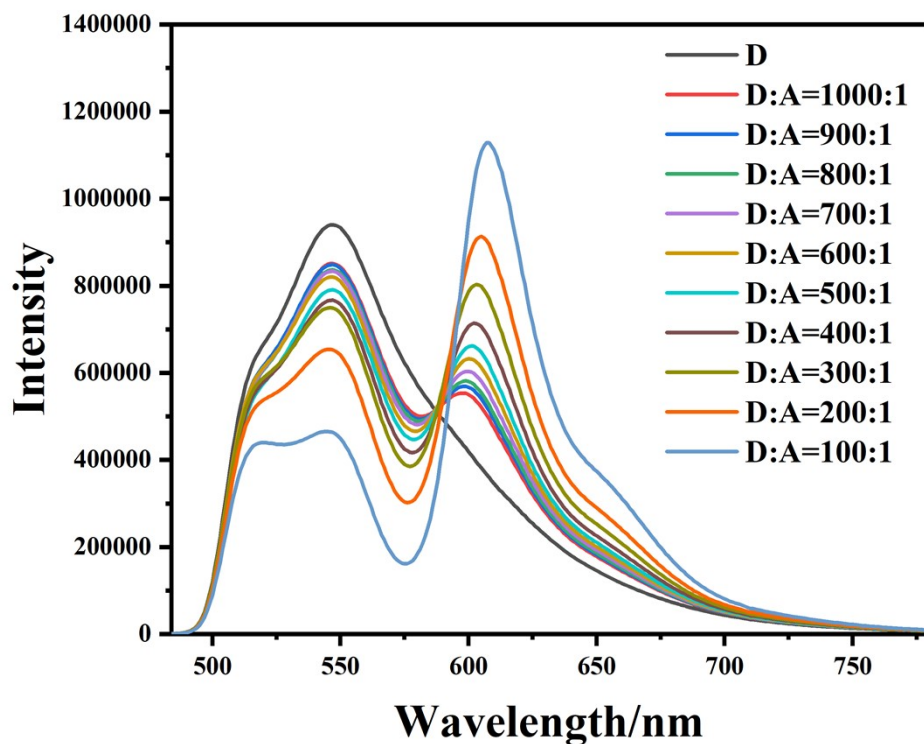


Fig. S17. Fluorescence spectra of PVA/PDA-SR101 in the DMSO and DMF binary solven with different content of SR101. (100:1, [PDA] = 1.5×10^{-6} mol, [SR101] = 1.5×10^{-8} mol, and $\lambda_{\text{ex}} = 357$ nm)

Energy-transfer efficiency (Φ_{ET}) was calculated from spectra using equation S1.

$$\Phi_{\text{ET}} = 1 - I_{\text{DA},357}/I_{\text{D},357} \text{ (eq. S1)}^{1-3}$$

Where I_{DA} and I_{D} are the fluorecence intensities of the excitation of PVA/PDA-SR101 assembly (donor and acceptor) and PDA assembly (donor), respectively at 357 nm.

The highest Φ_{ET} value was calculated as 50.72% in solvent, measured under the condition of [PDA] = 1.5×10^{-6} mol, [SR101] = 1.5×10^{-8} mol, and $\lambda_{\text{ex}} = 357$ nm.

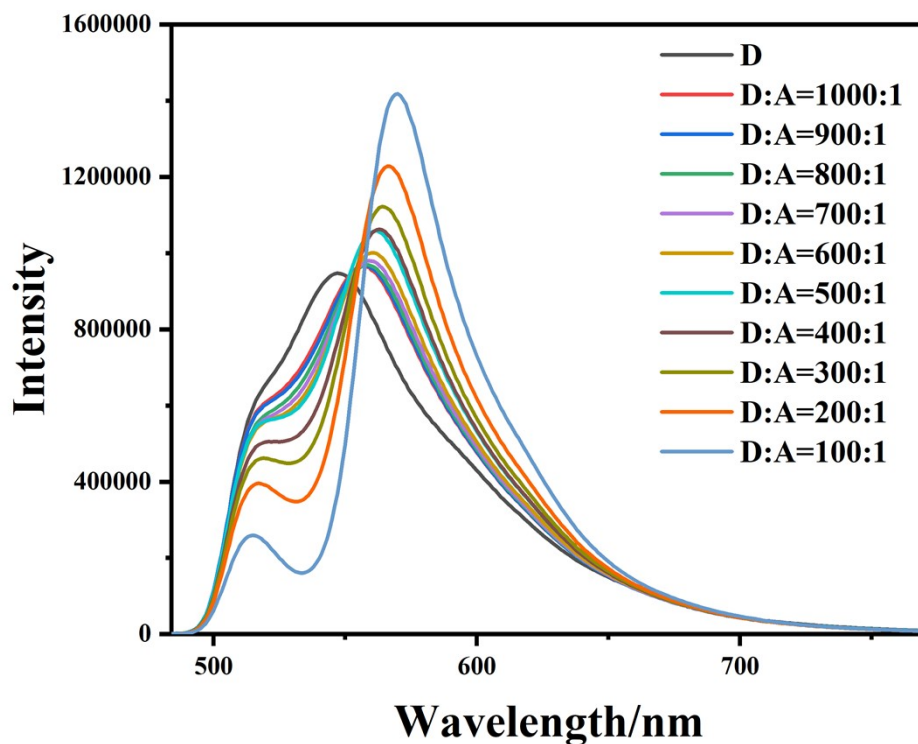


Fig. S18. Fluorescence spectra of PVA/PDA-R6G in the DMSO and DMF binary solven with different content of R6G. (100:1, [PDA] = 1.5×10^{-6} mol, [R6G] = 1.5×10^{-8} mol, and $\lambda_{\text{ex}} = 357$ nm)

Energy-transfer efficiency (Φ_{ET}) was calculated from spectra using equation S1.

$$\Phi_{\text{ET}} = 1 - I_{\text{DA},357}/I_{\text{D},357} \text{ (eq. S1)}^{1-3}$$

Where I_{DA} and I_{D} are the fluorecence intensities of the excitation of PVA/PDA-R6G assembly (donor and acceptor) and PDA assembly (donor), respectively at 357 nm.

The highest Φ_{ET} value was calculated as 61.37% in solvent, measured under the condition of [PDA] = 1.5×10^{-6} mol, [R6G] = 1.5×10^{-8} mol, and $\lambda_{\text{ex}} = 357$ nm.

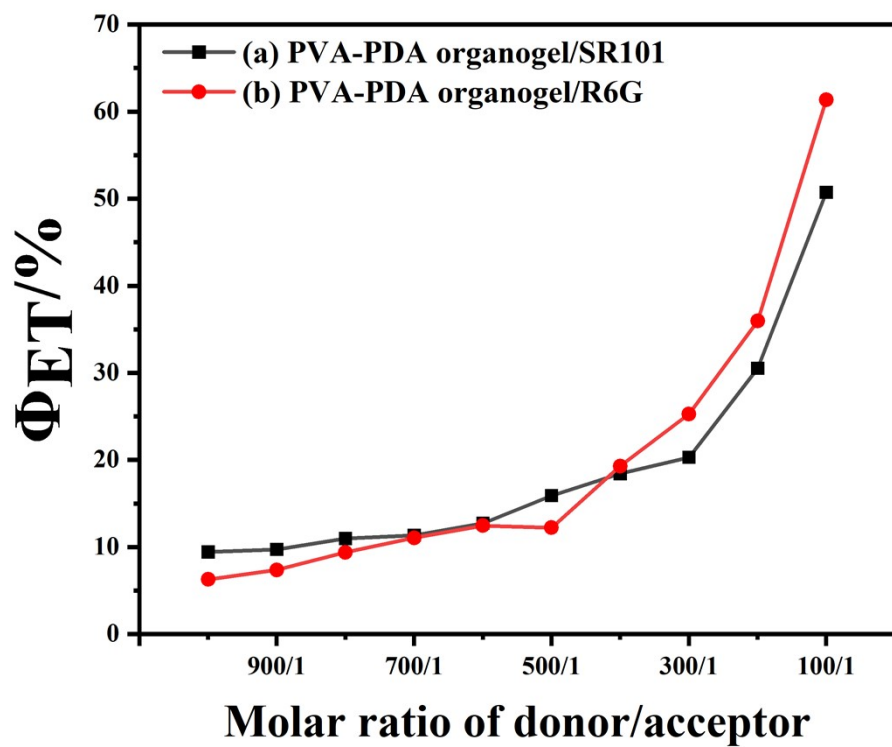


Fig. S19. Line chart of energy transfer efficiency of PVA/PDA/SR101 and PVA/PDA/R6G organogel at different proportions

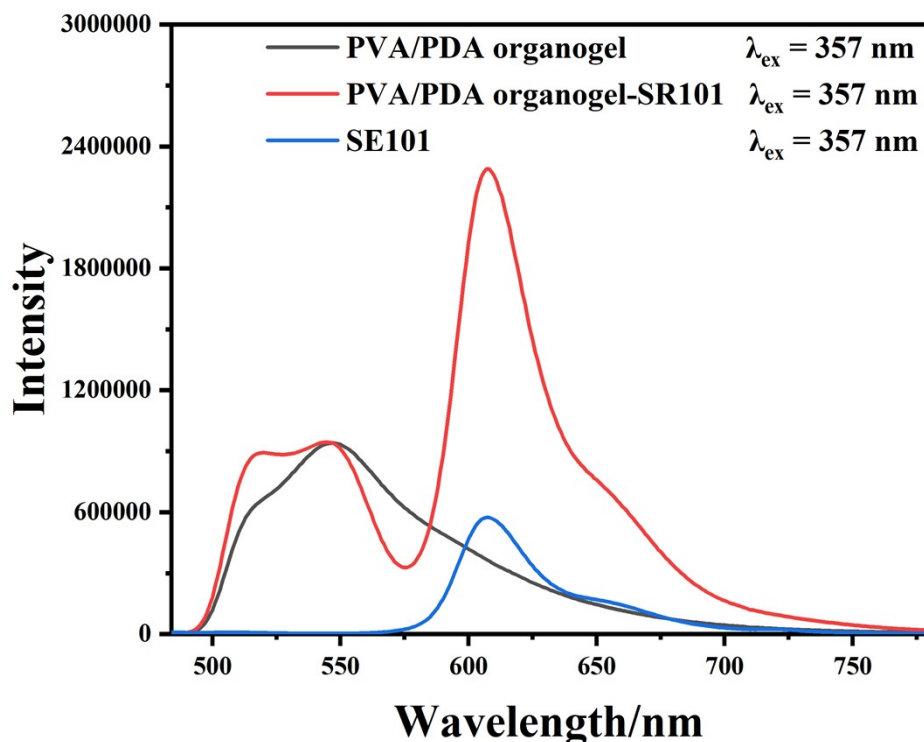


Fig. S20. Red line: Fluorescence spectra of PVA/PDA-SR101 in the DMSO and DMF binary solven, which was normalized according to the fluorescence intensity at 547 nm of the black line. ($\lambda_{\text{ex}} = 357 \text{ nm}$) ($[\text{PDA}] = 1.5 \times 10^{-6} \text{ mol}$, $[\text{SR101}] = 1.5 \times 10^{-8} \text{ mol.}$); the black line represents the fluorescence spectrum of PVA/Tmt.

The antenna effect (AE) was calculated based on the excitation spectra using equation S3.

$$\text{AE} = (I_{\text{DA},357} - I_{\text{D},357}) / I_{\text{A},357} \text{ (eq. S3)}$$

Where $I_{\text{DA},357}$ and $I_{\text{DA},357}$ are the fluorescence intensities at 608 nm with the excitation of the donor at 357 nm and the direct excitation of the acceptor at 357 nm, respectively. $I_{\text{D},357}$ is the fluorescence intensities at 608 nm of the PVA/PDA assembly, which was normalized with the PVA/PDA-SR101 assembly at 547 nm.

The antenna effect value was calculated as 3.3468 in the DMSO and DMF binary solven, measured under the condition of $[\text{PDA}] = 1.5 \times 10^{-6} \text{ mol}$, $[\text{SR101}] = 1.5 \times 10^{-8} \text{ mol.}$

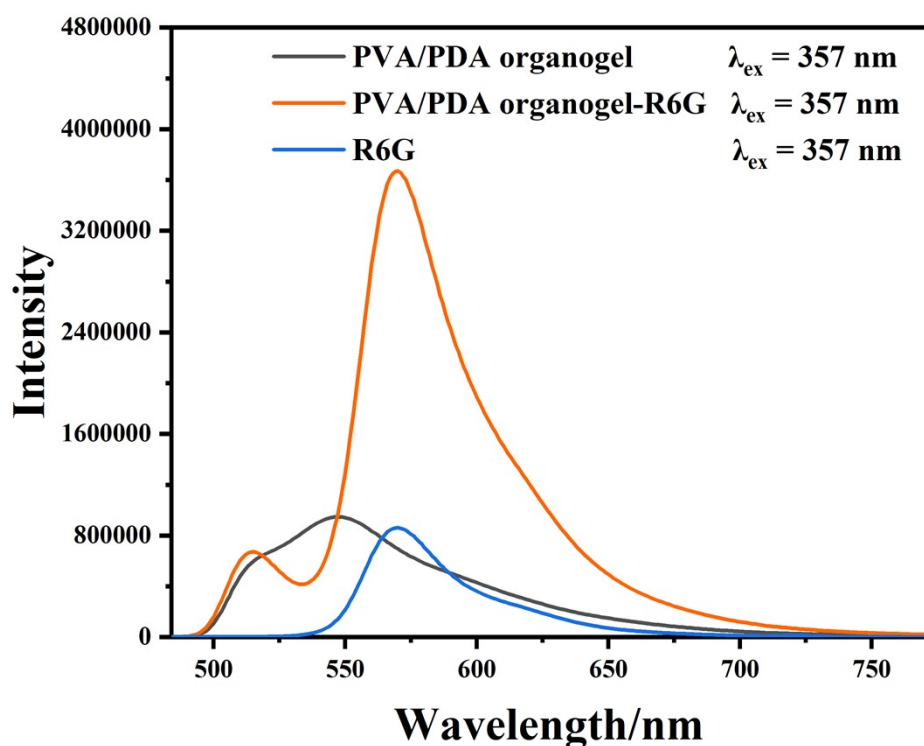


Fig. S21. Orange line: Fluorescence spectra of PVA/PDA-R6G in the DMSO and DMF binary solven, which was normalized according to the fluorescence intensity at 547 nm of the black line. ($\lambda_{\text{ex}} = 357 \text{ nm}$) ($[\text{PDA}] = 1.5 \times 10^{-6} \text{ mol}$, $[\text{R6G}] = 1.5 \times 10^{-8} \text{ mol}$.); the black line represents the fluorescence spectrum of PVA/PDA.

The antenna effect (AE) was calculated based on the excitation spectra using equation S3.

$$\text{AE} = (I_{\text{DA},357} - I_{\text{D},357}) / I_{\text{A},357} \text{ (eq. S3)}$$

Where $I_{\text{DA},357}$ and $I_{\text{D},357}$ are the fluorescence intensities at 570 nm with the excitation of the donor at 357 nm and the direct excitation of the acceptor at 357 nm, respectively. $I_{\text{D},357}$ is the fluorescence intensities at 570 nm of the PVA/PDA assembly, which was normalized with the PVA/PDA-R6G assembly at 547 nm.

The antenna effect value was calculated as 3.4564 in the DMSO and DMF binary solven, measured under the condition of $[\text{PDA}] = 1.5 \times 10^{-6} \text{ mol}$, $[\text{R6G}] = 1.5 \times 10^{-8} \text{ mol}$.

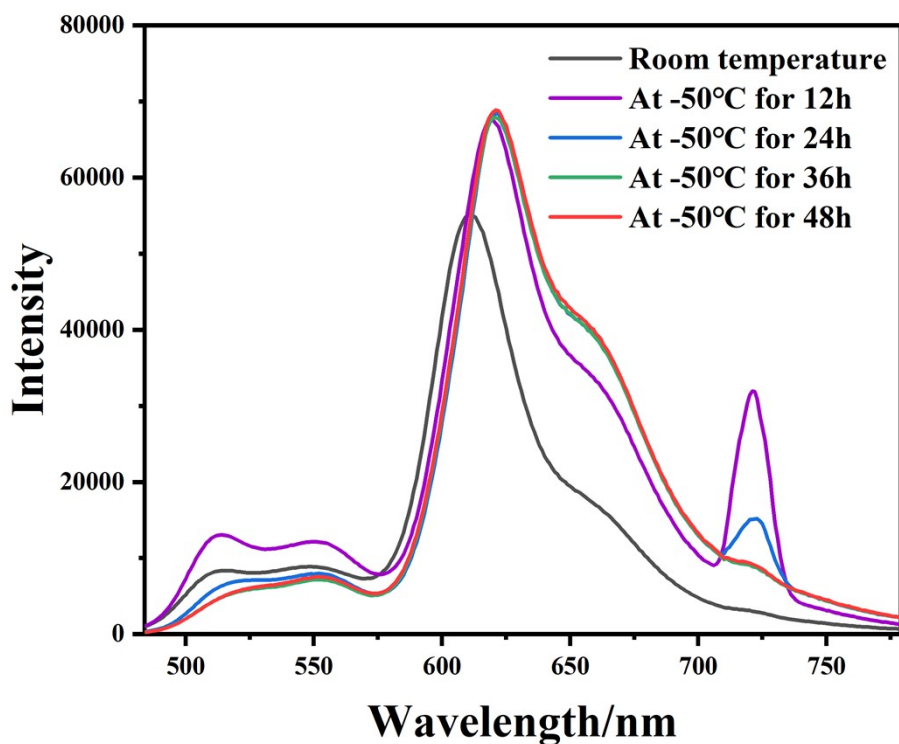


Fig. S22. Fluorescence spectra of PVA/PDA-SR101 in the DMSO and DMF binary solven at different temperature ($\lambda_{\text{ex}} = 357 \text{ nm}$) ($[\text{PDA}] = 1.5 \times 10^{-6} \text{ mol}$, $[\text{SR101}] = 1.5 \times 10^{-8} \text{ mol}$.)

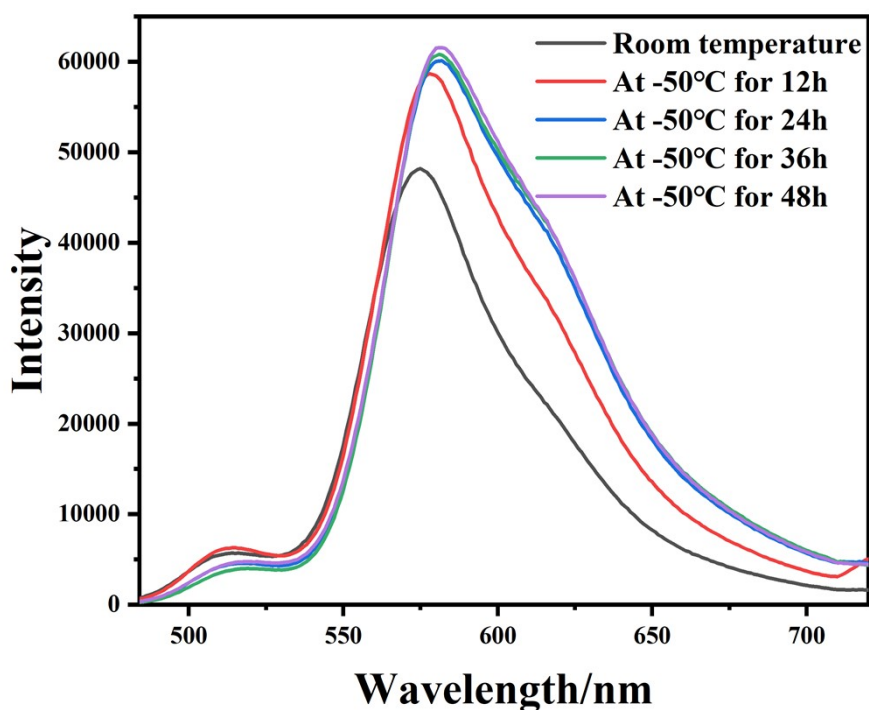


Fig. S23. Fluorescence spectra of PVA/PDA-R6G in the DMSO and DMF binary solven at different temperature ($\lambda_{\text{ex}} = 357 \text{ nm}$) ($[\text{PDA}] = 1.5 \times 10^{-6} \text{ mol}$, $[\text{R6G}] = 1.5 \times 10^{-8} \text{ mol}$.)

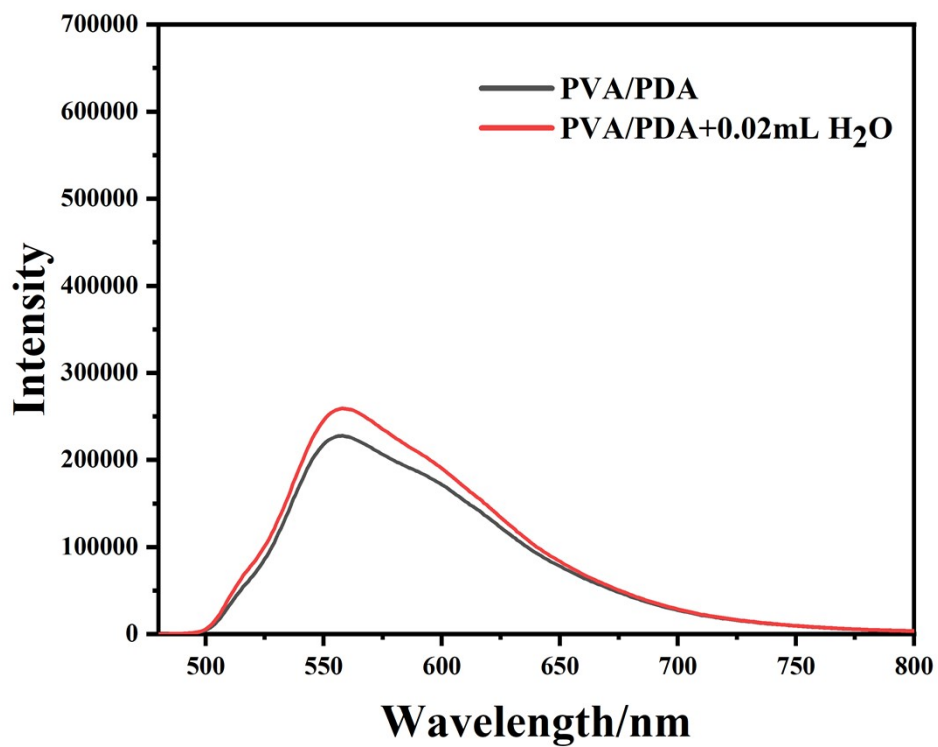


Fig. S24. Effect of 0.02 mL of water on fluorescence spectra of PVA/PDA

References

- (1) R. Gao and D. Yan, *Chem. Sci.*, 2017, **8**, 590–599.
- (2) S. Guo, Y. Song, Y. He, X. Hu and L. Wang, *Angew. Chem. Int. Ed.*, 2018, **57**, 3163–3167.
- (3) M. Hao, G. Sun, M. Zuo, Z. Xu, Y. Chen, X. Hu and L. Wang, *Angew. Chem. Int. Ed.*, 2020, **59**, 10095–10100.