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A multifunctional organogel for constructing artificial light harvesting systems with excellent energy transfer efficiency†

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Fluorescent gels with excellent physical properties were synthesised using polyvinyl alcohol (PVA)/telmisartan (Tmt) based on binary solvent. On this basis, artificial light-harvesting system with high energy-transfer efficiency and the antenna effect was constructed by adding the acceptors acridine yellow G and rhodamine B.

Nowadays, increasing attention is being paid to luminous energy as it is a 'green' and economical renewable energy source. Thus, an understanding of how to capture and use light energy is required. It was discovered that photosynthetic bacteria and green plants use photosynthesis for capturing, transferring and storing energy drawn from sunlight.^{1,2} This motivated researchers to develop artificial light-harvesting systems (ALHSs) for efficient light collection,^{3–11} and reports on ALHSs are increasing. Scientists have used energy-transfer efficiency (Φ_{ET}) and the antenna effect (AE) as parameters to evaluate the efficiency of ALHSs.^{12–15} Cao *et al.* reported conjugated polymers that contained a column aromatic unit.¹⁶ They used polymers as the primary material to bind a guest fluorescence molecule containing a triazole-alkyl-cyanide group and constructed an ALHS with an ultra-high AE. The AE can reach 35.9 and 90.4 in solutions and solid films, respectively. However, research has proven that high-efficiency ALHSs must fulfil three requirements: (1) the fluorescence spectrum of the donor should effectively overlap with the absorption band of the acceptor; (2) the donor must be sufficiently close to the recipient, with a distance of generally <10 nm; and (3) the spatial arrangement of the donor and recipient should be appropriate.^{17,18} Efficient ALHSs typically utilise complex self-assembled structures,¹⁹

such as nanocrystals, metal complexes, biohybrid complexes and dendritic polymers. These cases hinted that supramolecular gel systems can also help in the development of efficient gel ALHSs.^{20,21}

However, research indicates supramolecular gels formed *via* non-covalent intermolecular interactions are easily destroyed by external shocks, which considerably limits the application of gels. Thus, how to build a mechanism for efficient ALHSs has become a complex problem. Moreover, hydrogels and organogels exhibit excellent ion transport^{22,23} and adjustable mechanical properties owing to their unique three-dimensional mesh structure.²⁴ In addition, given the specificity of organogels, the desired properties, which include but are not limited to, self-repair,^{25–27} antibacterial²⁸ and frost resistance,^{29,30} can be achieved by adding functional units or modifying crosslinkers. Therefore, polymer organogels have been extensively researched as flexible new materials. In our previous research, we observed the excellent fluorescence properties of benzimidazole derivatives.³¹

Herein, we designed and synthesised a new polymer organogel with good fluorescence and physical properties. The carboxyl group and polyvinyl alcohol (PVA) can be cross-linked to form a stable polymer organogel in dimethyl sulfoxide (DMSO) through esterification at 120 °C. Then, we constructed efficient ALHSs with a high AE by adding the acceptors acridine yellow G (AYG) and rhodamine B (RhB), and confirmed the occurrence of energy transfer (Fig. 1).

The prediction that PVA and Tmt are cross-linked by esterification was demonstrated by ¹H nuclear magnetic resonance (¹HNMR) and Fourier transform infrared (FT-IR) (Fig. 2a). PVA's O–H proton signal was divided into three peaks: 4.302, 4.497 and 4.719 ppm (Fig. 2a(3)). However, in the PVA/Tmt organogel, the intensity of the signal peak of the O–H proton decreased evidently, and the O–H proton signals shifted from 4.497 to 4.539 ppm (Fig. 2a(1)), which proves that the hydroxyl groups in the PVA underwent a chemical reaction. In addition, the O–H proton signals of

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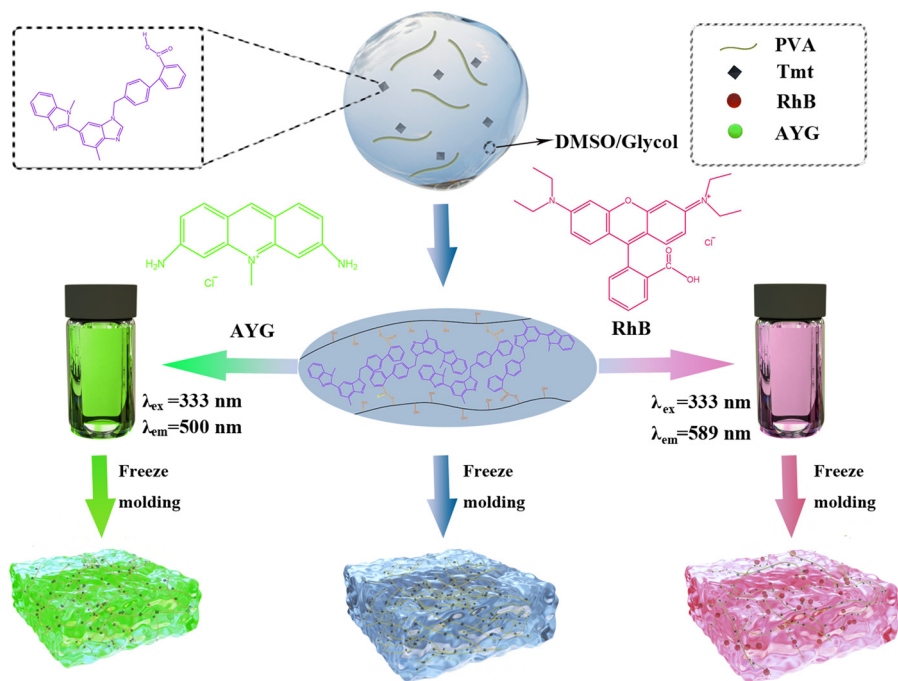


Fig. 1 Schematic of the formation, structure and intermolecular non-covalent interactions of the PVA/Tmt organogel and the prepared light-harvesting systems.

PVA shifted to a lower field at 4.539 ppm with the introduction of the electron-attracting group. In addition, some C–H proton signals of the PVA/Tmt organogel shifted by 0.058 ppm to a higher field (from 3.831 ppm to 3.773

ppm) as the oxygen atom formed a P– π conjugation with the carbonyl group. Then, electron delocalisation increased the C–H electron cloud density and decreased the chemical shift as the PVA hydroxyl connected to the carbonyl group. To further prove the conjecture that PVA and Tmt are cross-linked by esterification, we compared and analysed the Fourier transform IR spectroscopy (FT-IR) spectra of the solid PVA, the mixture of PVA and Tmt and the xerogel of the PVA/Tmt organogel (Fig. 2b). The typical peak of $\nu(\text{C}=\text{O})$ in Tmt appeared at 1704.28 cm^{-1} (Fig. 2b(3)), and that of $\nu(\text{C}=\text{O})$ in the PVA/Tmt organogel was at 1717.78 cm^{-1} (Fig. 2b(2)). Notably, the absorption band of $\nu(\text{C}=\text{O})$ shifted towards a higher wavenumber at 1717.78 cm^{-1} after the introduction of an electron-withdrawing group. In addition, an absorption band of $\nu(\text{C}-\text{O}-\text{C})$ was observed in the PVA/Tmt organogel at 1018.23 cm^{-1} (Fig. 2b(2)). The above analyses prove that the Tmt cross-linked with PVA through esterification.

We performed SEM to describe the morphological characteristics of the above samples (Fig. 2c–f). The xerogel of the PVA exhibited a layered morphology, which was observed *via* electron microscopy (Fig. 2c). Subsequently, given the esterification between PVA and Tmt, the morphology of the xerogel of the PVA/Tmt organogel exhibited an evident porous structure (Fig. 2d). Finally, after adding RhB and AYG to the mixture, the morphologies of the obtained xerogels became more densely porous and needle-like, respectively (Fig. 2e and f).

Subsequently, as can be observed in the charts shown in Fig. S1–S3,† the above three organogels had a considerably larger storage modulus (G') than loss modulus (G''). Moreover, the G' and G'' of the three above-mentioned

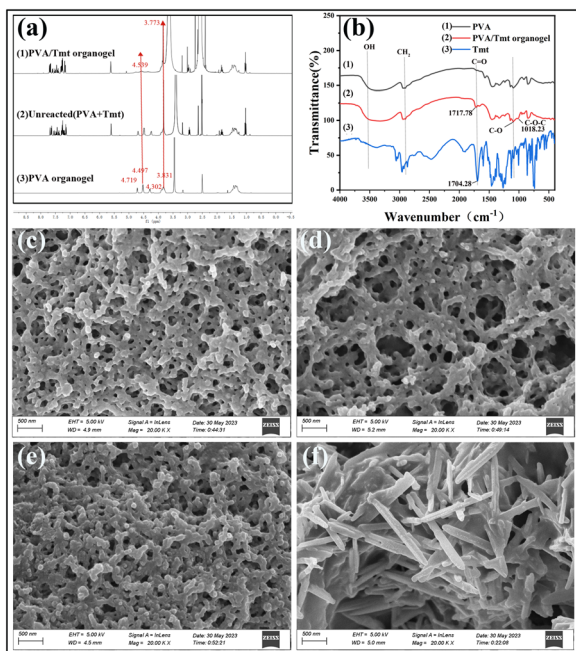


Fig. 2 (a) ^1H NMR and (b) FT-IR spectra of the different samples. Field-emission scanning electron microscopy (SEM) images of (c) PVA, (d) PVA/Tmt, (e) PVA/Tmt/RhB and (f) PVA/Tmt/AYG organogel samples.



organogels were parallel to the frequency axis. Thus, the PVA/Tmt, PVA/Tmt/AYG and PVA/Tmt/RhB organogels all exhibited excellent gel properties in the above analysis.

After allowing them to settle for a while, the organogel samples were obtained. Then, the mechanical properties of the organogels were evaluated. As displayed in Fig. 3a, the PVA/Tmt organogel can be customised into various shapes (numbers and letters) through moulds, and showed a bluish violet fluorescence under a UV lamp. In addition, the fluorescence intensity and colour of the PVA/Tmt organogel system evidently changed in different ways with the addition of AYG and RhB dyes. Illuminated with 365 nm UV lamps, the PVA/Tmt/AYG organogel glowed with yellowish green hues and the PVA/Tmt/RhB organogel glowed with bright pink hues. The organogels also presented outstanding puncture resistance in a series of physical and mechanical tests (Fig. 3d). Similarly, the organogels can withstand a wide range of mechanical deformations without visible cracks or any breakage (Fig. 3b). Further, these organogels achieved high elongation at break and tensile strength in the stretching experiment (Fig. 3f and g). The PVA/Tmt/RhB organogel can quickly achieve a stretching strain of more than 800% without visible cracks or any breakage (Fig. 3f). In comparison, the PVA/Tmt/AYG organogel stretched to 830% strain (Fig. 3g). Fig. 3e exhibits the deformation of the PVA/Tmt organogel during compression. The organogels remained intact, and no liquid overflowed from them under heavy compression, proving that organogels have remarkable

water-retaining capability and pressure resistance. Additionally, the compression test experiment proved their excellent pressure resistance (Fig. 3h). As presented in Fig. 3h, the pressure loads of the PVA/Tmt/RhB and PVA/Tmt/AYG organogels were 2.23 and 1.26 MPa, respectively. In addition, the organogels can successfully lift 2.1 kg without breaking in the load experiments (Fig. 3c).

The 'Tmt' type sample was turned into the 'PVA' type sample by sequentially cutting, heating at 90 °C and freezing. Using the same steps, the 'PVA' type sample can be turned into the 'Tmt' type sample (Fig. S4†). Moreover, the transmittances of the PVA/Tmt and PVA organogels in the visible range (350–800 nm) were tested using a UV spectrophotometer (Fig. S5†). The addition and reaction of Tmt molecules resulted in no substantial effect on the light transmittance of pure PVA organogels and enhanced that of other organogels. This finding is notably beneficial for visual abrasion applications.

To test the fluorescence properties of the obtained organogels, we cut them into sheets and used the patches to perform the fluorescence test. Fluorescence spectrometry revealed that the absorption band of the fluorescence dye AYG considerably overlapped with the emission band of the PVA/Tmt organogel (Fig. 4a). Therefore, the PVA/Tmt organogel was selected as a donor and AYG as the acceptor for the preparation of our ALHS. As displayed in Fig. 4b, the fluorescence intensity of the PVA/Tmt organogel gradually reduced at $\lambda = 376$ nm with the dropwise addition of AYG.

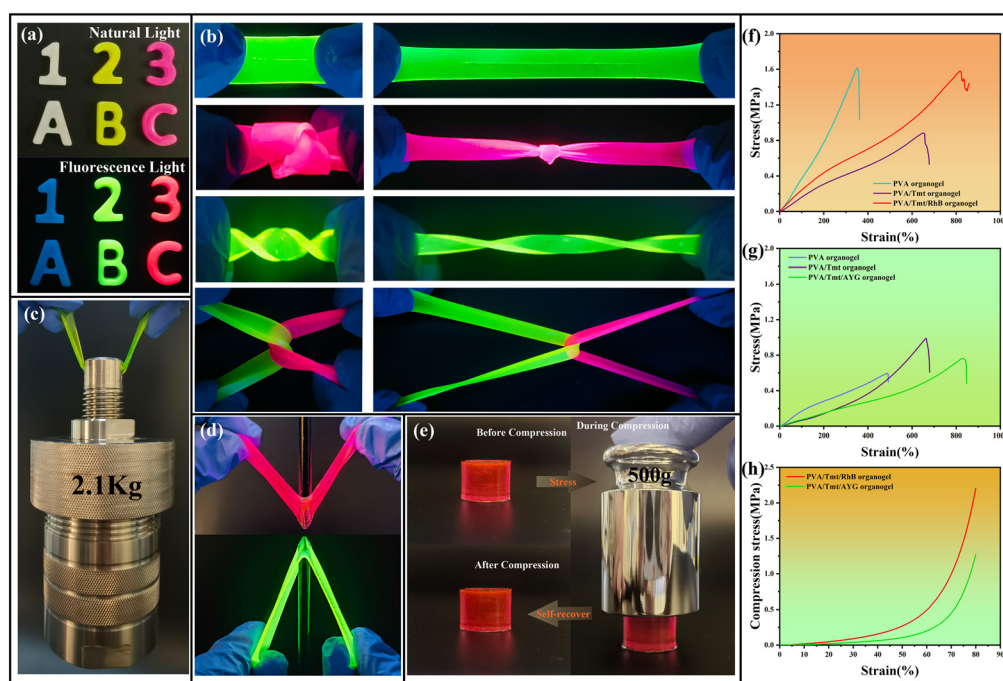
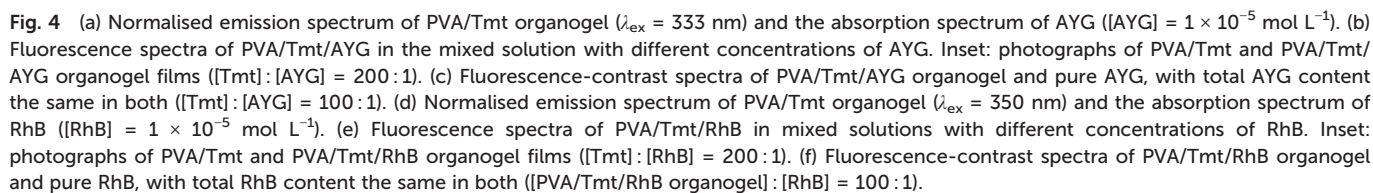


Fig. 3 (a) Photos of the organogels in different shapes under natural light and ultraviolet (UV) radiation. (b) Organogels can withstand a wide range of mechanical deformations. (c) PVA/Tmt/AYG organogels exhibited good load-bearing properties. (d) PVA/Tmt/RhB and PVA/Tmt/AYG organogels exhibited excellent puncture resistance. (e) Compression properties of the PVA/Tmt/RhB organogel. (f) Tensile stress-strain curve comparisons of the RhB organogel. (g) Tensile stress-strain curve comparisons of the AYG organogel. (h) Compression stress-strain curves of two organogels.





Similarly, we constructed an additional ALHS using RhB as the fluorescence acceptor given the substantial overlap between the absorption band of the fluorescence dye RhB and the emission band of the PVA/Tmt organogel (Fig. 4d). Fig. 4e shows that the fluorescence intensity of the PVA/Tmt organogel gradually decreased at $\lambda = 387$ nm with the dropwise addition of RhB. Furthermore, at an excitation wavelength of 350 nm, a new emission band appeared at $\lambda = 589$ nm. With the slow addition of RhB, the fluorescence intensity of the new emission band at $\lambda = 589$ nm gradually increased and reached a maximum at the molar ratio of $n_{\text{donor}}:n_{\text{acceptor}} = 100:1$. Based on the above phenomena, we designed additional experiments to prove that energy transfer occurred in the PVA/Tmt/RhB organogel. The fluorescence intensity of the pure acceptor (RhB) in the system at a molar ratio of 100:1 was measured (the quantity of RhB was not changed). Similar to the PVA/Tmt/AYG organogel, when the molar ratio was $n_{\text{donor}}:n_{\text{acceptor}} = 100:1$, the fluorescence intensity at $\lambda = 589$ nm was notably higher than that of the pure acceptor (RhB) (both had the same total content of RhB) in the comparison of the obtained fluorescence spectra ($n_{\text{donor}}/n_{\text{acceptor}} = 100:1$; pure RhB), evidencing the occurrence of the energy transfer process (Fig. 4f). Subsequently, the fluorescence lifetimes of the obtained samples were measured using the steady-state/lifetime spectrofluorometer. The results show that the decay curves of the obtained PVA/Tmt and PVA/Tmt/RhB organogels were fitted with a double exponential model. The fluorescence lifetimes of the PVA/Tmt organogel are $\tau_1 = 0.7645$ ns, $\tau_2 = 2.73$ ns, and $\tau = 1.27$ ns. The fluorescence lifetimes of the

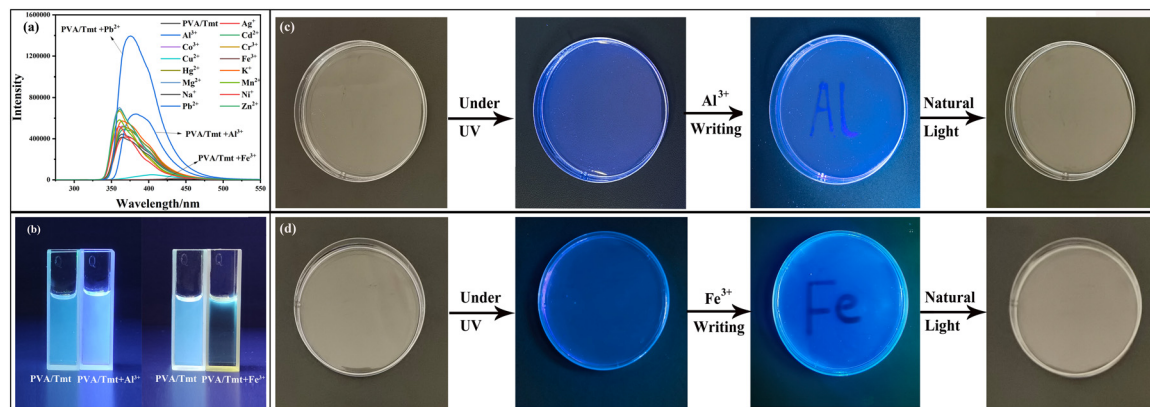


Fig. 5 (a) Fluorescence spectra of the PVA/Tmt organogel in the presence of equiv. metal ions (Cr^{3+} , Zn^{2+} , Co^{3+} , K^+ , Al^{3+} , Mn^{2+} , Hg^{2+} , Fe^{3+} , Mg^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Ni^{2+} , Ag^+ and Na^+ , 0.1 mol L^{-1}) ($\lambda_{\text{ex}} = 333 \text{ nm}$). (b) Photos of the PVA/Tmt, PVA/Tmt- Al^{3+} ($[\text{Al}^{3+}] = 5 \times 10^{-6} \text{ mol}$), PVA/Tmt and PVA/Tmt- Fe^{3+} ($[\text{Fe}^{3+}] = 5 \times 10^{-6} \text{ mol}$) under UV lamp irradiation. (c) The message written on the PVA/Tmt organogel using the Al^{3+} solution under natural light and UV lamps. (d) The message written on the PVA/Tmt organogel using the Fe^{3+} solution under natural light and UV lamps.

PVA/Tmt/AYG organogel are reduced to $\tau_1 = 0.7642 \text{ ns}$, $\tau_2 = 2.45 \text{ ns}$ and $\tau = 1.18 \text{ ns}$, which suggests that energy from the donor is transferred to the acceptor (Fig. S9 and S10, Table S2†). The fluorescence QY of the obtained samples was measured in a similar manner. The fluorescence QY of the PVA/Tmt/RhB organogel reached 51.06% at the selected wavelength range of 520–700 nm (Fig. S11†). All the above analyses confirmed the successful construction of a PVA/Tmt/RhB ALHS.

To evaluate the efficiency of the PVA/Tmt/AYG and PVA/Tmt/RhB ALHSs, the energy-transfer efficiency (Φ_{ET}) and AE were used as parameters. The Φ_{ET} values of the PVA/Tmt/AYG ALHS were 8.60%, 11.45%, 16.40%, 20.13%, 27.07%, 35.97%, 46.80%, 59.20%, 70.20% and 82.77% when the donor-to-acceptor molar ratios were 1000:1, 900:1, 800:1, 700:1, 600:1, 500:1, 400:1, 300:1, 200:1 and 100:1, respectively (Fig. S12†). Similarly, the Φ_{ET} values for the PVA/Tmt/RhB ALHS were calculated to be 0.13%, 0.96%, 1.42%, 2.48%, 3.87%, 4.51%, 5.28%, 6.67%, 10.18% and 16.58%, when the molar ratios of the donor-to-acceptor were 1000:1, 900:1, 800:1, 700:1, 600:1, 500:1, 400:1, 300:1, 200:1 and 100:1, respectively (Fig. S13†). Thus, the Φ_{ET} values substantially increased with the dropwise addition of AYG into the PVA/Tmt organogel system and reached a staggering peak of 82.77% when the molar ratio of donor-to-acceptor was 100:1 (Fig. S14(a)†). With the dropwise addition of RhB to the PVA/Tmt organogel system, the Φ_{ET} values increased remarkably as well, with a final peak of 16.58% attained when the molar ratio of the donor-to-acceptor was 100:1 (Fig. S14(b)†). In addition, analysis of the normalised intensity revealed that the AE of the PVA/Tmt/AYG and PVA/Tmt/RhB ALHSs were 16.8690 and 1.7889, respectively, indicating that the PVA/Tmt/AYG ALHS had an excellent AE (Fig. S15 and S16†). These results demonstrate the great efficiency and economy of the PVA/Tmt/AYG ALHS. Overall, from the above analyses, the PVA/Tmt/AYG and PVA/Tmt/RhB ALHSs exhibited good light-capturing effect.

The effects of metal ions on the fluorescence properties of the PVA/Tmt organogels were tested using nitrate solutions with the same concentration of Na^+ , Ni^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Cu^{2+} , Fe^{3+} , Co^{2+} , Al^{3+} , Cr^{3+} , K^+ , Mg^{2+} , Ag^+ or Mn^{2+} . With the addition of Al^{3+} , the fluorescence spectrum of the PVA/Tmt organogel redshifted (Fig. 5a), accompanied with the colour emission changing from bluish purple to green under 333 nm UV light (Fig. 5b). In addition, the fluorescence intensity of the PVA/Tmt organogel doubled with the addition of Pb^{2+} (Fig. 5a). Moreover, the PVA/Tmt organogel was quenched after the addition of Fe^{3+} (Fig. 5a and b), due to the paramagnetism causing fluorescence quenching of the PVA/Tmt organogel by Fe^{3+} .^{32,33} Prompted by this finding, we attempted to write on the top of the PVA/Tmt organogel using an aqueous solution containing Al^{3+} and Fe^{3+} , due to the toxicity of Pb^{2+} . Notably, the fluorescence changed from bluish violet to dark blue under a 333 nm UV light when the aqueous solution containing Al^{3+} was used to write on the PVA/Tmt organogel, which means that the ' Al^{3+} ' writing can be observed (Fig. 5c). However, no such phenomenon can be observed under natural light instead of UV light, suggesting that the ' Al^{3+} ' writing cannot be retained under natural light. In addition, fluorescence quenching could be clearly observed when the aqueous solution containing Fe^{3+} was used to mark the PVA/Tmt organogel, no such phenomenon could be observed when natural light was used instead of UV light (Fig. 5d). Based on the above findings, ' Al^{3+} ' and ' Fe^{3+} ' can be written on the PVA/Tmt organogel, which is only visible under the 333 nm UV light. Thus, the PVA/Tmt organogel can be used as a writing and information anticounterfeiting material.

Conclusions

Fluorescent gels with unique mechanical and physical properties were synthesised using two ratios of PVA/Tmt based on DMSO–ethylene glycol binary solvent. The prepared



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