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One-pot preparation of nonconventional luminescent polymer gels driven by polymerization†

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Nonconventional chromophores are good candidates for preparing luminous gels because their luminescence is usually enhanced in the aggregated state. In this work, a simple one-pot strategy for polymerization-induced gelation of polymer fluorescent gels was developed, and a self physically crosslinked luminous gel **PUHG** based on a non-conjugated/nonconventional luminous polyurethane derivative was obtained. Detailed experimental and theoretical studies probed the physical properties and luminescence principles of **PUHG**'s aggregated state. Molecular dynamics simulations suggest that abundant non-covalent interactions and physical entanglement between polyurethane chains are the main driving forces of gel formation and the source of luminescence. **PUHG** displays stable photophysical properties, environmental tolerance, good adhesion properties and processability, leading to the validation of patterning applications of **PUHG** on different organic/inorganic substrates. This work broadens the application range of nonconventional luminous polymers and provides a simple route for large-scale preparation of fluorescent gel soft materials.

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Introduction

Gels are very promising flexible materials with the advantages of flexible and tuneable physical and chemical properties, adjustable mechanical properties and viscoelasticity, and they have excellent application prospects in fields such as biomedical engineering, agriculture, food industry, soft robotics, etc.^{1–5} Therefore, new luminous gel soft materials, which combine the benefits of luminescence and gel properties, can play a vital role in high-tech applications where they are receiving increased attention.^{6–9} However, the development of such materials is still relatively slow. One of the major challenges is the aggregation-caused quenching (ACQ) that occurs when conventional chromophores are aggregated in the solid state or in high concentrations in solutions.^{10–13} Gels assume solid

and liquid characteristics concurrently, and a large part of a gel consists of a network of partially aggregated states, giving the properties of a quasi-solid.¹⁴ The confined space inside gels will inevitably cause conventional aromatic or π -conjugated chromophores to accumulate and interact strongly, which sometimes leads to the ACQ effect.¹⁵ This has greatly limited the development of fluorescent gels with broad application prospects, and brings a lot of adverse effects into their production.

The development of nonconventional luminescent materials (NCLMs) has overcome the ACQ dilemma faced by conventional luminescent materials.^{16–20} Crucially, the emission from NCLMs does not rely on chromophores with large π -conjugated structures. Instead, the emission comes from the spatial electron delocalization formed by the mutual aggregation of electron-rich or lone pair electron groups such as hydroxyl, ester, carbonyl, amide and so on, and the ensuing conformational solidification.^{21–25} The spatial electron aggregation principle of NCLMs is partly consistent with the semi-aggregation property of gels. In addition, NCLMs have the advantages of simple synthesis, low cost, easy structural regulation, good processability and large-scale production,^{26–30} which make them excellent candidates for the preparation of fluorescent gels. The polymerization-induced emission strategy^{31–33} is important and very relevant to the present work.

Fluorescent gels have many advantages. From the viewpoint of processability they have excellent plasticity, and due to their

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high stability in the aggregation state they can be processed into structures with a specific shape and size by injection molding and other methods which are suitable for the laboratory or commercial production. Gel-state materials are generally easy to handle because they do not spill, scatter or fly like powders, and are not prone to leak like solutions.^{34–39} At present, the acquisition of many fluorescent gels relies on embedding chromophores into the three-dimensional network of the gel, which relaxes the threshold for the preparation of luminous gels.^{40–43} However, these doped gels face many problems. For example, chromophore molecules may interact with other gel components, affecting the stability and controllability of the gel structure. The preparation of composite gels may require more complex synthesis and preparation methods, involving a multi-step process, increasing the difficulty of the experiments, especially for commercial scale-up.⁴⁴ Therefore, research on luminous gels should focus on developing single molecules that can be used as gelators and chromophores concurrently. Polymer gels typically have the advantage of increased mechanical strength compared to supramolecular gels that are formed from small molecules.⁴⁵

In this study, a fluorescent self physically crosslinked polymer gel was obtained *via* a simple one-pot reaction. Compared with conventional methods, the one-pot protocol needs fewer steps, thus simplifying the preparation process. It can use raw materials more efficiently, save resources and costs, and help reduce the chemical waste generated, which is in line with the principles of green chemistry. Moreover, self-crosslinked gel preparation often does not require external additives or catalysts, reducing dependence on external substances.

Results and discussion

Synthesis

Through a simple one-pot reaction of heptaethylene glycol, poly(ethylene glycol) monomethyl ether and trimethylhexamethylene diisocyanate (Fig. 1a) the self-crosslinked polyurethane derivative fluorescent gel (named **PUHG**, Fig. 1a and Table S1†) was prepared. The ¹H nuclear magnetic resonance (NMR) spectrum showed that **PUHG** has a clear fine structure (Fig. S1†). The FT-IR spectrum showed the N–H stretching vibration absorption peak at 3340 cm⁻¹, C–H asymmetric and symmetrical vibration peaks at 2881 and 2955 cm⁻¹, and C=O stretching vibration absorption peak at 1643 cm⁻¹; is the stretching vibration absorption peak of C–O–C is at 1105 cm⁻¹. The combination of the characteristic NH and CO peaks of the carbamate [–NHCOO–] functional group confirmed the successful synthesis of the polyurethane derivative (Fig. S2†). X-ray diffraction (XRD) data (Fig. S3†) show that a wide diffused diffraction peak unique to polyurethane derivatives appears at the diffraction angle of 18°. This semi-crystalline structure can enhance the physical binding of materials, which is conducive to their luminescence.⁴⁶ The average molecular weight and polydispersion index of **PUHG** were 8333 and

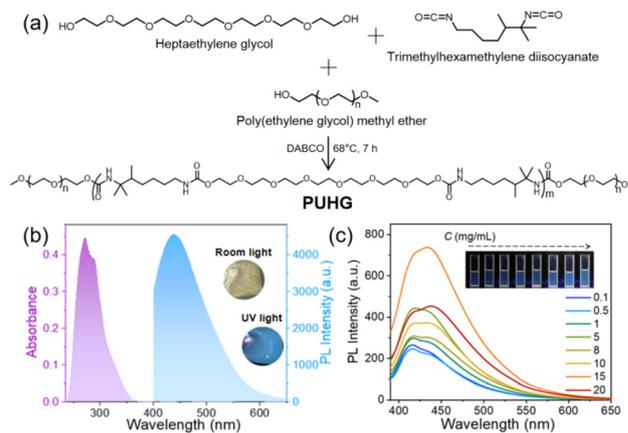


Fig. 1 (a) Synthetic route to the polyurethane derivative **PUHG**. (b) Absorption and emission (photoluminescence, PL) spectra of **PUHG** in the gel state. Insert: Photograph of **PUHG** glowing under room light and 365 nm UV light. (c) Emission of **PUHG**/DMSO solutions with different concentrations. $\lambda_{\text{ex}} = 365$ nm; Insert: Corresponding photographs taken under 365 nm UV light.

4.37, respectively, obtained by gel permeation chromatography (GPC).

Due to the chemical structure of the diol monomer (heptaethylene glycol), **PUHG** has a relatively flexible linear structure and contains a large number of O and N heteroatoms, which is very conducive to enhancing emission through the overlap of lone pairs of electrons. **PUHG** appeared as a transparent gel-like object under room light and as a bright blue, fluorescent gel under a 365 nm UV lamp (Fig. 1b). In comparison, the optical and mechanical properties of heptaethylene glycol monomer are mediocre (Fig. S4†). Therefore, we project a chain-extension type of addition polymerization reaction, for amplifying the effect of polymerization on the material's properties.

Photophysical characterization and mechanical property

The absorption and emission peak of **PUHG** is at λ_{max} 280 and 438 nm, respectively, showing a large Stokes shift of >150 nm (Fig. 1b and S4†), which can reduce the re-excitation caused by light. **PUHG** exhibits the common excitation-dependent properties of non-conjugated polymers (Fig. S5†).²⁶ The optical properties, including the excited state lifetime (6.18 ns) and quantum yield (0.8%) are listed in Table S1 in ESI.† To understand the luminous mechanism of **PUHG** in detail **PUHG**/DMSO solutions at different concentrations were monitored. Both the emission and absorption showed a concentration-dependent enhancement as the solution concentration gradually increased from 0.1 mg mL⁻¹ to 15 mg mL⁻¹ (Fig. 1c and S6†). This is because the aggregation behavior of **PUHG** chains leads to enhanced electron delocalization. However, with the further increase in concentration, **PUHG** chains gather randomly, and more heterogeneous electron delocalization is generated in the aggregates. At 20 mg mL⁻¹, **PUHG**'s emission shows a distinct change, slightly broadening and red-shifting,



yet the strength is reduced as observed previously with different aggregating fluorophores.^{47–49}

The illustration in Fig. 1c is the corresponding luminescent enhanced photograph. In addition, **PUHG** maintained good excitation-dependent emission properties even in dilute solutions as low as 0.1 mg mL^{-1} (Fig. S7†).

Heptaethylene glycol monomer and the product **PUHG** were observed by scanning electron microscopy (SEM) to explore the relationship between the properties of the compounds and their microscopic aggregation features (Fig. 2). Quantified heptaethylene glycol monomer and **PUHG** were dispersed in ethanol (20 mg mL^{-1}). The two samples were sufficiently dispersed by the vortex instrument to observe clearly their micromorphology. At the same magnification, heptaethylene glycol monomer showed a very dispersed blocky structure (Fig. 2a). In contrast, **PUHG** showed a slightly folded and ruptured membrane structure (Fig. 2b). In addition, thicker nanowire entanglements were observed (Fig. 2c and d). The above results show that the material's microstructure changed considerably after only one step of chain extension addition polymerization, which further affects the macroscopic emission properties.

To better understand the effects of polymerization and aggregation behavior, **PUHG** solutions with different concentrations were selected for quantitative SEM measurements and dynamic light scattering (DLS) monitoring (Fig. 3 and S8†). At the same magnification, 0.5 mg mL^{-1} samples showed sparse nanosphere structures (Fig. 3a). When the sample concentration increased successively, the microstructure showed an increasing trend of aggregation, until at 20 mg mL^{-1} aggregation and large nano-aggregates appear (Fig. 3b–d and S8†) and the polydispersity index increases with increasing concentration (Fig. S8†). Combined with the emission profile in Fig. 1c, we can infer that in the low concentration range, the aggregation behavior enhances the emission intensity. In the

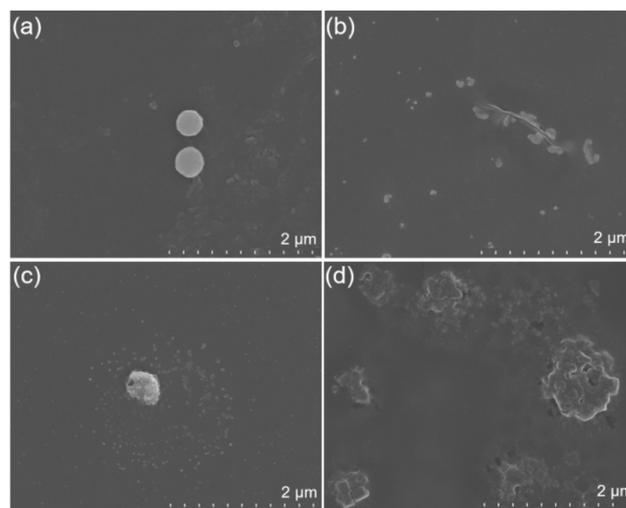


Fig. 3 SEM images of (a) 0.5 mg mL^{-1} , (b) 5 mg mL^{-1} , (c) 8 mg mL^{-1} , (d) 20 mg mL^{-1} of **PUHG**/ethanol solutions.

high concentration range, the aggregation behavior causes the emission wavelength to redshift. This property is commonly observed with non-conjugated polymers.^{16,17,26} Compared with the conventional aggregation-induced luminescence induced by molecular motion restriction, the nontraditional intrinsic luminescence (NTIL) of non-conjugated polymers is realized through the spatial electron conjugation of nonconventional chromophores. Hence, the increased concentration has a more significant influence on their NTIL emission behavior.

The theoretical calculations of **PUHG** system were conducted using Compass III force field. **PUHG** molecules with two repeating units were initially structurally optimized, annealed, and then molecular dynamics simulation with a simulation time of 5000 ps was implemented (Fig. S9–S12†).^{50–54} Various non-covalent interaction forces and chain-to-chain interactions were calculated *via* radial distribution functions. As shown in Fig. 4a, there are abundant N–C=O, N–C–O, N–C(O)O, C=O–C–O and inter-chain interactions within the **PUHG** system. These interactions make **PUHG** prone to inter- and intra-chain aggregation behavior, which is conducive to the through-space communication, conjugation of electrons and physical (non-covalent) crosslinking. These effects should be responsible for the gelation and luminescence of **PUHG**. A statistical analysis of the trend of the non-short interactions in the **PUHG** system over time shows that their energies reach equilibrium within 100 ps and then change little over time (Fig. S10†). The calculated cut-off distance of the hydrogen bond in the equilibrium structure was 3.43 \AA (Fig. S11†), and the bond angle of the formed hydrogen bond was defined as $90\text{--}180$ degrees, which was used as the criterion of the hydrogen bond for subsequent statistics on the number of hydrogen bonds. The statistical results show that with the change of time, the number of hydrogen bonds in the whole system is in dynamic equilibrium (Fig. 4b and S12†). The above results prove that there are many strong and stable

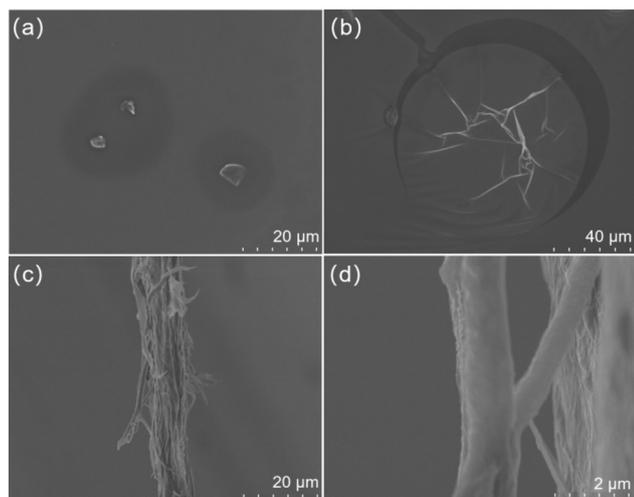


Fig. 2 SEM images of 20 mg mL^{-1} (a) heptaethylene glycol monomer, and **PUHG** (b–d) dispersed in ethanol.



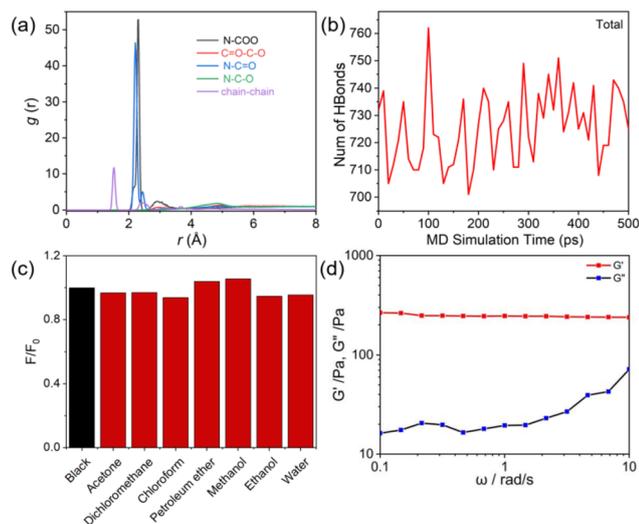


Fig. 4 (a) Radial distribution function of PUHG by molecular dynamics simulation. (b) The number of total hydrogen bonds over time. (c) Fluorescence changes of pure PUHG (black) and PUHG treated with different solvents (red). (d) The elastic modulus (G') and viscosity modulus (G'') at different frequencies of PUHG.

non-covalent interactions in the system, which provides a solid molecular foundation for the stability and function of PUHG. These tight non-covalent interaction networks not only enhance the intermolecular binding force, but also make PUHG molecular chains tend to entwine and aggregate with each other, and finally bring enhanced photoluminescence and self-gelation properties. To characterize the dynamic rheology of PUHG at different time scales, the strain was set at 1%, and the angular frequency (ω) was 100–0.1 rad s^{-1} . The change curves of elastic modulus (G') and viscosity modulus (G'') at different frequencies were obtained by a frequency scanning test. As shown in Fig. 4d, $G' > G''$, and G' and G'' have no intersection, and G' is not affected by frequency changes, indicating that PUHG is a complete gel sample.⁵⁵

PUHG application

The environmental tolerance of fluorescent gels in practical applications is also an important index. After 30 min infiltration of PUHG with acetone, dichloromethane, chloroform, petroleum ether, methanol, ethanol and water, PUHG still main-

tained excellent luminescence (Fig. 4c), which indicated that PUHG has good environmental tolerance and could be used in practical applications. Therefore, as a proof-of-concept, we tested the adhesion of PUHG on different organic/inorganic substrates, including paper, glass, plastic, wood and tinfoil. PUHG exhibited effective adhesion on these substrates. In addition, thanks to the flexibility and deformability of PUHG, it can be molded into any shape which is retained after the mold is removed (Fig. 5). These results prove the excellent processability of PUHG.

Conclusions

In conclusion, fluorescent gels materials have great potential for applications and for fundamental research because of their excellent photophysical properties, adhesion and plasticity. They are rising stars in luminous materials. However, due to the tight internal structure of gel materials, conventional chromophores usually face the dilemma of luminescence quenching after aggregation, so the development of such materials has been minimal. In this work, we developed a polymerization-induced self physically crosslinked polymer gel (PUHG) based on a nonconventional luminescent polyurethane derivative *via* a one-pot reaction. The ultra-flexible alkoxy chain favors non-covalent interactions and physical entanglement which are responsible for PUHG's gelation and luminescence behavior. Due to its excellent adhesion, processability, and fluorescence stability, PUHG was successfully applied to patterning on different substrates. This work provides a universal strategy for the facile, rapid and large-scale preparation of luminous gels.

Author contributions

Nan Jiang: Investigation, data curation, formal analysis, visualization, writing original draft; Ke-Xin Li, Chang-Yi Zhu: data curation, formal analysis, visualization. Yu-Wei Sun: validation; Xin Pu and You-Liang Zhu: software; Yan-Hong Xu: conceptualization, funding acquisition, project administration, resources; Martin R. Bryce: project administration, resources, supervision, writing-review & editing.

Data availability

The data associated with this article are available in the manuscript and ESI files.† Additional data can be obtained upon request to the authors.

Conflicts of interest

The authors declare no competing financial interest.

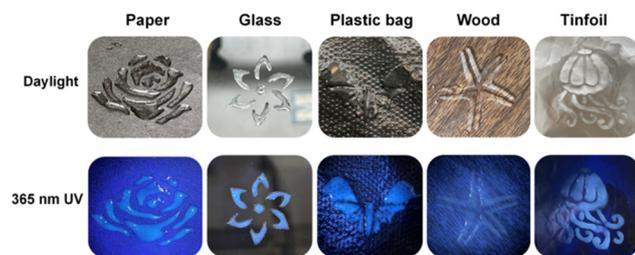


Fig. 5 Fluorescent patterns of PUHG adhering to paper, glass, plastic, wood and tinfoil under daylight and an ultraviolet lamp.



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