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## Supplementary Information

### One-Pot Preparation of Nonconventional Luminescent Polymer Gels Driven by Polymerization

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## 1. Experimental details

### General

The UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. The fluorescence spectra were recorded on a Hitachi F-4700 spectrometer and Edinburgh Instruments FLS-1000 spectrometer. The fluorescence lifetimes ( $\tau$ ) and fluorescence quantum yields were recorded using an Edinburgh Instruments FLS-1000 spectrometer. Using an integrating sphere to obtain all the light emitted by the sample, the quantum yield was determined by comparing the number of emitted photons with the number of absorbed photons.  $^1\text{H}$  NMR spectra were recorded on a Varian 400 MHz spectrometer. The  $^1\text{H}$  NMR spectra were referenced internally to the residual proton resonance in  $\text{DMSO-}d_6$  ( $\delta$  2.5 ppm). The molecular weights of the polyurethane were determined by gel permeation chromatography (GPC) on a Waters 410 instrument with monodispersed polystyrene as the reference and THF as the eluent at 35 °C. Scanning electron microscope (SEM) images were obtained using a JEOL model JSM-6700 instrument operating at an accelerating voltage of 5.0 kV. The samples were prepared by placing microdrops of the solution on a holey carbon copper grid. X-ray diffraction (XRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on a glass substrate.

### Molecular dynamics simulation method

In Materials Studio (MS) the initial model of the molecule was constructed using the "Amorphous Cell" module, and the initial density was set to 1.0 g/cm<sup>3</sup>. Periodic boundary conditions were used, i.e., boxes were used in MS to represent the environment outside the molecule. 70 molecules were invested in the construction process. The structure was then iterated with energy minimization using the Smart algorithm to rule out unreasonable contact cases, such as overlapping parts and overly dense contact between molecules. In this step, the conformation with the lowest energy was selected as the starting point for the subsequent molecular dynamics simulation. Then, the optimized cells were annealed for 1000 cycles within the temperature range of 300-600 K under NPT ensemble conditions, and the configuration with the lowest energy was selected for molecular dynamics simulation. Finally, NPT dynamics simulations were used to obtain the physical properties of the system, such as

density, volume, kinetic energy and potential energy, resulting in the final equilibrium structure. The NPT dynamics simulation was performed at 298.15 K with a total duration of 5000 ps and each time step of 1 femtosecond.

In the simulation, the Compass III force field was used to calculate the interatomic interactions within the system. The long-range electrostatic interaction terms were solved by the PPPM method with an accuracy of 0.001 kcal·mol<sup>-1</sup>. The van der Waals interaction force was calculated using an atom-based method. At the same time, to control the system temperature, the Nose-Hoover thermostat and the Berendsen constant pressure were used to maintain the pressure stability. All molecular dynamics simulations were performed using a time step of 1 femtosecond. In summary, in this process, the initial model was built using Amorphous Cell module in Materials Studio. Through steps such as energy minimization and dynamic simulation, the balanced structure and physical properties of the system were obtained. The interaction was calculated using the Compass III force field, with appropriate temperature and pressure control, providing strong support for further molecular modelling studies.<sup>1,2</sup>

### Radial distribution function

The calculation equation for radial distribution function (RDF) can be described as:

$$g(r) = \lim_{dr \rightarrow 0} \frac{p(r)}{4\pi \left( \frac{N_{pairs}}{V} \right) r^2 dr}$$

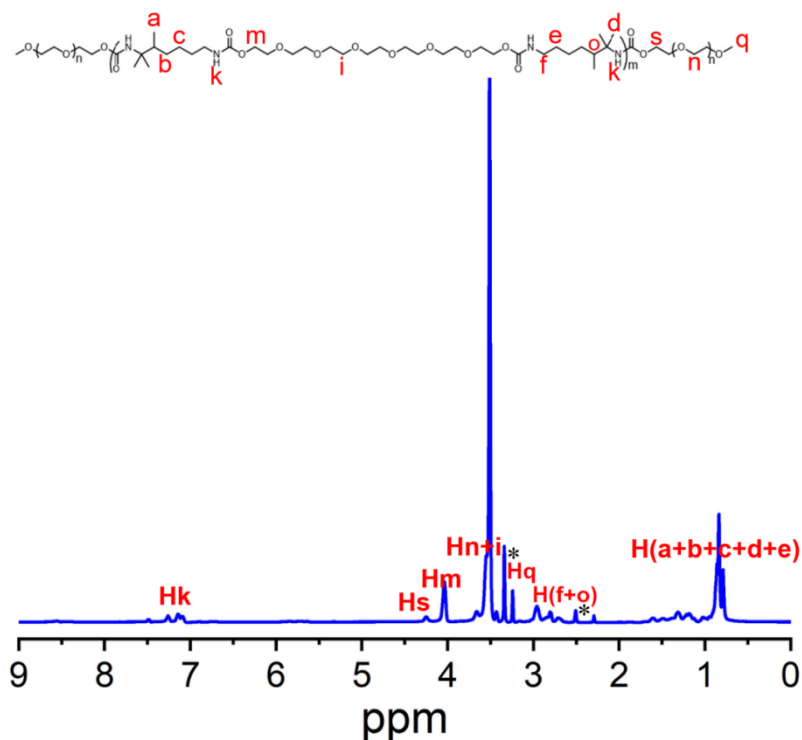
where  $r$  is the distance between each atom pair,  $g(r)$  is radial distribution function,  $p(r)$  is the average number of atom pairs.  $N_{pairs}$  is the total number of atom pairs,  $V$  is the volume of the simulation cell.<sup>3,4</sup>

### Synthesis of PUHG

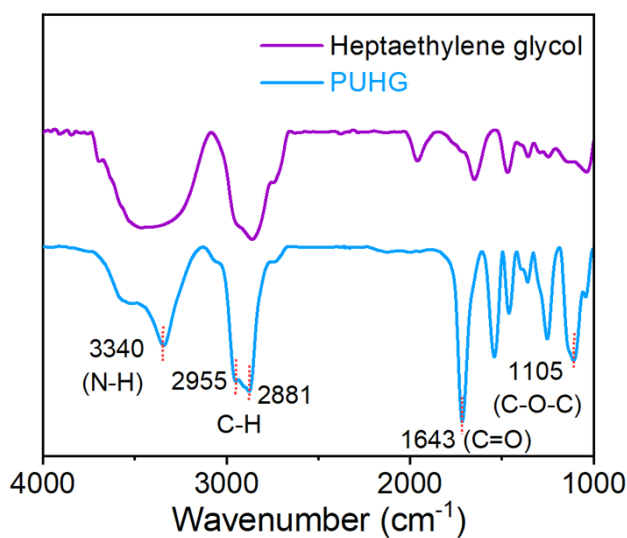
A mixture of heptaethylene glycol (2.565 g, 7.86 mmol), poly(ethylene glycol) monomethyl ether ( $M_w = 200$  g mol<sup>-1</sup>; 2.352 g, 5.94 mmol), anhydrous THF (6 mL), trimethylhexa-1,6-diyl diisocyanate (2.277 g, 10.83 mmol) and DABCO (0.035 g, 0.315 mmol) were added to a dried two-neck round-bottom flask. The solution was heated at 68°C for 7 h under nitrogen atmosphere. After that time the clear solution became significantly viscous, indicating the polymerization reaction had occurred. The crude product was dissolved in chloroform and then reverse precipitated from excess diethyl ether. Then the product was dried under vacuum for 24 h to obtain the resulting **PUHG** (4.03 g); yield 56%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  [ppm]): 7.26 (s, 2H), 7.12 (s, 2H), 4.2 (s, 4H), 3.4-3.6 (broad, PEG protons), 3.24 (s, 3H; PEG

terminal  $-OCH_3$  protons), 2.6-3.1 (broad, 3H), 0.7-1.6 (broad, 15H). FTIR:  $3340\text{ cm}^{-1}$  (N-H),  $2881$  and  $2955\text{ cm}^{-1}$  ( $-CH_2-$  asymmetric and symmetric stretch),  $1643\text{ cm}^{-1}$  (C=O),  $1105\text{ cm}^{-1}$  (C-O-C stretch PEG).  $M_n$ : 8333;  $M_w$ : 36485;  $M_p$ : 11869; PD: 4.37.

## 2. Structural characterization



**Fig. S1**  $^1\text{H}$  NMR spectrum of **PUHG** in  $\text{DMSO-}d_6$  (\* indicates peaks from the solvent and water).



**Fig. S2** FTIR spectra of heptaethylene glycol monomer and **PUHG**.

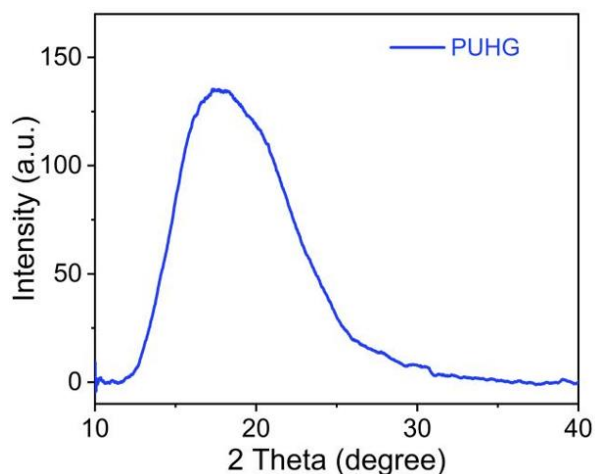


Fig. S3 XRD pattern of **PUHG**.

### 3. Photophysical properties

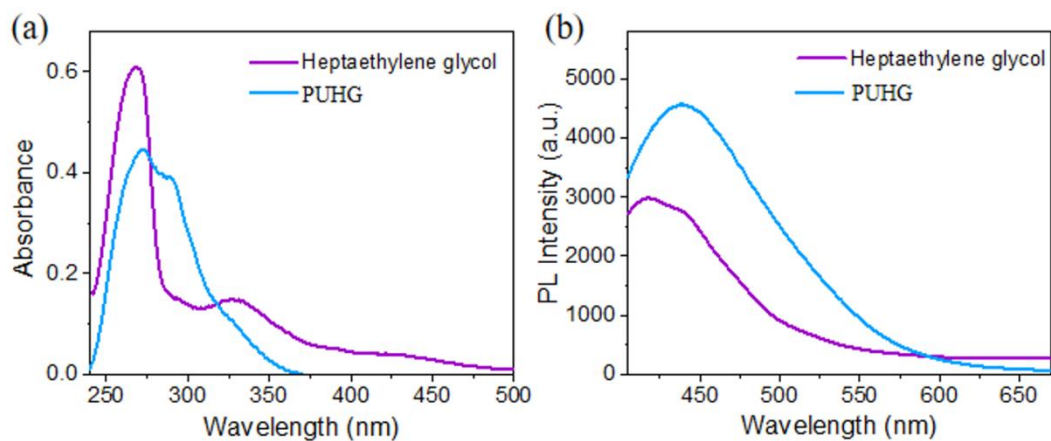


Fig. S4 (a) UV-vis absorption spectra of heptaethylene glycol monomer and **PUHG**. (b) Fluorescence spectra of heptaethylene glycol monomer and **PUHG** at 365 nm excitation.

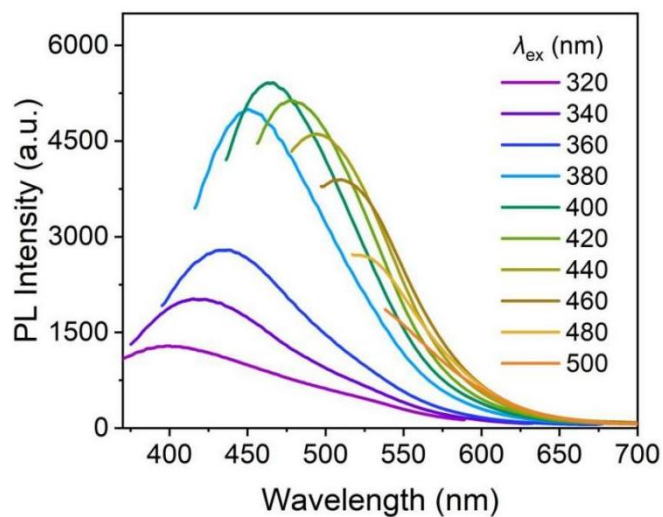
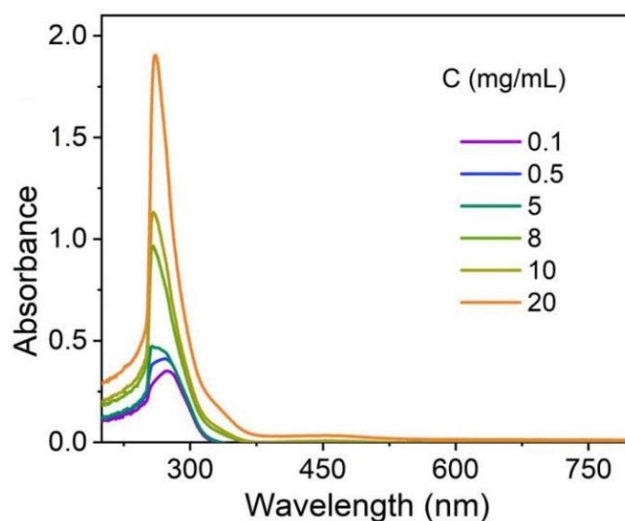
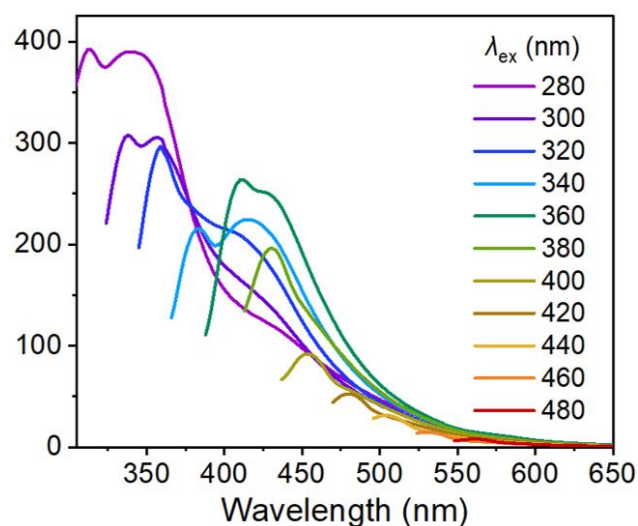


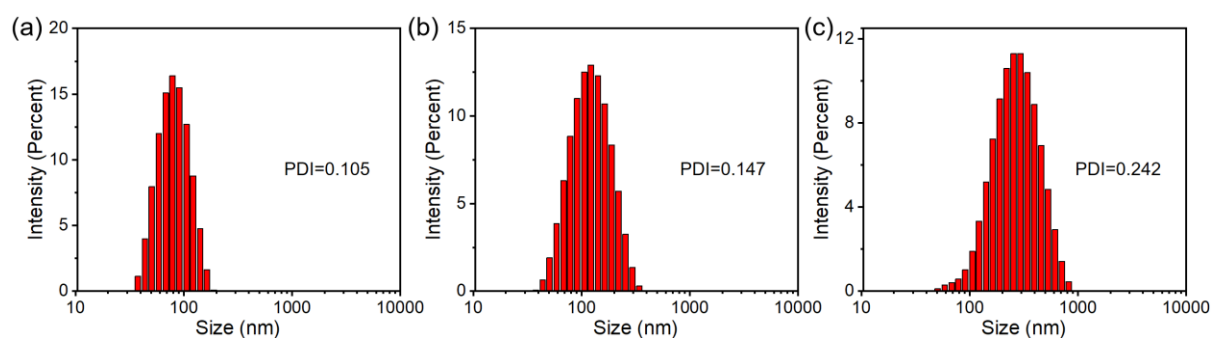
Fig. S5 Fluorescence spectra of **PUHG** at varying  $\lambda_{ex}$ .



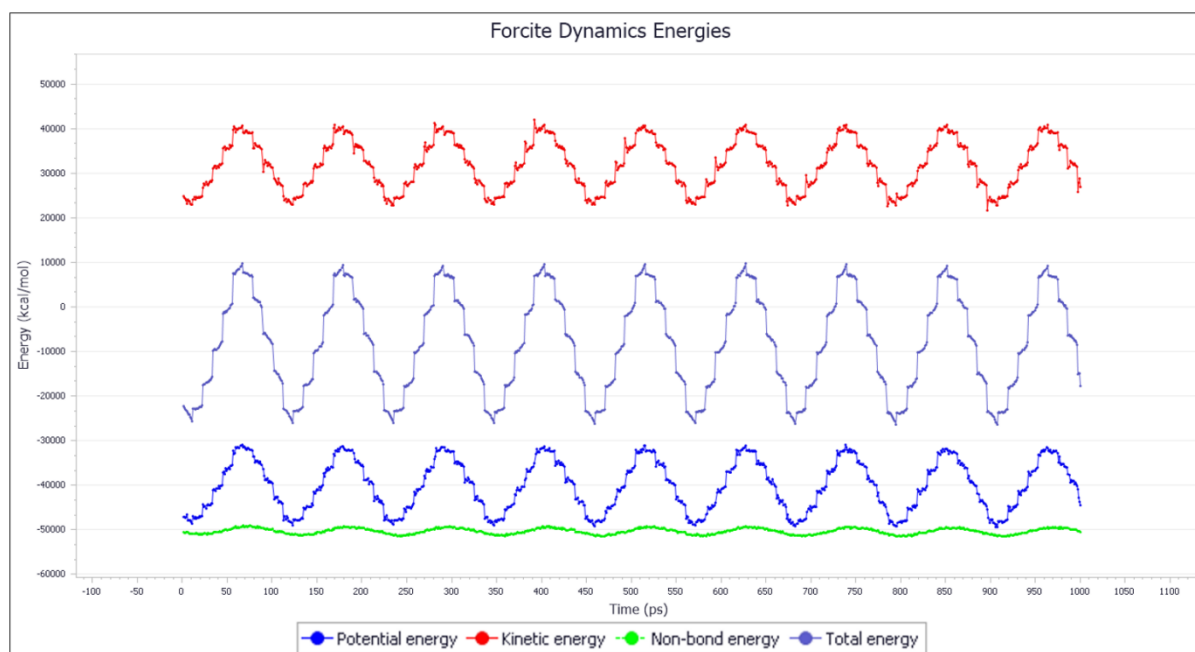
**Fig. S6** UV-vis absorption spectra of **PUHG/DMSO** solution with different concentrations.



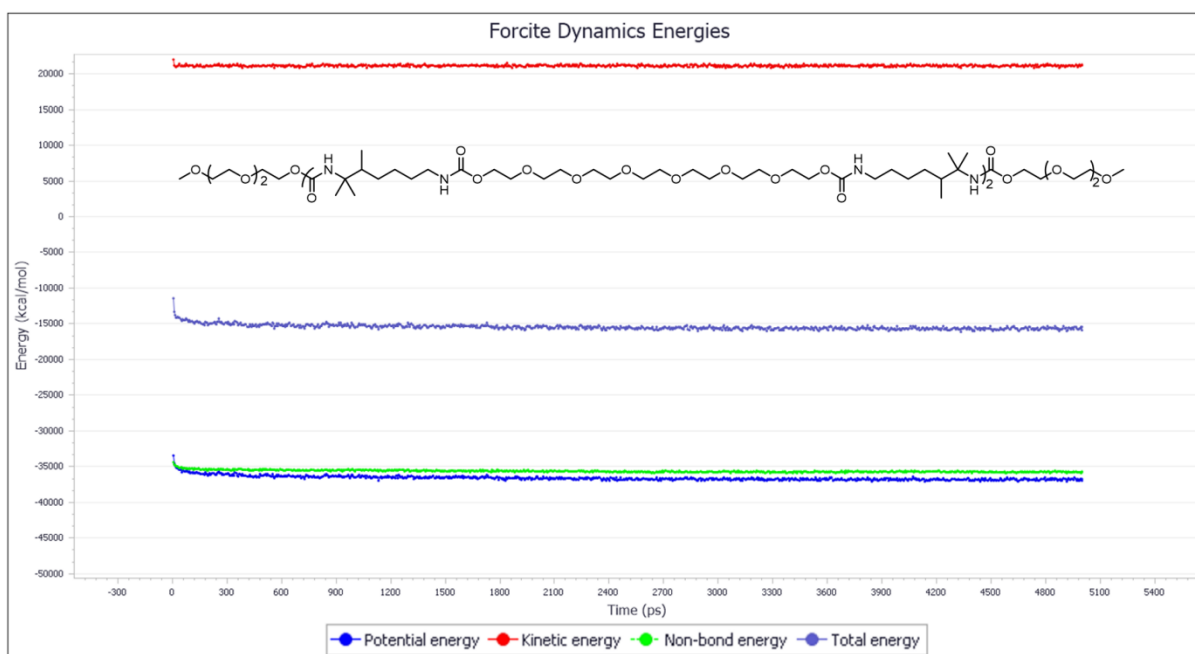
**Fig. S7** Emission spectra of 0.1 mg mL<sup>-1</sup> **PUHG/DMSO** solution at varying  $\lambda_{\text{ex}}$ .



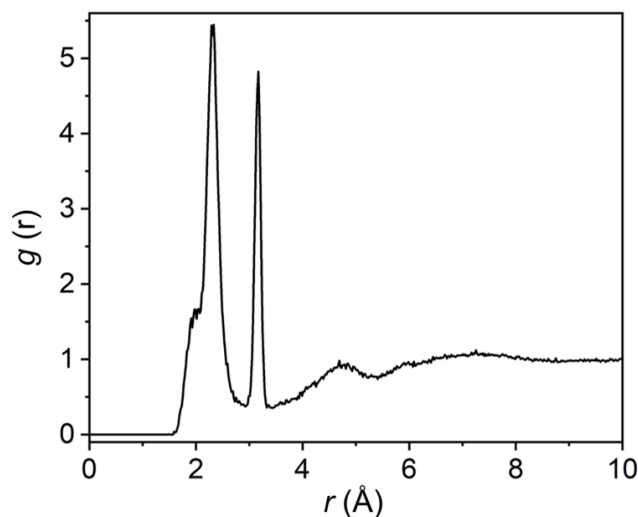
**Fig. S8** DLS particle size map of **PUHG** (a) 0.5 mg mL<sup>-1</sup>, (b) 5 mg mL<sup>-1</sup> and (c) 8 mg mL<sup>-1</sup> in pure DMSO solution.



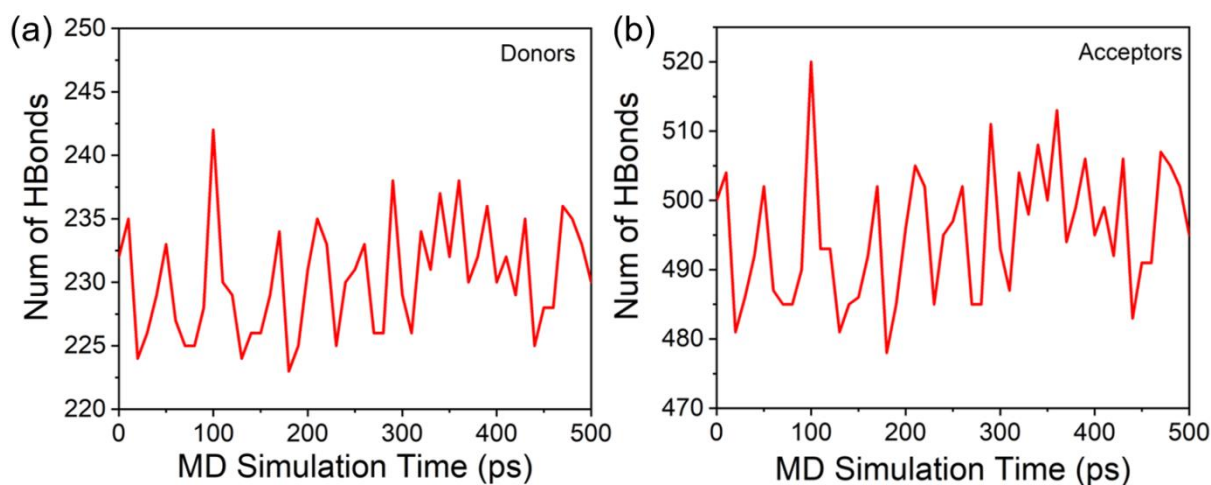
**Fig. S9** Diagram of the energy change of the PUHG system undergoing annealing.



**Fig. S10** The variation trend of various energies in the simulation system over time. Insert: the specific structure of the model molecules.



**Fig. S11** The cut-off distance of the hydrogen bonds.



**Fig. S12** The number of hydrogen bonds (a) donors and (b) acceptors over time.

**Table S1.** Optical properties of **PUHG** in the gel state.

|             | $\lambda_{\text{abs}}$ | $\lambda_{\text{em}}^{\text{a}}$ | Lifetime <sup>b</sup> | Quantum Yield |
|-------------|------------------------|----------------------------------|-----------------------|---------------|
| <b>PUHG</b> | 273 nm                 | 438 nm                           | 6.18 ns               | 0.8%          |

<sup>a</sup> $\lambda_{\text{ex}}=365$  nm; <sup>b</sup> $\lambda_{\text{ex}}=365$  nm,  $\lambda_{\text{em}}=438$  nm.

#### 4. References

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