# **Supplementary Information**

The role of ring-type structures in nonconventional luminescent polyurethane

derivatives

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#### 1. Experimental details

## General

The UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. The fluorescence spectra, fluorescence lifetimes ( $\tau$ ) and fluorescence quantum yields were recorded on an Edinburgh Instruments FLS-1000 spectrometer. Using an integrating sphere to obtain all the light emitted by the sample, the quantum yields were determined by comparing the number of emitted photons with the number of absorbed photons. <sup>1</sup>H NMR spectra were recorded on a Varian 400 MHz spectrometer. The <sup>1</sup>H NMR spectra were referenced internally to the residual proton resonance in DMSO- $d_6$  ( $\delta$  2.5 ppm). The molecular weights of the polyurethanes 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. Dynamic light scattering (DLS) images were obtained using a Malvern Panalytical Zetasizer Lab instrument. All the photos were taken with an iPhone 15. X-ray diffraction (XRD) patterns of the samples were obtained with a Rigaku DMax 2000 instrument. The pixel painting was designed by the authors and assembled using PowerPoint. The molds for painting were designed by the authors using Adobe Illustrator and engraved by a HUIBANG-LASER HB-4060 non-metal laser engraving machine.

#### **PU** solution preparation for SEM test

Different concentrations of PUs/DMSO solutions (0.1-20 mg mL<sup>-1</sup>) were prepared and transferred into 5 mL centrifuge tubes. The centrifuge tubes were shaken thoroughly on a vortex mixer until the samples were completely dissolved. Shaking of the centrifuge tubes was continued for another 30 minutes. The angle and force of the centrifuge tube was adjusted every 10 minutes to ensure that the samples were fully dispersed in the DMSO solution. 1 mL of the prepared PUs/DMSO solution was dispersed in 1 mL of ethanol. Continued use of the vortex mixer dispersed the sample and prevented PU nanoparticles from aggregating in the solution. The samples were dropped onto a holey carbon copper grid, the solvent was evaporated overnight, and finally, the SEM instrument was used to observe the nanoaggregate structure

caused by the evaporation of the solvent.

#### Preparation of water-soluble nanoparticles PU3 NPs

The water-soluble nanoparticles were prepared by a solvent exchange method. Firstly, derivative **PU3** (1 mg) was dissolved in methanol (1 mL), then the mixture was slowly dropped into deionized water (10 mL) and the methanol was volatilized by stirring at a constant speed for 24 h. After the methanol was completely volatilized, the mixture was placed in a dialysis bag and the residual methanol was removed. Then a 0.22  $\mu$ m filter head was used to filter and to obtain uniformly dispersed nanoparticles.

#### Cell Culture.

Mouse hippocampal neuronal (HT22) cells were regularly checked for mycoplasma contamination. HT22 cells were cultured in Dulbecco's Modified Eagle's Medium (DMEM) (Gibco®, Grand Island, NY, USA) supplemented with 10% fetal bovine serum (FBS) (Gibco®), penicillin (100 U mL<sup>-1</sup>), and streptomycin (100  $\mu$ g mL<sup>-1</sup>) and the cultures were maintained at 37 °C in a humidified atmosphere containing 5% CO<sub>2</sub>. Cells were divided into three groups for treatment with H<sub>2</sub>O<sub>2</sub> (200  $\mu$ M): (i) control group; (ii) HT22 cells were incubated with H<sub>2</sub>O<sub>2</sub> alone for 24 h; and (iii) HT22 cells were incubated with **PU3 NPs** for 24 h and then treated with H<sub>2</sub>O<sub>2</sub> for another 24 h.

#### In Vitro Cell Cytotoxicity Test.

The HT22 cells were maintained in Ham's F12K medium with heparin (0.1 mg mL<sup>-1</sup>), endothelial cell growth supplement (ECGS) (0.05 mg mL<sup>-1</sup>), 10% FBS, 1% *L*-glutamine and 1% penicillin/streptomycin at 37°C containing 5% CO<sub>2</sub>. For in vitro cytotoxicity tests, HT22 cells were seeded into 96 well plates with a density of  $1 \times 10^4$  per well. After 24 h, the cells were incubated with **PU3 NPs** for another 24 h. The MTT assay was conducted following the standard protocol. [MTT is 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide].

#### **Pixel Painting and Security Ink Applications.**

**Pixel Painting:** Prepare A wall of pixel paintings was made up of small square plates, and the PU powder was placed into the corresponding small square plates in order according to the

names (**PU1**, **PU2** or **PU3**) in Fig. S20. Under sunlight and UV light, the pixel painting presents different colors.

**Security Ink**: After the synthesis was completed, a reverse precipitation treatment was carried out on the crude product, and then it was used as ink directly, without drying. The state of the ink (thin or thick) can be adjusted by adding DMSO solvent in an appropriate amount and stirring. The drawing was then made on the target substrate (glass, paper, wood, aluminum, non-woven fabric) using the mold shown in Fig. S21.

#### **Computational Methodology**

The initial models of **PU1**, **PU2** and **PU3** were built by the Packmol program and 50 model molecules of **PU1** or **PU2/PU3** (m = 2 and n = 2) were placed in the orthogonal box. The model structure **PU1** or **PU2/PU3** was optimized at the PBE0-D3(BJ)/def2-SVP level of theory<sup>1-4</sup> using Gaussian 16 (Revision C.01)<sup>5</sup> and no imaginary frequency was checked by frequency calculations. The restrained electrostatic potential (RESP) atomic charges were generated by Multiwfn.<sup>6</sup> Force field parameters were adopted from the General Amber Force Field (GAFF).<sup>7</sup>

Molecular dynamics (MD) simulations were performed using the GROMACS (version 2022.5) package<sup>8</sup> and topology file and forcefield parameters were created by Sobtop.<sup>9</sup> The long-range electrostatic interactions were handled by the particle-mesh Ewald (PME) method and the cutoff value of van der Waals interactions was set to 10.0 Å.<sup>10</sup> After energy minimization, the three systems were heated up from 0 K to 300 K in the 1.0 ns simulations. Subsequently, the 50.0 ns MD simulations (MD1) were conducted in the NPT ensemble at 300 K using the v-rescale thermostat method<sup>11</sup> and the Berendsen protocol.<sup>12</sup> Next, the three systems were heated up to synthetic temperatures of 338 K, 338 K and 403 K, respectively, with the 50.0 ns of MD simulations (MD2). Finally, the temperature of the three systems dropped to 300 K and unrestrained MD simulations for 50.0 ns (MD3) were performed.

Natural transition orbitals (NTOs) were calculated at the NEVPT2(6,6)/def2-TZVP/MM level of theory. Electron-hole distribution was obtained based on NTO results. The snapshots were taken from MD3 and optimized at the CAM-B3LYP-D3/def2-SVP level of theory by the Tcl-Chemshell program (version 3.7.1)<sup>13</sup> where the QM region was treated by ORCA program (version 5.0.4)<sup>14</sup> and MM region was treated by DL poly program<sup>15</sup> with electrostatic

embedding scheme. Active spaces used for multi-reference calculations were selected by standard workflow of MOKIT<sup>16</sup> based on the optimized structure, including: 1) RHF/def2-TZVP single point calculation was performed with background charges, and the wavefunction was checked to be stable by Gaussian16; 2) CIS/def2-TZVP calculation with background charges was performed for the lowest 7 states based on previous RHF wavefunction and all excitation components with contribution larger than 10<sup>-5</sup> were considered, and 3) Active spaces were determined based on NTOs obtained in CIS calculations.<sup>17, 18</sup> NEVPT2/MM calculations were performed by the PySCF package (version 2.5.0).<sup>19</sup>

#### Synthesis of PU1

A mixture of 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (2.393 g, 7.86 mmol), poly(ethylene glycol) monomethyl ether ( $M_w = 200$  g mol<sup>-1</sup>; 1.188 g, 5.94 mmol), anhydrous THF (5 mL), trimethylhexa-1,6-diyl diisocyanate (2.277 g, 10.83 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.035 g, 0.315 mmol) were added to a dried two-neck round-bottom flask. The solution was heated at 75°C for 8 h under nitrogen atmosphere. After that time the clear solution became significantly viscous, indicating the polymerization 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 **PU1** (3.66 g); yield 62%.

### Synthesis of PUX

A mixture of 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (2.393 g, 7.86 mmol), poly(ethylene glycol) monomethyl ether ( $M_w = 200$  g mol<sup>-1</sup>; 1.188 g, 5.94 mmol), anhydrous DMSO (5 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 130°C for 17 h under nitrogen atmosphere. After that time the clear solution became significantly viscous, indicating the polymerization 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 **PUX** (3.94 g); yield 67%.

#### Synthesis of PU2

A mixture of 1,4-dioxane-2,5-diol (0.944 g, 7.86 mmol), poly(ethylene glycol) monomethyl ether ( $M_w = 200 \text{ g mol}^{-1}$ ; 1.188 g, 5.94 mmol), anhydrous THF (5 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 75°C for 8 h under nitrogen atmosphere. After that time the clear solution became significantly viscous, indicating the polymerization 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 **PU2** (2.83 g); yield 64%.

#### Synthesis of PU3

A mixture of 1,4-dioxane-2,5-diol (0.944 g, 7.86 mmol), poly(ethylene glycol) monomethyl ether ( $M_w = 200 \text{ g mol}^{-1}$ ; 1.188 g, 5.94 mmol), anhydrous DMSO (5 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 130°C for 8 h under nitrogen atmosphere. After that time the clear solution became significantly viscous, indicating the polymerization 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 **PU3** (2.69 g); yield 61%.







Fig. S2 Synthetic route to the polyurethane derivative PU2 and PU3.

## 2. Structural characterization



Fig. S3 <sup>1</sup>H NMR spectrum of PU1 in DMSO- $d_6$ , with residual solvent proton resonance.



Fig. S4 <sup>1</sup>H NMR spectrum of **PUX** in DMSO- $d_6$ , with residual solvent proton resonance.



Fig. S5 <sup>1</sup>H NMR spectrum of PU2 in DMSO- $d_6$ , with residual solvent proton resonance.



Fig. S6 <sup>1</sup>H NMR spectrum of **PU3** in DMSO- $d_6$ , with residual solvent proton resonance.



Fig. S7 (a) FT-IR spectra of PU1, PU2 and PU3 in solid state. (b) FT-IR spectra of PU1, PU2 and PU3 solutions at 0.1 mg mL<sup>-1</sup> in DMSO. XRD patterns of (c) PU1, (d) PU2, (e) PU3 and (f) PUX.

3. Photophysical properties and morphology



Fig. S8 UV-vis absorption spectra of PU1, PU2 and PU3 in solid state.



**Fig. S9** SEM images of 20 mg mL<sup>-1</sup> diol monomers dispersed in ethanol (a) 3,9-bis(1,1dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane, (b) 1,4-dioxane-2,5-diol.



Fig. S10 SEM images of 20 mg mL $^{-1}$  (a) PU1, (b) PU2 and (c) PU3 dispersed in ethanol.



Fig. S11 PL spectra of PUX and PU1 in solid state.



Fig. S12 Concentration-dependent PL spectra of (a) PU1, (b) PU2, and (c) PU3 in DMSO.



Fig. S13 Normalized emission spectra of (a) PU1, (b) PU2, and (c) PU3 in Acetonitrile (ACN), Methanol (MeOH), Acetone (AC) and Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solvent (3 mg mL<sup>-1</sup>). UV-vis absorption spectra of (d) PU1, (e) PU2 and (f) PU3 in DMSO solution at different concentrations.



**Fig. S14** SEM images of (a) 0.1 mg mL<sup>-1</sup>, (b) 5 mg mL<sup>-1</sup>, (c) 10 mg mL<sup>-1</sup>, (d) 20 mg mL<sup>-1</sup> of **PU1** in DMSO solution.



**Fig. S15** SEM images of (a) 0.1 mg mL<sup>-1</sup>, (b) 5 mg mL<sup>-1</sup>, (c) 10 mg mL<sup>-1</sup>, (d) 20 mg mL<sup>-1</sup> of **PU2** in DMSO solution.



Fig. S16. DLS particle size maps of (a-c) PU1, (d-f) PU2, and (g-i) PU3 in ethanol at 0.1, 5, and 20 mg mL<sup>-1</sup>.

Table S1 Molecular weight and polydispersity data of the PUs from GPC.

	PU1	PU2	PU3
$M_{ m n}$	1451	1427	1292
$M_{ m w}$	1877	1963	1882
$M_{ m P}$	804	800	779
PD	1.29	1.38	1.46

Table S2 Optical properties of the PUs in the solid state.

	$\lambda^{\max}_{abs}$	$\lambda^{\max}_{em}^{a}$	Lifetime <sup>a</sup>	Quantum Yield
PU1	370 nm	440 and 475 nm	3.78 and 5.15ns	3.2%
PU2	512 nm	455 and 590 nm	1.96 and 3.41ns	1.5%
PU3	688 nm	585 nm	0.94 ns	1.4%

 $^{a}\lambda_{ex}=365$  nm.

## 4. Theoretical calculations



Fig. S17 Counts of hydrogen bonds during the three-stage MD simulations. Initial 5.0 ns is excluded in the statistics due to nonequilibrium reasons. Average counts for each stage are marked in red.



Fig. S18 n  $\rightarrow \pi^*$  excited state energy shift influenced by the external electrostatic field (EEF).

## 5. Applications



Fig. S19 Cell viability was measured after HT22 cells were treated with different concentrations of PU3 NPs in water for 24 h.



Fig. S20 A schematic of the materials (PU1, PU2 and PU3) and arrangement used in a pixel

painting.



Fig. S21 Molds used in painting on different materials.



Fig. S22 (a) Architectural designs drawn by PU2 on non-woven fabrics under daylight and under an ultraviolet lamp. (b) A drawing of the leaning tower of Pisa on paper by PU1, PU2 and PU3 under daylight and under an ultraviolet lamp.

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