

Supporting Information

Blue-emitting thermoreversible oligourethane gelators with aggregation-induced emission properties

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1. Experimental details

General:

Materials obtained from commercial suppliers were used without further purification unless otherwise stated. All glassware, syringes, magnetic stirring bars and needles were thoroughly dried in a convection oven. ^1H NMR spectra were recorded at 25 °C on a Varian 500 MHz spectrometer and were referenced internally to the residual proton resonance in $\text{DMSO-}d_6$ (δ 2.5 ppm). The molecular weights of the oligomers were calculated from their ^1H NMR spectra, as described in the sections below. UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Photoluminescence spectra were collected on an Edinburgh FLS920 spectrophotometer.

Synthesis of OU Derivatives:

OU Derivatives were synthesized according to a similar method used in previous work.¹

OUHDI. A mixture of 4,4'-sulfonyldiphenol (2.62 mmol), polyethylene glycol mono-methyl ether ($M_w = 200 \text{ g mol}^{-1}$; 1.98 mmol), anhydrous acetonitrile (8 mL), hexamethylene diisocyanate (3.61 mmol) and DABCO (0.105 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 the clear solution became significantly viscous, the product was precipitated from excess diethyl ether. Then the product was dried under vacuum for 24 h to obtain **OUHDI**. Yield: 69%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$, δ [ppm]): 7.1-8.0 (broad, 8H; 4,4'-sulfonyldiphenol protons), 6.9 (broad, 4H), 4.03 (s, 4H), 3.4-3.68 (broad, PEG protons), 3.3 (s, 3H; PEG terminal $-\text{OCH}_3$ protons), 3.1-2.9 (broad, 4H), 1.2-1.6 (broad, 4H). FTIR: 3342 cm^{-1} (N-H), 2858 and 2933 cm^{-1} ($-\text{CH}_2-$ asymmetric and symmetric stretch), 1712 cm^{-1} (C=O), 1105 cm^{-1} (C-O-C stretch PEG). $M_w = 4192 \text{ g mol}^{-1}$.

OUHMDI. The synthetic procedure for **OUHMDI** was the same as **OUHDI**, except monomer methylene-bis(4-cyclohexyl isocyanate) was used instead of hexamethylene diisocyanate. Yield: 65%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$, δ [ppm]): 7.25-8.0 (broad, 8H; 4,4'-sulfonyldiphenol protons), 6.85 (broad, 2H), 3.85 (s, 2H), 4.05 (s, 2H), 3.40-3.60 (broad, PEG protons), 3.25 (s,

3H; PEG terminal $-OCH_3$ protons), 2.5-1.20 (broad, 10H). FTIR: 3313 cm^{-1} (N-H), 2856 and 2930 cm^{-1} ($-CH_2-$ asymmetric and symmetric stretching), 1703 cm^{-1} (C=O), 1106 cm^{-1} (C-O-C stretching PEG). $M_w = 1749\text{ g mol}^{-1}$.

OUTDI. The synthetic procedure for **OUTDI** was the same as **OUHDI**, except monomer 2,4-diisocyanatotoluene was used instead of hexamethylene diisocyanate. Yield: 63%. $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ [ppm]): 8.85-9.0 (broad, 2H), 6.55-8.0 (broad, 8H; 4,4-sulfonyldiphenol protons), 4.2 (s, 4H), 3.45-3.7 (broad, PEG protons), 3.4 (s, 3H; PEG terminal $-OCH_3$ protons), 1.95-2.25 (broad, 3H). FTIR: 3305 cm^{-1} (N-H), 2873 and 2937 cm^{-1} ($-CH_2-$ asymmetric and symmetric stretching), 1736 cm^{-1} (C=O), 1104 cm^{-1} (C-O-C stretching PEG). $M_w = 2775\text{ g mol}^{-1}$.

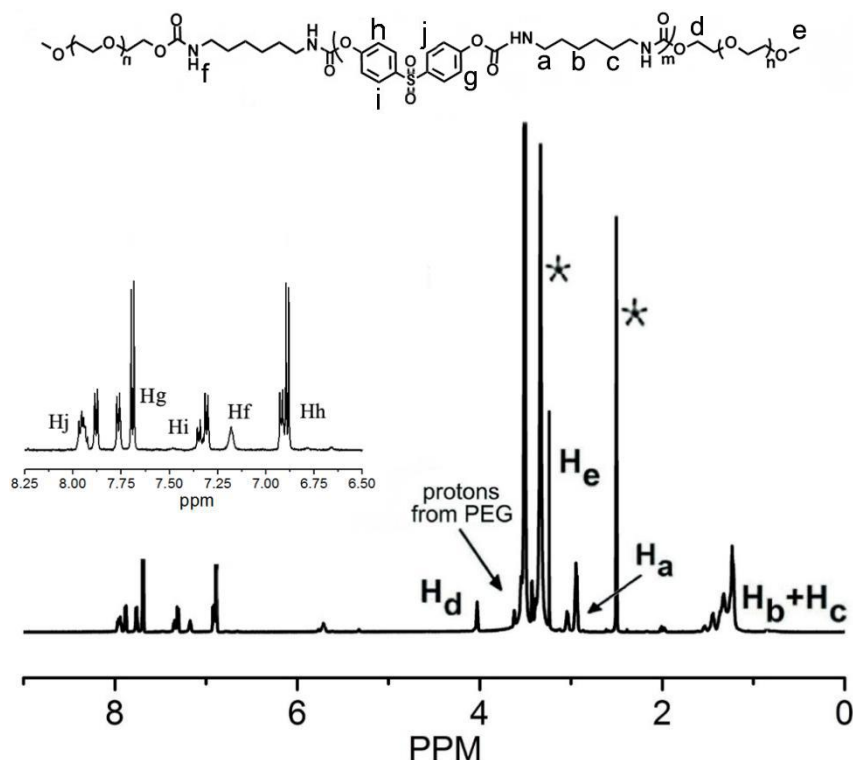


Fig. S1 $^1\text{H NMR}$ spectrum of **OUHDI** in $\text{DMSO-}d_6$ (* indicates peaks from the solvent and water)

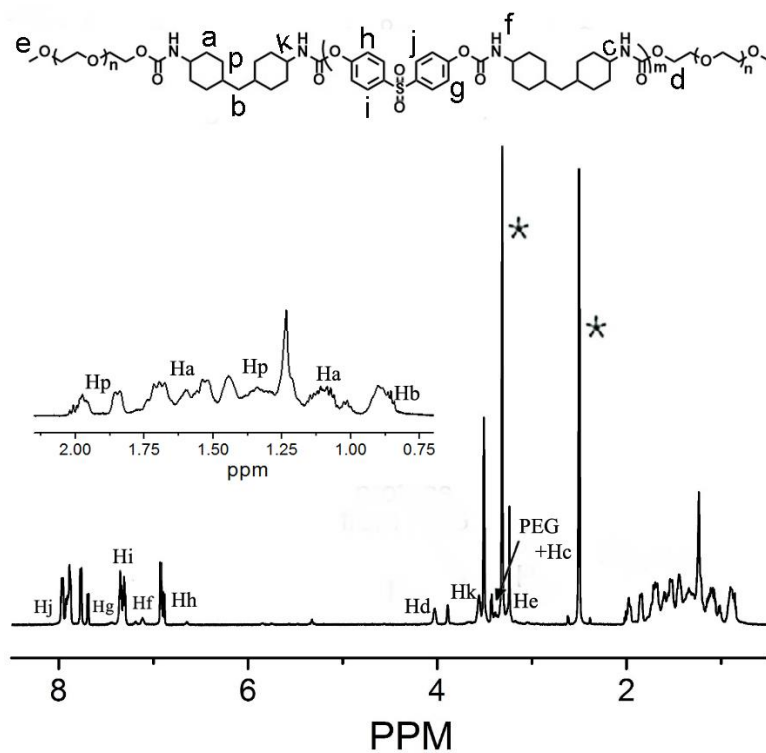


Fig. S2 ^1H NMR spectrum of **OUHMDI** in $\text{DMSO-}d_6$ (* indicates peaks from the solvent and water)

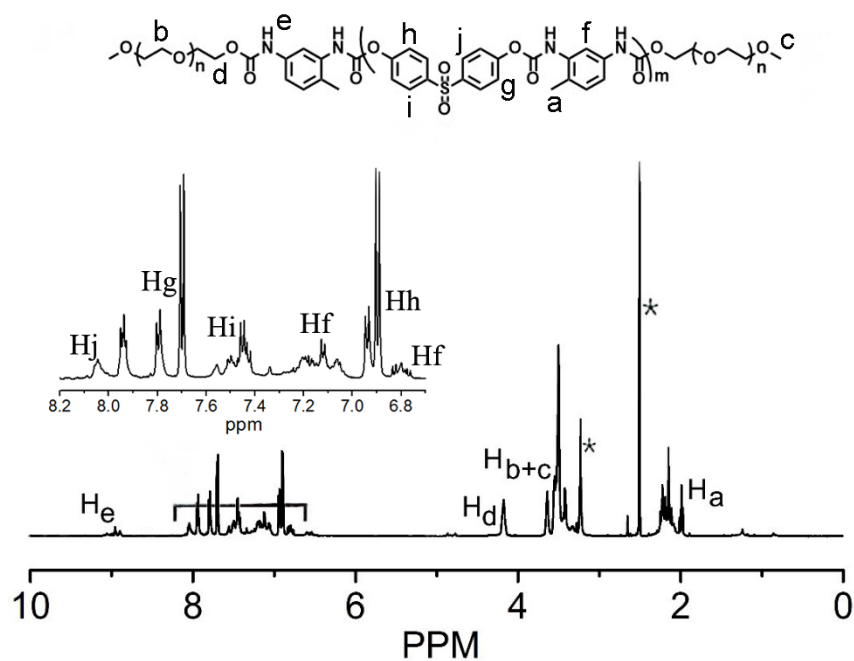
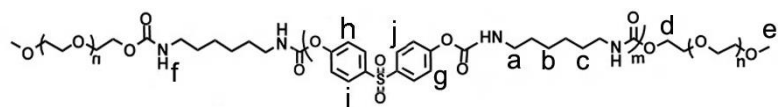


Fig. S3 ^1H NMR spectrum of **PUTDI** in $\text{DMSO-}d_6$ (* indicates peaks from the solvent and water)

Molecular Weight Calculation:

For co-polymers and oligomers with higher polarity, it is difficult to find a suitable standard solution for determining their molecular weights by gel permeation chromatography (GPC) experiments. Therefore, nuclear magnetic resonance (NMR) spectroscopy is often used to calculate the number-average molecular weight.² Specifically, end-substituent analysis is used to compare the integral values of the polymer end-substituent and the characteristic peaks of the main chain repeat element. In this way the average number of repeat units (degree of polymerization), and hence the molecular weight of polymer are calculated. The premise is to assume that each chain has the same end group at both ends. Low molecular weight polymers and oligomers give accurate results, but the data will be less accurate for higher molecular weights. This method requires the unambiguous assignment of specific protons in the ¹H NMR spectrum. The integral ratio of different characteristic peaks and terminal groups was used to calculate the number of repeat units in the oligomer chains.



For example, in **OUHDI**, the characteristic peaks of hydrogens in the main chains (Ha/Hh) and the methyl end group (He) were chosen to calculate the integral ratio and obtain the degree of polymerization (m). In addition, 'n' is known. Finally, the molecular weight can be obtained by adding up each of these parts.

Gelation studies:

The OU (8 wt %) was dissolved in *N,N*-dimethylformamide (DMF) under heating. A clear solution was obtained and allowed to cool down to room temperature. After 10-20 min, a transparent gel formed. Similar experiments done with dimethyl sulfoxide (DMSO), or dimethylacetamide (DMAc) solvent, gave spontaneous gelation in all cases.

Determination of Critical Gelation Concentration:

The PU (8 wt%) was gradually added to a measured amount of DMF and heated to make a clear solution. Gelation was confirmed by an inversion method after 10 min. Up to a certain

concentration, gelation was noticed, which even after a prolonged wait, no gelation occurred. This concentration is considered as a critical gelation concentration.

Determination of T_{gel} :

A closed vial containing the gel was placed on a digital display heater. The temperature was gradually increased from 20 °C, and the existence of the gel was examined by tilting the vial. At a given temperature, the gel no longer was stable when the vial was inverted. This temperature was recorded as the gel-to-sol melting temperature (T_{gel}).

Rheological Experiments:

Gels (8 wt%) were prepared and stored at room temperature for 12 h before rheological experiments were performed in an Anton-Paar MCR 302 rheometer. Stress-amplitude sweep measurements were used to record the gel strength. The runs were carried out at a constant oscillation frequency of 1 Hz at 25 °C.

Urea Addition Experiments:

Gels (8 wt %) were prepared in DMF and then urea (10 eq.) was added to the gel vial, and then the mixture was heated to make a clear solution and then cooled to room temperature. It was observed that after urea addition the gel did not form again.

The preparation method of films:

3.5 wt% of **OUHDI** sol was poured on a PTFE board, and placed under vacuum several times to remove all the air bubbles. The sample was then heated at 60 °C for 4 h and dried in a vacuum oven.

The preparation method of stereoscopic molds:

A small amount of **OUHDI** powder was placed in a vial and a few drops of DMF were added to the vial. Heating the mixture with a hair-dryer quickly dissolved the powder. The cycle of adding more **OUHDI** powder and heating was repeated a few times until a sticky gel appeared in the bottom of the vial. This sticky gel was then placed in the mold using a plastic dropper.

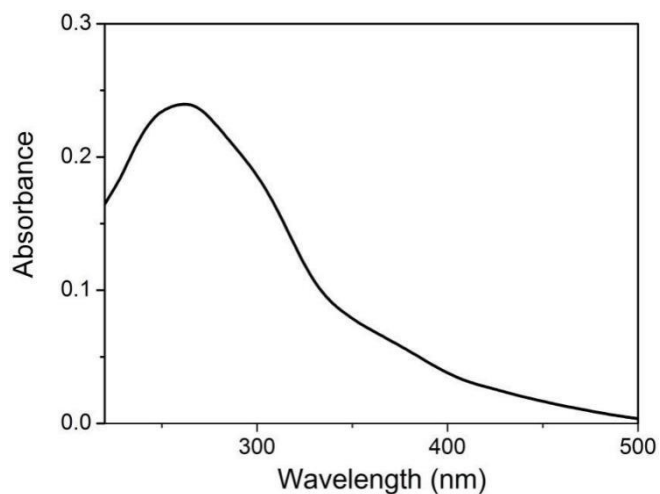


Fig. S4 Absorption spectrum of **OUHDI** in the solid state.

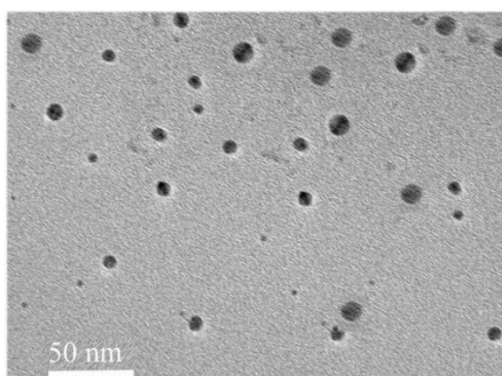


Fig. S5 TEM image of nanoaggregates of **OUHDI** formed in acetone-H₂O mixture with 90% water fraction (10^{-5} M).

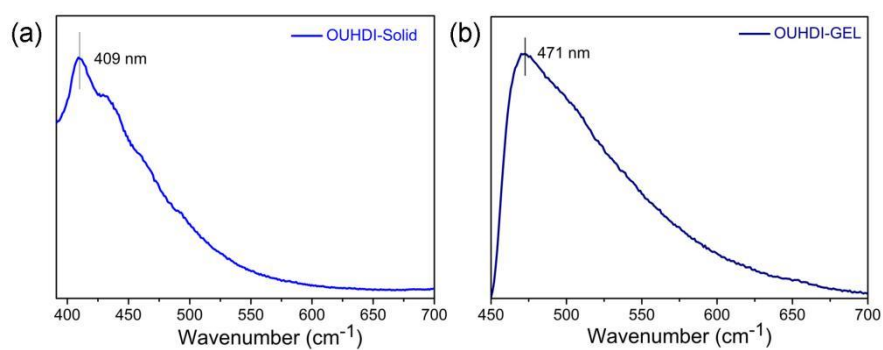


Fig. S6 (a) PL spectra of **OUHDI** solid. (b) PL spectra of **OUHDI** gel. ($\lambda_{\text{ex}} = 365$ nm)

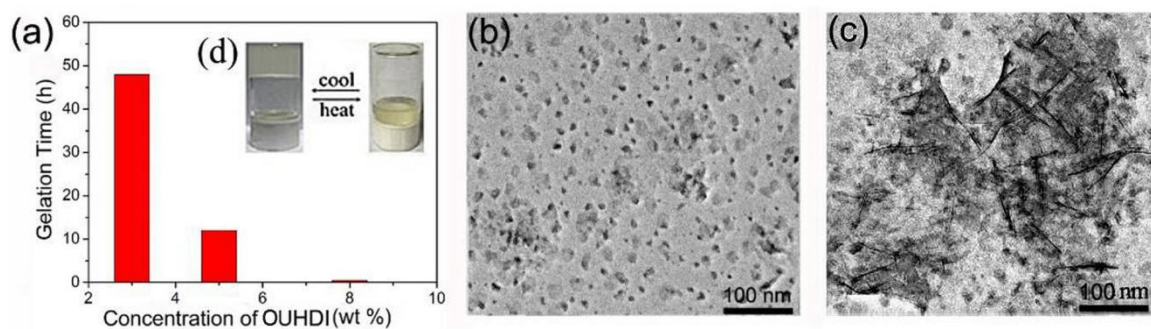


Fig. S7 (a) Variation of gelation time with concentration of **OUHDI**. TEM images of (b) freshly prepared solution and (c) aged (48 h, room temperature) gel of **OUHDI** in DMF ($c = 0.2$ wt %). (d) sol-gel transition of **OUHDI** in DMF.

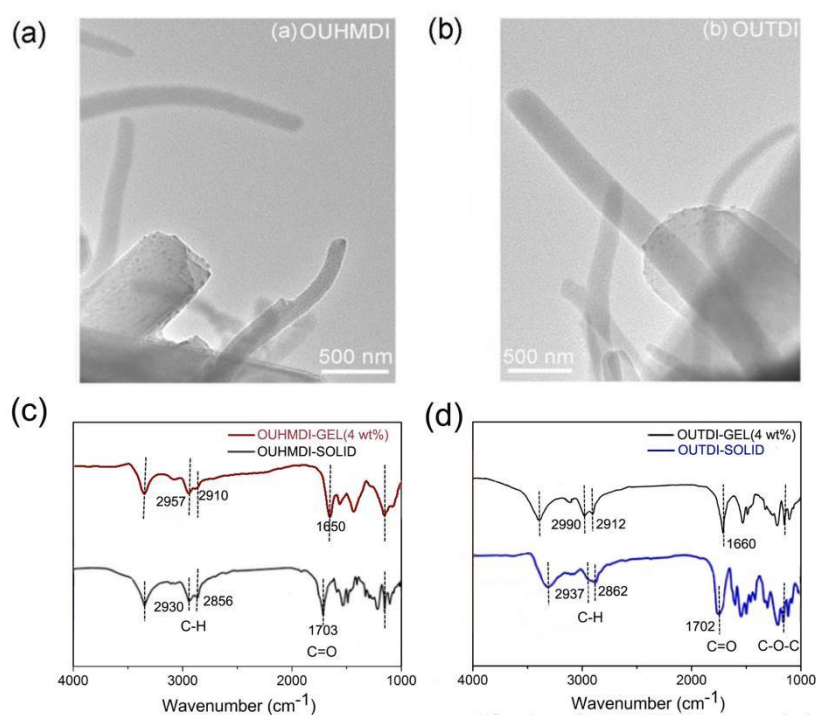


Fig. S8 TEM images of nanotubes (a) **OUHMDI** (b) **OUTDI** formed in 0.8 wt% DMF solution. (c) FTIR spectra of **OUHMDI** in solid and gel states. (d) FTIR spectra of **OUTDI** in solid and gel states.

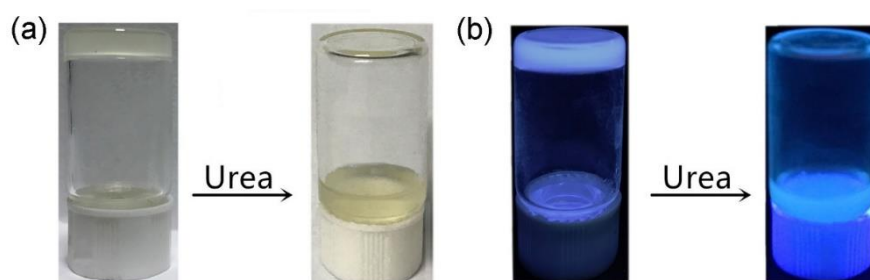


Fig. S9 Urea (10 eq. with respect to the repeat unit of OU) mediated gel-to-sol transformation of **OUHDI** gel in DMF under (a) sunlight (b) UV light.

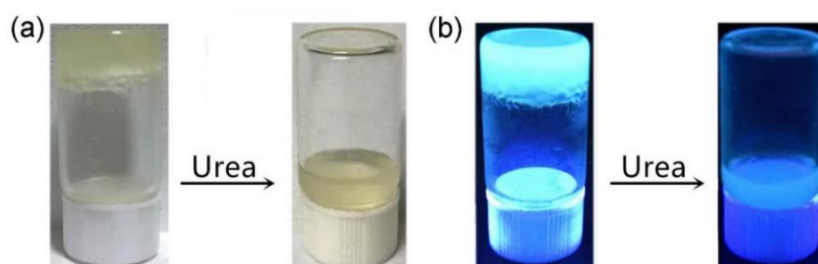


Fig. S10 Urea (10 eq. with respect to the repeat unit of OU) mediated gel-to-sol transformation of **OUHMDI** gel in DMF under (a) sunlight (b) UV light.

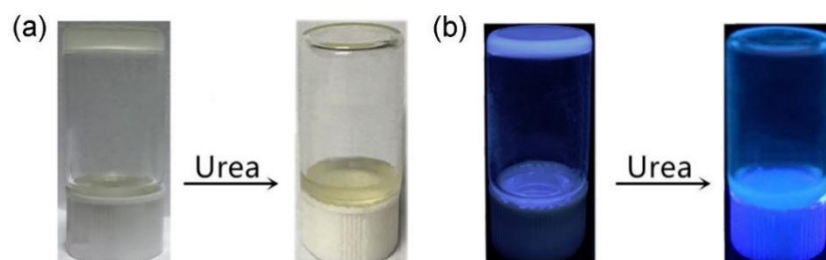


Fig. S11 Urea (10 eq. with respect to the repeat unit of the OU) mediated gel-to-sol transformation of **OUTDI** gel in DMF under (a) sunlight (b) UV light.

Table S1: Observation of gelation tests of **OUs** in different solvents ($c = 8$ wt%).

DMF	DMSO	DMAC	CHCl ₃	THF	MCH	Acetone
Gel	Gel	Gel	Sol	Sol	Precipitate	Sol

Table S2: Gelation Data of the OUs.

Oligourethane	CGC (wt %)	T_{gel} ($^{\circ}$ C) ^a	ΔH_{m} (kJ mol^{-1})	G' (Pa)	G'' (Pa)	σ (Pa)
OUHDI	3.5	99	20.3	101.3	1.2	1.5
OUHMDI	4	96	18.4	83.0	17	0.7
OUTDI	4.3	83	15.0	28.1	2.4	0.5

^a Concentration of gelator = 8 wt%

References

- 1 N. Jiang, G. F. Li, W. L. Che, D. X. Zhu, Z. M. Su and M. R. Bryce, *J. Mater. Chem. C*, 2018, **6**, 11287-11291.
- 2 T. F. Page, W. E. Bresler, *Anal. Chem.*, 1964, **10**, 1981-1985.