Supporting Information

Supramolecular oligourethane gels as light harvesting antennae: achieving multicolour luminescence and white-light emission through FRET

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Experimental Section

Chemicals and Materials:

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 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 FLS1000 spectrophotometer. Rheological properties were measured by a TA DHR-2 rheometer, using 25 mm parallel plates geometry with a gap size of ~1 mm.

Synthetic Methods:

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

OUB. A mixture of 3,4-dihydroxybenzoic acid (2.62 mmol), polyethylene glycol mono-methyl ether ($M_n = 200 \text{ g mol}^{-1}$; 1.98 mmol), anhydrous THF (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 7 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 **OUB**. Yield: 68%. ¹H NMR (500 MHz, DMSO- d_6 , δ [ppm]): 9.85 (s, 1H), 8.52-8.14 (s, 2H), 7.9-6.7 (broad, 3H), 4.05 (s, 4H), 3.7-3.35 (broad, PEG protons), 3.24 (s, 3H; PEG terminal -OCH₃ protons), 3.15-2.90 (broad, 4H), 1.65-1.15 (broad, 8H). FTIR (OUB-solid): 3375 cm⁻¹ (N-H), 2932 and 2859 cm⁻¹ (-CH₂- asymmetric and symmetric stretch), 1716 cm⁻¹ (C=O), 1110 cm⁻¹ (C-O-C stretch PEG). $M_n = 2096 \text{ g mol}^{-1}$.

OUG. The synthetic procedure for **OUG** was the same as **OUB**, except monomer Genistein was used instead of 3,4-dihydroxybenzoic acid. Yield: 63%. ¹H NMR (500 MHz, DMSO- d_6 , δ [ppm]):12.90-12.80 (broad, 1H) 8.7-6.2 (broad, 7H), 4.03 (s, 2H), 3.63-3.48 (broad, PEG protons), 3.23 (s, 3H; PEG terminal -OCH₃ protons), 3.14-2.90 (broad, 4H), 1.60-1.20 (broad, 8H). FTIR (OUG-solid): 3336 cm⁻¹ (N-H), 2859 and 2930 cm⁻¹ (-CH₂- asymmetric and symmetric stretching), 1725 cm⁻¹ (C=O), 1041 cm⁻¹ (C-O-C stretching PEG). M_n =2982 g mol⁻¹.

OUR. The synthetic procedure for **OUR** was the same as **OUB**, except monomer 1,5dihydroxyanthraquinone was used instead of 3,4-dihydroxybenzoic acid. Yield: 68%. ¹H NMR (500 MHz, DMSO- d_6 , δ [ppm]): 8.0-5.6 (broad, 6H), 4.05 (s, 4H), 3.25 (s, 3H; PEG terminal -OCH₃ protons), 3.45-3.37 (broad, PEG protons), 3.0-2.9 (broad, 4H). 1.50-1.15 (broad, 8H). FTIR (OUR-solid): 3314 cm⁻¹ (N-H), 2873 and 2939 cm⁻¹ (-CH₂- asymmetric and symmetric stretching), 1709 cm⁻¹ (C=O), 1100 cm⁻¹ (C-O-C stretching PEG). M_n =1603 g mol⁻¹.

Preparation of Gels:

The hybrid or single gelator was placed in a glass bottle with dimethyl sulfoxide (DMSO) solution. The mixture was sonicated and heated to 90-120 °C to make a homogeneous solution

and then cooled to room temperature to produces gels.

Microscopic morphology:

The scanning electron microscopy (SEM) images were obtained using a HITACHI SU8010. A small portion of the gel was placed on a glass coverslip and dried in a vacuum oven at 90 °C. The sample was observed through the SEM instrument operating at 5 kV after platinum coating.

Computational details:

The ground-state equilibrium structures of **OUB**, **OUR** and **OUG** were obtained at B3LYP/6-31G (d,p) level, with no harmonic frequencies in the vacuum state. In addition, the HOMO and LUMO levels evaluated by B3LYP are close to the experimental values. All calculations were performed with the Gaussian 16 program. In order to explore the interface model, MD simulations were carried out by using GROMACS program with general AMBER force field (GAFF). The restrained electrostatic potential (RESP) data were obtained in Multiwfn. During the whole process, after initial energy minimization and the isothermal-isobaric (NPT) eventually reach equilibrium. Then we selected an interface model from the final cluster in the box which has good π - π stacking and further optimized using the mechanical/molecular mechanics (QM/MM) approach. In addition, the QM part was calculated at the B3LYP/6-31G (d, p) level.

The energy transfer and charge transfer rate were calculated with semiempirical Marcus formula.

$$k = \frac{1}{\hbar} H_{12}^2 \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left[-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right]$$
(1)

Here energy transfer electronic coupling of **OUB/OUG**, **OUB/OUR** and **OUG/OUR** were evaluated by B3LYP/6-31G (d,p) method in Gaussian 16 software. Nelson's four-point method was used to calculate λ

$$\lambda = \lambda_1 (H) + \lambda_2 (G) = \left[E \left({}^{3}H_{fc} \right) - E \left({}^{3}H_{opt} \right) \right] + \left[E \left({}^{1}G_{fc} \right) - E \left({}^{1}G_{opt} \right) \right]$$
(2)

Where opt and fc represent the optimized states and Franck-Condon excited states, respectively. The spin multiplicity is labeled as the superscript. The Gibbs free energy difference in the process of energy transfer can be straightforwardly obtained from the energy difference between the optimized ³H-G and H-³G states.

$$\Delta G = \left({}^{1}E_{H} + {}^{3}E_{G}\right) - \left({}^{3}E_{H} + {}^{1}E_{G}\right)$$
(3)

Molecular Weight Calculations:

It is known that the number-average molecular weight (M_n) of end-functional polymers/oligomers can be obtained accurately using ¹H NMR spectroscopy for end-group analysis.² The M_n of OUs were characterized through ¹H NMR spectra, in which all peaks could

be assigned unambiguously (see the description in the supporting information). By comparing the integration of the peak for He (terminal groups -CH₃ protons) and Hc (repeating unit -CH₂ protons), the degree of polymerization (DP) can be found, and the M_n can be calculated according to the following equation:

$\overline{M}_{n} = M \overline{DP} + 2M_{EG}$

where M and M_{EG} are the molecular weights of the repeat unit and end-group, respectively.

Structural Characterization of OUs



Fig. S1 ¹H NMR spectrum of OUB in DMSO- d_6 (* indicates peaks from the solvent and water)



Fig. S2 ¹H NMR spectrum of OUG in DMSO- d_6 (* indicates peaks from the solvent and water)



Fig. S3 ¹H NMR spectrum of OUR in DMSO- d_6 (* indicates peaks from the solvent and water)



Fig. S4 (a) FTIR spectra of OUs in the solid state. (b) Powder XRD patterns of **OUB**, **OUG** and **OUR**.



Fig. S5 Variation of G' and G'' as a function of angular velocity for **OUB** gel (c = 1 wt%).



Fig. S6 (a) Gel-to-sol transformation and effect of adding urea to OUB gel (c = 4 wt%) under UV light. (b) Emission spectra of OUB gel at varied concentrations.

Photophysical Properties of OUs



Fig. S7 Normalized absorbance and emission spectra of OUB, OUG and OUR gels.



Fig. S8 PL spectra of OUs in the sol, solid and gel states. (a) OUB at $\lambda_{ex} = 340$ nm. (b) OUG at $\lambda_{ex} = 380$ nm. (c) OUR at $\lambda_{ex} = 420$ nm.

Table S1 Photophysical characteristics of OUB, OUG and OUR.

	$\lambda_{em}{}^{a}(nm)$	$\lambda_{em}{}^{b}(nm)$	$\lambda_{em}^{c}(nm)$	$\tau^{c}(ns)$
OUB	387	384/400/421	401/429/479	18.7
OUG	463	440/482/593	413/442/495/534	12.5
OUR	583	555/610/653	596/616/631/656	16.9

 $^{\rm a}$ Measured in solution state. $^{\rm b}$ Measured in solid state. $^{\rm c}$ Measured in gel state at N_2 atmosphere.



Fig. S9 FTIR spectra of OUs in THF/DMSO solution and in the gel/solid state. Black circles represent the free C=O; Green circles represent the hydrogen bonded C=O.



Fig. S10 SEM images of OUB in DMSO with different concentration (a) 0.02 wt % (b) 0.2 wt % (c) 1 wt %.



Fig. S11 SEM image of the (a) OUG gel (b) OUR gel (c) OUB+OUG gel (d) OUG+OUR gel.



Fig. S12 Absorption spectra of OUs in the sol and gel states.



Fig. S13 (a) Emission spectra of OUB (10⁻³ M) solution with the addition of OUG (10⁻⁵ M) solution at $\lambda_{ex} = 365$ nm. (b) Emission spectra of OUB (10⁻³ M) solution with the addition of OUR (10⁻⁵ M) solution at $\lambda_{ex} = 365$ nm. (c) Emission spectra of OUG (10⁻³ M) solution with the addition of OUR (10⁻⁵ M) solution at $\lambda_{ex} = 365$ nm. (d) Emission spectra of OUB gel (c = 4 wt%) mixed with 10% OUR gel (c = 4 wt%) at $\lambda_{ex} = 365$ nm. (e) Emission spectra of a mixture of OUB gel (c = 4 wt%) and 2% OUG gel (c = 4 wt%) with the addition of OUR (10⁻³ M) solution at $\lambda_{ex} = 365$ nm. (f) Emission spectra of OUB gel (c = 4 wt%) before and after ultraviolet irradiation for 5 days ($\lambda_{ex} = 365$ nm).



Fig. S14 Emission spectra of hybrid gels and their photographs under a UV torch with excitation at 365 nm. (a) **OUB/OUG/OUR** of 1:10.2:1.2, (b) **OUB/OUG/OUR** of 1:5.54:3.42, (c) **OUG/OUR** of 6:1. (The ratio is the mass ratio.)

Table S2. Calculated the recombination energy λ (eV), Gibbs free energy difference ΔG (eV), energy transfer rate k_{ET} (s⁻¹) of the OUG-OUR, OUB-OUG and OUB-OUR interface.

Hybrid gel	λ_{ET}	ΔG_{ET}	K_{ET}
OUG-OUR (1:2.38 mol%)	1.39	-0.65	1.88×10^{13}
OUB-OUG (1.08:1 mol%)	1.19	-0.71	5.03×10 ¹³
OUB-OUR (2.33:1 mol%)	1.12	-1.52	2.23×10^{14}

References

- S1 N. Jiang, D. Zhu, Z. Su and M. R. Bryce, J. Mater. Chem. C, 2020, 8, 5137-5142.
- S2 M. J. Robb, D. Montarnal, N. D. Eisenmenger, S.-Y. Ku, M. L. Chabinyc and C. J. Hawker, *Macromolecules*, 2013, 46, 6431-6438.