

## Supporting Information

### **Co-Organizing Synthesis of Heterogeneous Nanostructure through Photo-Cleavage of Pre-Stabilized Self-Assembly**

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## 1. General Information

All the solvents and chemicals are commercial available. Chemicals were used without further purification; solvents were further purified by Ultimate Solvent System (Nikko Hansen, Japan) before use.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in deuterated solvent on a Bruker Advance 400 MHz spectrometer. The  $^1\text{H}$  NMR chemical shift ( $\delta$ ) are given in ppm referring to internal standard tetramethylsilane (TMS). All coupling constants ( $J$ ) are given in Hz.

## 2. Experimental Procedures

*TEM images:* Aliquots (10  $\mu\text{L}$ ) of sample solution were added into a glow discharge copper grid (400 mesh) coated with thin carbon film and incubated for 30 s at room temperature. After removing excess solution, the grid was washed with deionized water three times and then stained with 2.0% (w/v) uranyl acetate (UA) by exposing the grid in three drops of UA solution for 30 s. TEM images were captured at high vacuum on transmission electron microscope JEM-1230R (JEOL, Japan).

*SEM images:* Aliquots (10  $\mu\text{L}$ ) of sample solution were added into on silicon wafer, freeze dried overnight, and sprayed with a thin gold layer. SEM images were taken on a scanning electron microscope FEI Quanta 250 FEG.

*HPLC and UV-Vis absorption:* The Photo-cleavage monitoring of **1** and **2** ( $2 \times 10^{-4}$  mol/L) under different photo irradiation time was tested by using a Agilent 1260 Infinity HPLC and UV-Vis spectrophotometer (Cary 60 UV-Vis, Agilent), respectively.

*CD measurements:* Circular dichroism (CD) spectra of all the samples were collected on a spectrometer JASCO J-820 CD with bandwidth of 1.0 nm in the ultraviolet (UV) region (190-400 nm) using a 0.1 mm quartz cuvette.

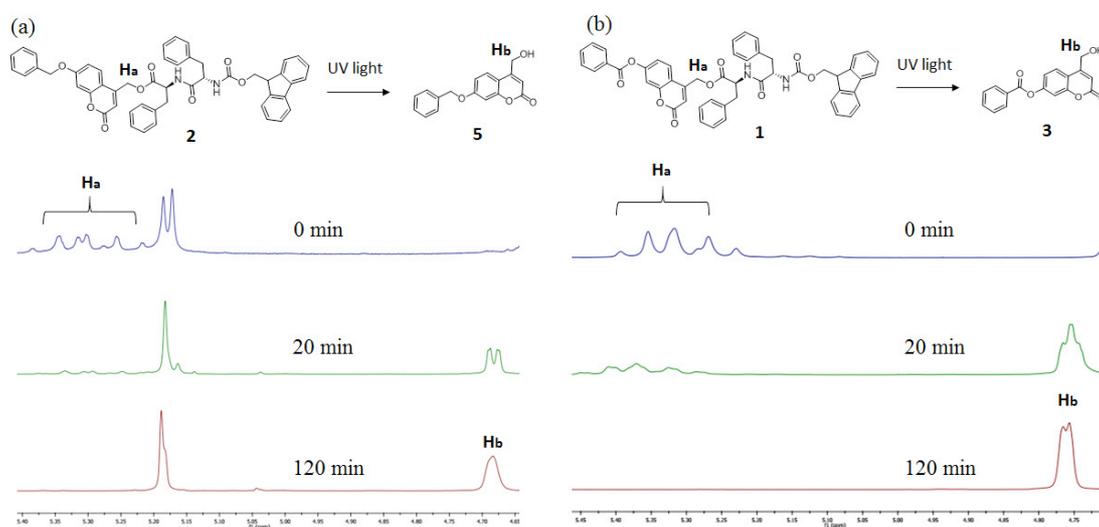
*Single crystal X-ray diffraction:* Single crystal structures of **4** and **5** were used according to the reported literatures, respectively.<sup>[1, 2]</sup>

Single crystal **3** suitable for X-ray diffraction was obtained by slow evaporation of n-hexane/ dichloromethane (v/v 1:2) solution at room temperature. The X-ray diffraction data for the single crystals were collected on a Rigaku XtaLab PRO instrument ( $\omega$ -scan mode) using graphite monochromated MoK $\alpha$  radiation (0.71073 Å). The diffractometer was equipped with a Rigaku GN2 low temperature system (air cooling type) and data were collected at 93 K. The performance mode of the microfocus sealed X-ray tube was 50 kV, 0.60 mA. Suitable crystals of appropriate dimensions were mounted on loops in random orientations. Preliminary unit cell parameters were determined with three sets of total 30 narrow frame scans. Data collection: images were indexed and integrated using CrysAlisPro data reduction package (version 1.171.39.7b, Rigaku Oxford Diffraction, 2015). Final cell constants were determined by global refinement of reflections from the complete data set. Data were corrected for systematic errors and absorption using the ABSPACK module. The structures were solved by the intrinsic phasing method using SHELXT-2014/5 and refined by the full matrix least-squares on  $F^2$  using SHELXL-2014/7.<sup>[3]</sup> Non-hydrogen atoms were refined anisotropically. Hydrogen atoms except “H3” were inserted at the calculated positions and refined as riding atoms. The crystal data, data collection and structure refinement details are summarized in Table S1, S2 and Figure

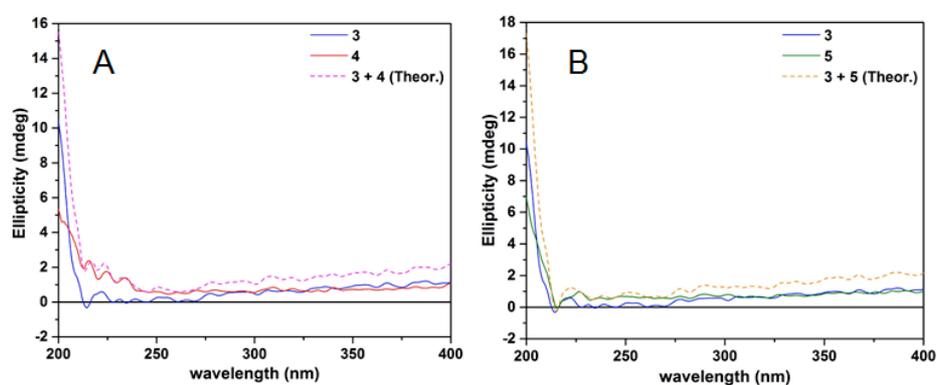
S5, S6.

Crystallographic data for the investigated compound **3** have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1531717.

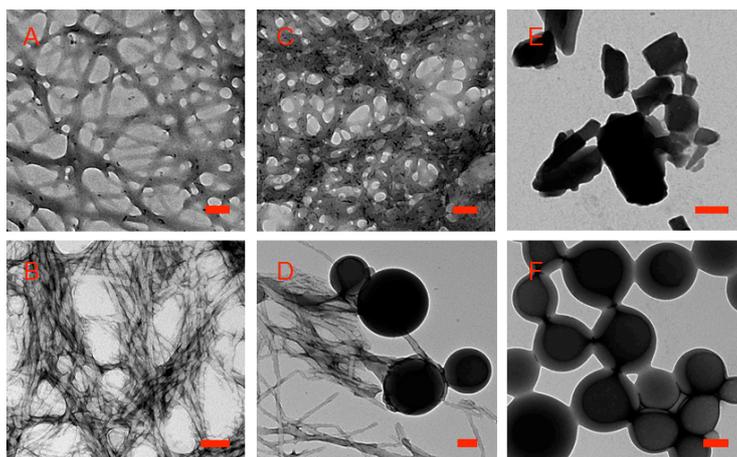
### 3. Additional Experimental Data and Figures



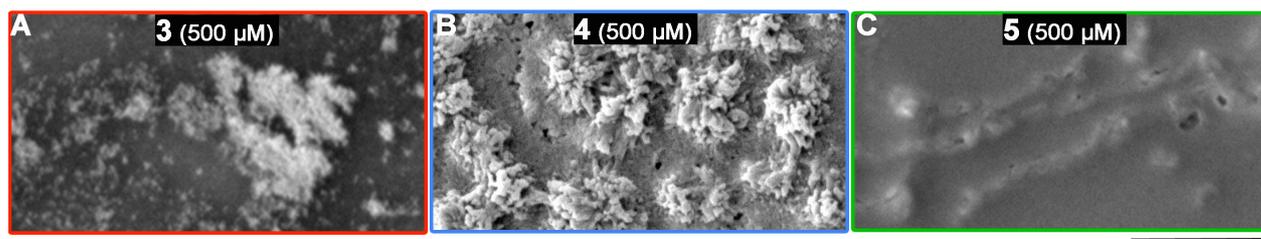
**Figure S1.** <sup>1</sup>H NMR spectra comparisons before and after photo-cleavage of **2** (a) and **1** (b).



**Figure S2.** CD spectra of (A) **3**, **4**, and **3+4**, (B) **3**, **5**, and **3+5** at 500  $\mu$ M (each component's concentration) in H<sub>2</sub>O/DMSO = 3:2 solution.



**Figure S3.** TEM images of self-assemblies of **1** (A), and **2** (B) separately at 500  $\mu\text{M}$  in DMSO/H<sub>2</sub>O (v/v = 2:3). TEM images of **3/4** mixture (C, E) and **4/5** mixture (D, F) in DMSO/H<sub>2</sub>O (v/v = 2:3) obtained from photo irradiation of **1** and **2**. Scale bar is 100 nm.



**Figure S4.** SEM images of **3** (A), **4** (B), and **5** (C) at 500  $\mu\text{M}$  in DMSO/H<sub>2</sub>O (v/v = 2:3). Scale bar is 1  $\mu\text{m}$ .

**Table S1.** *Crystal data and structure refinement for 3.*

Identification code	shelx	
Empirical formula	C <sub>17</sub> H <sub>12</sub> O <sub>5</sub>	
Formula weight	296.27	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.1640(4) Å	a = 85.162(4)°.
	b = 9.2165(5) Å	b = 82.217(4)°.
	c = 10.1606(5) Å	g = 81.222(5)°.
Volume	655.52(6) Å <sup>3</sup>	

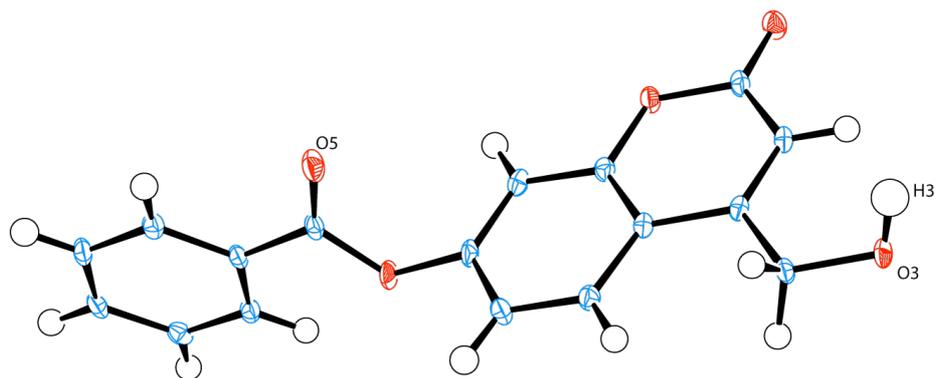
Z	2
Density (calculated)	1.501 Mg/m <sup>3</sup>
Absorption coefficient	0.112 mm <sup>-1</sup>
F(000)	308
Crystal size	0.217 x 0.065 x 0.046 mm <sup>3</sup>
Theta range for data collection	2.900 to 28.000°.
Index ranges	-9<=h<=8, -10<=k<=12, -13<=l<=12
Reflections collected	8284
Independent reflections	2901 [R(int) = 0.0696]
Completeness to theta = 25.242°	99.8 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2901 / 0 / 203
Goodness-of-fit on F <sup>2</sup>	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.1359
R indices (all data)	R1 = 0.0613, wR2 = 0.1434
Extinction coefficient	n/a
Largest diff. peak and hole	0.463 and -0.319 e.Å <sup>-3</sup>

**Table S2.** *Hydrogen bonds for 3 [Å and °].*

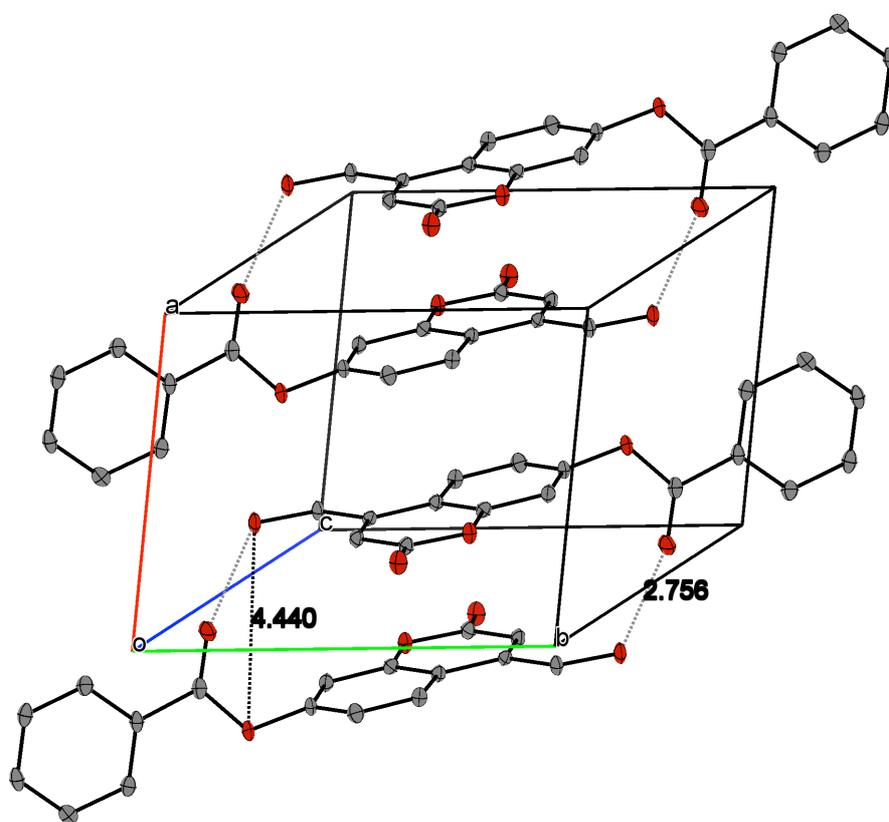
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3)...O(5)#1	0.87(2)	1.98(2)	2.7561(16)	148(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1



**Figure S5.** ORTEP diagram showing 50 % probability anisotropic displacement ellipsoids of non-hydrogen atoms for **3**.

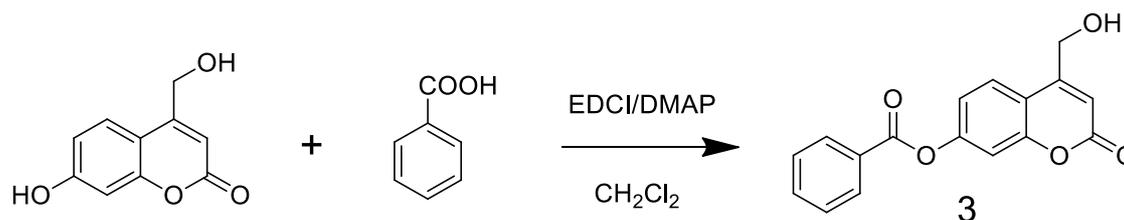


**Figure S6.** Illustration of the intermolecular packing in **3**.

#### 4. Synthesis and Characterizations

**Synthesis of 4 and 5.** Compounds **4** and **5** were synthesized according to literature methods, respectively. <sup>[1, 2]</sup>

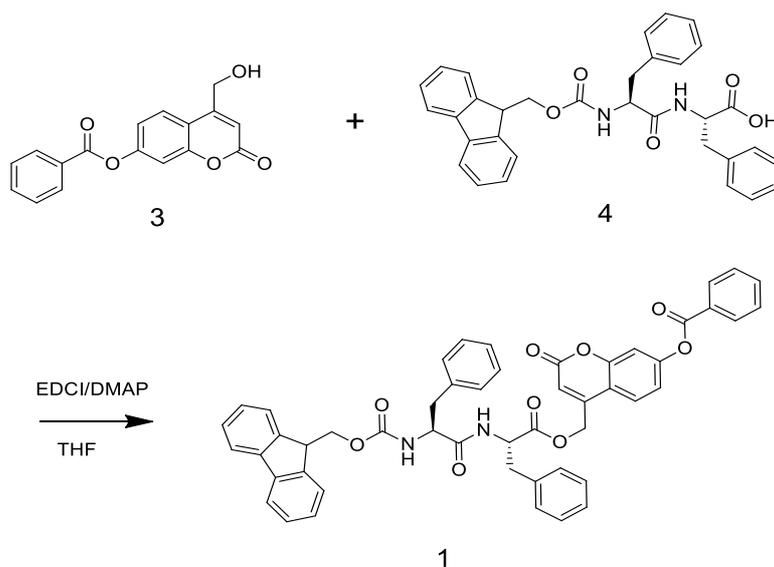
**Synthesis of 3.** A  $\text{CH}_2\text{Cl}_2$  solution (20ml) of 7-hydroxy-4-(hydroxymethyl)-2H-chromen-2-one (0.39 g, 2 mmol), <sup>[2]</sup> benzoic acid (0.24 g, 2 mmol), 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI) (0.38 g, 2 mmol) and 4-dimethylaminopyridine (DMAP) (24 mg, 0.2 mmol) was stirred at room temperature for 12 hours (Scheme S1). The resulting solution was washed with deionized water (3 x 5 ml) and then the organic layer was collected. The solvent was removed under vacuum and the resulting precipitate was purified by column chromatography ( $\text{CH}_2\text{Cl}_2/\text{EA} = 6/1$ ), yielding **3** as a white solid (0.26 g, 45%). <sup>1</sup>H NMR (400MHz, d-DMSO)  $\delta = 8.17$  (d,  $J = 0.8$  Hz, 2H), 7.77-7.83 (m, 2H), 7.64 (t,  $J = 0.8$  Hz, 2H), 7.50 (d,  $J = 0.4$  Hz, 1H), 7.33-7.36 (dd,  $J_1 = 0.4$  Hz  $J_2 = 0.4$  Hz, 1H), 6.49 (s, 1H), 5.71 (t,  $J = 0.8$  Hz, 1H), 4.81 (d,  $J = 0.4$  Hz, 2H). <sup>13</sup>C NMR (400MHz,  $\text{CDCl}_3$ )  $\delta = 164.72, 160.50, 156.80, 154.16, 153.48, 135.07, 134.88, 130.51, 129.58, 129.04, 125.99, 119.09, 115.90, 111.04, 110.69, 59.64$ .



**Scheme S1.** Synthetic route to **3** through EDCI/DMAP condensation reaction.

**Synthesis of 1.** A THF solution (20ml) of **3** (0.29 g, 1 mmol), **4** (0.80 g, 1.5 mmol), 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI) (0.29 g, 1.5 mmol) and 4-dimethylaminopyridine (DMAP) (12 mg, 0.1 mmol) was stirred at room temperature for 48 hours (Scheme S2). The resulting solution was washed with deionized water (3 x 5 ml) and then the organic layer was collected. The solvent was removed and the resulting precipitate was purified by column chromatography ( $\text{CH}_2\text{Cl}_2/\text{EA} = 10/1$ ) yielding **1** as a white solid (0.35 g, 43%). <sup>1</sup>H NMR (400MHz, d-DMSO)  $\delta = 8.63$  (d,  $J = 0.8$  Hz, 1H), 8.09 (d,  $J = 0.8$  Hz, 2H), 7.79 (t,  $J = 0.8$  Hz, 2H), 7.71 (t,  $J = 0.8$  Hz, 2H), 7.53-7.58 (m, 5H), 7.44 (t,  $J = 0.4$  Hz, 1H), 6.95-7.40 (m, 14H), 6.39 (d,  $J = 1.6$  Hz, 1H), 5.26-5.42 (m, 2H), 4.59-4.66 (m, 1H), 4.19-4.26 (m,

1H), 4.00-4.11 (m, 4H), 2.98-3.12 (m, 2H), 2.84-2.88 (m, 1H), 2.61-2.70 (m, 1H). <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>) δ = 172.57, 172.35, 171.40, 164.67, 159.88, 156.26, 156.22, 154.24, 153.71, 149.83, 144.31, 144.22, 141.16, 138.57, 137.45, 137.36, 134.89, 130.51, 129.81, 129.74, 129.64, 129.58, 129.00, 128.82, 128.76, 128.53, 128.13, 127.57, 127.20, 126.76, 126.46, 125.89, 125.81, 120.61, 119.25, 115.39, 112.75, 111.15, 66.20, 62.26, 56.33, 55.45, 54.37, 47.03.



**Scheme S2.** Synthetic route to 1 through EDCI/DMAP condensation reaction.

**Synthesis of 2.** 2 was synthesized in a similar way to that of 1 by replacing 3 with 5. Yield a white solid (57%). <sup>1</sup>H NMR (400MHz, d-DMSO) δ = 8.60 (dd,  $J_1 = 0.4$  Hz  $J_2 = 0.8$  Hz, 1H), 7.80 (dd,  $J_1 = 0.4$  Hz  $J_2 = 0.8$  Hz, 2H), 7.46-7.57 (m, 3H), 6.92-7.40 (m, 22H), 6.20 (d,  $J = 1.6$  Hz, 1H), 5.14-5.31 (m, 4H), 4.59 (t,  $J = 0.8$  Hz, 1H), 3.95-4.22 (m, 4H), 2.95-3.10 (m, 2H), 2.80-2.89 (m, 1H), 2.59-2.65 (m, 1H). <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>) δ = 172.72, 171.54, 171.14, 167.39, 161.95, 161.19, 160.37, 159.16, 158.34, 155.29, 153.34, 152.93, 144.48, 144.32, 144.21, 142.21, 141.11, 136.77, 129.79, 129.72, 129.64, 129.04, 128.64, 128.52, 128.40, 128.12, 127.56, 127.16, 126.75, 126.44, 126.36, 120.58, 115.59, 113.42, 111.45, 110.88, 73.36, 70.42, 69.46, 66.12, 51.93, 46.95.

## 5. Molecular Modeling

Models of 3, 4 and 5 were created based on the single crystal diffraction data. The

models of 1, and 2 were created starting from single crystal model of 3, 4 and 5. The geometrical energy minimization scans were performed using Forcite module of Materials Studio for the molecular packings before and after photo-cleavage. After energy minimization, the hydrogen bond calculation of Materials Studio was applied to both models.

## 6. Reference

1. Raeburn, J.; Mendoza-Cuenca, C.; Cattoz, B. N.; Little, M. A.; Terry, A. E.; Cardoso, A. Z.; Griffiths, P. C.; Adams, D. J. The effect of solvent choice on the gelation and final gel properties of Fmoc-diphenylalanine. *Soft Matter* **2015**, *11*, 927.
2. Ji, W.; Liu, G. F.; Wang, F.; Zhu, Z.; Feng, C. L. Galactose-decorated light-responsive hydrogelator precursors for selectively killing cancer cells. *Chem. Commun.* **2016**, *52*, 12574.
3. Sheldrick, G. M. A short history of SHELX. *Acta Cryst. A* **2008**, *64*, 112.