## **Electronic Supplementary Information**

# Phase-controlled supramolecular photochirogenesis in cyclodextrin nanosponges

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#### **Experimental**

**Materials. 1Z** and **2ZZ** (purchased from Wako) were purified by fractional distillation. CDNSs **3**, **4** and **5** were prepared as triethylammonium salts by reacting  $\beta$ - or  $\gamma$ -CD with pyromellitic dianhydride (PDA) in the presence of triethylamine in dimethyl sulfoxide at room temperature, and purified by Soxhlet extraction with acetone, as reported previously.<sup>1</sup> Other chemicals were commercially available and used as received.

**Instruments and methods**. Elemental analyses were performed on a Thermo Scientific Flash EA1112 instrument. FT-IR, UV-vis and CD were recorded on Perkin-Elmer Spectrum 100, JASCO V-560 and JASCO J-820 spectrometer, respectively. TG-DTA analyses were performed on a TA Instruments 2050 TGA V5.4A instrument. High resolution magic angle spinning (HRMAS) <sup>1</sup>H NMR spectra were obtained in D<sub>2</sub>O at 500 MHz with a Bruker Avance 500 instrument. The particle size distributions of CDNSs were measured at 25 °C by monitoring the scattered light at 173° by using a Malvern Instruments Zetasizer Nano dynamic light-scattering (DLS) instrument. The size and shape of the precipitates in suspension were optically observed by using an AS ONE DN-107T digital microscope.

**Photolysis.** Sample (3 mL) in a quartz cell was placed in a UNISOKU CoolSpek USP-203CD cryostat and irradiated at 254 ±10 nm or 313 ±10 nm under a nitrogen atmosphere at a given temperature with an Asahi Spectra Max-301 monochromated light source (a 300-W xenon lamp fitted with a band-pass filter). The photolyzed sample was poured onto an aqueous KOH (10%) solution (3 mL), and the resulting mixture was extracted with pentane (1 mL). After the gas chromatographic (GC) analysis of an aliquot for the *E/Z* ratio on a Shimadzu GC-2014 fitted with a CBP-20 column (0.25 mm  $\phi$  x 25 m, 60 °C), the organic layer was extracted with an aqueous silver nitrate solution (2 mL) at 0 °C. The aqueous phase was washed twice with pentane (1 mL) and then added to an aqueous ammonia (28%) solution at 0 °C, and the liberated cyclooctene was extracted with pentane (0.5 mL). The ee was determined by chiral GC equipped with a Supelco  $\beta$ -DEX 225 column (0.25 mm  $\phi$  x 30 m).

Sample	% C	% N	% H
β-CDNS <b>3</b> (CD:PDA = 1:2)	46.82	2.35	6.38
β-CDNS <b>4</b> (CD:PDA = 1:4)	51.11	3.13	6.64
γ-CDNS <b>5</b> (CD:PDA = 1:4)	48.54	2.75	6.29

 Table S1. Elemental analyses of CDNSs



**Fig. S1**. FT-IR spectrum of  $\beta$ -CDNS **3** (CD:PDA = 1:2).



Fig. S2. FT-IR spectrum of  $\beta$ -CDNS 4 (CD:PDA = 1:4).



**Fig. S3**. FT-IR spectrum of  $\gamma$ -CDNS **5** (CD:PDA = 1:4).



Fig. S4. Thermogravimetric and differential thermal analysis of  $\beta$ -CDNS 3 (CD:PDA = 1:2).



Fig. S5. Thermogravimetric and differential thermal analysis of  $\beta$ -CDNS 4 (CD:PDA = 1:4).



Fig. S6. Thermogravimetric and differential thermal analysis of  $\beta$ -CDNS 5 (CD:PDA = 1:4).

#### Water contents determined by TG-DTA analyses

The water contents in the CDNS samples **3-5** were determined from the weight loss observed in the thermogravimetric (TG) analysis (Figs. S4-S6). Based on our previous experience in the TG analyses of various CD samples including other CDNSs, the water contents were evaluated from the weight loss observed at temperatures of up to 150°C (corresponding to the first plateau where the weight became constant, indicating that the water in the sample was completely removed), as shown in Table S2.

Table S2. Water contents determined from the weight

loss observed in TG analyses

Sample	Water content/%
$\beta$ -CDNS <b>3</b> (CD:PDA = 1:2)	7.6
$\beta$ -CDNS <b>4</b> (CD:PDA = 1:4)	6.5
γ-CDNS <b>5</b> (CD:PDA = 1:4)	5.8

#### **CD:PDA ratios in CDNSs 3-5**

The CD:PDA ratios in CDNSs **3-5** were evaluated by using the C/H/N composition determined by the elemental analysis (EA) (Table S1) and the water content (% H<sub>2</sub>O) determined by thermogravimetric (TG) analysis (Table S2), according to the following procedures.

First, the % compositions of carbon and hydrogen attributable to the CD and PDA moieties in CDNS (shown in the last two columns in Table S3) were calculated by subtracting the C/H contributions of triethylamine (% NEt<sub>3</sub>, which was estimated from the % N value) in CDNS from the experimental C/H values determined by EA. Then, by using the theoretical C/H/N/O compositions of CD, PDA, H<sub>2</sub>O and NEt<sub>3</sub> (Table S4), the contents of CD, PDA, NEt<sub>3</sub> and H<sub>2</sub>O in each CDNS were calculated with an assumption that all of the observed carbon and hydrogen contents originate from the CD, PDA, NEt<sub>3</sub> and H<sub>2</sub>O contained in each CDNS. The total weight of these components amounted to 95-99%, validating the calculation procedures and also indicating the presence of relatively small amounts of impurities in the samples. Another interesting result is the molar PDA/CD ratios of 3.3 for **3** and 4.9-5.1 for **4** and **5**, which were appreciably higher than the original PDA/CD ratios (2 and 4, respectively) employed upon preparation, indicating highly efficient cross-linking of CD by PDA linker.

	EA			% NEt <sub>3</sub>	% H <sub>2</sub> O	% C	% H
Sample	% C	% H	% N	determined by EA	determined by TG	assignable to CD + PDA	assignable to CD + PDA
β-CDNS <b>3</b> (CD:PDA = 1:2)	46.82	6.38	2.35	17.0	7.6	34.69	2.99
β-CDNS <b>4</b> (CD:PDA = 1:4)	51.11	6.64	3.13	22.7	6.5	34.96	2.52
γ-CDNS <b>5</b> (CD:PDA = 1:4)	48.54	6.29	2.75	19.9	5.8	34.35	2.66

Table S3. Contents of carbon and hydrogen attributable to CD and PDA in CDNSs 3-5

		1	1		
Compound	% C	% H	% N	% O	
CD	44.45	6.22	0	49.34	
PDA	55.07	0.92	0	44.01	
$H_2O$	0	11.19	0	88.81	
NEt <sub>3</sub>	71.22	14.94	10.67	0	

Table S4. Theoretical C/H/N/O compositions for each component

**Table S5.** Compositions of each component by weight and molar PDA/CD ratios in CDNSs calculated by assuming  $%C_{obs} = \Sigma (%C_{CD} + %C_{PDA} + %C_{NEt3})$  and  $%H_{obs} = \Sigma (%H_{CD} + %H_{PDA} + %H_{NEt3} + %H_{H2O})$ 

		DA · / · · · · · · · · · · · · · · · · ·		503 = (73)	=-CD $+$ $+$ $=$ $-1$ $DA$ $+$	(01-INEL) : (01-INEL)
Sampla	% NEt <sub>3</sub>	% NEt <sub>3</sub> % H <sub>2</sub> O		eight	Molar ratio	Total % weight of
Sample	by EA	by TG	CD	PDA	PDA/CD	$CD + PDA + NEt_3 + H_2O$
β-CDNS <b>3</b> (CD:PDA = 1:2)	17.0	7.6	43.9	27.5	3.3	96.0
β-CDNS <b>4</b> (CD:PDA = 1:4)	22.7	6.5	35.4	34.9	5.1	99.5
γ-CDNS <b>5</b> (CD:PDA = 1:4)	19.9	5.8	38.1	31.6	4.9	95.4



**Fig. S7.** Dynamic light scattering profiles (number of particles) of  $\beta$ -CDNS **3** in aqueous solution at CDNS/H<sub>2</sub>O = 0.2 and 1.0 mg/mL.



Fig. S8. Dynamic light scattering profiles (number of particles) of  $\beta$ -CDNS 4 in aqueous solution at CDNS/H<sub>2</sub>O = 0.2 and 1.0 mg/mL.



Fig. S9. Dynamic light scattering profiles (number of particles) of  $\gamma$ -CDNS 5 in aqueous solution at CDNS/H<sub>2</sub>O = 0.2 and 1.0 mg/mL.



Fig. S10. Photographs of the suspensions of (a) 4 and (b) 5 at  $CDNS/H_2O = 2 \text{ mg/mL}$ .



Fig. S11. UV (top) and CD (bottom) spectra of 3 at 6 x  $10^{-5}$ , 0.5 and 2.0 g/mL (CDNS/H<sub>2</sub>O) measured at 25 °C.



Fig. S12. UV (top) and CD (bottom) spectra of 4 at 6 x  $10^{-5}$ , 0.1, 0.3 and 0.6 g/mL (CDNS/H<sub>2</sub>O) measured at 25 °C.



Fig. S13. UV (top) and CD (bottom) spectra of 5 at 6 x 10<sup>-5</sup> and 0.9 g/mL (CDNS/H<sub>2</sub>O) measured at 25 °C.

High resolution magic angle spinning (HRMAS) <sup>1</sup>H NMR spectroscopic study of  $\gamma$ -CDNS 5 in the presence of (Z,Z)-1,3-Cyclooctadiene (2ZZ)

The microenvironmental changes around substrate **2ZZ** caused upon interaction with  $\gamma$ -CDNS **5** in the ground state were examined by high resolution magic angle spinning (HRMAS), which was expected to provide information about the substrate located in the polymer matrix where the photoisomerization takes place. Two samples were prepared for the HRMAS NMR measurement:

1) Sample A:  $\gamma$ -CDNS (0.5 g/mL) swollen with D<sub>2</sub>O (gel state)

2) Sample B: sample A + 2ZZ (25 mg/mL) (gel state)

The rotor (sample container) was filled with each sample of 50  $\mu$ L volume and spun at 4 kHz to acquire the <sup>1</sup>H NMR spectra of samples **A** and **B** shown in Fig. S14.



**Fig. S14**. HRMAS <sup>1</sup>H NMR spectra of samples **A** (top) and **B** (bottom). **2ZZ** signals are highlighted by asterisk, while the residual HOD is indicated by W and triethylammonium in CDNS by TEA.

As shown in Fig. S14, sample **A** (spectrum 1) exhibited broad signals of  $\gamma$ -CDNS at 3.3-4.3 ppm and the anomeric proton at 5.1 ppm, while sample **B** (spectrum 2) showed the sharp signals (indicated by asterisks) due to **2ZZ** in addition to the broad  $\gamma$ -CDNS signals. **2ZZ** at room temperature is known to undergo fast conformational equilibria achieving C<sub>2v</sub> symmetry on the NMR time-scale to afford only 4 signals, assignable to H<sub>a</sub>, H<sub>b</sub>, H<sub>c</sub> and H<sub>d</sub> protons (see the structure below) as anticipated; the methylene protons H<sub>d</sub> and H<sub>c</sub> at 1.45 and 2.13 ppm, respectively, and the vinylic protons H<sub>b</sub> and H<sub>a</sub> at 5.53 and 5.72 ppm, respectively in nice agreement with the literature data for **2ZZ** in cryogenic solvents.<sup>2</sup>



The well resolved NMR spectrum observed for the substrate in highly viscous CDNS gel **5** indicates that **2ZZ** is freely moving on the NMR time-scale within the polymeric gel under the condition employed. This conclusion was confirmed by a T2 filtration experiment, where the pulse sequence used was a basic spin-echo sequence (Carr-Purcell-Meiboom-Gill), which allows filtration of all the fast-decaying components of the magnetization to acquire the information about the magnetization associated with the fast moving molecules. The spectrum acquired under the T2 filtering condition is shown in Fig. S15 (top) along with the normal acquisition (bottom) for comparison. The main outcome of the T2 filtering was the enhancement of the signal intensity of the mobile species and the virtual suppression of the residual signals of the polymer. Thus, the sharp peaks labelled with an asterisk confirm that **2ZZ** is freely moving in the polymeric gel.

Additionally, the presence of 4 signals for **2ZZ** means that the interaction with the polymer is fast on the NMR time-scale, since a slow inclusion equilibrium of **2ZZ** with the CD cavities in CDNS would lead to the observation of a double set of the NMR signals.



Fig. S15. T2-filtered (top) and normal (bottom) HRMAS <sup>1</sup>H NMR spectra of sample B.

CDNS	Phase	[CDNS]	Irradiation time/h	E/Z	% ee
3	sol	0.0002	1	0.03	+7.5
		0.0003	1	0.05	+3.5
		0.0004	1	0.04	+2.5
	suspension	0.0015	1	0.07	+0.9
	F	0.003	- 1	0.05	0.0
		0.010	1	0.05	-0.8
	flowing gel	0.050	- 1	0.07	-1.0
	no wing ger	0.50	2	0.02	-19
		1.00	2	0.02	-3.5
		1.67	2	0.01	-6.8
	gel	2.00	2	0.01	-7.6
	801	2.50	2	0.01	-7.2
4	sol	0.0002	1	0.03	+2.7
		0.0005	1	0.05	+1.9
	suspension	0.001	1	0.07	0.0
	1	0.005	1	0.05	-0.6
		0.050	1	0.05	-1.1
	flowing gel	0.10	1	0.07	-2.8
	00	0.25	2	0.02	-4.1
		0.50	2	0.02	-6.2
	gel	0.625	2	0.02	-9.5
	8	0.80	2	0.01	-8.7
		1.00	2	0.01	-5.2
5	sol	0.0002	1	0.03	-4.8
		0.0005	1	0.05	-1.4
	suspension	0.001	1	0.07	0.0
		0.050	1	0.05	-0.3
	~	0.20	1	0.05	-0.2
	flowing gel	0.50	1	0.07	-0.4
		0.85	2	0.02	-0.7
	gel	1.00	2	0.01	-0.6
-		1.67	2	0.01	-0.6

 Table S6. Enantiodifferentiating photoisomerization of 1Z sensitized by CDNSs 3-5

<sup>*a*</sup> Photoirradiation was performed under  $N_2$  at 0.5 °C in a quartz cell with a Max-301 (254 nm) light source.



**Fig. S16.** The ee profile of **1E** as a function of the concentration of CDNS **3** (top), **4** (middle) and **5** (bottom) upon enantiodifferentiating photoisomerization of **1Z**. The pink, yellow, blue and violet regions represent the solution, suspension, flowing gel and rigid gel states, respectively; see Table S6 for the original data.

CDNS	Phase	[CDNS]	Tempera-	Irradiation	F/Z	% 66
CDIG		/g mL <sup>-1</sup>	ture/°C	time/h	L/L	70 00
3	sol	0.0002	0.5	1	0.03	+4.7
		0.0003	0.5	1	0.05	+4.0
		0.0004	0.5	1	0.04	+1.5
		0.0005	0.5	1	0.06	0.0
	suspension	0.001	0.5	1	0.07	0.0
	I I I I I I I I I I I I I I I I I I I	0.010	0.5	1	0.05	0.0
	flowing gel	0.050	0.5	1	0.07	+1.0
	nowing ger	0.050	0.5	1	0.03	+1.5
		0.10	0.5	1	0.02	1.5
		0.30	0.5	1	0.02	+1.7
		0.30	0.5	2	0.02	+2.0
		1.00	0.3	2	0.02	+2.8
		1.67	0.5	2	0.01	+4.3
	gel	2.00	0.5	2	0.01	+6.1
4	aal	2.50	0.5	2	0.01	+6.5
4	SOI	0.0002	0.5	1	0.05	+4.9
		0.0003	0.5	1	0.04	+3.0 +1.8
	suspension	0.001	0.5	1	0.05	+0.5
	suspension	0.010	0.5	1	0.08	+1.3
		0.10	0.5	1	0.03	+1.7
	flowing gel	0.20	0.5	1	0.02	+2.7
		0.40	0.5	2	0.02	+4.1
	gel	0.625	0.5	2	0.01	+11.1
		0.625	-10	3	0.01	+4.0
		0.80	0.5	2	0.01	+10.6
		1.00	0.5	2	0.01	+11.3
-	,	1.50	0.5	2	0.01	+6.0
5	sol	0.0002	0.5	1	0.13	+0.7
	suspension	0.001	0.5	1	0.11	0.0
		0.030	0.5	1	0.14	+0.4
	flowing gel	0.20	0.5	1	0.03	+0.3 +2.0
	nowing gei	0.50	0.5	2	0.02	+2.0 +4.7
		0.85	0.5	$\frac{1}{2}$	0.02	+7.2
	gel	1.000	0.5	3	0.007	+13.3
	0	1.25	10	3	0.007	+5.6
		1.25	0.5	3	0.005	+13.0
		1.25	-5	3	0.006	+9.5
		1.25	-10	3	0.006	+7.7
		1.67	0.5	3	0.007	+12.6
		2.50	0.5	3	0.007	+9.6
		1.25	-5	3	0.007	$+7.9^{b}$

### Table S7. Enantiodifferentiating photoisomerization of 2ZZ sensitized by CDNS 3-5

<sup>*a*</sup> Photoirradiation was performed under  $N_2$  in a quartz cell with a Max-301(313 nm) light source.

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