

## **-Supplementary Materials-**

# Water Content-Dependent Switching of the Bending Behavior of Photoresponsive Hydrogels Composed of Hydrophilic Acrylamide-Based Main Chains and Hydrophobic Azobenzene

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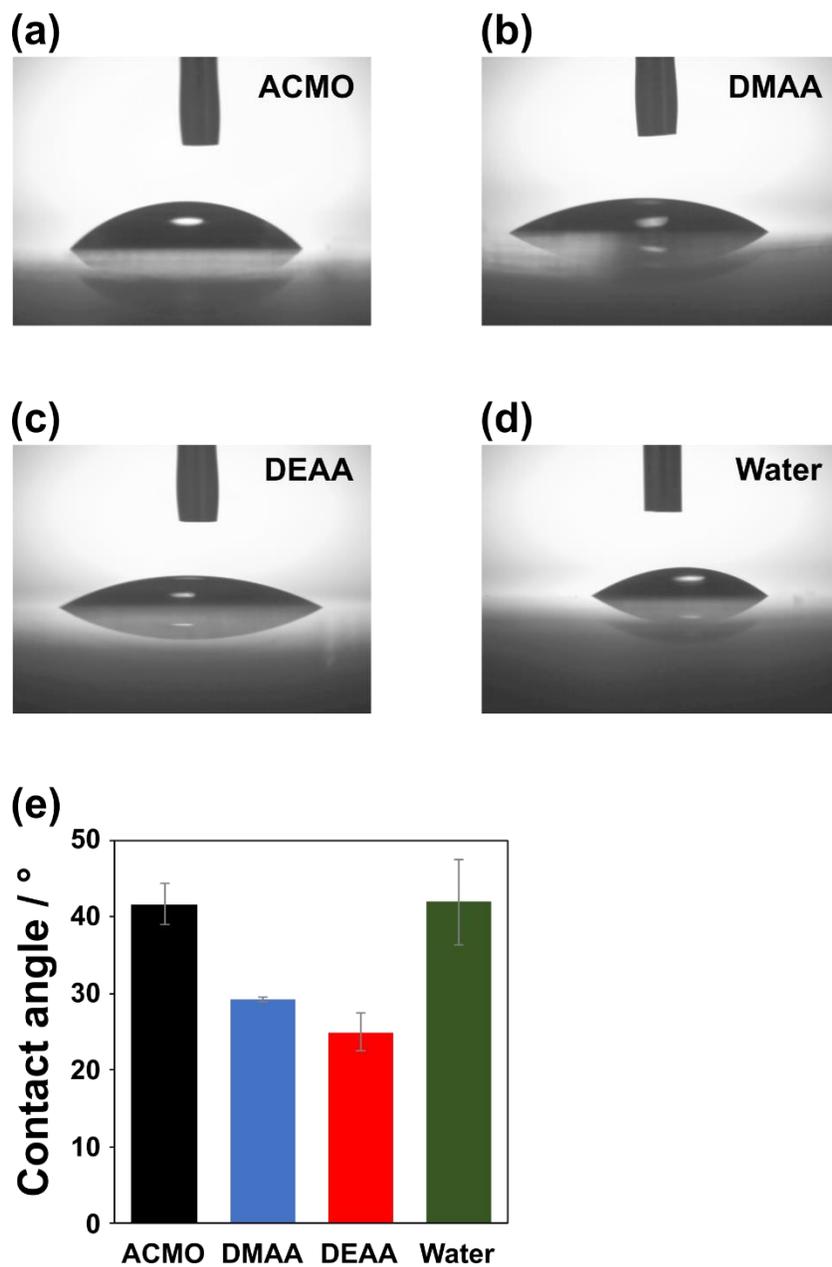
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## 1. Contact angles of acrylamide-type monomers and water on a glass substrate



**Figure S1.** Photographs of various droplets on a glass substrate such as (a) ACMO, (b) DMAA, (c) DEAA, and (d) water. (e) Contact angles of three liquid acrylamide-based monomers and water as a reference on a glass substrate.

## 2. Preparation of photoresponsive hydrogels (PR-Azo)

**Table S1.** Amounts of reagents used in the preparation of PACMO-Azo.

ACMO / $\mu\text{L}$ (mmol)	AzoAAm / mg (mmol)	APS / mg (mmol)
750 (6.0)	31 (0.12)	6.9 (0.030)

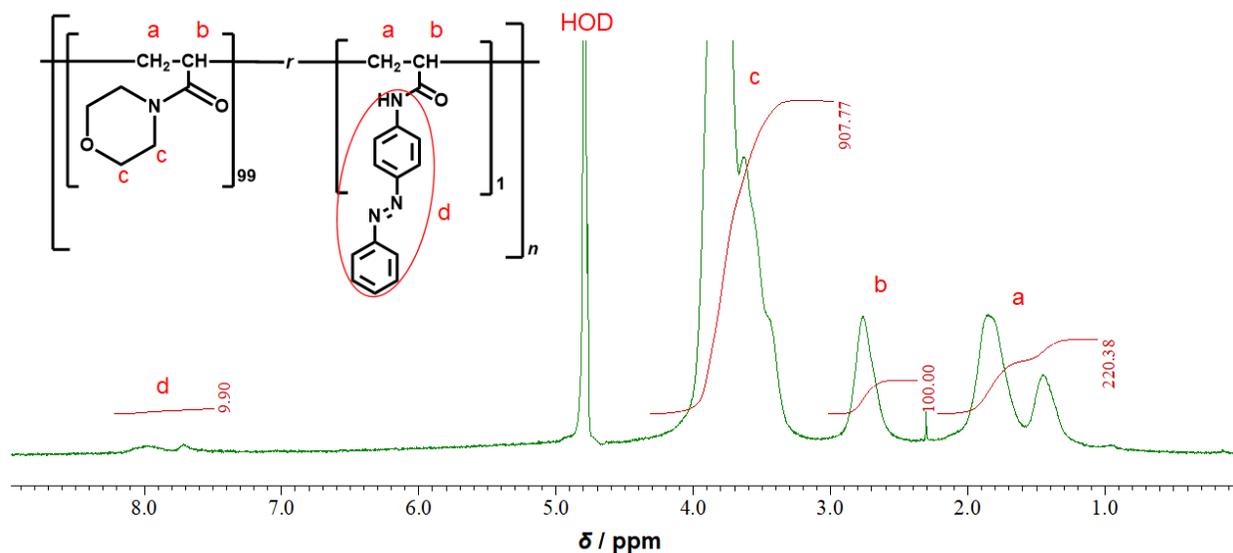
**Table S2.** Amounts of reagents used in the preparation of PDMAA-Azo.

DMAA / $\mu\text{L}$ (mmol)	AzoAAm / mg (mmol)	APS / mg (mmol)
750 (7.3)	37 (0.15)	8.5 (0.037)

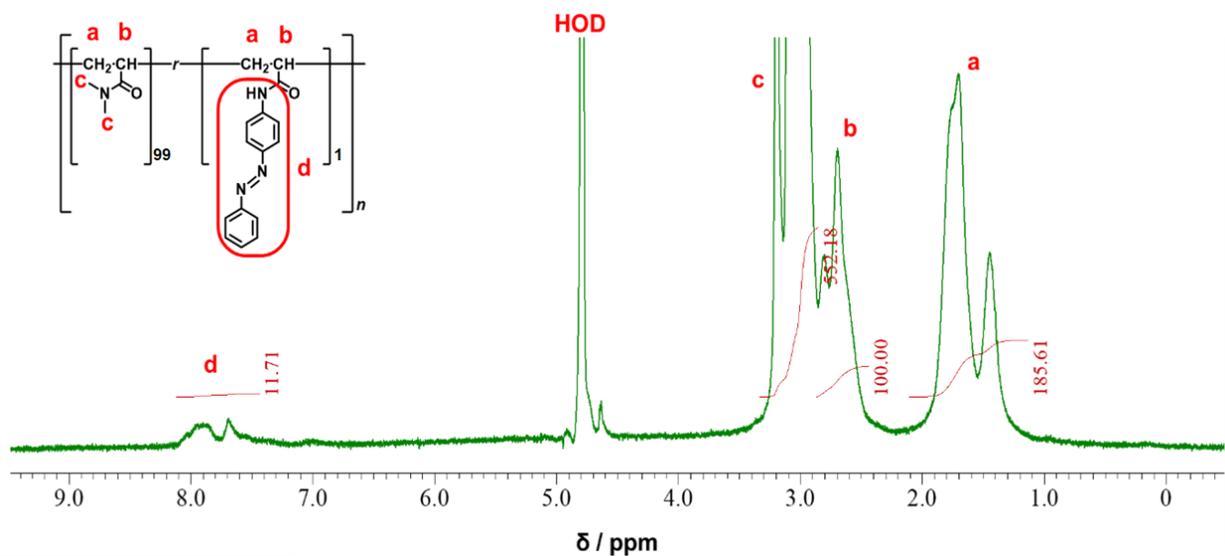
**Table S3.** Amounts of reagents used in the preparation of PDEAA-Azo.

DEAA / $\mu\text{L}$ (mmol)	AzoAAm / mg (mmol)	APS / mg (mmol)
750 (5.4)	28 (0.11)	6.3 (0.028)

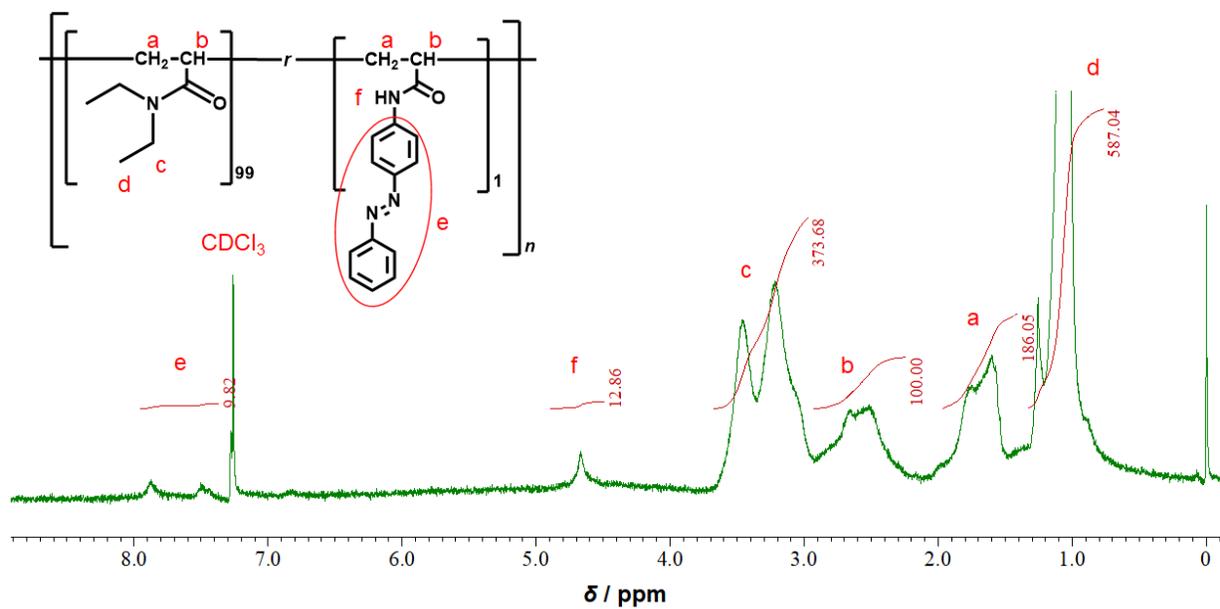
### 3. FGMAS NMR spectra of PR-Azo hydrogels



**Figure S2.**  $^1\text{H}$  FGMAS NMR spectrum of PACMO-Azo swollen in  $\text{D}_2\text{O}$  (7 kHz spinning speed, 400 MHz, 25  $^\circ\text{C}$ ). Based on the integral ratio of the  $H_b$  and  $H_d$  peaks, PACMO-Azo contained 1.1% azobenzene.

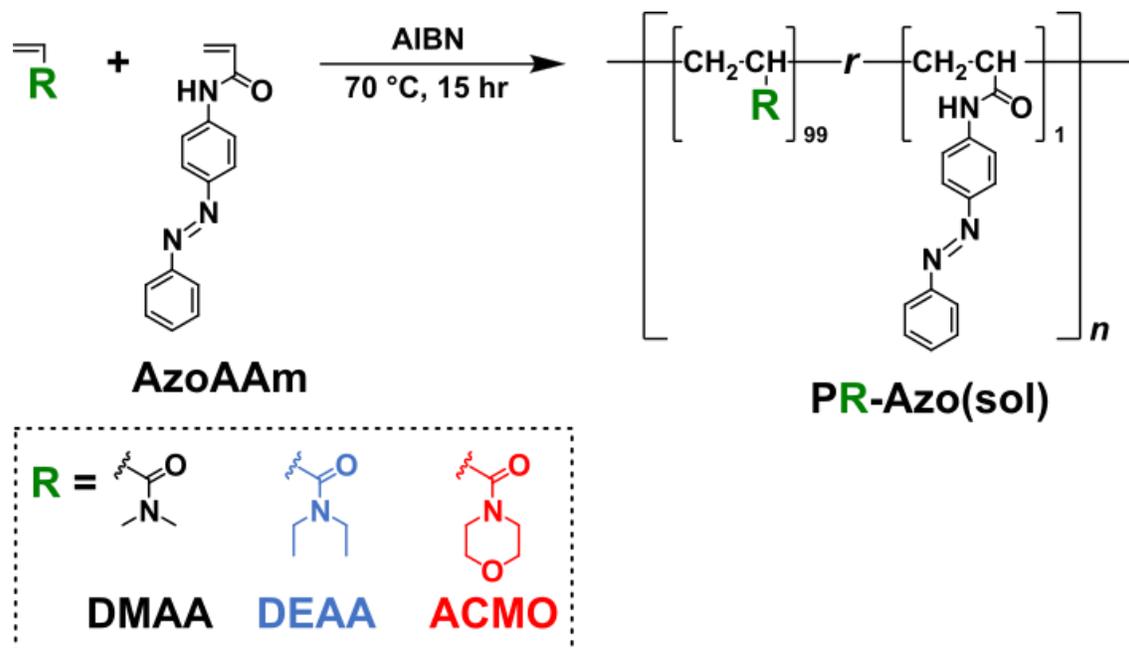


**Figure S3.**  $^1\text{H}$  FGMAS NMR spectrum of PDMAA-Azo swollen in  $\text{D}_2\text{O}$  (7 kHz spinning speed, 400 MHz, 25  $^\circ\text{C}$ ). Based on the integral ratio of the  $H_b$  and  $H_c$  peaks, PDMAA-Azo contained 1.3% azobenzene.



**Figure S4.**  $^1H$  FGMAS NMR spectrum of PDEAA-Azo swollen in  $CDCl_3$  (7 kHz spinning speed, 400 MHz, 25 °C). Based on the integral ratio of the  $H_b$  and  $H_d$  peaks, PDEAA-Azo contained 1.2% azobenzene.

#### 4. Preparation of water-soluble photoresponsive polymers (PR-Azo(sol))



**Figure S5.** Preparation scheme of water-soluble photoresponsive polymers (PR-Azo(sol)).

**Table S4.** Amounts of reagents used in the preparation of water-soluble PACMO-Azo(sol).

ACMO / mg (mmol)	AzoAAm / mg (mmol)	AIBN / mg (mmol)
4400 (31)	160 (0.65)	7.6 (0.046)

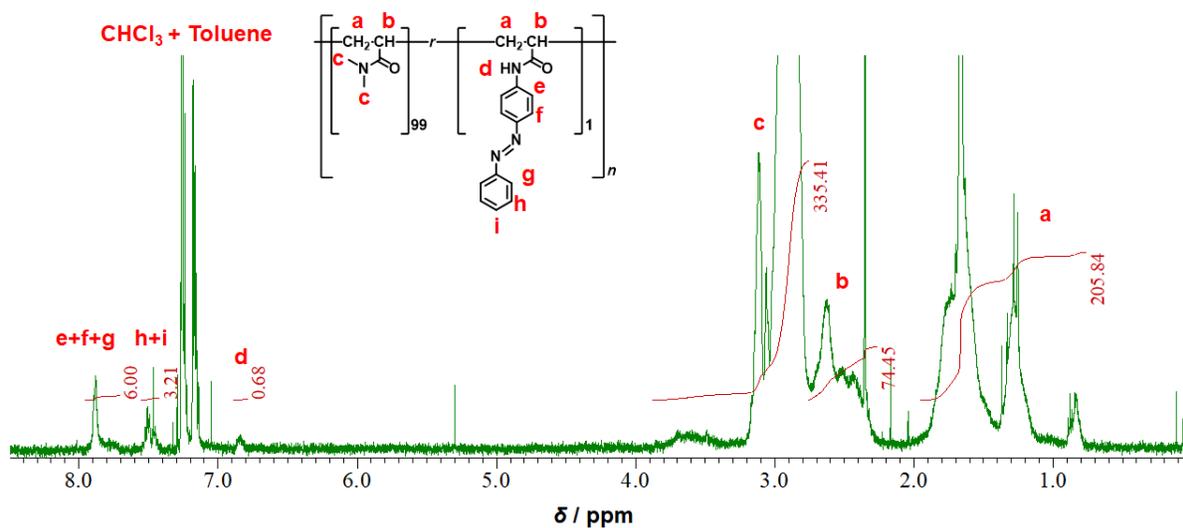
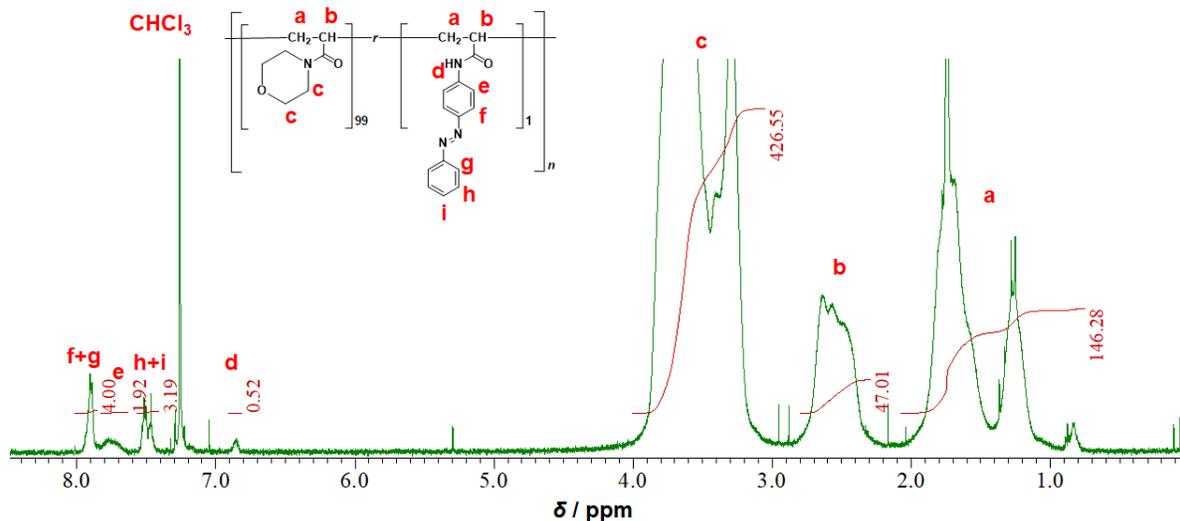
**Table S5.** Amounts of reagents used in the preparation of water-soluble PDMAA-Azo(sol).

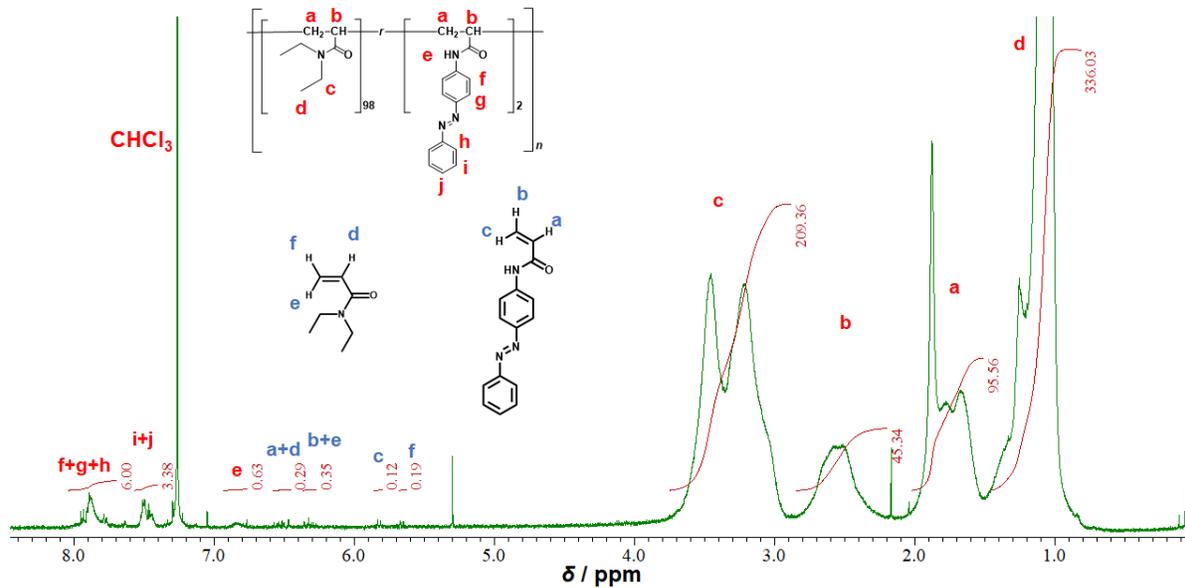
DMAA / mg (mmol)	AzoAAm / mg (mmol)	AIBN / mg (mmol)
3900 (39)	200 (0.80)	9.1 (0.055)

**Table S6.** Amounts of reagents used in the preparation of water-soluble PDEEA-Azo(sol).

DEEA / mg (mmol)	AzoAAm / mg (mmol)	AIBN / mg (mmol)
3700 (29)	150 (0.59)	7.4 (0.045)

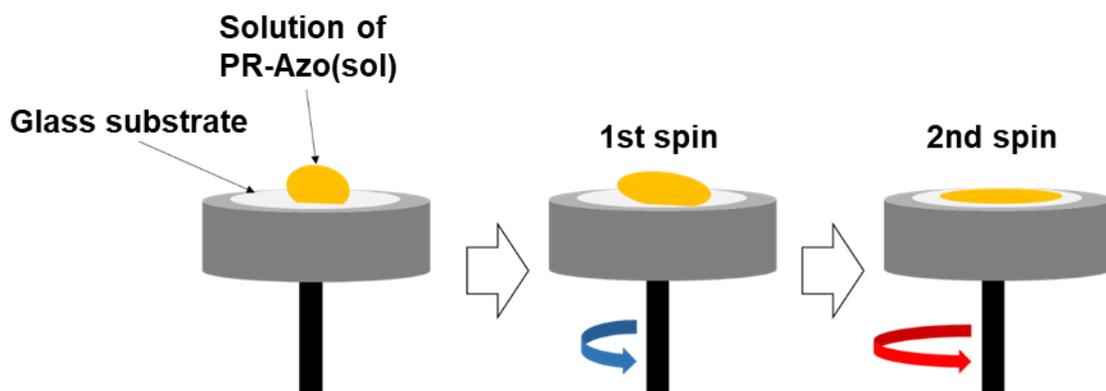
## 5. NMR spectra of water-soluble PR-Azo(sol)





**Figure S8.** <sup>1</sup>H NMR spectrum of water-soluble PDEAA-Azo(sol) in CDCl<sub>3</sub> (500 MHz, 25 °C). Based on the integral ratio of the  $H_b$  and  $H_{f+g}$  peaks, The azobenzene content in water-soluble PDEAA-Azo(sol) was 2.2%. Unreacted AzoAAM and DEAA remained at concentrations of 12% and 0.4% in PDEAA-Azo(sol), respectively.

## 6. Preparation of a thin film on a glass substrate by spin coating

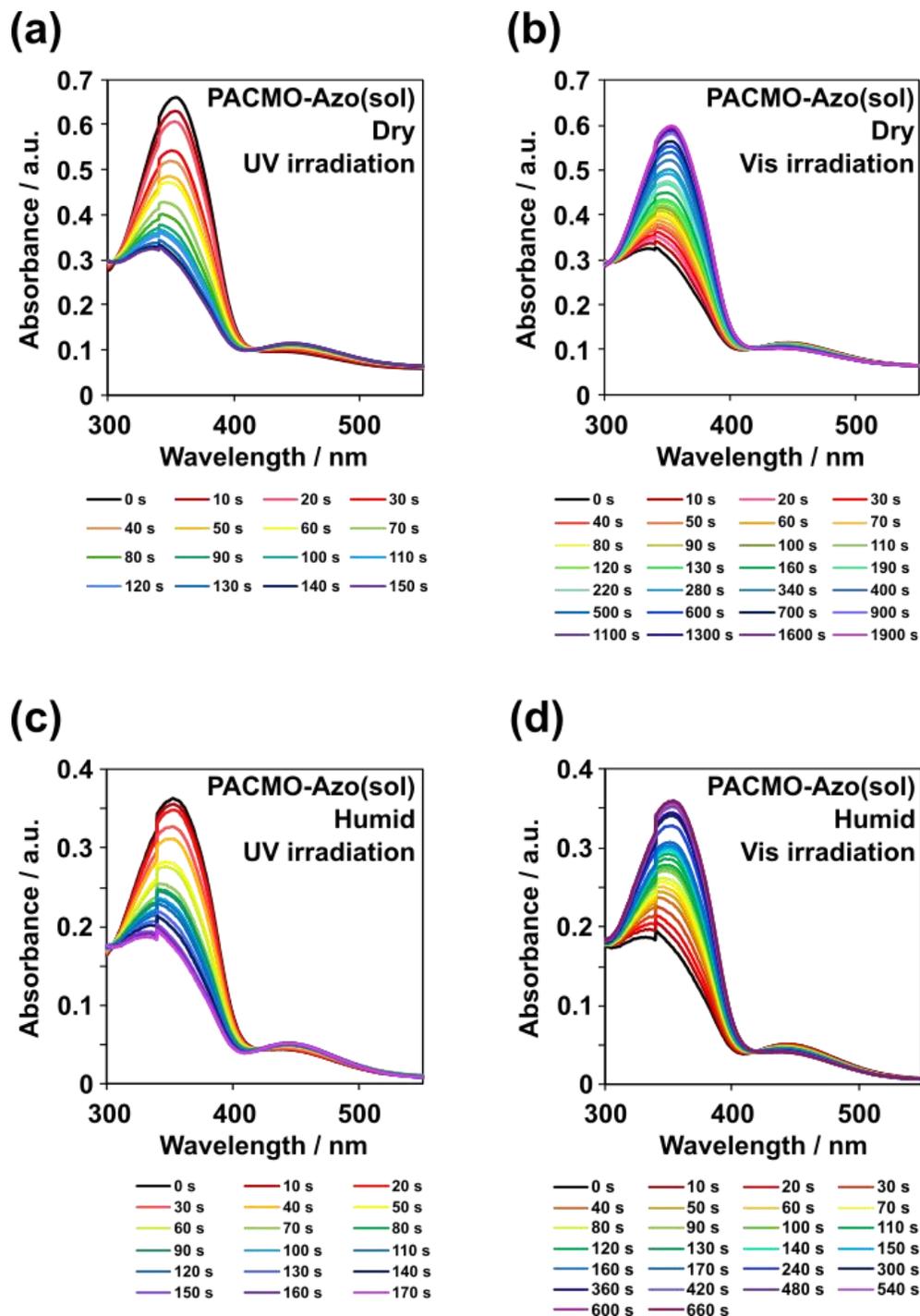


**Figure S9.** Illustration showing how to prepare a thin film of PR-Azo(sol) on a glass substrate.

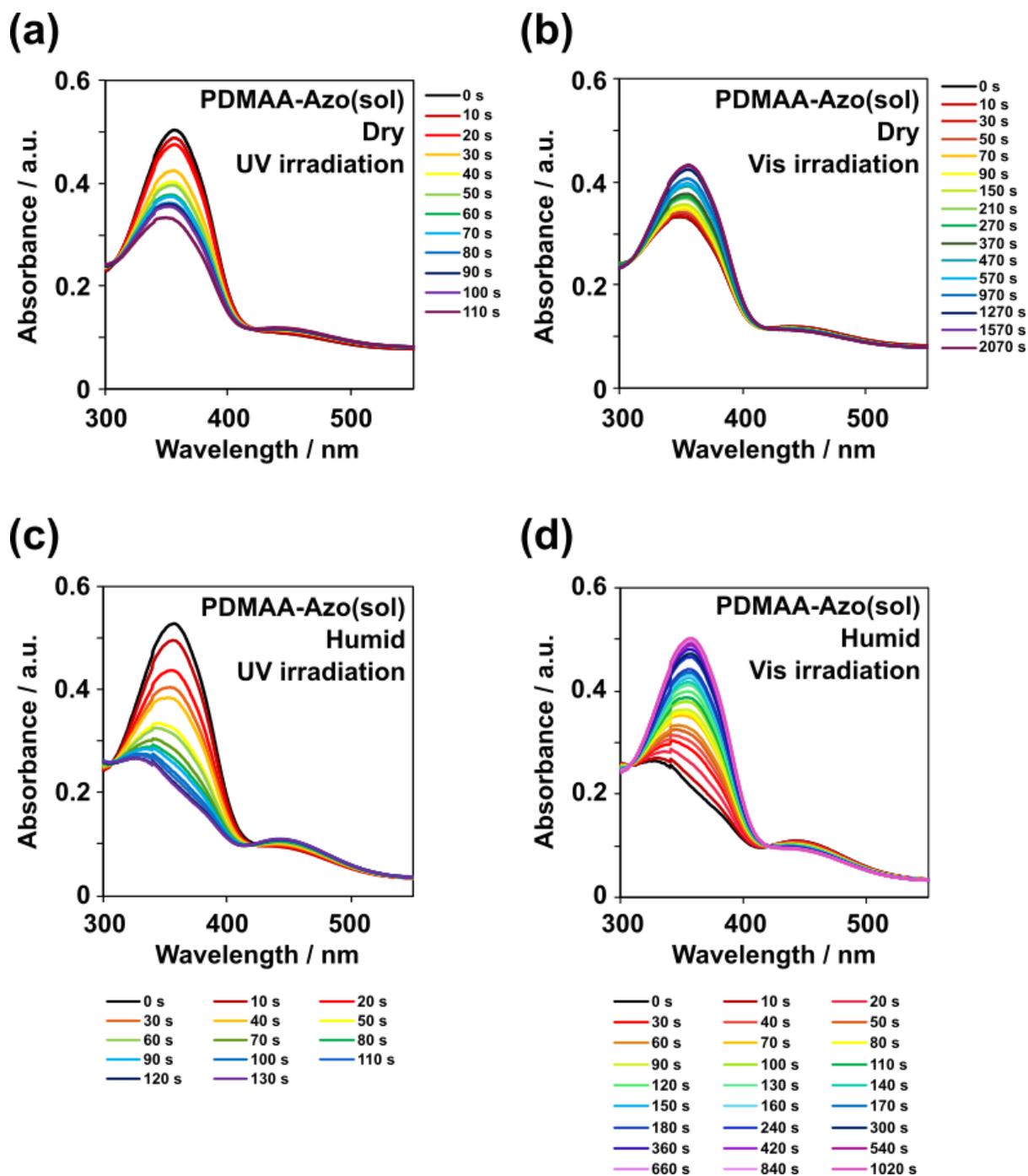
**Table S7.** Preparation conditions of PR-Azo(sol) thin films.

<b>R</b>	<b>Solution concentrations / wt%</b>	<b>Rotation conditions</b>
<b>DMAA</b>	8	1st spin: 4000 rpm for 5 s 2nd spin: 8000 rpm for 15 s
<b>DEAA</b>	8	1st spin: 2000 rpm for 5 s 2nd spin: 8000 rpm for 15 s
<b>ACMO</b>	6	1st spin: 4000 rpm for 5 s 2nd spin: 8000 rpm for 15 s

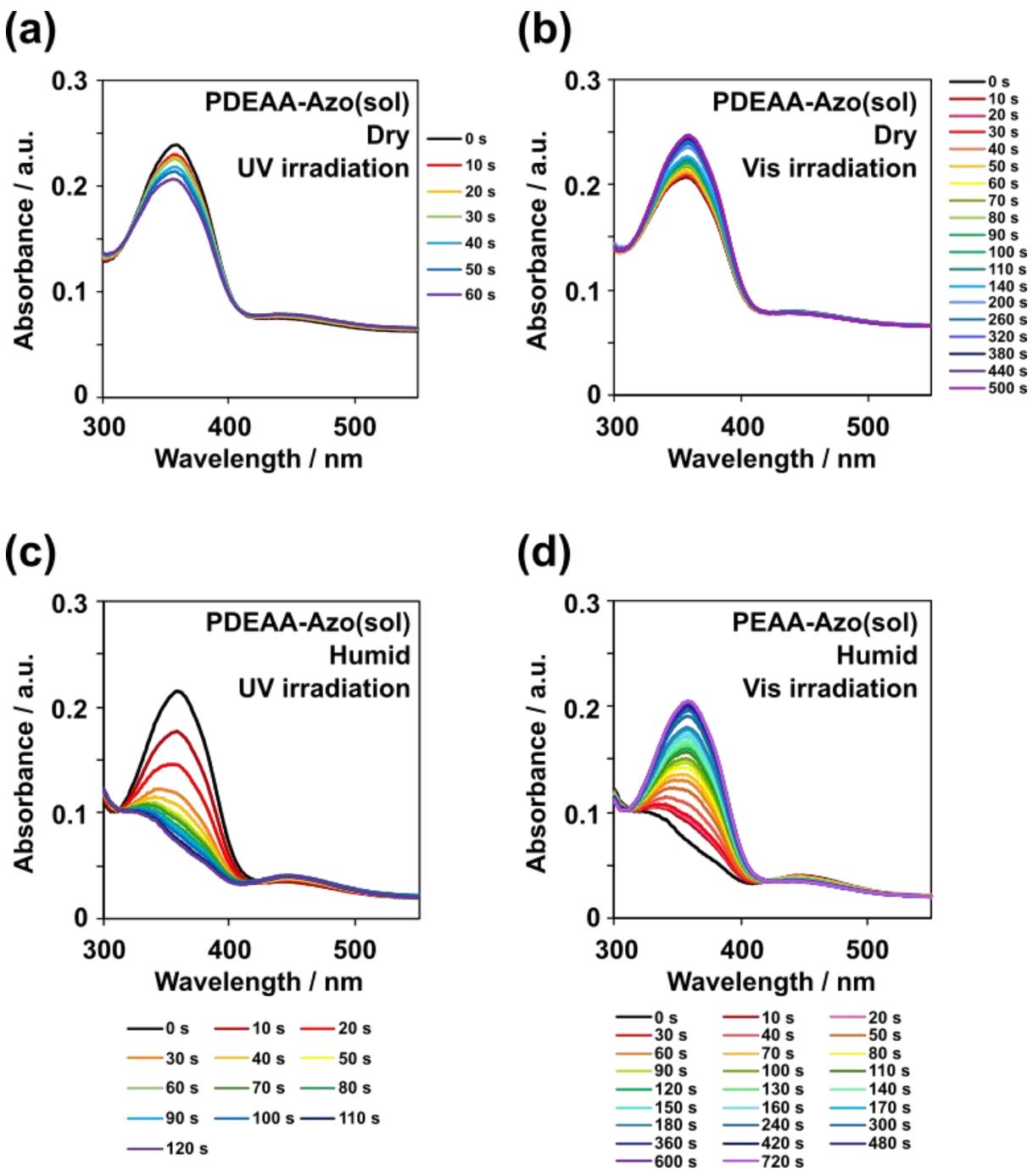
7. Changes in UV–Vis spectra of PR-Azo(sol) during light irradiation in dry and humid environments



**Figure S10.** Changes in the UV–Vis spectra of PACMO-Azo(sol) in a dried state upon (a) UV light irradiation and (b) subsequent Vis light irradiation. Similar changes in the UV–Vis spectra of PACMO-Azo(sol) stored in a humid environment upon (c) UV light irradiation and (d) subsequent Vis light irradiation.



**Figure S11.** Changes in the UV–Vis spectra of PDMAA-Azo(sol) in a dried state upon (a) UV light irradiation and (b) subsequent Vis light irradiation. Similar changes in the UV–Vis spectra of PDMAA-Azo(sol) stored in a humid environment upon (c) UV light irradiation and (d) subsequent Vis light irradiation.



**Figure S12.** Changes in the UV–Vis spectra of PDEAA-Azo(sol) in the dried state upon (a) UV light irradiation and (b) subsequent Vis light irradiation. Similar changes in the UV–Vis spectra of PDEAA-Azo(sol) stored in a humid environment upon (c) UV light irradiation and (d) subsequent Vis light irradiation.

8. Kinetic studies of azobenzene in PR-Azo(sol) during light irradiation in dry and humid environments

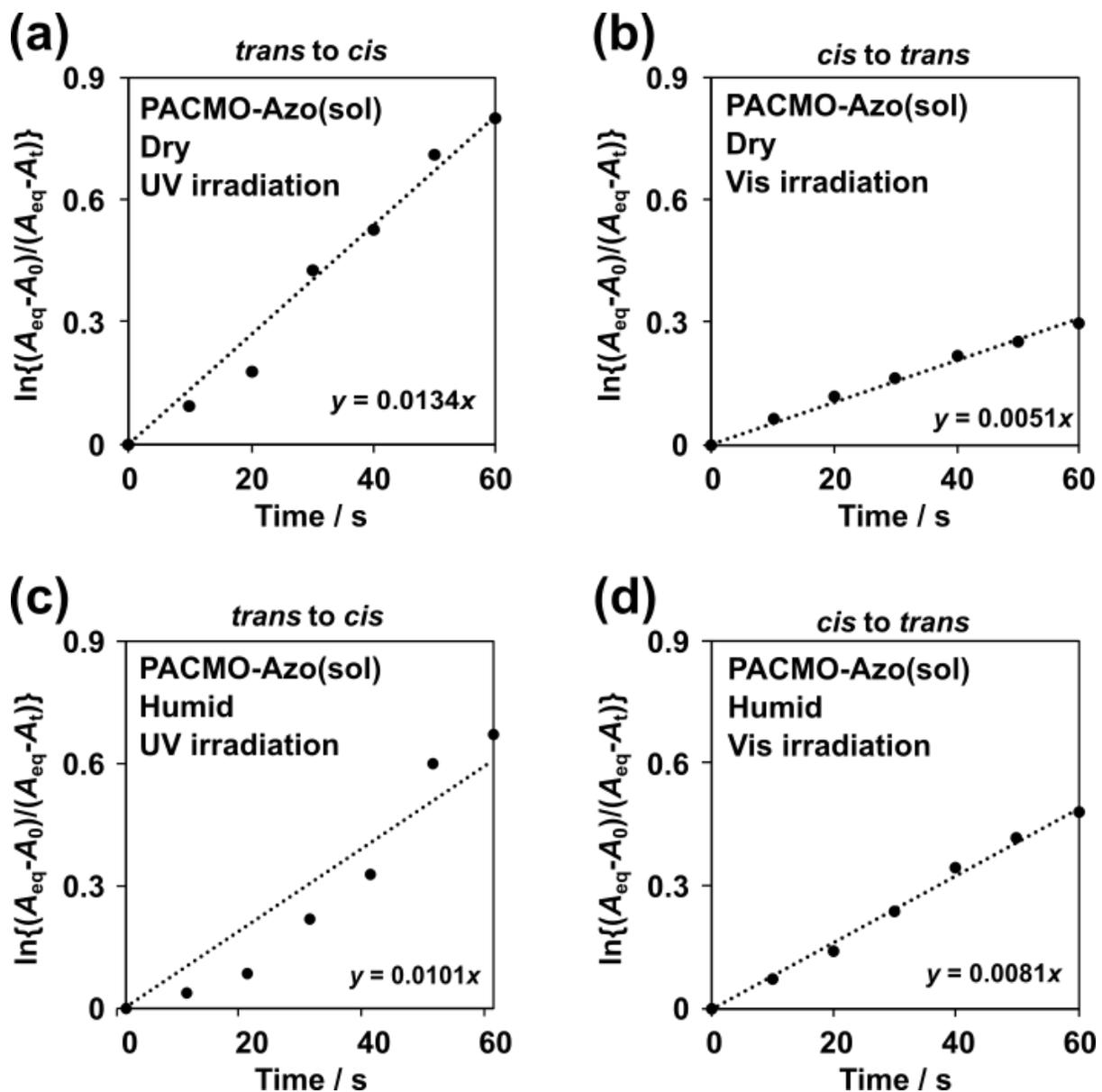
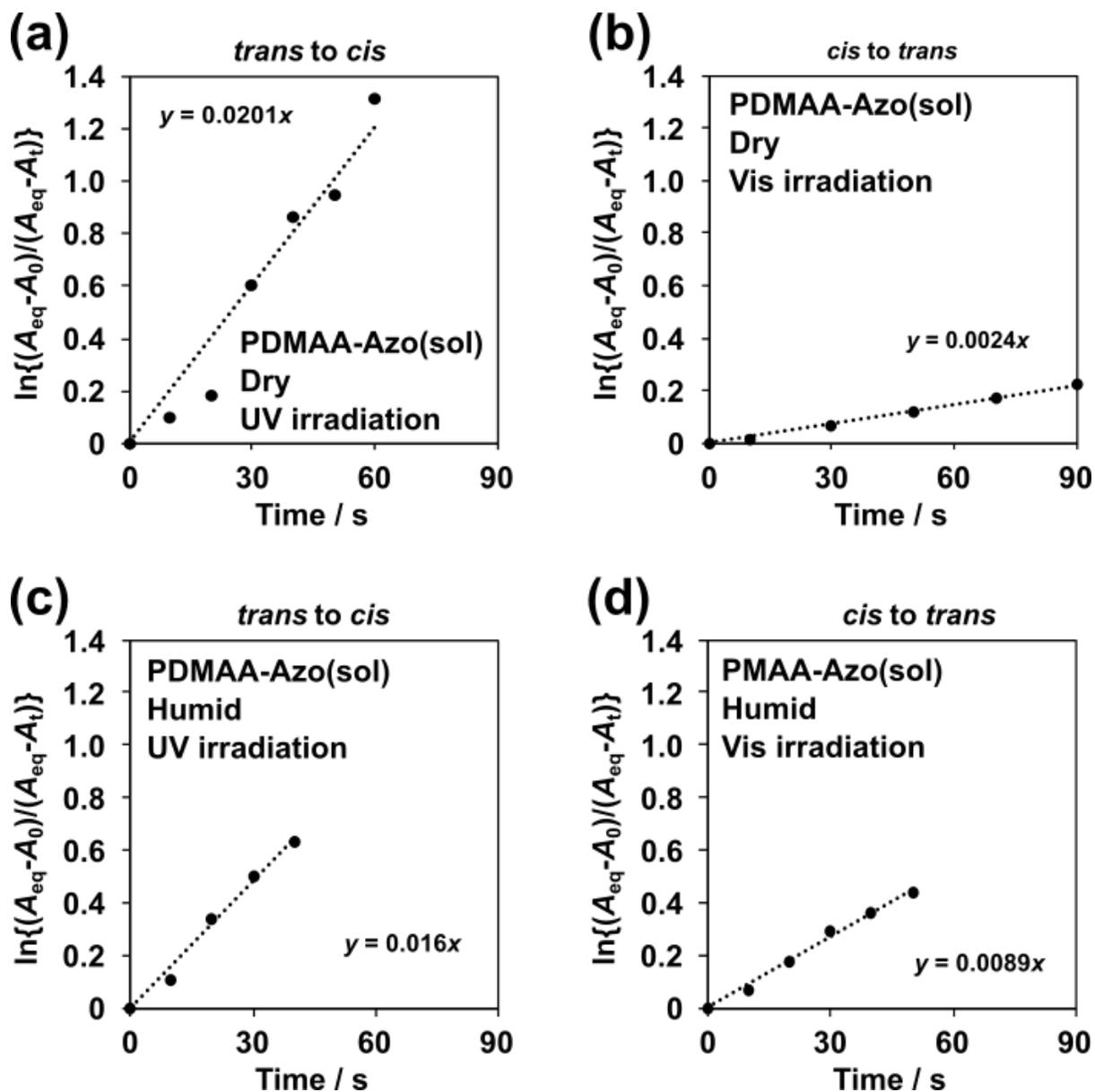
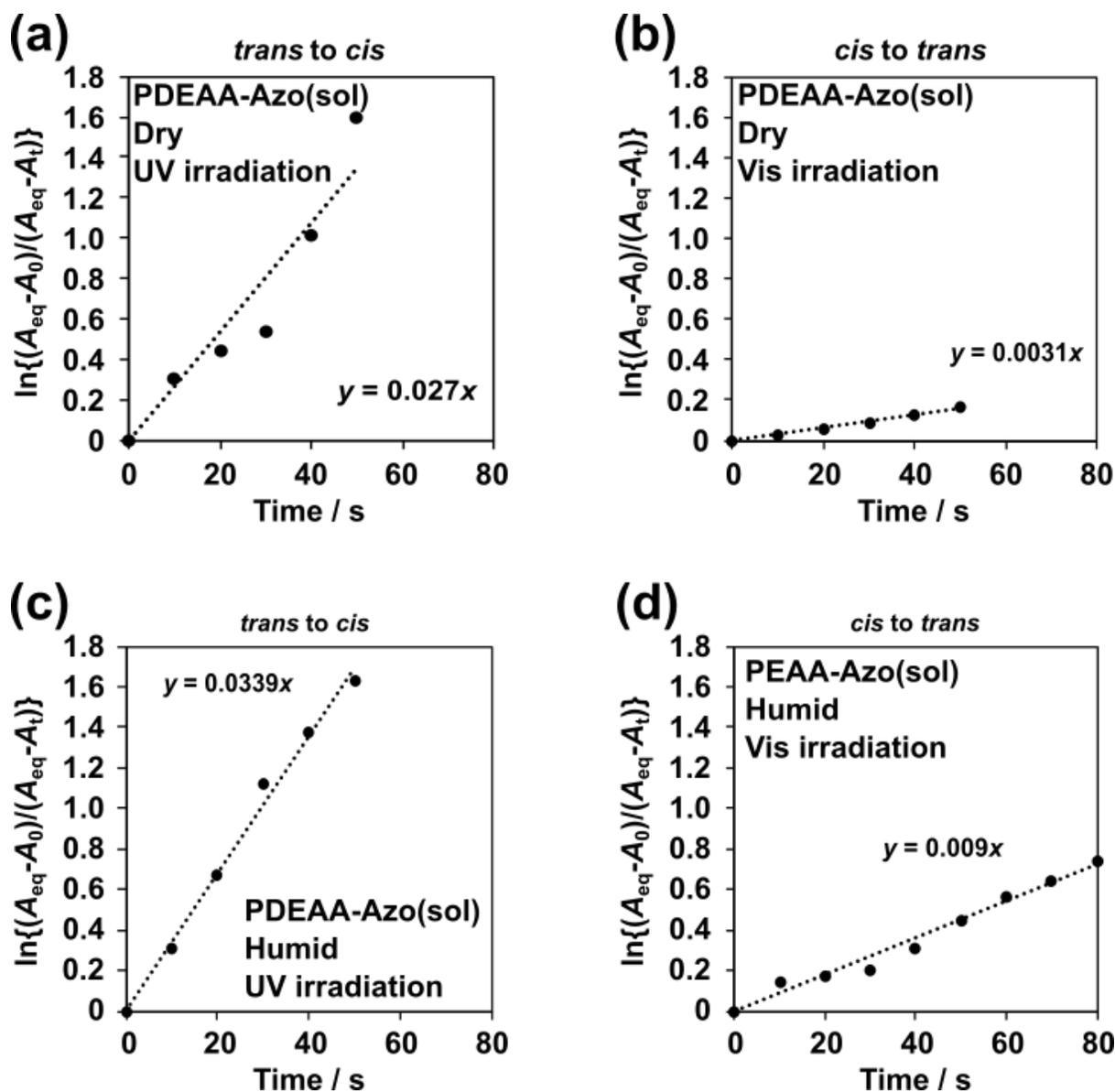


Figure S13. Pseudo-first-order plots for PACMO-Azo(sol) (a) in the dry state upon UV irradiation, (b) in the dry state upon subsequent Vis light irradiation, (c) in the humid state upon UV irradiation, and (d) in the humid state upon subsequent Vis light irradiation



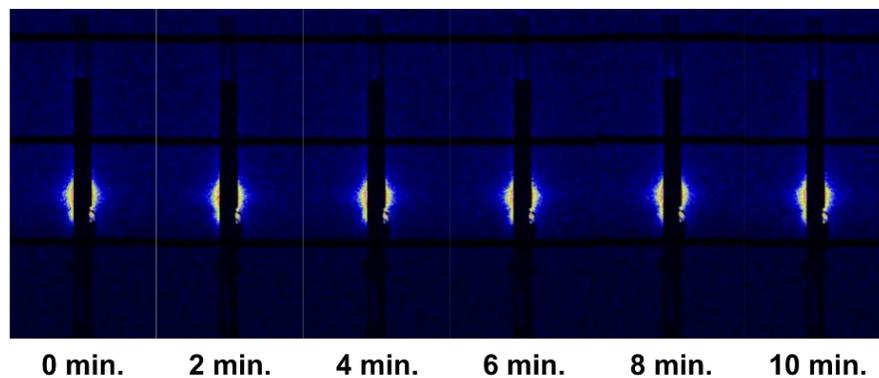
**Figure S14.** Pseudo-first-order plots of PDMAA-Azo(sol) (a) in the dry state upon UV irradiation, (b) in the dry state upon subsequent Vis light irradiation, (c) in the humid state upon UV irradiation, and (d) in the humid state upon subsequent Vis light irradiation.



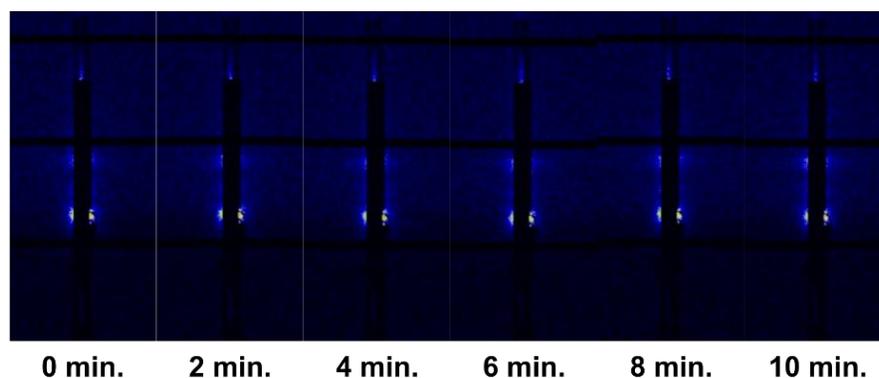
**Figure S15.** Pseudo-first-order plots of PDEAA-Azo(sol) (a) in the dry state upon UV irradiation, (b) in the dry state upon subsequent Vis light irradiation, (c) in the humid state upon UV irradiation, and (d) in the humid state upon subsequent Vis light irradiation.

9. 2D GISAXS scattering patterns of PR-Azo(sol) during UV light irradiation in dry and humid environments

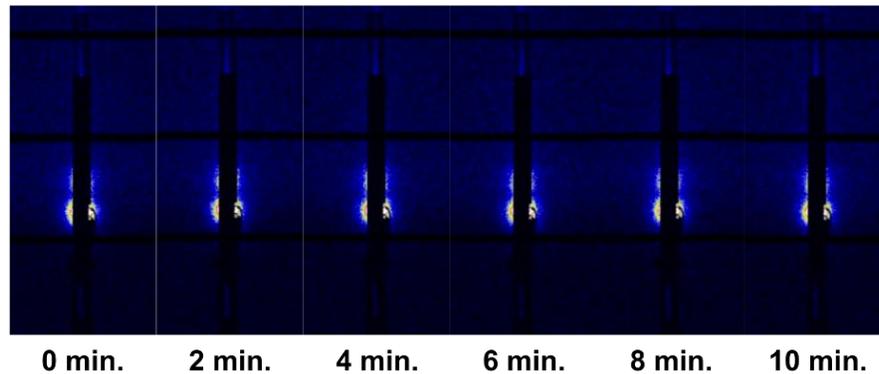
(a) PACMO-Azo(sol) Dry



(b) PDMAA-Azo(sol) Dry



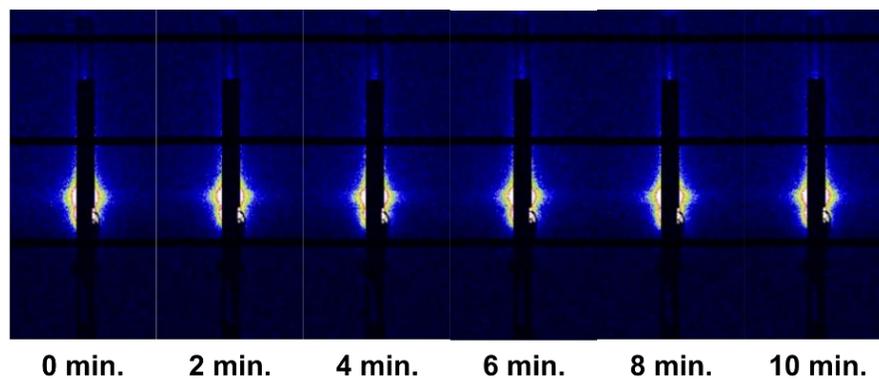
(c) PDEAA-Azo(sol) Dry



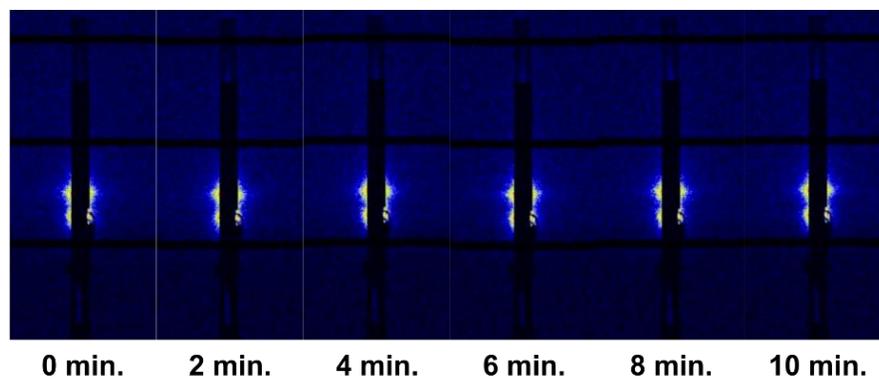
Time for UV light irradiation

Figure S16. 2D GISAXS scattering patterns of (a) PACMO-Azo(sol), (b) PDMAA-Azo(sol), and (c) PDEAA-Azo(sol) in the dry state upon UV irradiation for 10 minutes.

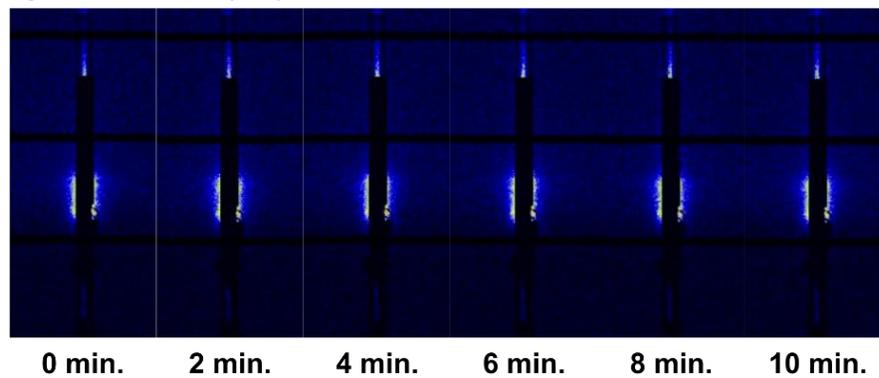
**(a)** PACMO-Azo(sol) Humid



**(b)** PDMAA-Azo(sol) Humid



**(c)** PDEAA-Azo(sol) Humid



Time for UV light irradiation

**Figure S17.** 2D GISAXS scattering patterns of (a) PACMO-Azo(sol), (b) PDMAA-Azo(sol), and (c) PDEAA-Azo(sol) in the humid state upon UV irradiation for 10 minutes.