

Supporting Information for:

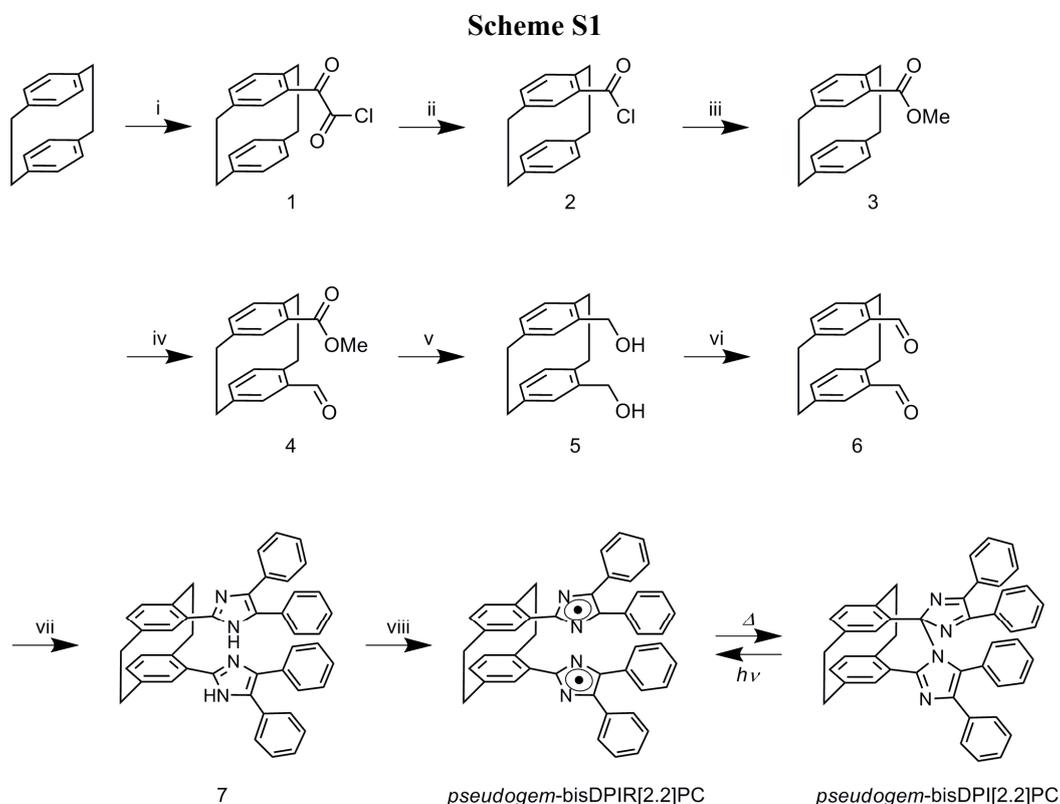
A fast photochromic molecule that colors only under UV light

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1. Synthesis



Reagents and condition: (i) $(\text{COCl})_2$, AlCl_3 , CH_2Cl_2 , $-20\text{ }^\circ\text{C}$ to $-10\text{ }^\circ\text{C}$, 20 min; (ii) PhCl , reflux, 2 h; (iii) MeOH , $40\text{ }^\circ\text{C}$, 10 min; (iv) TiCl_4 , $\text{CH}_3\text{OCHCl}_2$, CH_2Cl_2 , $-20\text{ }^\circ\text{C}$ to $-10\text{ }^\circ\text{C}$ \rightarrow r.t., 16 h; (v) LiAlH_4 , THF , $60\text{ }^\circ\text{C}$, 6 h; (vi) DDQ , dioxane, r.t., 2 h; (vii) benzil, AcONH_4 , AcOH , $90\text{ }^\circ\text{C}$, 2 days; (viii) $\text{K}_3[\text{Fe}(\text{CN})_6]$ aq, KOH , benzene, r.t., 2h.

Materials: All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Wakogel[®] C-300). All reagents except methanol and benzil were purchased from TCI, Wako Co. Ltd., Aldrich Chemical Company, Inc, and ACROS Organics, and were used without further purification. Methanol was distilled under nitrogen on the appropriate drying reagent prior to use. Benzil was recrystallized from ethanol. All reaction solvents were distilled on the appropriate drying reagents prior to use.

[2.2]Paracyclophane-4-glyoxyloyl chloride (1), [2.2]Paracyclophane-4-carbonyl chloride (2), and 4-methoxycarbonyl[2.2]paracyclophane (3) were prepared according to a literature procedure.^{S1}

***pseudogem*-Formyl(methoxycarbonyl)[2.2]paracyclophane (4)** were prepared according to a literature procedure.^{S2}

pseudogem-Bis(hydroxymethyl)[2.2]paracyclophane (5) and *pseudogem*-bisformyl[2.2]paracyclophane (6) were prepared according to a literature procedure.^{S3}

pseudogem-Bis(4,5-diphenyl-1*H*-imidazol-2-yl)[2.2]paracyclophane (7). 6 (56.1 mg, 0.212 mmol), benzil (90.0 mg, 0.428 mmol) and ammonium acetate (412 mg, 5.35 mmol) were stirred at 90 °C in acetic acid (2 mL) for 2 days. The reaction mixture was cooled to 0 °C, and neutralized with aqueous NH₃, when form a white precipitate. The precipitate was filtered, and washed with water. The residue was recrystallized from ethanol to give a white needle, 82.9 mg (60 %). ¹H NMR (DMSO-*d*₆, 500 MHz): δ 11.65 (s, 2H), 7.30-7.00 (m, 22H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.61 (dd, *J* = 6.0, 2.0 Hz, 2H), 4.59-4.50 (m, 2H), 3.16-3.01 (m, 6H). HRMS *m/z* calcd for C₄₆H₃₇N₄ [M + H]⁺: 645.3018, found: 645.3010. Anal. Calcd for C₄₆H₃₆N₄: C, 85.68; H, 5.63; N, 8.69. found: C, 85.51; H, 5.84; N, 8.59.

pseudogem-BisDPI[2.2]PC. Under nitrogen, 7 (44.0 mg, 0.0682 mmol) was dissolved in benzene (40 mL). Over 10 min, a solution of potassium ferricyanide (2.80 g, 11.1 mmol) and KOH (1.26 g, 22.5 mmol) in water (30 mL) was added dropwise, and the reaction mixture was vigorously stirred at room temperature for 2 h. The aqueous phase was separated, and extracted with benzene. The combined organic phases were washed with water, and then dried over Na₂SO₄. The solution was filtrated and evaporated to give a yellow amorphous solid, which was recrystallized from ethanol to give a white plate, 40.0 mg (91 %). ¹H NMR (CD₃CN, 500 MHz): δ 7.57-7.49 (m 2H), 7.45-7.36 (m, 3H), 7.32-7.17 (m, 9H), 7.14-7.02(m, 7H), 6.80 (s, 1H), 6.70 (d, *J* = 1.5 Hz, 2H), 6.56-6.48 (m, 2H), 4.49-4.37 (m, 1H), 3.35-2.91 (m, 7H). HRMS *m/z* calcd for C₄₆H₃₅N₄ [M + H]⁺: 643.2862, found: 643.2884. Anal. Calcd for C₄₆H₃₄N₄ · EtOH: C, 83.69; H, 5.85; N, 8.13. found: C, 83.63; H, 6.00; N, 8.08.

2. X-ray Crystallographic Analysis

The diffraction data of the single crystal of *pseudogem*-bisDPI[2.2]PC was collected on the Bruker APEX II CCD area detector (MoK_α, λ = 0.71073 nm). During the data collection, the lead grass doors of the diffractometer were covered to exclude the room light. The data refinement was carried out by the Bruker APEXII software package with SHELXT program.^{S4} All non-hydrogen atoms were anisotropically refined.

3. Experimental Detail for Laser Flash Photolysis

The laser flash photolysis experiments were carried out with a Unisoku TSP-1000 time-resolved spectrophotometer. A Continuum Minilite II Nd:YAG (Q-switched) laser with the third harmonic at 355 nm (ca. 8 mJ per 5 ns pulse) was employed for the excitation light. The probe beam from a Hamamatsu 150-W xenon short arc lamp (L2195) was guided with an optical fiber scope to be arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored

with a Hamamatsu R2949 photomultiplier tube through a spectrometer (Unisoku MD200). Sample solutions were deaerated by argon bubbling prior to the laser flash photolysis experiments.

4. Kinetics for the Thermal Back-Reaction

From the first-order kinetic plot shown in Figure S4, the rate constants were obtained at each temperature. The rate constants are summarized in Table S2. The Eyring plot over a temperature ranging from 5 °C to 40 °C are shown in Figure S5.

5. Movie for the Photochromic Color Change in Solution

The benzene solution of *pseudogem*-bisDPI[2.2]PC (0.1 M) in a quartz cuvette (1mm × 10mm × 40mm) was irradiated with UV light at 20.5 °C. UV irradiation was carried out using a Keyence UV-400 series UV-LED (UV-50H type), equipped with a UV-L6 lens unit (365 nm, irradiation power 300 mW/cm²). The movie was taken with a digital SLR camera (Nikon D90) equipped with a micro lense (AF Micro-Nikkor 60 mm F2.8D).

6. Photochromism in Amorphous and Crystal States

Figure S6 shows the XRD pattern of the film spin-coated on a nickel plate from the chloroform solution of *pseudogem*-bisDPI[2.2]PC. No diffraction peaks attributable to that of crystalline state supports that the spin-coated film is in the amorphous solid state. Figure S7 shows the DSC profile of the spin-coated film, where a clear shift in the baseline was observed at 140-150 °C. This change in the heat capacity is a characteristic feature of the glass transition. The microstructure of the spin-coated film was also studied using SEM microscopy (Figure S8). This observation also supports the amorphous character of the spin-coated film. Figure S9 shows the time profile of the transient absorbance at 400 nm of the amorphous film measured at 25 °C.

Though the single crystal does not show the photochromic color change at room temperature due to their fast bleaching rate in crystal, the photochromic reaction can proceed at 90 K. Upon UV irradiation at 90 K, the color of the single crystal changes from colorless to blue (Figure S10). Therefore we have carried out the X-ray crystallographic measurement under dark at 90 K. We found that the photochromic reaction in crystal is reversible without any degradation of crystallinity. We have attempted to reveal the molecular structure of the colored species by the X-ray crystallographic study. Unfortunately, thus far no change has been detected in the diffraction pattern, suggesting that only a small layer on the outside of the crystal has reacted.

7. References

- S1. Psiorz, M. & Schmid, R. *Chem. Ber.* **120**, 1825-1828 (1987).
- S2. Zitt, H.; Dix, I.; Hopf, H. & Jones, G. P. *Eur. J. Org. Chem.* 2298-2307 (2002).

- S3. Sergeeva, V. E.; Rozenberg, I. V.; Antonov, Y. D.; Vorontsov, V. E.; Starikova, A. Z.; Fedyanin, V. I. & Hopf, H. *Chem. Eur. J.* **11**, 6944-6961 (2005).
- S4. (a) Sheldrick GM. *SHELXS-97* and *SHELXL-97* 1997; University of Gottingen, Germany. (b) Sheldrick GM. *SADABS* 1996; University of Gottingen, Germany.

8. Acknowledgement

We thank Daisuke Kato of Aoyama Gakuin University for help with X-ray crystallographic analysis.

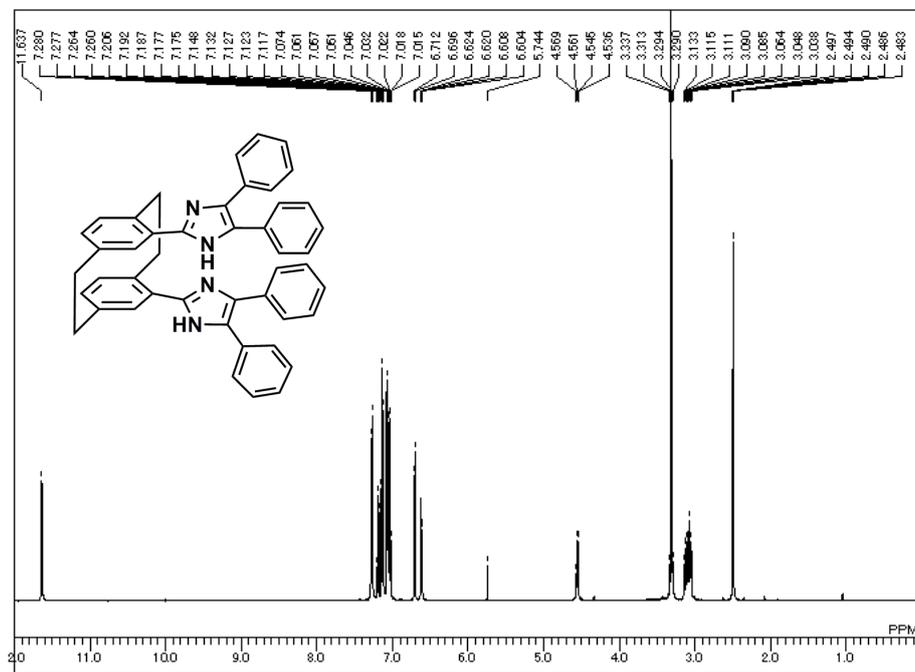


Figure S1. ¹H NMR Spectrum of **7** in DMSO-d₆.

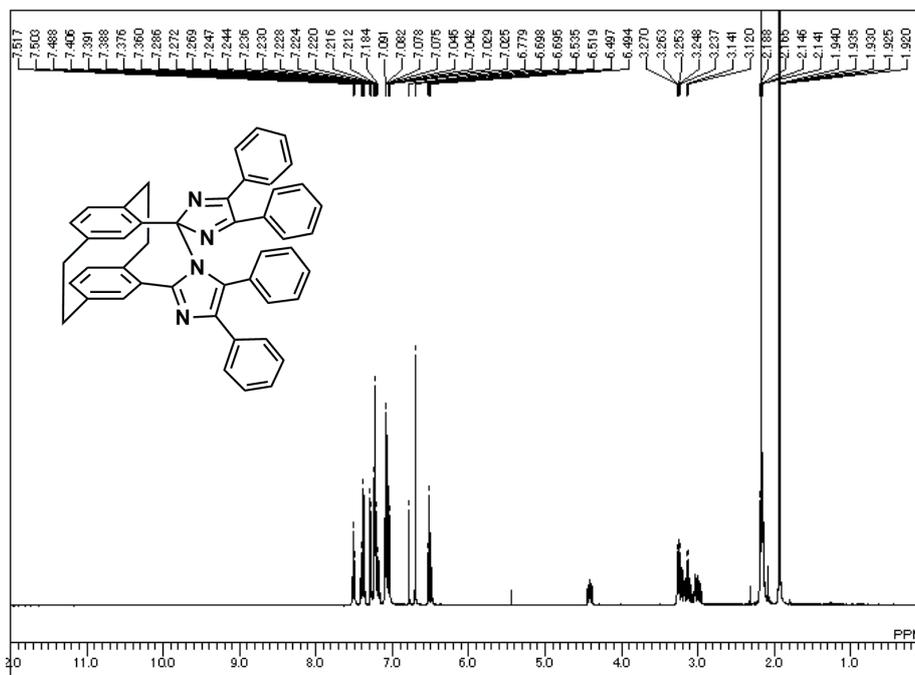


Figure S2. ¹H NMR Spectrum of *pseudogem*-bisDPI[2.2]PC in CD₃CN.

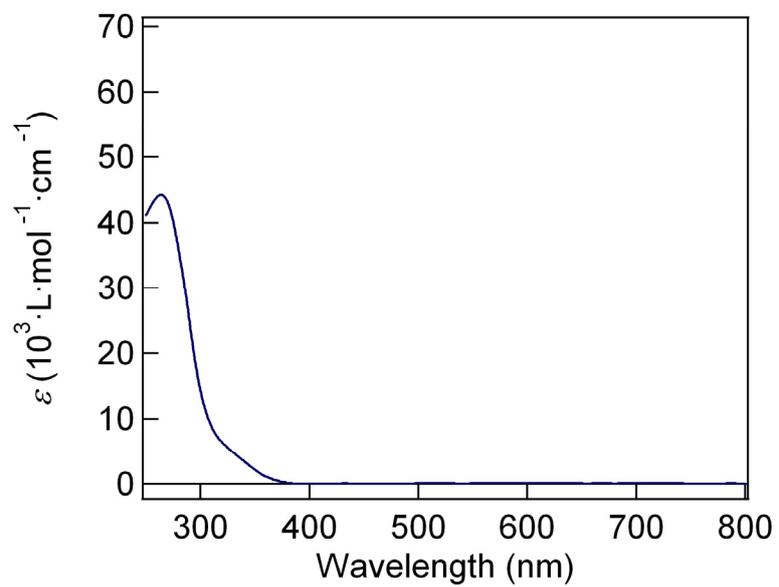


Figure S3. UV-Vis absorption spectrum of *pseudogem*-bisDPI[2.2]PC in acetonitrile (1.01×10^{-5} M) measured at 298 K.

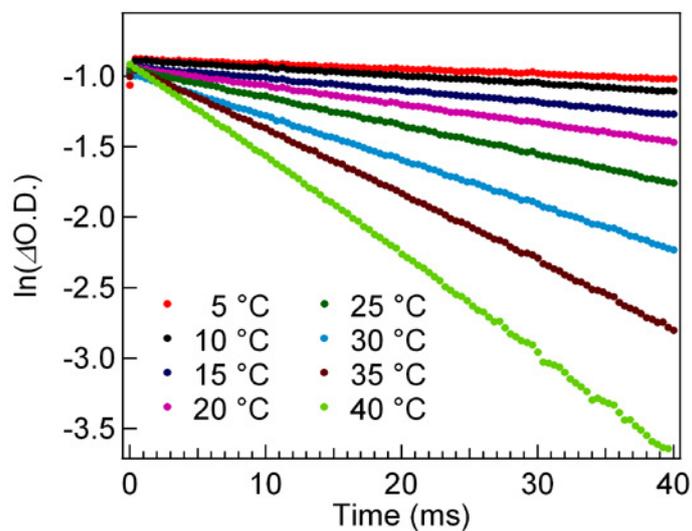


Figure S4. First-order kinetic profiles of the colored species generated from *pseudogem*-bisDPI[2.2]PC monitored at 400 nm in degassed benzene solution (1.5×10^{-4} M).

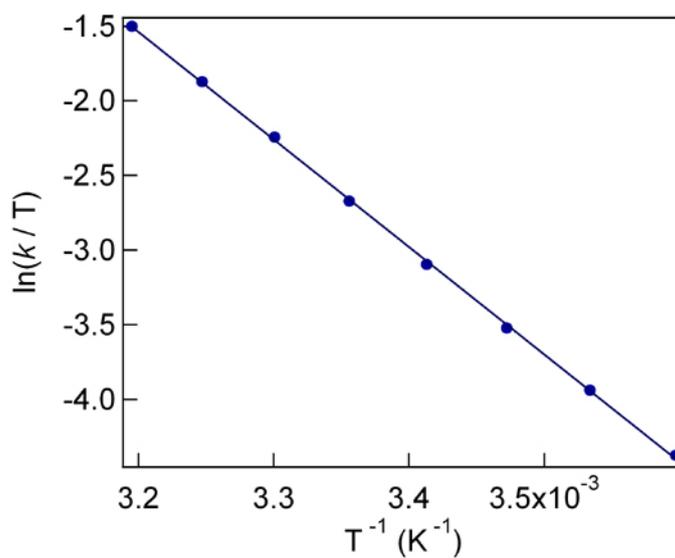


Figure S5. Eyring plot for the thermal back-reaction of the colored species generated from *pseudogem*-bisDPI[2.2]PC in degassed benzene solution (1.5×10^{-4} M).

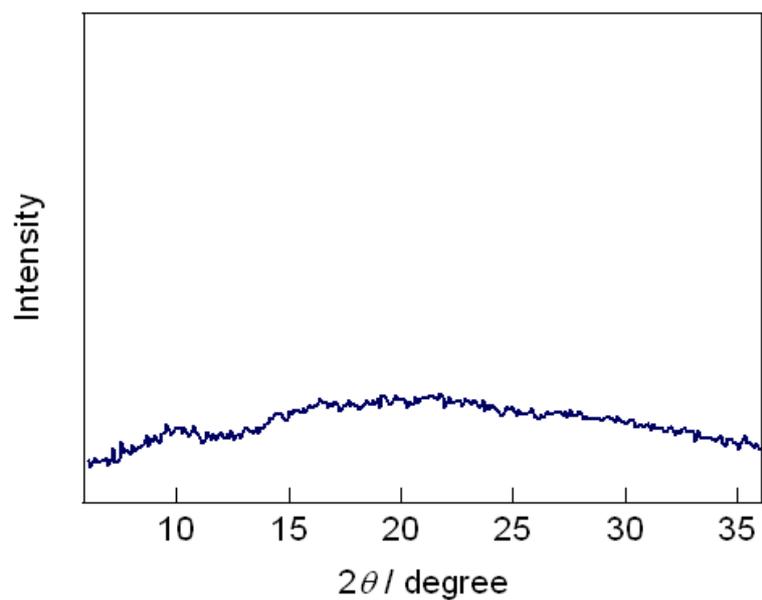


Figure S6. XRD pattern of the film spin-coated on a nickel plate from the chloroform solution of *pseudogem*-bisDPI[2.2]PC.

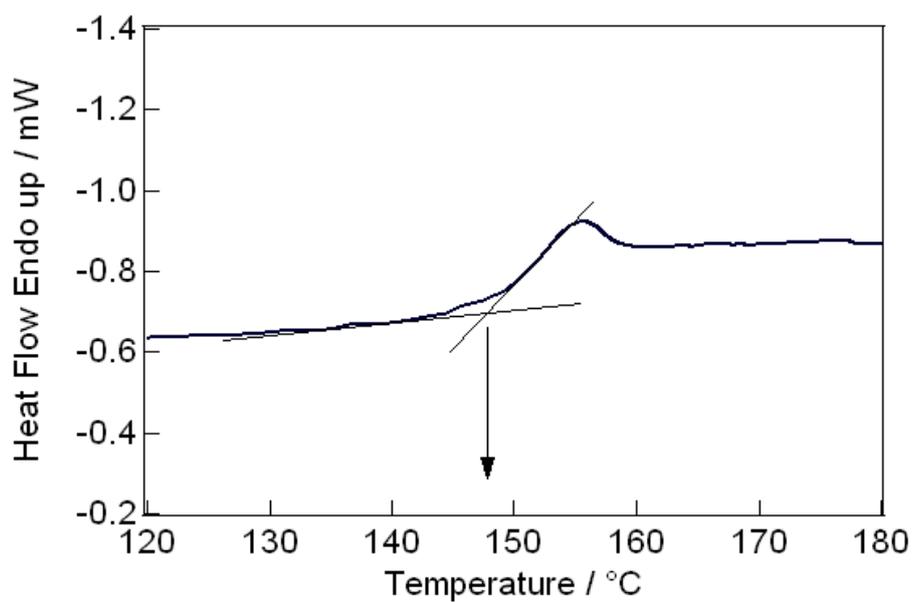


Figure S7. DSC profile of the spin-coated film with temperature scanning rate of 10 °C/min.

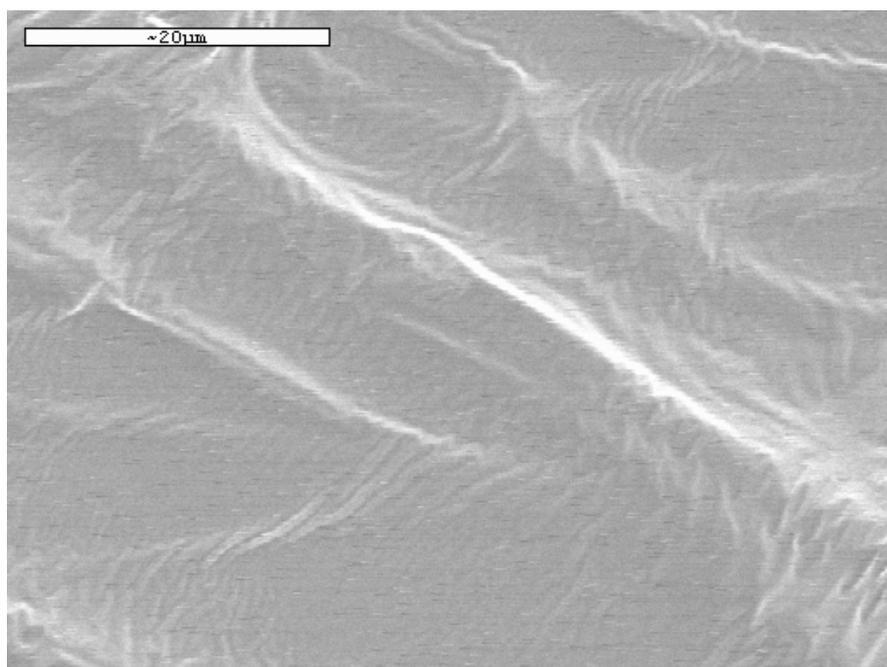


Figure S8. SEM image of the spin-coated film on a glass substrate.

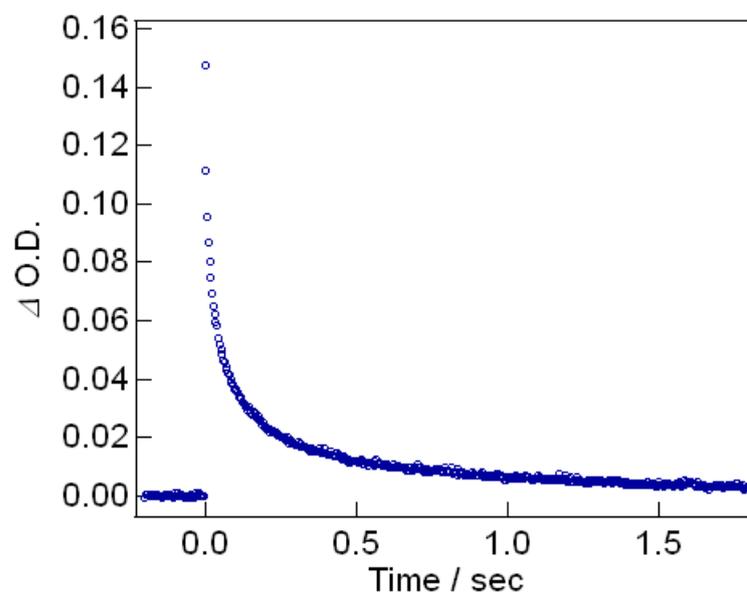


Figure S9. Decay profile of the colored species generated from *pseudogem*-bisDPI[2.2]PC, monitored at 400 nm in the amorphous film at 25 °C.

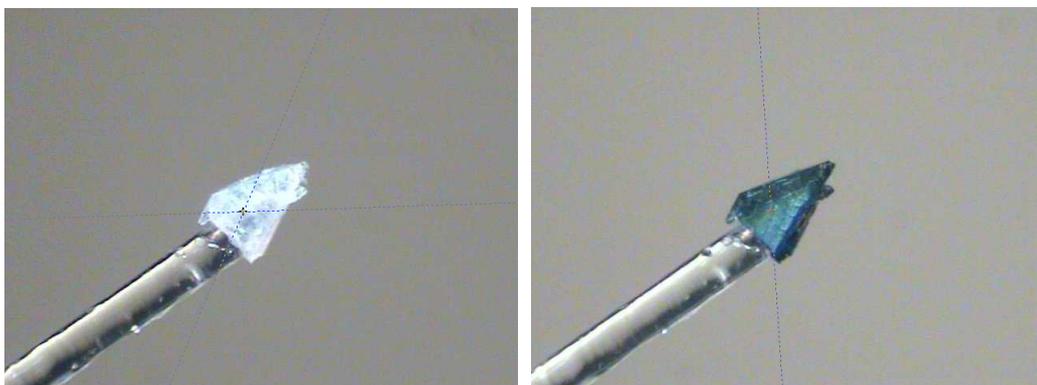


Figure S10. Photographs of the single crystal of *pseudogem*-bisDPI[2.2]PC (left) before light irradiation, and (right) after UV irradiation (365 nm) at 90 K.

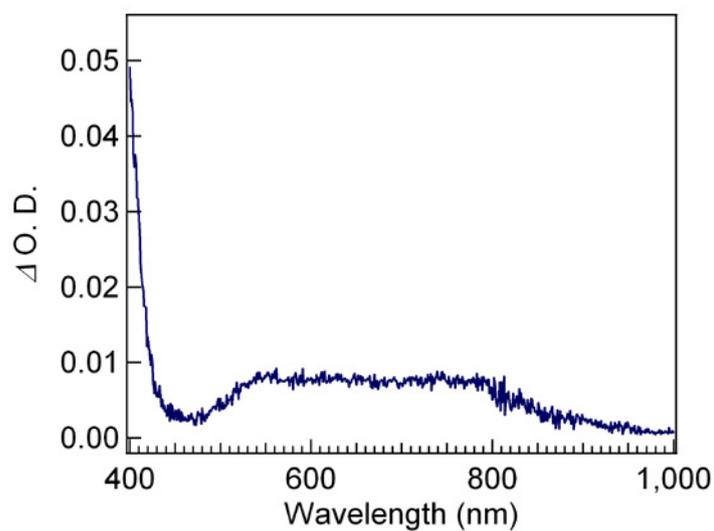


Figure S11. Transient vis-NIR absorption spectrum of the PMMA film doped with 20 wt% of *pseudogem*-bisDPI[2.2]PC measured at 25 °C with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5ns; power, 4 mJ/pulse).

Table S1. X-ray crystallographic data of *pseudogem*-bisDPI[2.2]PC.

Identification code	<i>pseudogem</i> -bisDPI[2.2]PC	
Empirical formula	C ₄₈ H ₃₇ N ₅	
Formula weight	683.83	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.620(4) Å	α = 90°.
	b = 13.468(3) Å	β = 113.326(3)°.
	c = 18.643(5) Å	γ = 90°.
Volume	3601.3(15) Å ³	
Z	4	
Density (calculated)	1.261 Mg/m ³	
Absorption coefficient	0.075 mm ⁻¹	
F(000)	1440	
Crystal size	0.30 x 0.23 x 0.21 mm ³	
Theta range for data collection	1.42 to 28.58°.	
Index ranges	-20 ≤ h ≤ 20, -17 ≤ k ≤ 15, -13 ≤ l ≤ 24	
Reflections collected	20143	
Independent reflections	8228 [R(int) = 0.0319]	
Completeness to theta = 27.92°	89.5 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9855 and 0.9794	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8228 / 0 / 479	
Goodness-of-fit on F ²	1.016	
Final R indices [I > 2σ(I)]	R1 = 0.0422, wR2 = 0.1056	
R indices (all data)	R1 = 0.0605, wR2 = 0.1125	
Largest diff. peak and hole	0.358 and -0.284 e.Å ⁻³	

Table S2. First-order rate constants for the thermal back-reaction of *pseudogem*-bisDPI[2.2]PC.

T / K	k / s^{-1}
278	3.5
283	5.5
288	8.5
293	13.3
298	20.6
303	32.1
308	47.4
313	69.7