

SUPPLEMENTARY INFORMATION

**Photosalient Effect and Photodimerization of Mono- and Dicationic
Organic Salts Incorporated in 4-Styrylpyridine**

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Reagents

All reagents and solvents were purchased from Tokyo Kasei Co. and Wako Pure Chemical Industries and used without further purification. Compounds **1** and **2** were prepared following the previous method, with minor modifications.[ref 8 in the main text]

Preparation of single crystal

(*E*)-1-benzyl-4-styrylpyridin-1-ium bromide ([*bsp*]Br) (**1**)

4-Styrylpyridine (1.0 mmol) and benzyl bromide (1.0 mmol) were dissolved in acetonitrile (100 mL) in an amber glass flask and stirred at 60 °C for 1 day. The resulting solution was then cooled to ambient temperature, forming colorless plate-like crystals. Yield, 0.27 g (97%).

1,1'-((2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene))bis(4-((*E*)-styryl)pyridin-1-ium) dibromide, ([*tpbmbsp*]Br₂) (**2**)

4-Styrylpyridine (1.0 mmol) and 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (0.50 mmol) were dissolved in acetonitrile (100 mL) in an amber glass flask and stirred at 70 °C for 1 day. After the solution was cooled to ambient temperature and left to stand for 1 week, pale-yellow block-like crystals were obtained. Yield, 0.18 g (70 %).

Anal. calc. for C₃₈H₄₄Br₂N₂O₃: C, 61.96; H, 6.02; N, 3.80%. Found: C, 62.03; H, 6.39; N, 3.50%.

1_UV

After exposing powder **1** to UV light for 4 hours, it was dissolved in a methanol solution with a drop of *c*-HBr and allowed to evaporate slowly to give block-like crystals suitable for single-crystal structural analysis.

2_UV

The photodimerized crystals **2_UV** were prepared and crystallized under natural light.

Physical measurements

¹H NMR spectra were measured using a JEOL400 MHz spectrometer in DMSO-*d*₆. Elemental analyses were performed on an Elementar Vario Micro Cube analyzer. Single-crystal X-ray diffraction data was collected with a XtaLAB Synergy Custom. The structures were solved by direct methods (SHELXT¹) and refined by full-matrix least-squares refinement using the SHELXL² program. Hydrogen atoms were refined geometrically using a riding model. □ In the crystallographic determination of compound **2**, it was impossible to determine satisfactory coordinates for the hydrogen atoms at water oxygen O2. Crystallographic data are summarized in Table S1. Powder X-ray diffraction data (PXRD) were collected on a RIGAKU RINT-UltimaIII (40 kV/40 mA) X-ray diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2 θ range of 2–30° with a step width of 1.0°. Electronic absorption spectra in the solid state were measured using a V650 spectrometer (JASCO). The photosalient of crystals were recorded using a SHODENSHA digital camera.

Supplementary data

Table S1. Crystallographic data

Compound	1	1_UV	2	2_UV
formula	C ₂₀ H ₁₈ Br ₁ N ₁	C ₄₀ H ₄₀ Br ₂ N ₂ O ₂	C ₃₈ H ₄₁ Br ₂ N ₂ O _{1.50}	C ₇₆ H ₇₆ Br ₄ N ₄
formula weight	352.26	740.56	709.55	1365.04
crystal system	triclinic	triclinic	triclinic	triclinic
space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> / Å	6.8963(2)	9.6895(3)	12.1902(4)	12.2770(5)
<i>b</i> / Å	10.2829(3)	9.7559(4)	15.9154(5)	16.0596(7)
<i>c</i> / Å	12.8595(4)	10.9467(3)	18.7119(7)	18.7305(15)
α / °	76.412(3)	97.487(3)	69.469(3)	68.905(6)
β / °	83.264(2)	105.034(3)	73.203(3)	71.723(6)
γ / °	70.536(3)	118.199(4)	89.616(3)	89.945(3)
<i>V</i> / Å ³	834.98(5)	840.99(6)	3236.5(2)	3245.5(4)
<i>Z</i>	2	1	4	2
<i>T</i> / K	120	120	120	120
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0371	0.0340	0.0615	0.1046
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0820	0.0724	0.1396	0.2462
<i>R</i> ₁ (all data)	0.0484	0.0415	0.0960	0.1792
<i>wR</i> ₂ (all data)	0.0852	0.0747	0.1577	0.2908
G.O.F.	1.192	1.055	1.044	1.026
CCDC	2358683	2358684	2358685	2358686

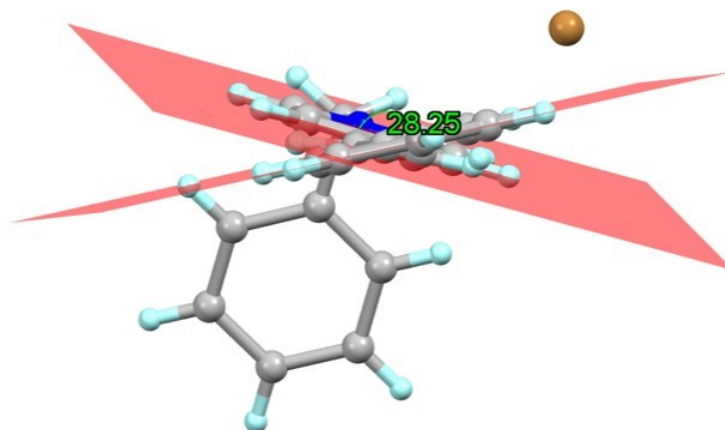


Fig. S1 Dihedral angle of **1** between pyridinium and the benzene in the 4spy moiety.

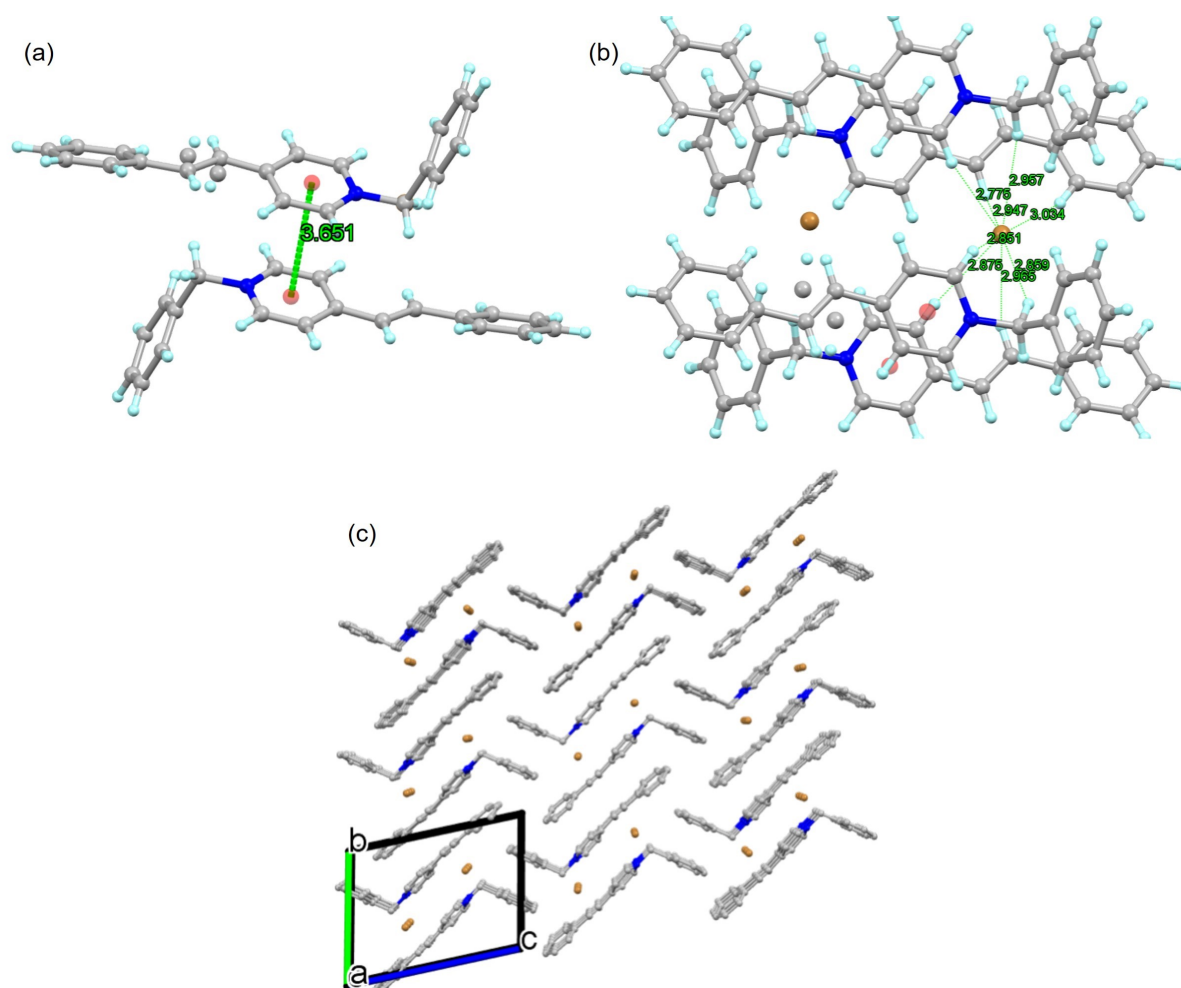


Fig. S2 (a) π --- π interactions between pyridinium rings in crystal **1**. (b) Intermolecular interactions around a bromide ion in crystal **1**. (c) Packing structure of crystal **1** viewed down a -axis.

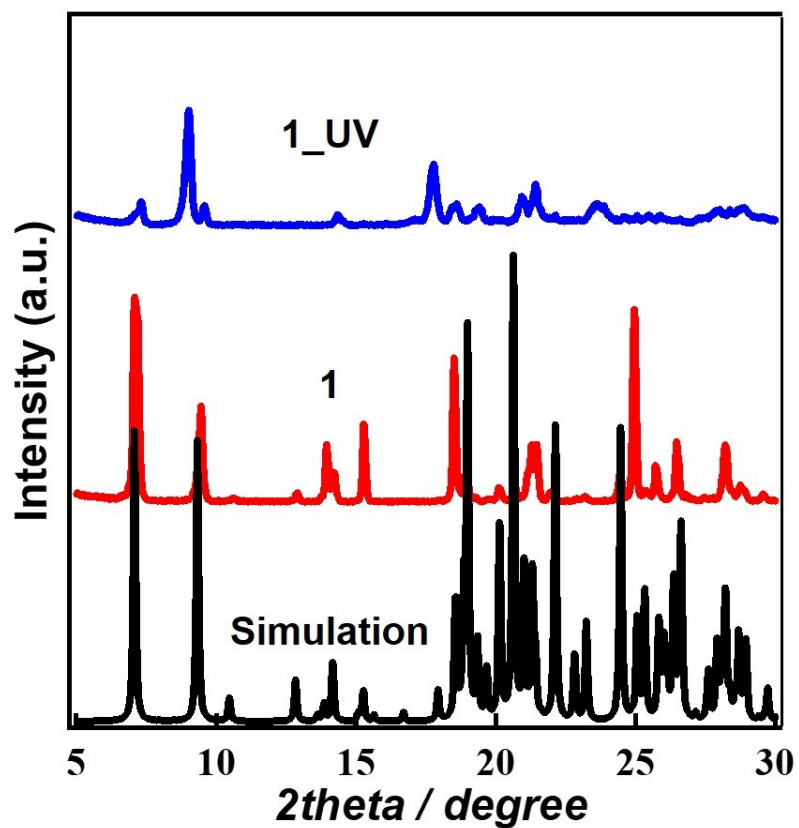


Fig. S3 Powder X-ray diffraction pattern of compound 1.

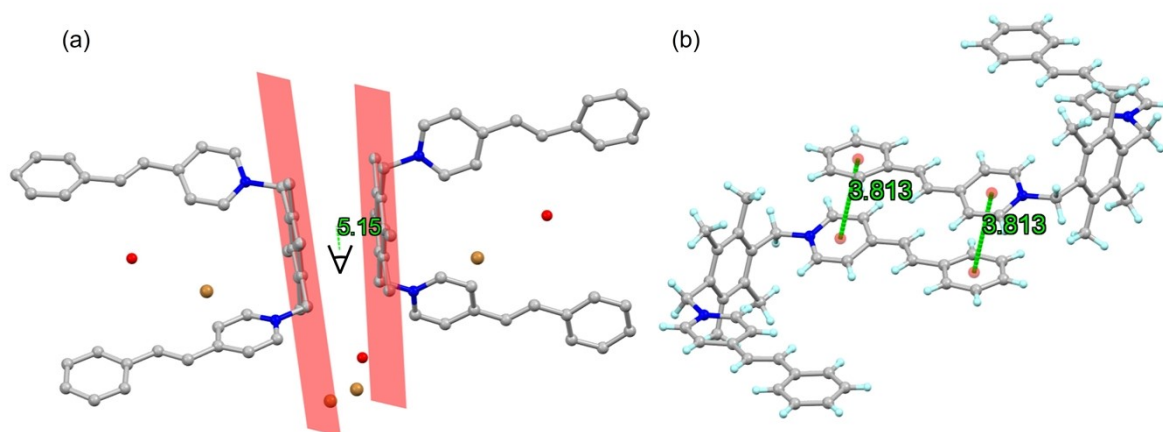


Fig. S4 Crystal structure of 2. (a) The durenium moieties have slightly oblique π --- π interactions with a dihedral angle of 5.15° to the adjacent ones. (b) The styrylpyridinium moieties are stacked head-to-tail with the adjacent ones, resulting in π --- π interactions between pyridinium and benzene.

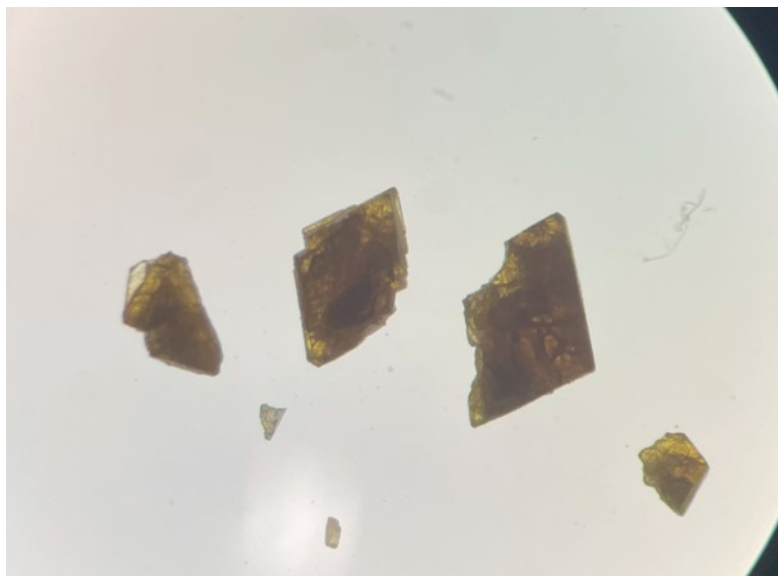


Fig. S5 Crystal image of **2** under microscope.

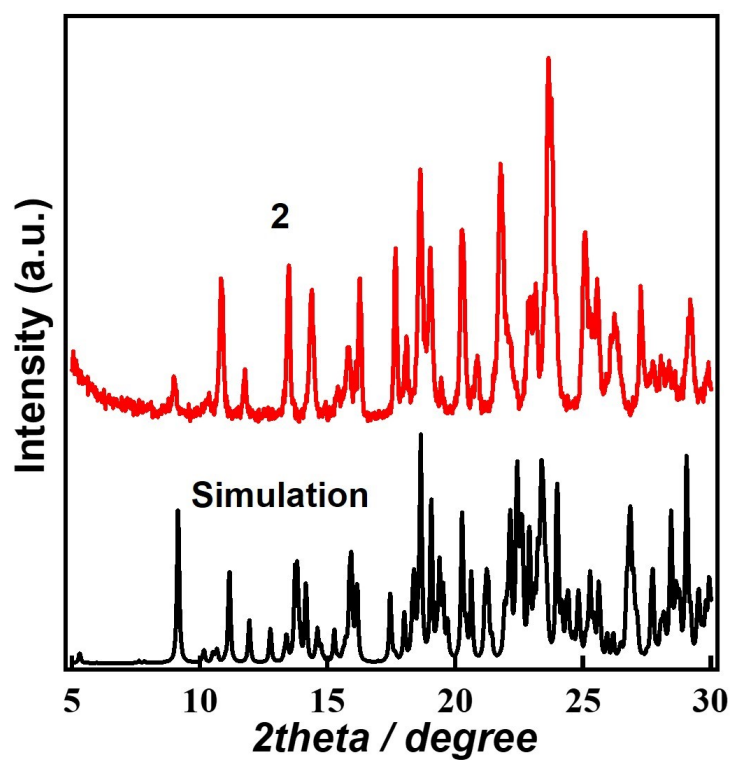


Fig. S6 Powder X-ray diffraction pattern of compound **2**.

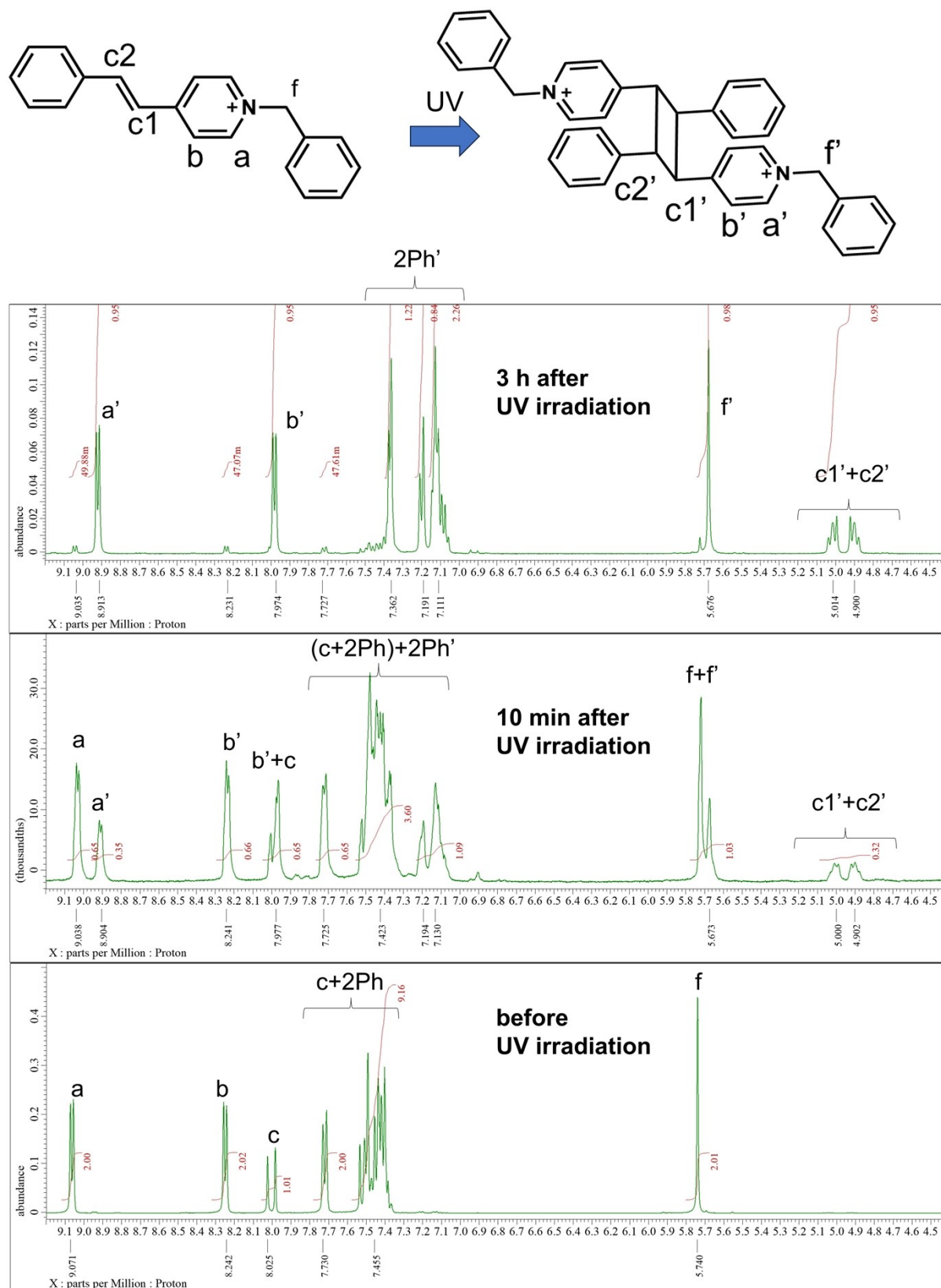


Fig. S7 ^1H NMR spectra of **1** before and after exposure to UV light for 10 min and 180 minutes.

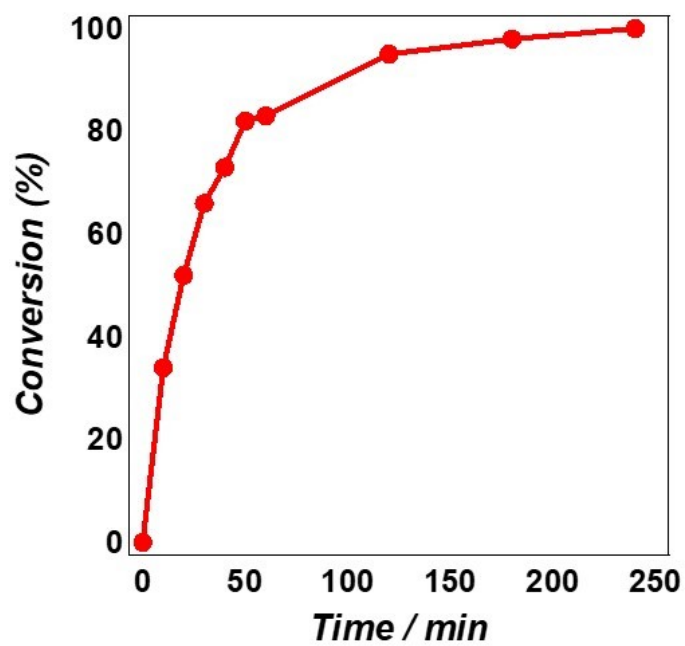


Fig. S8 Percentage of time-dependent photodimerization conversion under UV light exposure for **1**.

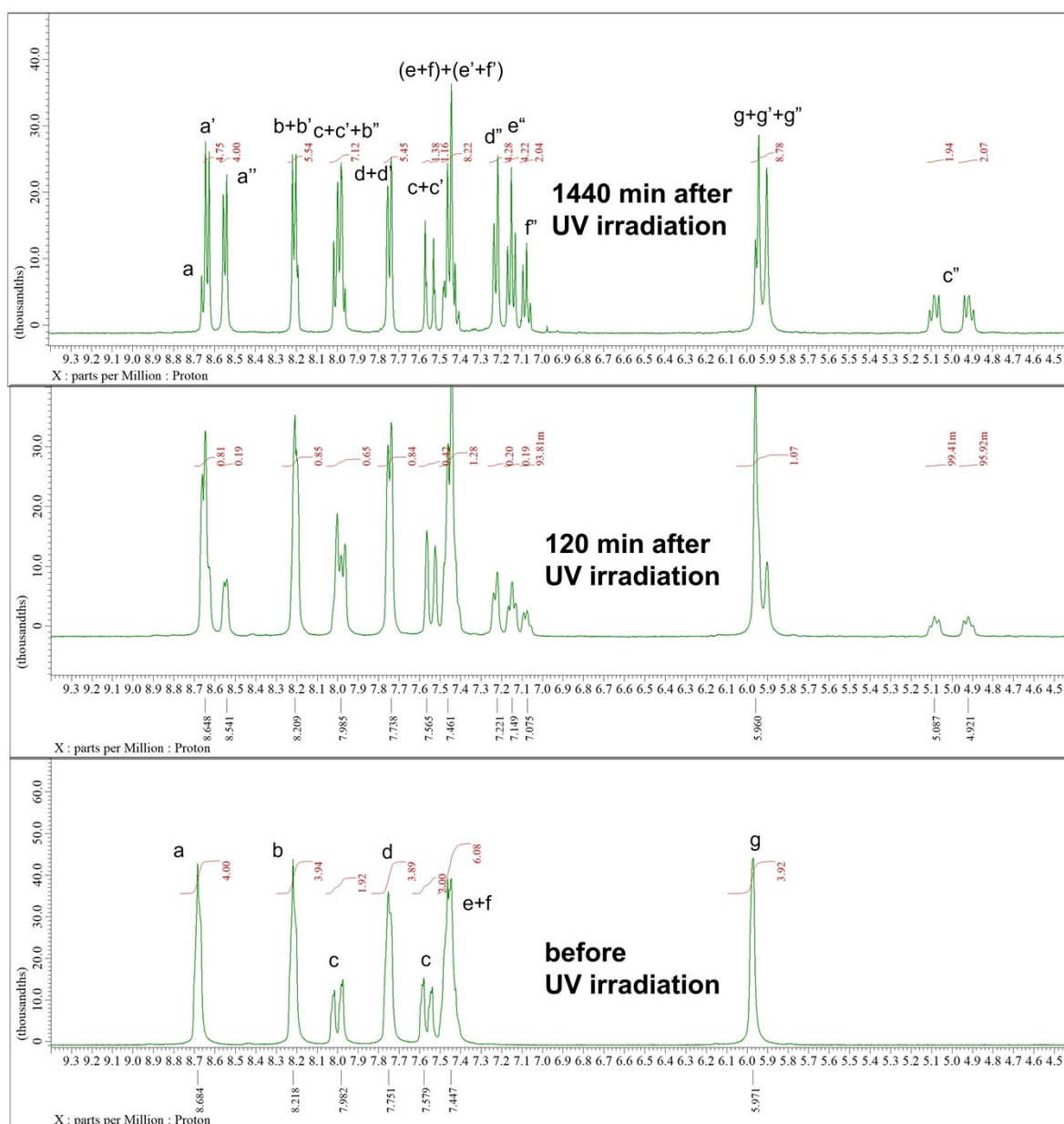
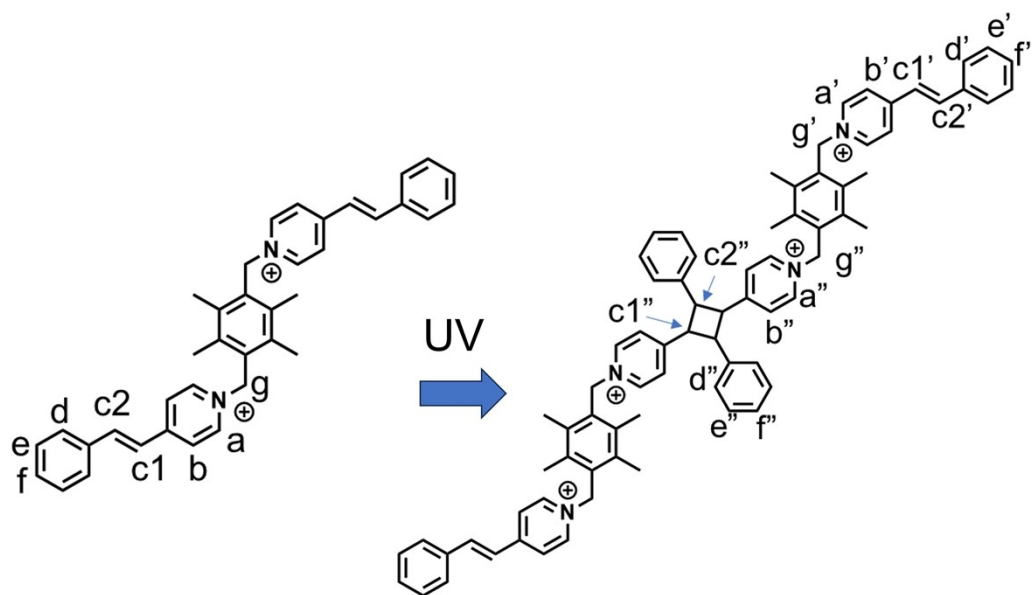


Fig. S9 ^1H NMR spectra of **2** before and after exposure to UV light for 120 and 1440 minutes.

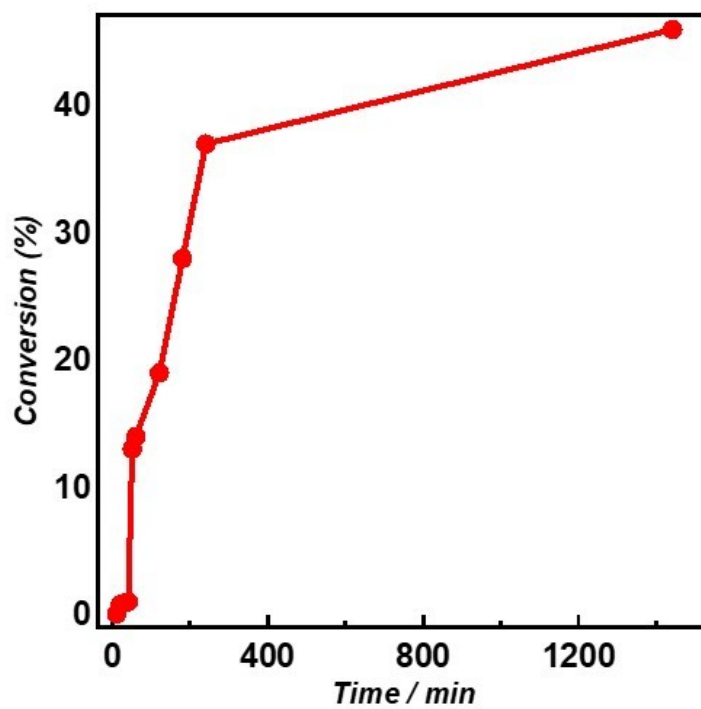


Fig. S10 Percentage of time-dependent photodimerization conversion of olefin under UV light exposure for **2**.

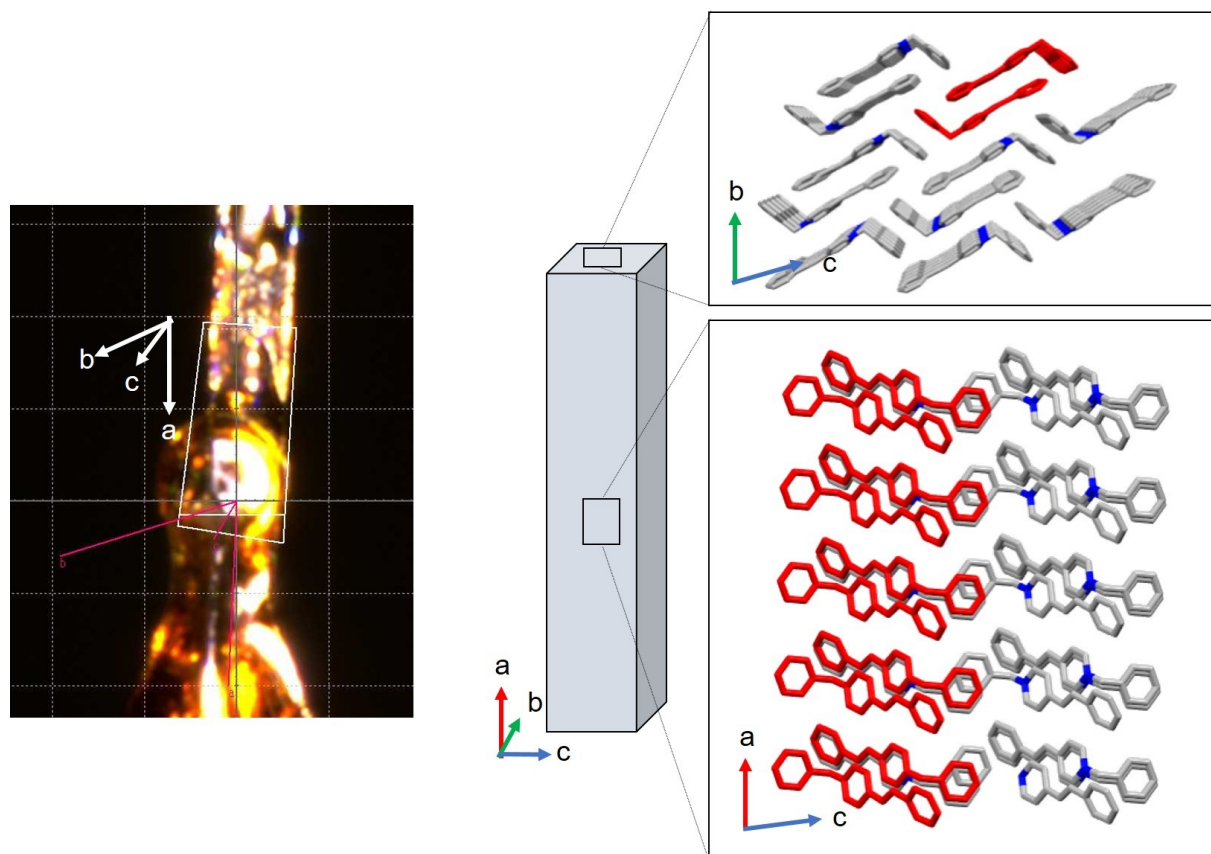


Fig. S11 Face index of **1** and its corresponding integrated structure. Bromide ions are omitted for clarity.

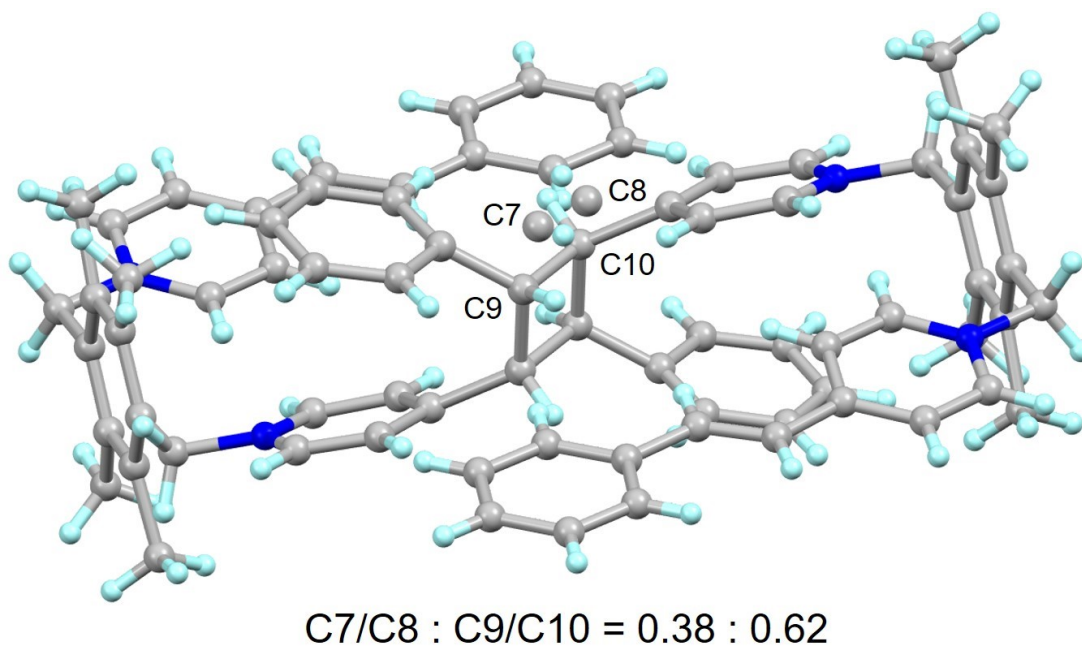


Fig. S12 Disordered bonds of **2_UV** between C7/C8 and C9/C10 and their ratios. C7/C8 indicates unreacted C=C bonds.

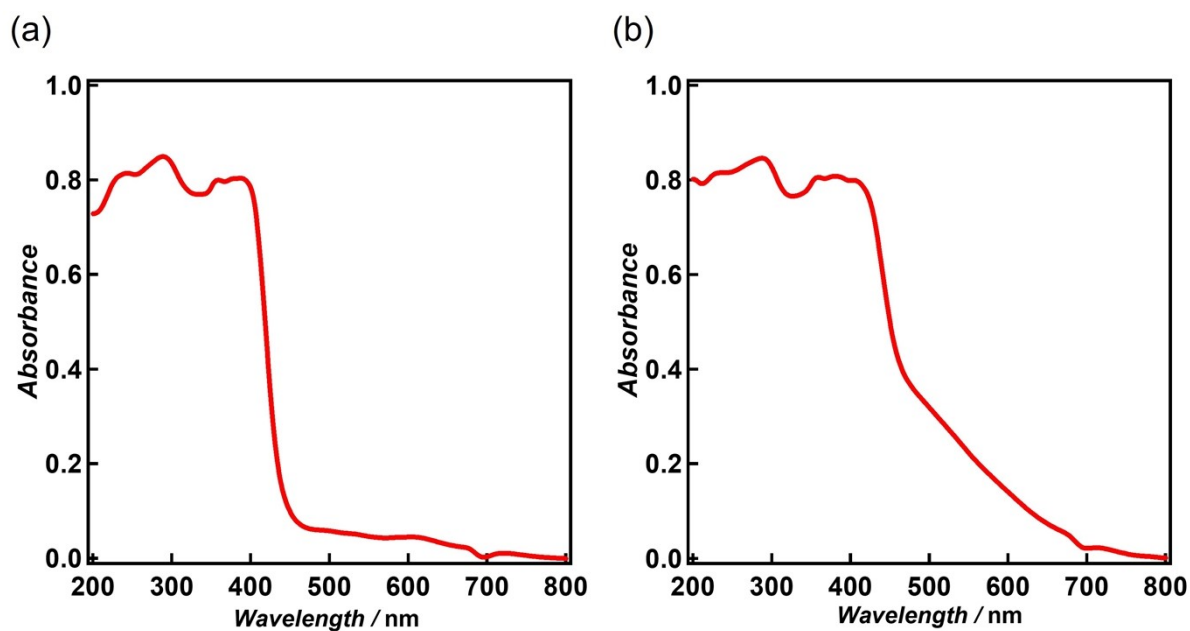


Fig. S13 UV spectra in the solid state for compounds **1** (a) and **2** (b)

References

1. G. M. Sheldrick, SHELXT – Integrated Space-Group and Crystal-Structure Determination, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3–8.
2. G. M. Sheldrick, Crystal Structure Refinement with SHELXL. *Acta Crystallogr Sect. C* 2015, **71**, 3–8.