Supplementary Information

Photosalient [2+2] Photodimerization in Metal Chloride-Templated Organic Crystals

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Experimental

Materials and Instruments.

All chemicals and solvents used in the preparation were obtained from Tokyo Kasei Co. and Wako Pure Chemical Industries, Ltd. and were used without further purification.

Preparation of Ebpe_In, Ebpe_Bi, Ebpe_Sb, Ebpe_Sn and Ebpe_In_UV

Ebpe_In

1,2-Di(4-pyridyl)ethylene (0.018 g, 0.1 mmol) and indium oxide (0.056g, 0.2 mmol) were placed in separate 100 mL beakers, each containing 20 mL of 12 M hydrochloric acid. The mixtures were heated and stirred at 100 ℃ until dissolved. The solutions were then combined in a 100 mL beaker and stirred for an additional 20 minutes. After standing for one week, the resulting colorless crystal was collected by suction filtration. (yield: 48%, 0.027 g). Calcd for $[H_2Ebpe][InCl_5(H_2O)]\cdot 3H_2O$, C, 26.28; H, 3.68; N, 5.11. Found C, 26.2; H, 2.90; N, 4.58%.

Ebpe_Bi

Replacing the metal source with bismuth oxide (Bi_2O_3) and following the same procedure as for Ebpe_In, colorless crystals were obtained. (0.021 g, yield: 19%). Calcd for $[H_2Ebpe]_2[Bi_2Cl_{10}]$ C, 25.27; H, 2.12; N, 4.91. Found C, 25.06; H, 2.19; N, 4.43%.

Ebpe_Sb

Replacing the metal source with antimony oxide (Sb_2O_3) and following the same procedure as for Ebpe_In, yellow crystals were obtained. (0.03 g, yield: 57%). Calcd for $[H_2Ebpe][SbCl_5]$ C, 29.83; H, 2.50; N, 5.80. Found C, 29.52; H, 2.60; N, 5.42%.

Ebpe_Sn

Replacing the metal source with tin(II) chloride ($SnCl_2$) and following the same procedure as for Ebpe_In, colorless crystals were obtained. (0.033 g, yield: 61%). Calcd for $[H_2Ebpe][SbCl_5]$ C, 27.95; H, 2.35; N, 5.43. Found C, 27.47; H, 2.41; N, 4.92%.

Ebpe_In_UV

After UV irradiation (25 mW/cm²) of **Ebpe_In** powder for 3 hours, the sample was dissolved in 20 mL of water, followed by the addition of a drop of 12 M hydrochloric acid. After standing for one month, transparent block-shaped crystals were obtained. Due to the limited amount of crystals obtained, no further characterization beyond single-crystal X-ray analysis was performed.

Physical measurements

Single-crystal X-ray diffraction data were collected using an XtaLAB Synergy instrument. The structures were determined through direct methods with SHELXT[1] and refined using the SHELXL program, employing full-matrix least-squares refinement.[2] Hydrogen atoms were refined geometrically with a riding model. Detailed crystallographic data are summarized in Table S1. Elemental analyses were conducted using an Elementar Vario Micro Cube analyzer. PXRD data were obtained on a RIGAKU RINT-Ultima III X-ray diffractometer (40 kV/40 mA) using Cu Kα radiation (λ = 1.5406 Å) across a 2ϑ range of 2–30°, with a step width of 1.0°.

Supplementary data

Table S1. Crystallographic data.

Compound	**Ebpe_In**	**Ebpe_Bi**	**Ebpe_Sb**	**Ebpe_Sn**	**Ebpe_In_UV**
formula	$C_{12}H_{16}Cl_5InN_2O_2$	$C_{24}H_{24}Bi_2Cl_{10}N_4$	$C_{96}H_{100}Cl_{40}N_{16}OSb_8$	$C_{12}H_{12}Cl_6N_2Sn$	$C_{24}H_{32}Cl_7InN_4O_4$
formula weight	512.354	1140.971	3886.151	515.668	803.532
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	tetragonal
space group	*C2/c*	*C2/c*	$C222_1$	*I2/a*	*P 4/n*
a / Å	18.6884(5)	18.4183(11)	11.2944(5)	7.1093(3)	13.3333(5)
b / Å	13.4365(4)	12.9016(8)	37.3407(14)	14.9953(5)	13.3333(5)
c / Å	14.1149(4)	13.7365(9)	15.8762(7)	32.2219(13)	8.8676(6)
α / º	90	90	90	90	90
β / º	95.665(3)	93.937(5)	90	91.529(3)	90
γ / º	90	90	90	90	90
V / Å^3	3527.04(17)	3256.4(4)	6695.6(5)	3433.8(2)	1576.45(14)
Z	8	4	2	8	2
T / K	120	120	120	120	120
R_1 [I > 2σ(I)]	0.0169	0.0210	0.0204	0.0357	0.0268
wR_2 [I > 2σ(I)]	0.0412	0.0503	0.0486	0.0656	0.0736
R_1 (all data)	0.0183	0.0234	0.0212	0.0459	0.0283
wR_2 (all data)	0.0418	0.0512	0.0490	0.0679	0.0743
G.O.F.	1.0446	1.0455	1.0347	1.0602	1.0207
CCDC	2425108	2425110	2425111	2425112	2425113

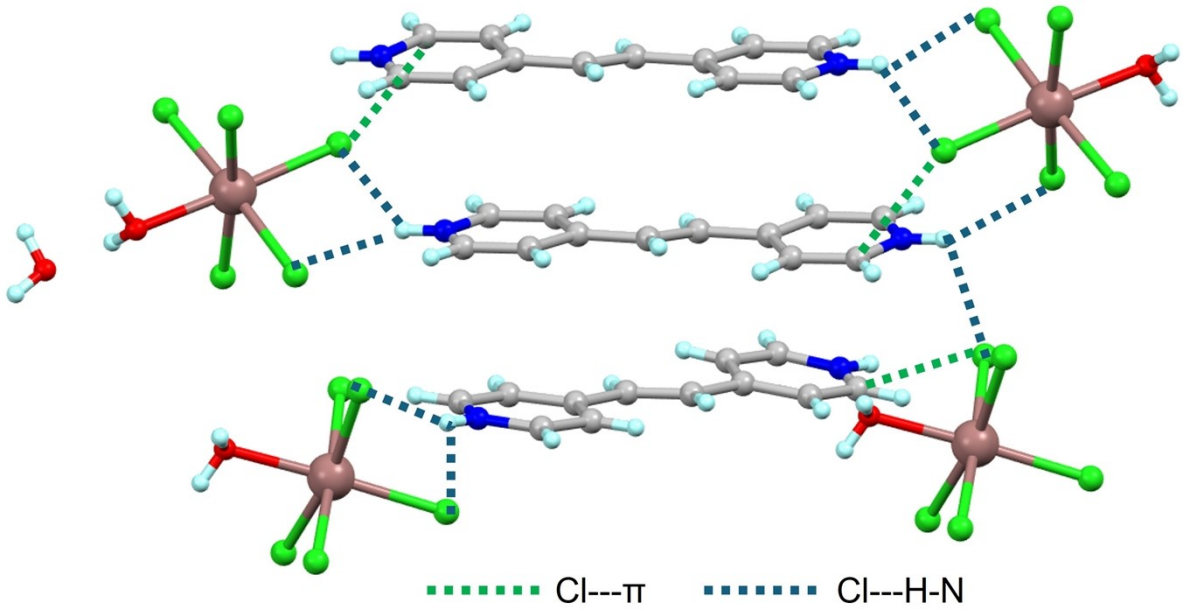

Fig. S1 Intermolecular interactions around $[H_2\mathbf{Ebpe}]^{2+}$ in **Ebpe_In**.

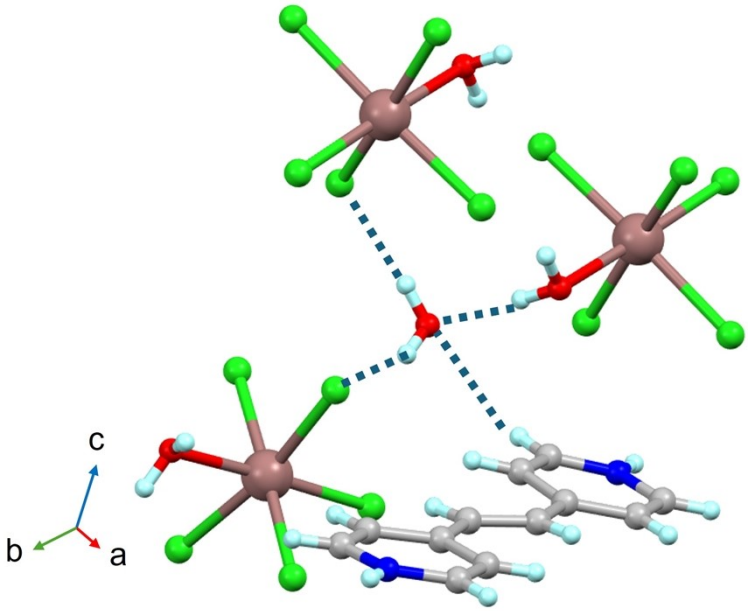

Fig. S2 (a) Intermolecular interactions around a water molecule.

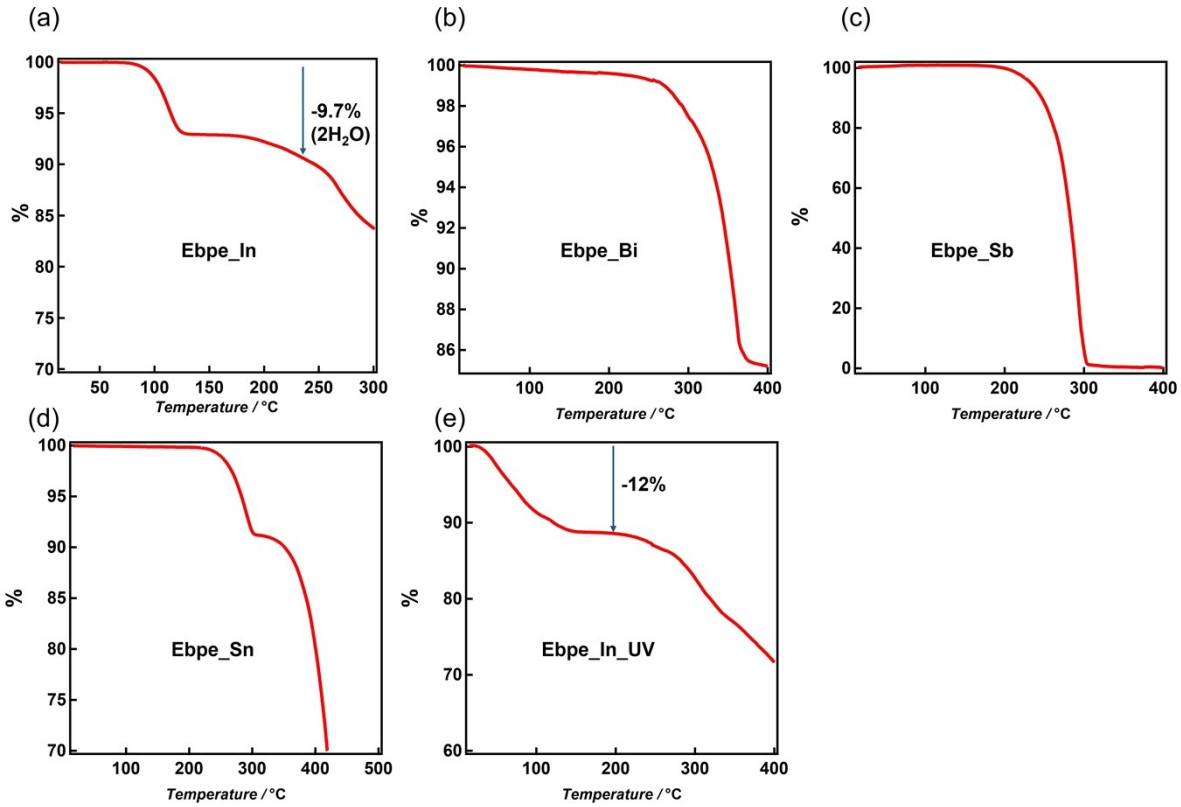

Fig. S3 (a) Thermogravimetric analysis (TGA) of Ebpe shows a 9.7% weight loss, corresponding to two water molecules, as confirmed by single-crystal structural analysis. (b–d) TGA profiles for **Ebpe_Bi**, **Ebpe_Sb**, and **Ebpe_Sn**, respectively. (e) TGA results for **Ebpe_In_UV** indicate a 12% weight loss attributed to five water molecules believed to be adsorbed from ambient moisture.

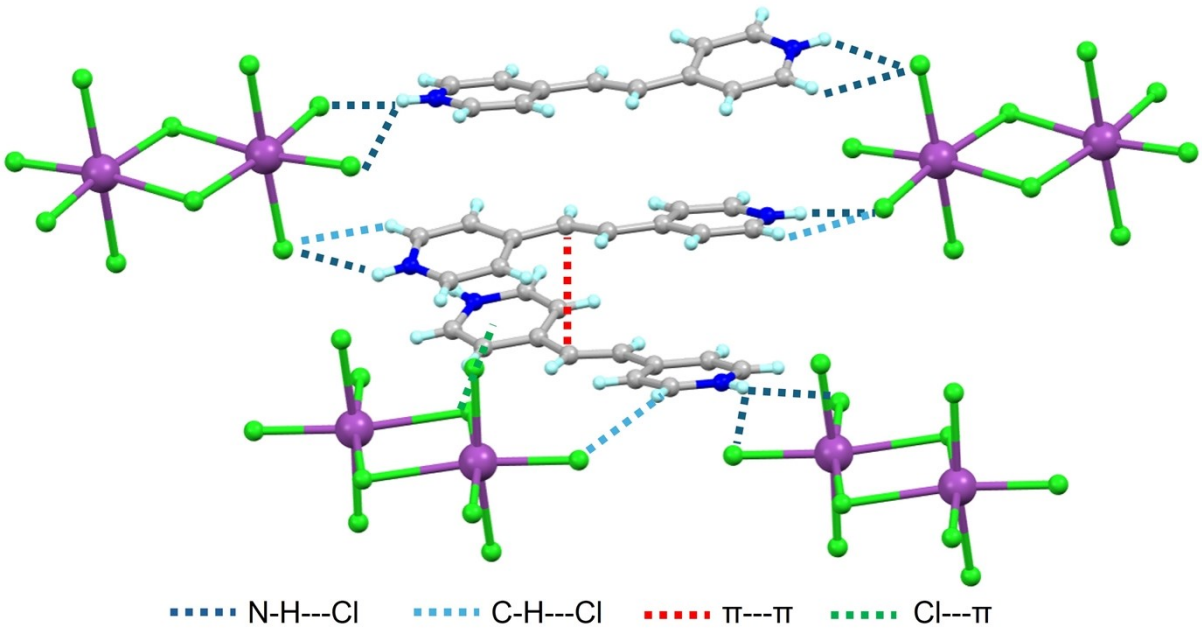

Fig. S4 Intermolecular interactions around $[H_2\mathbf{Ebpe}]^{2+}$ in **Ebpe_Bi**.

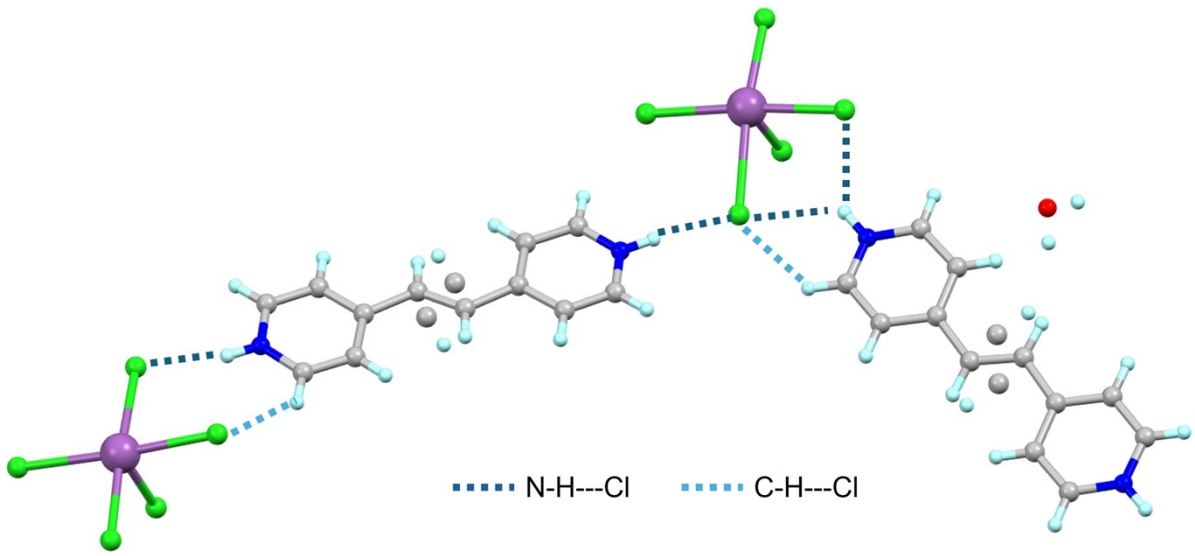

Fig. S5 Intermolecular interactions around $[H_2\mathbf{Ebpe}]^{2+}$ in **Ebpe_Sb**.

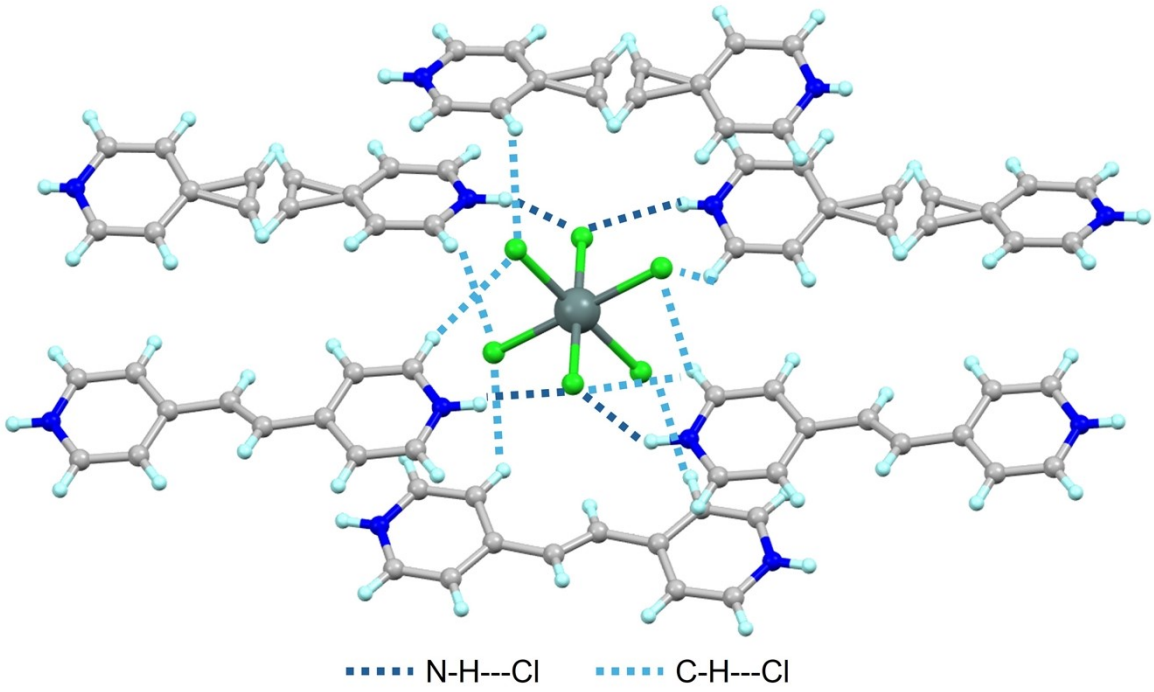

Fig. S6 Intermolecular interactions around $[SnCl_6]^{2-}$ in **Ebpe_Sn**.

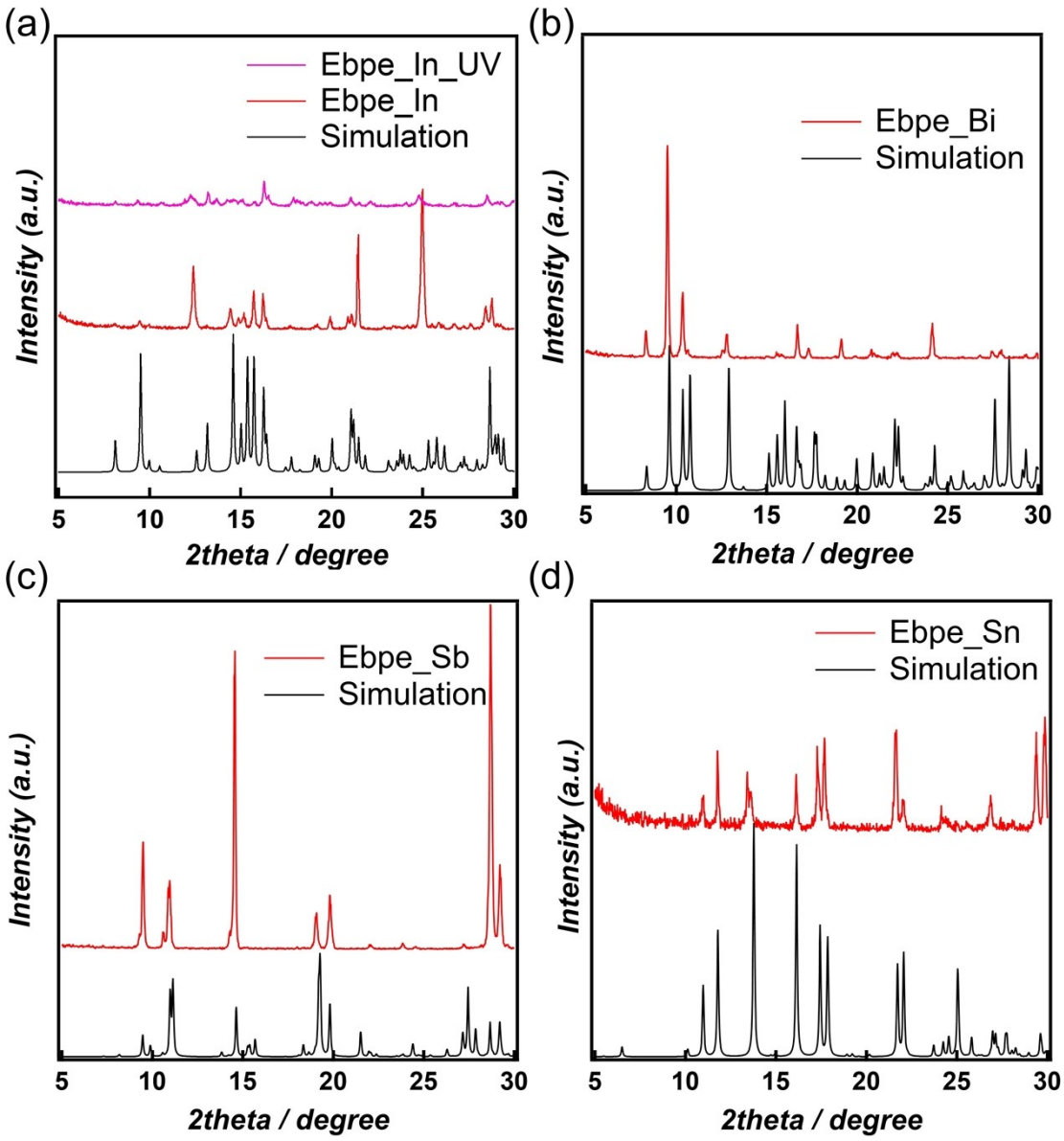

Fig. S7 Experimental and simulated PXRD patterns of **Ebpe_In** (a), **Ebpe_Bi** (b), **Ebpe_Sb** (c), and **Ebpe_Sn** (d).

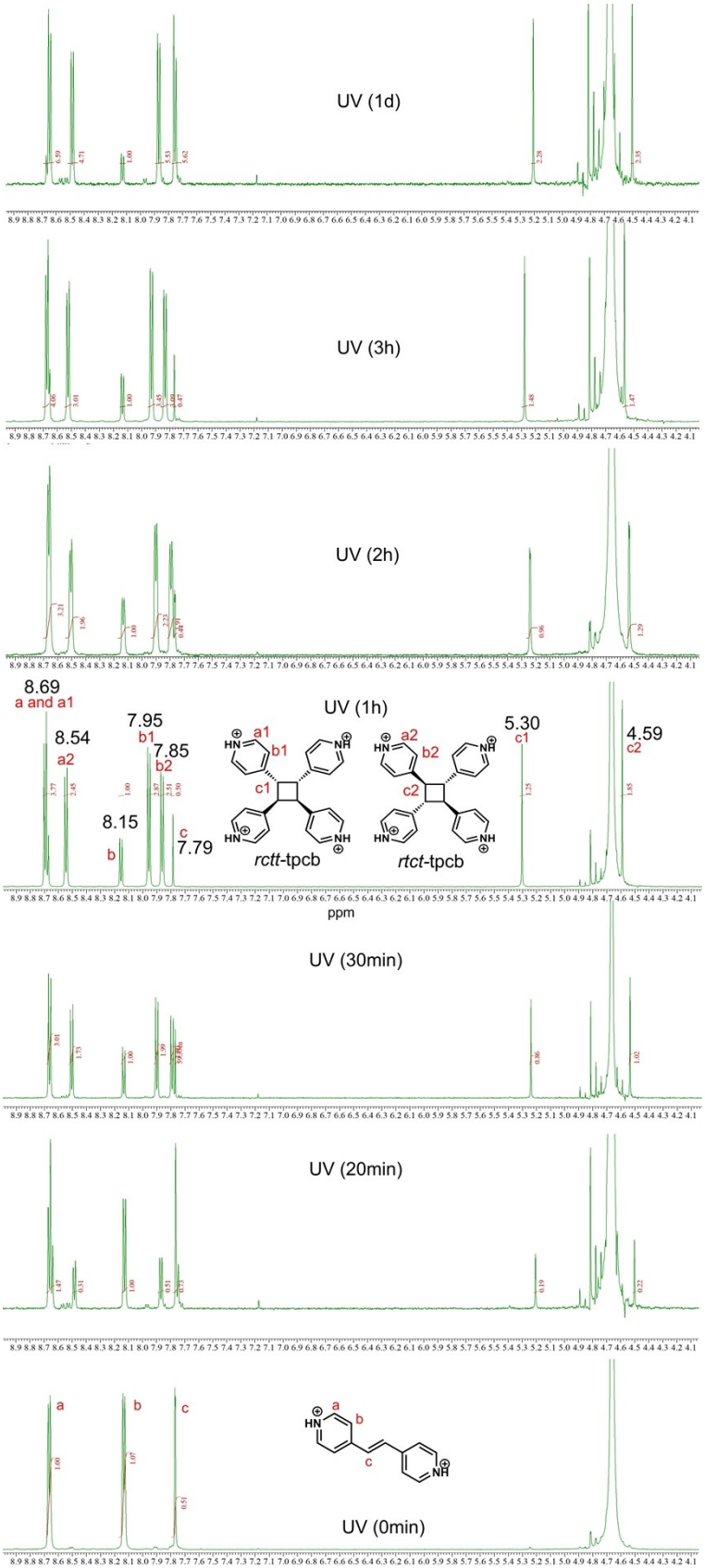

Fig. S8 Time-dependent ^{1}H NMR spectra with integration values of **Ebpe_In** crystalline powder irradiated with UV light for 0, 20, 30, 60, 120, 180, and 1440 minutes (measured in D_2O).

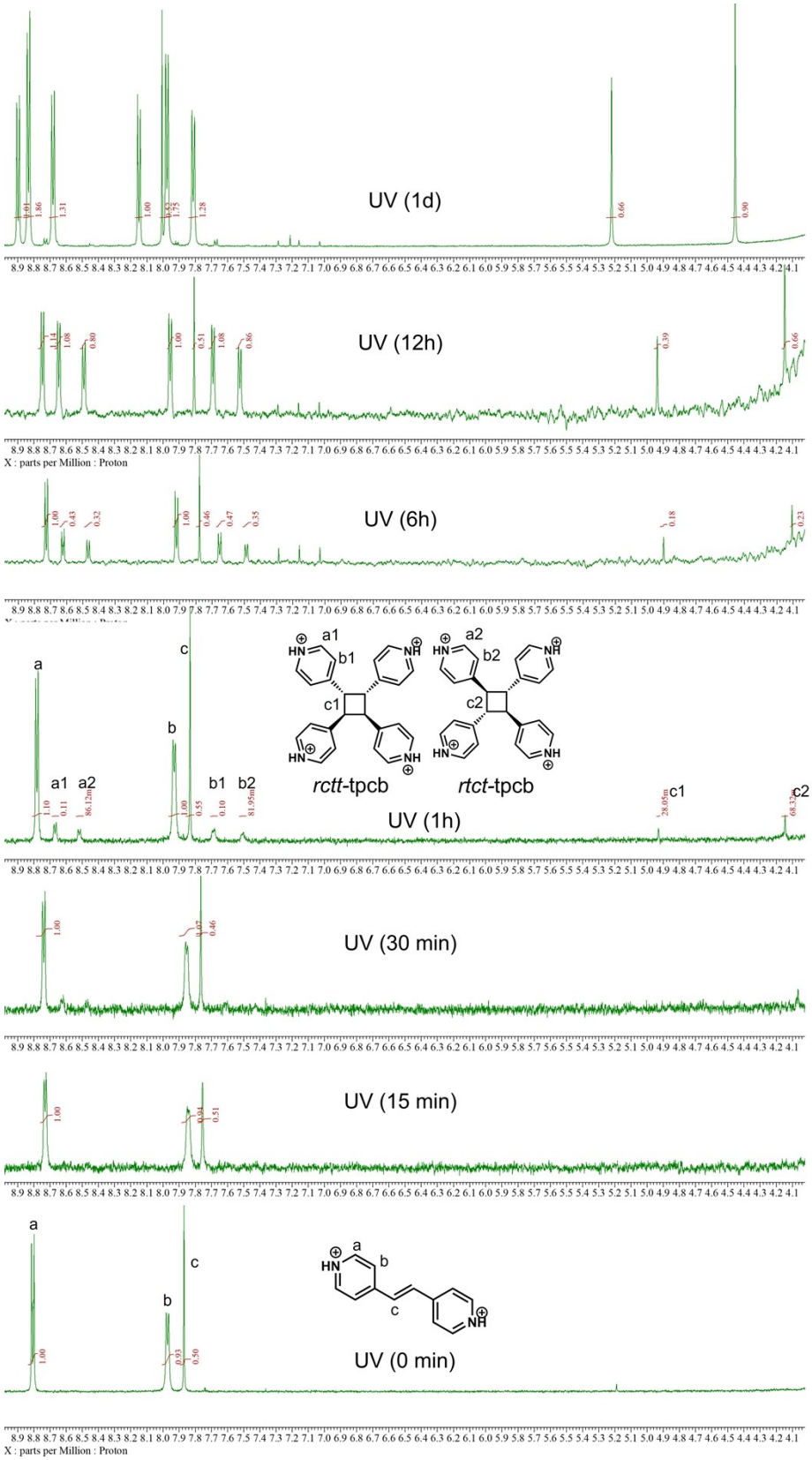

Fig. S9 Time-dependent ^{1}H NMR spectra with integration values of **Ebpe_In** crystalline powder irradiated with UV light for 0, 15, 30, 60, 360, 720, and 1440 minutes (measured in DMSO-d_6).

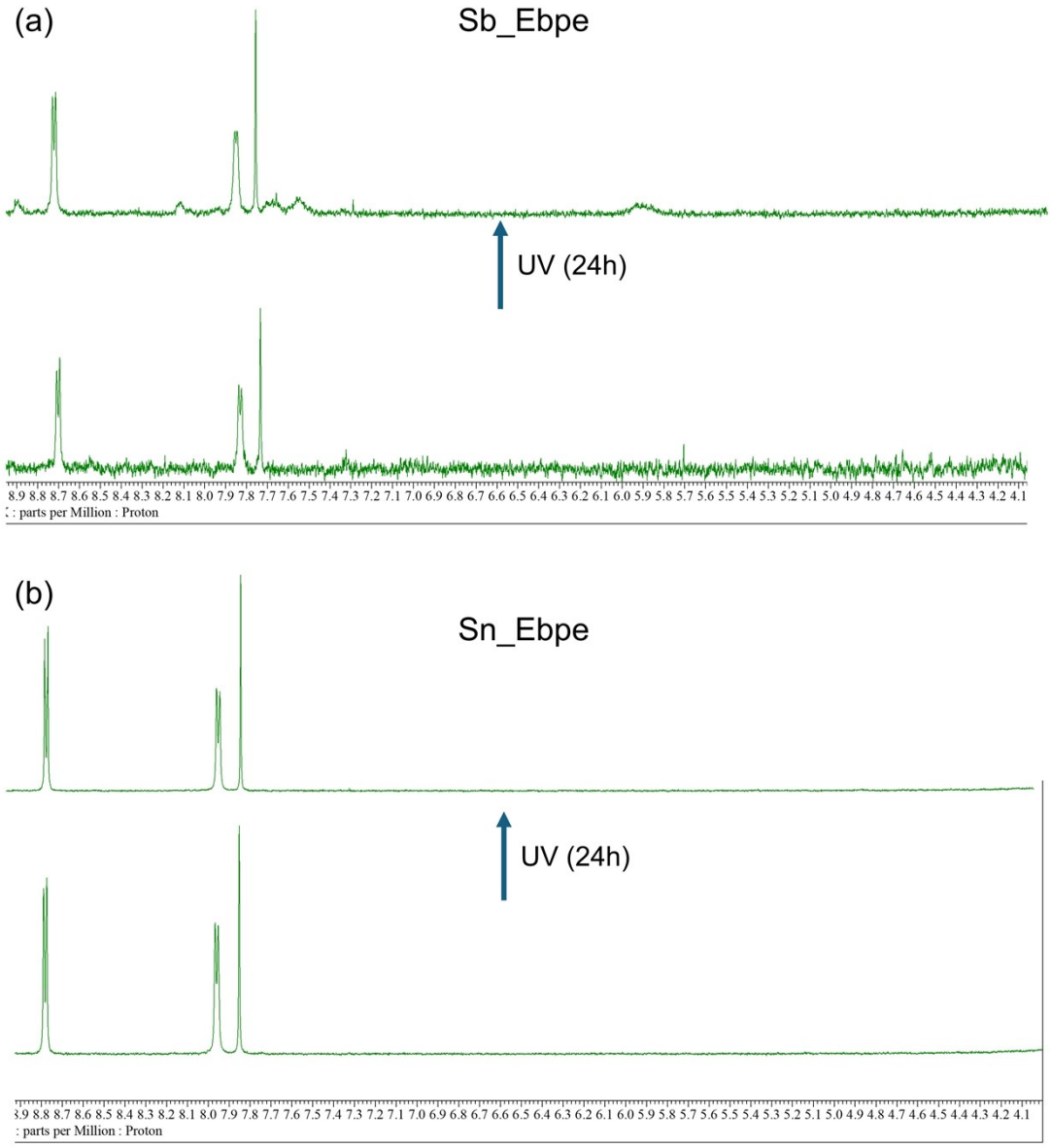

Fig. S10 ^{1}H NMR spectra of **Sb_Ebpe** (a) and **Sn_Ebpe** (b) before and after UV irradiation (24 h) (measured in DMSO-d_6).

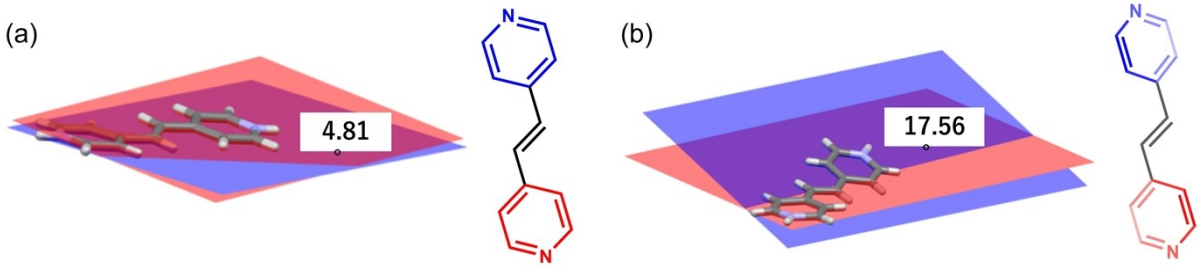

Fig. S11 Dihedral angle between pyridine rings in (a) **Ebpe_In** and (b) **Ebpe_Bi**.

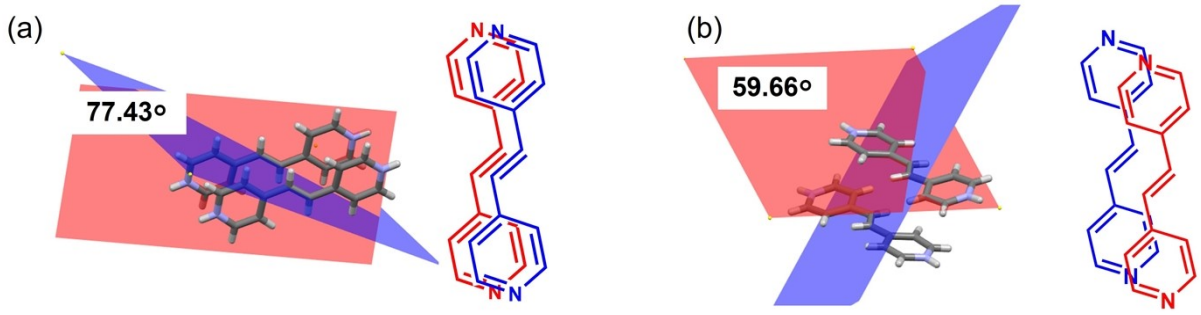

Fig. S12 Dihedral angle between the plane containing C–C=C–C and the plane containing the C=C bonds of two molecules in **Ebpe_In** (a) and **Ebpe_Bi** (b).

References

1. G. M. Sheldrick, *Acta Crystallogr, Sect. A* 2015, 71, 3–8.
2. G. M. Sheldrick, *Acta Crystallogr Sect. C* 2015, 71, 3–8.