

SUPPLEMENTARY INFORMATION

Photosalient ionic cocrystal composed of trimesic acid and 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.

Preparation

4-Styrylpyridine was prepared according to the reported procedure^[S11] and was characterized by a ¹H NMR spectrum using JEOL 400 MHz spectrometer in DMSO-d₆.

Trimesic acid and 4-styrylpyridine were dissolved in a mixed solvent of methanol/chloroform at a mole ratio of 1:2, of which mixture was slowly evaporated at ambient temperature to give colorless plate-like crystals.

Physical measurements

Single-crystal X-ray diffraction data for **1** was collected with a Rigaku Saturn 70. The structures were solved by direct methods (SHELXT^{S12}) and refined by full-matrix least-squares refinement using the SHELXL^{S13} program. Hydrogen atoms were refined geometrically using a riding model. 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 2θ range of 2–30° with a step width of 1.0°. Luminescence spectra of powder samples were recorded on a SHIMADZU RF-5300PC spectrofluorophotometer. The movie 2 is long and has been trimmed.

Refinement and disorder treatment

The molecule **1** is disordered over two orientations and the refinement was constrained to sum to unity. The disorder components C28 and C29 in the entire molecule were located from the difference map, of which occupancy were refined to 0.701 / 0.299.

Supplementary data

Table S1. Crystallographic data of **1**.

Compound	1
formula	C ₉ H ₅ O ₆ , C ₁₃ H ₁₂ N, C ₁₃ H ₁₁ N
formula weight	572.59
crystal system	Monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	8.6213(5)
<i>b</i> / Å	36.7554(16)
<i>c</i> / Å	9.9466(6)
α / °	90
β / °	113.343(7)
γ / °	90
<i>V</i> / Å ³	2893.9(3)
<i>Z</i>	4
<i>T</i> / K	293
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0633
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1399
<i>R</i> ₁ (all data)	0.0989
<i>wR</i> ₂ (all data)	0.1597
G.O.F.	1.075
CCDC	2222089

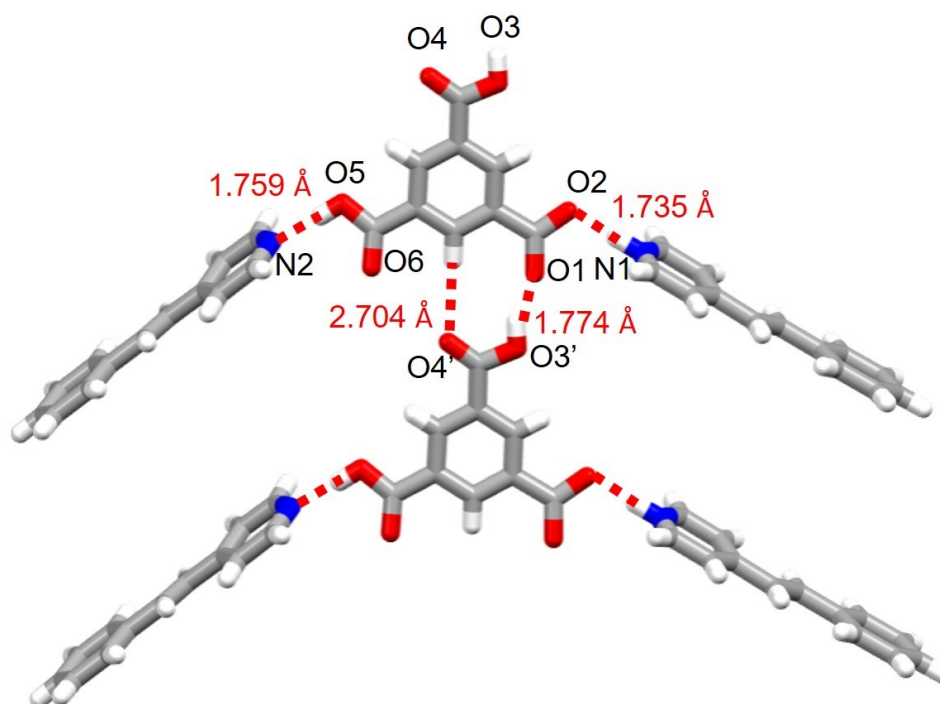


Fig. S1 Intermolecular interactions and distances around H_2tma^- .

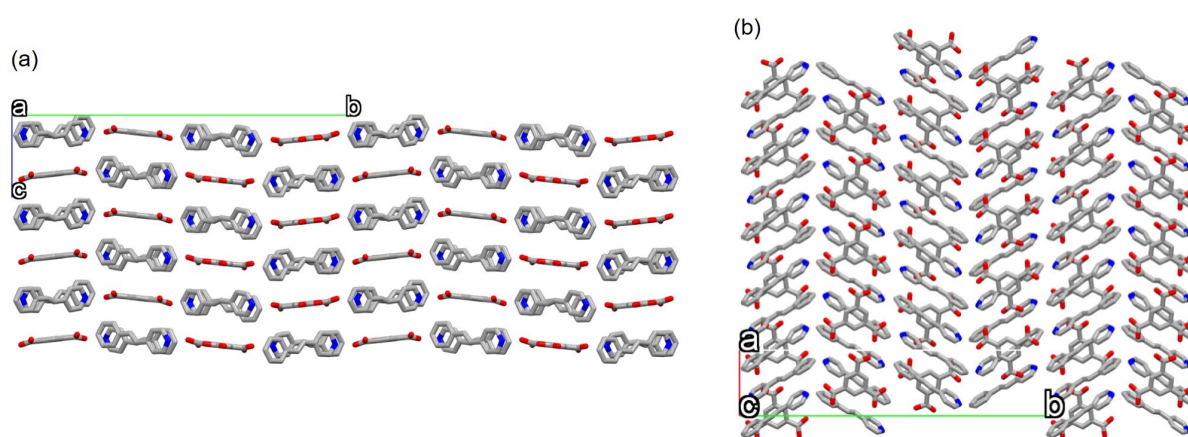


Fig. S2 Packing structures viewed down a -axis (a) and c -axis (b).

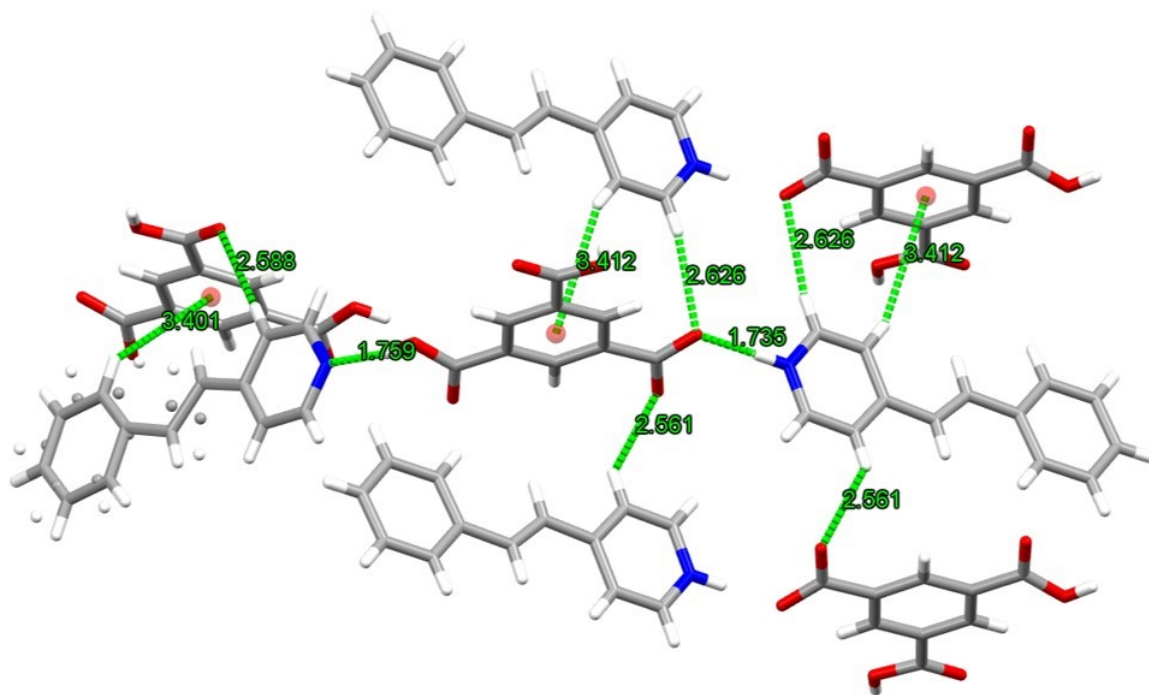


Fig. S3 Various intermolecular interactions around 4-spyH⁺ and 4-spy.

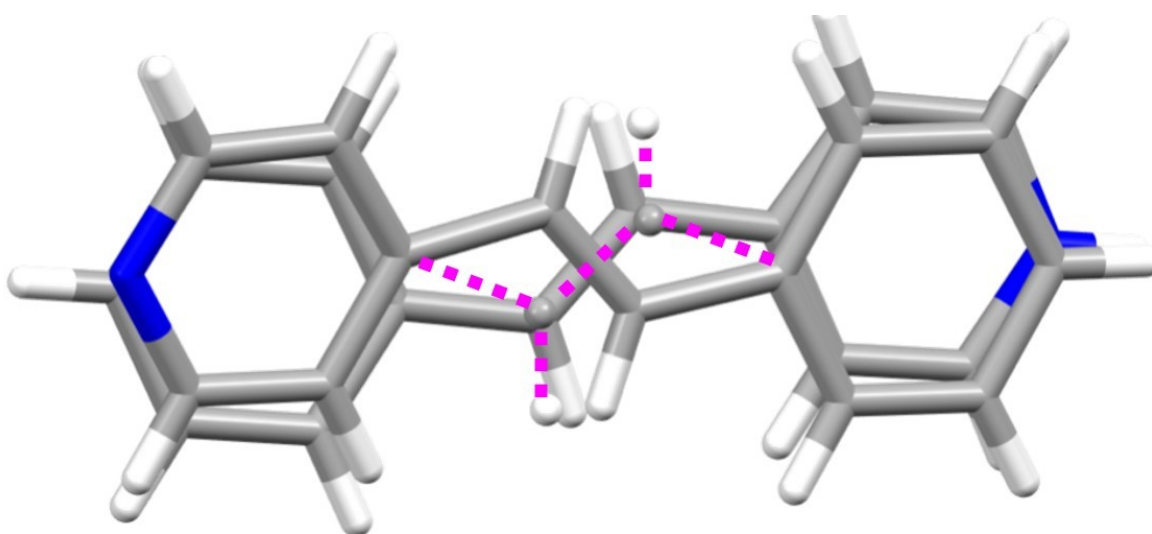


Fig. S4 The C=C double bonds of 4-spy and 4-spyH⁺ are mainly arranged in a crisscross shape, of which the minority are parallel and the disordered ratio is approximately 7:3. The pink dashed line represents covalent bonds with disordered atoms.

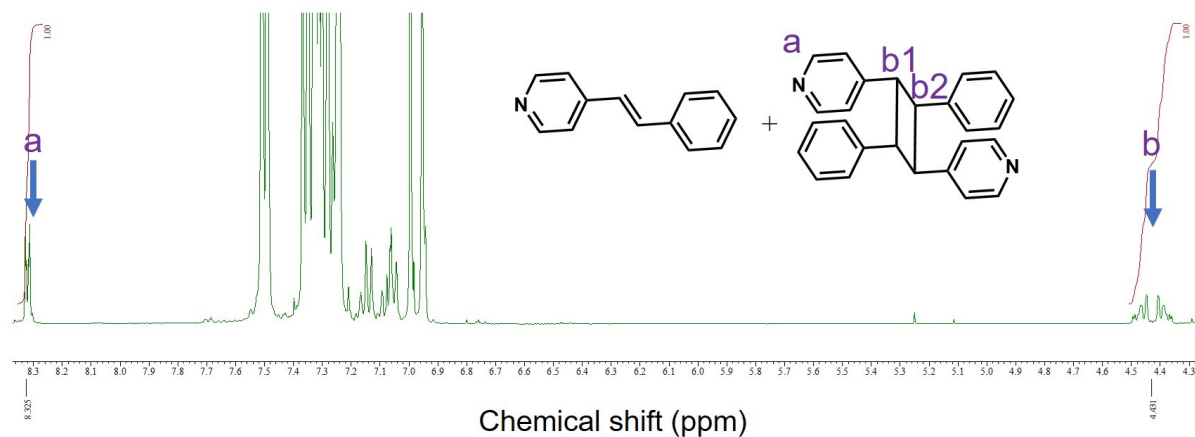


Fig. S5 ^1H NMR of photodimerized **1** after removal of trimesic acid. Photodimerized **1** was dissolved in 1 M NaOH solution and extracted with CHCl_3 . The NMR spectrum was measured in CDCl_3 and consistent with the *anti* head-tail product revealed by ref. 9e.

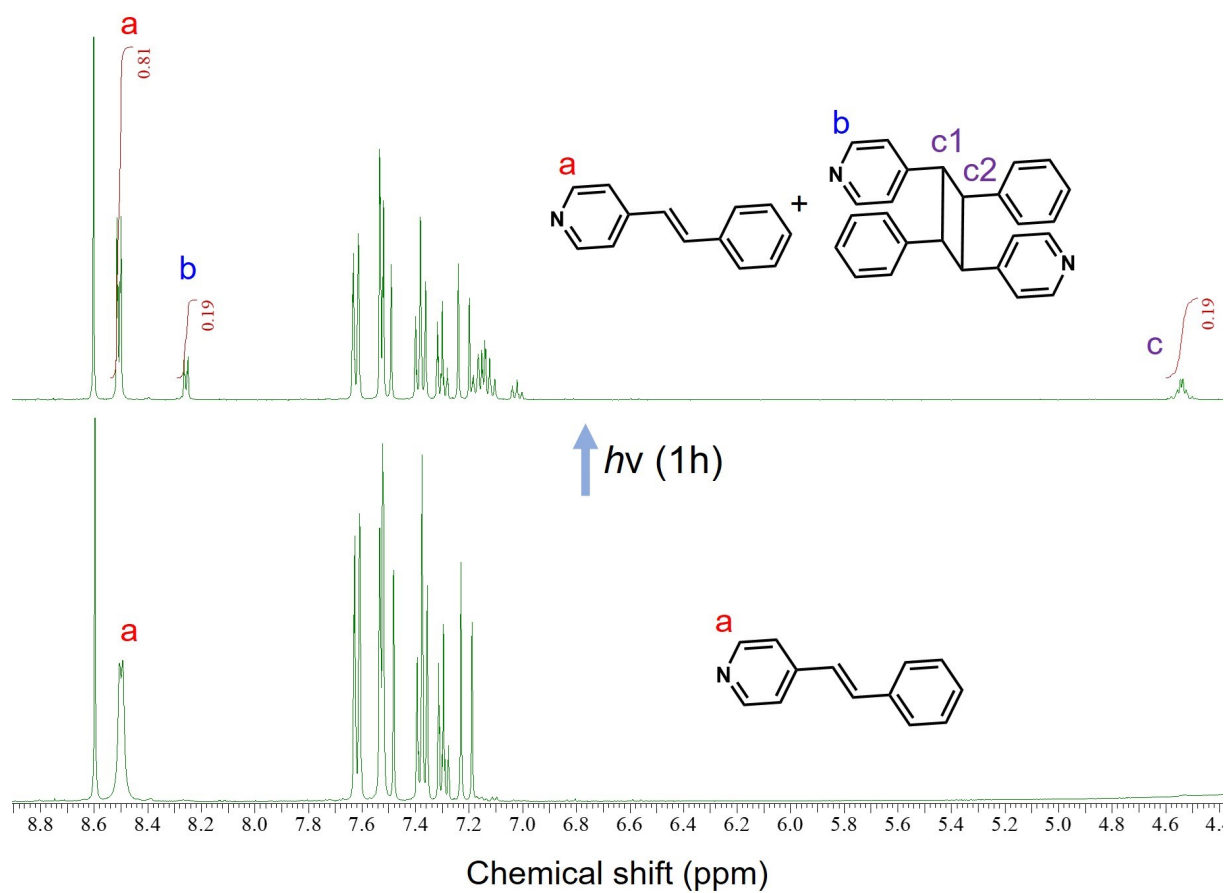


Fig. S6 The integration after exposure to UV light for 1 hour.

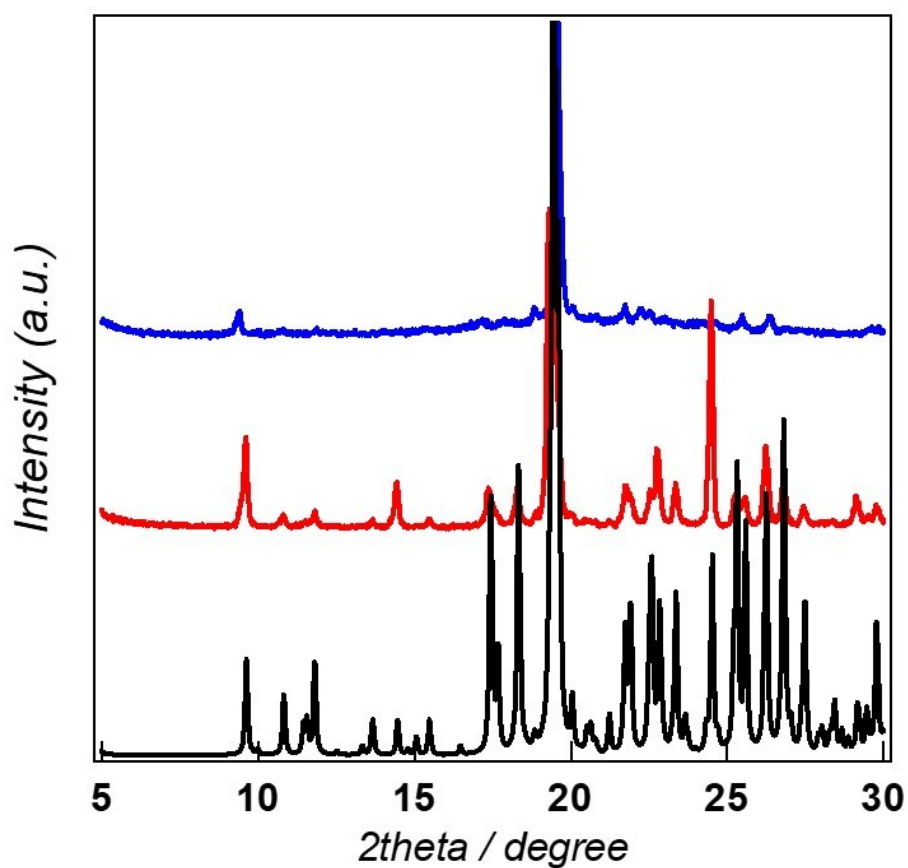


Fig. S7 Powder X-ray diffraction patterns for crystalline powder of **1** (red line), after UV irradiation for 3 h (blue line) and simulation from CIF (black line).

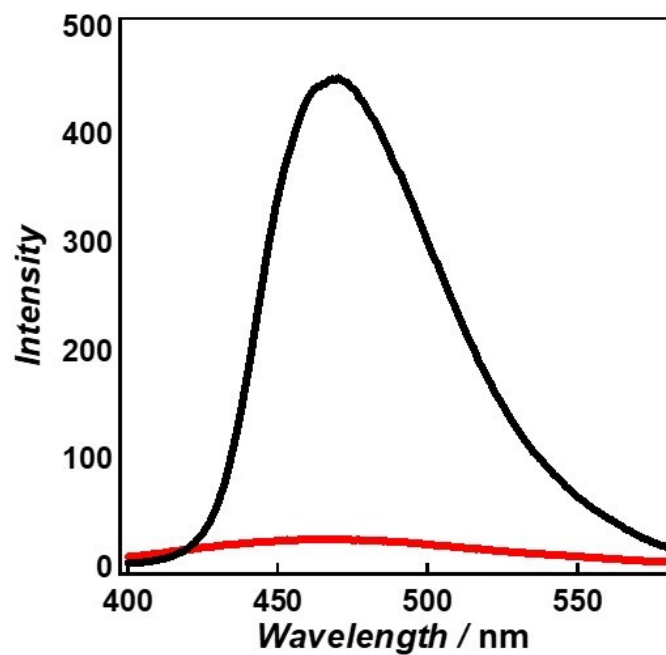


Fig. S8 Luminescent spectra of crystalline powder **1** (black line) and after UV irradiation for 24 h (red line).

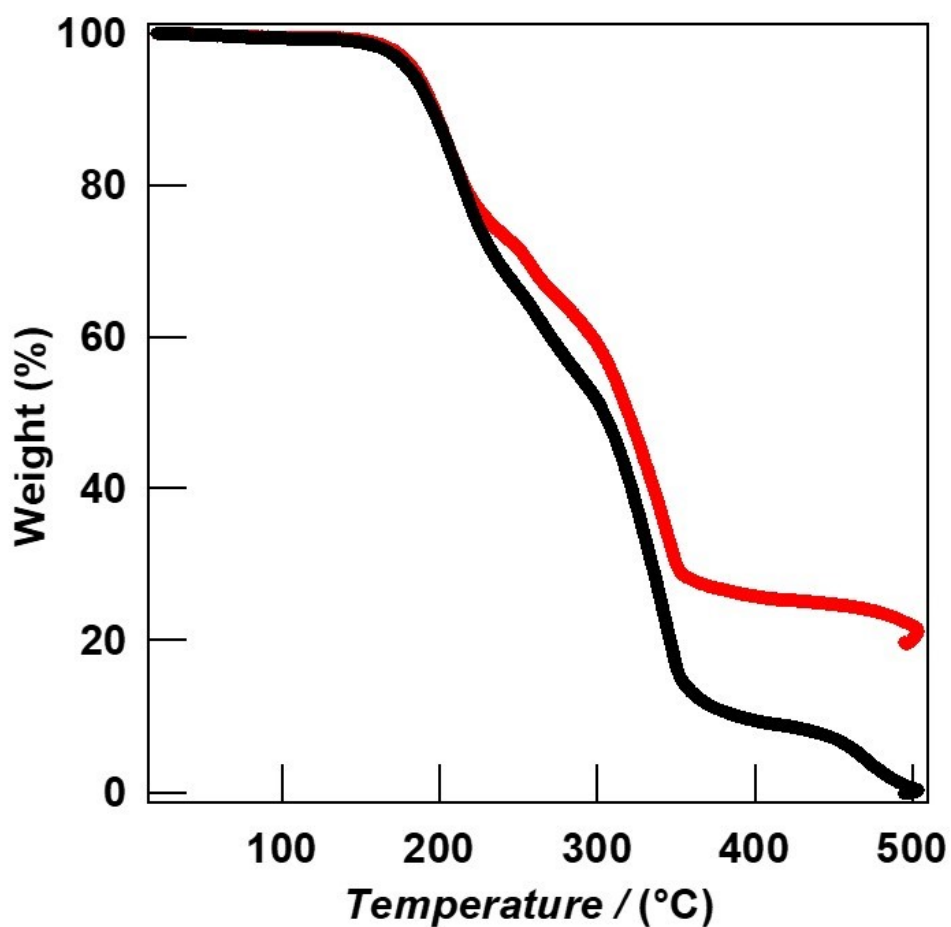


Fig. S9 Thermogravimetric analysis of **1** (black line) and after UV irradiation for 3 h (red line).

References

- [1] L. S. Matos, R. C. Amaral, and N. Y. Murakami Iha, *Inorg. Chem.*, 2018, **57**, 9316–9326.
- [2] G. M. Sheldrick, SHELXT – Integrated Space-Group and Crystal-Structure Determination, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3–8.
- [3] G. M. Sheldrick, Crystal Structure Refinement with SHELXL. *Acta Crystallogr Sect. C* 2015, **71**, 3–8.