Electronic Supplementary Material (ESI) for CrystEngComm.


# Supplementary Materials

## Photoreactive salt cocrystal: $N^+$-H···N hydrogen bond and cation-π interactions support a cascade-like photodimerization of a 4-stilbazole

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**Supplementary Information:**

## S1. Experimental section

**Materials**:

*Trans*-1-(4-pyridyl)-2-(phenyl)ethylene or 4-stilbazole (**4-stilbz**) was prepared according to a published procedure.[1] Ammonium hexafluorophosphate (**$NH_4PF_6$**) was purchased from Sigma-Aldrich. Solvents were purchased from Sigma-Aldrich. Solid reagents and solvents were used without further purification. Salt cocrystals of [**4-stilbz·(4-stilbzH$^+$)($PF_6^-$)**] were generated by mixing an ethanol (1 mL) solution of **$NH_4PF_6$** (18 mg, 0.11mmol) with **4-stilbz** (40 mg, 0.22 mmol) in tetrahydrofuran (4 mL). Single crystals as colorless irregular prism-like specimen were obtained after a period of 3 days via evaporation.

**Instruments and methods:**

The photodimerization was carried out in an ACE Glass photochemistry cabinet using a 450 W Hanovia medium-pressure mercury lamp with a broad wavelength distribution. Approximately 40-48% of total energy radiated is in the UV of the spectrum, 40-43% in the visible, and the balance in the IR. The single-crystal-to-single-crystal transformation was performed by irradiating single crystals in a UV light gel nail dryer (36 W, wavelength distribution: 380-480 nm with a peak at 365 nm). All single-crystal X-ray diffraction data were collected on a Bruker Nonius APEX II Kappa single-crystal X-ray diffractometer using MoKα radiation (λ=0.71073 Å) with APEX II detector. Single crystals were mounted in paratone oil on a Mitegen magnetic mount. Lorentz and polarization corrections with programs from the APEXII package were used for data reduction. Structure solution and refinement were completed using SHELXL[2] and SHELXT[3], respectively within the Olex2[4] graphical user interface. Non-hydrogen atoms were refined with anisotropically. Pyridium hydrogens were located in a difference map and refined freely. Other hydrogen atoms were positioned geometrically and refined using a riding model. Powder X-ray diffraction data were measured on samples mounted on glass slides using a Bruker D8 Advance X-ray diffractometer with CuK$\alpha_1$ radiation (λ = 1.54056 Å) typically in the range of 5−35° two-theta (scan type: locked coupled; scan mode: continuous; step size: 0.02°). The equipment was operated at 40 kV and 30 mA. NMR spectra were collected using a Bruker AVANCE 300 NMR spectrometer operating at 300 MHz. DMSO-$d_6$ was used as NMR solvent. All NMR data were processed with Mnova suite.

## S2. Single-crystal X-ray diffraction data

**Table S1.** Crystallographic parameters for [**4-stilbz**·(**4-stilbzH**$^+$)(**PF$_6^-$**)] (**298 K**).

| | |
|---|---|
| Empirical formula | $C_{26}H_{23}F_6N_2P$ |
| Formula weight | 508.43 |
| Temperature/K | 298.15 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.8408(11) |
| b/Å | 11.1512(11) |
| c/Å | 11.3568(11) |
| α/° | 84.292(5) |
| β/° | 75.957(5) |
| γ/° | 69.533(5) |
| Volume/Å$^3$ | 1247.6(2) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.353 |
| μ/mm$^{-1}$ | 0.172 |
| F(000) | 524.0 |
| Crystal size/mm$^3$ | 0.38 × 0.38 × 0.22 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.114 to 49 |
| Index ranges | -9 ≤ h ≤ 12, -12 ≤ k ≤ 13, -13 ≤ l ≤ 13 |
| Reflections collected | 5701 |
| Independent reflections | 3922 [$R_{int}$ = 0.0214, $R_{sigma}$ = 0.0396] |
| Data/restraints/parameters | 3922/53/436 |
| Goodness-of-fit on F$^2$ | 1.073 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0550, $wR_2$ = 0.1465 |
| Final R indexes [all data] | $R_1$ = 0.0889, $wR_2$ = 0.1637 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.25/-0.23 |
| CCDC deposition number | 2025376 |

**Table S2.** Crystallographic parameters for [**4-stilbz**·(**4-stilbzH**$^+$)(**PF$_6^-$**)] (**125K**).

| | |
|---|---|
| Empirical formula | $C_{26}H_{23}F_6N_2P$ |
| Formula weight | 508.43 |
| Temperature/K | 125.15 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.6906(11) |
| b/Å | 11.0302(11) |
| c/Å | 11.0850(11) |
| α/° | 84.721(5) |
| β/° | 76.416(5) |
| γ/° | 70.095(2) |
| Volume/Å$^3$ | 1194.6(2) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.414 |
| μ/mm$^{-1}$ | 0.179 |
| F(000) | 524.0 |
| Crystal size/mm$^3$ | 0.38 × 0.38 × 0.24 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.78 to 52.958 |
| Index ranges | -13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13 |
| Reflections collected | 15560 |
| Independent reflections | 4886 [$R_{int}$ = 0.0335, $R_{sigma}$ = 0.0414] |
| Data/restraints/parameters | 4886/5/327 |
| Goodness-of-fit on F$^2$ | 1.021 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0488, $wR_2$ = 0.1090 |
| Final R indexes [all data] | $R_1$ = 0.0704, $wR_2$ = 0.1231 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.52/-0.30 |
| CCDC deposition number | 2052940 |

**Table S3.** Crystallographic parameters for [**2**(**4-stilbz**)·(**4-pyr-ph-cb2H**$^+$)(**2PF$_6^-$**)].

| | |
|---|---|
| Empirical formula | $C_{26}H_{23}F_6N_2P$ |
| Formula weight | 508.43 |
| Temperature/K | 150.15 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.930(7) |
| b/Å | 11.296(8) |
| c/Å | 11.859(9) |
| α/° | 87.742(10) |
| β/° | 83.324(9) |
| γ/° | 65.023(9) |
| Volume/Å$^3$ | 1197.6(15) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.441 |
| μ/mm$^{-1}$ | 0.188 |
| F(000) | 535.0 |
| Crystal size/mm$^3$ | 0.3 × 0.21 × 0.19 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.458 to 46.998 |
| Index ranges | -11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13 |
| Reflections collected | 10862 |
| Independent reflections | 3517 [$R_{int}$ = 0.1342, $R_{sigma}$ = 0.1564] |
| Data/restraints/parameters | 3517/183/355 |
| Goodness-of-fit on F$^2$ | 0.912 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0995, $wR_2$ = 0.2101 |
| Final R indexes [all data] | $R_1$ = 0.2222, $wR_2$ = 0.2546 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.57/-0.35 |
| CCDC deposition number | 2025377 |

## S3. Hydrogen-bond table.

**Table S3**. Hydrogen-bond metrics for [**4-stilbz·(4-stilbzH$^+$)(PF$_6^-$)**] (**298K**), [**4-stilbz·(4-stilbzH$^+$)(PF$_6^-$)**] (**125K**), and [**2(4-stilbz)·(4-pyr-ph-cb2H$^+$)(2PF$_6^-$)**].

| Crystal/parameters | D-H· · · A | *d*(D-H) (Å) | *d*(H· · · A) (Å) | *d*(D· · · A) (Å) | $\vartheta$(D-H· · · A) (deg) | symmetry code |
|---|---|---|---|---|---|---|
| [**4-stilbz·(4-stilbzH$^+$)(PF$_6^-$)**] **(298 K)** | C14^a-H14^a· · ·F5^a | 0.930(2) | 2.502(9) | 3.34(3) | 151(3) | -x, -y+1, -z+1 |
| | C18^a-H18^a· · ·F1 | 0.930(2) | 2.601(2) | 3.52(2) | 168(2) | x+1, y, z |
| | C5^a-H5^a· · ·F1 | 0.930(6) | 2.512(6) | 3.42 (7) | 165(4) | x+1, y, z |
| | C2^a-H2^a· · ·F5^a | 0.930(5) | 2.635(9) | 3.53(9) | 162(5) | x+1, y, z-1 |
| | C4^a-H4^a· · ·F6^a | 0.930(8) | 2.491(6) | 3.41(9) | 168(5) | -x+1, -y+1, -z+1 |
| | C2B^b-H2B^b· · ·F2 | 0.930(3) | 2.623(2) | 3.21(3) | 122(2) | x+1, y, z-1 |
| | C14B^b-H14B^b· · ·F1 | 0.930(2) | 2.526(2) | 3.28(2) | 138(3) | x+1, y, z |
| | N1^a-H1^a· · ·N2^a | 1.010(4) | 1.716(4) | 2.72(2) | 170(3) | |
| [**4-stilbz·(4-stilbzH$^+$)(PF$_6^-$)**] **(125 K)** | C10-H10· · ·F007 | 0.950(2) | 2.594(2) | 3.54(3) | 173(7) | x-1, y, z |
| | C11-H11· · ·F002 | 0.950(9) | 2.419 (2) | 3.33(3) | 160(3) | -x+1, -y+1, -z+1 |
| | C13-H13· · ·F005 | 0.950(9) | 2.596(3) | 3.48(4) | 155(3) | -x+1, -y+1, -z+2 |
| | C14-H14· · ·F002 | 0.950(9) | 2.498(2) | 2.70(2) | 160(2) | -x+1, -y+1, -z+1 |
| | N1-H1· · ·N2 | 0.971(9) | 1.739(2) | 2.70(2) | 169(1) | |
| [**2(4-stilbz)·(4-pyr-ph-cb2H$^+$)(2PF$_6^-$)**] | N1-H1· · ·N2 | 1.000(7) | 1.761(8) | 2.68 (9) | 152(6) | -x+1, -y+1, -z+1 |

## S4. NMR spectral data

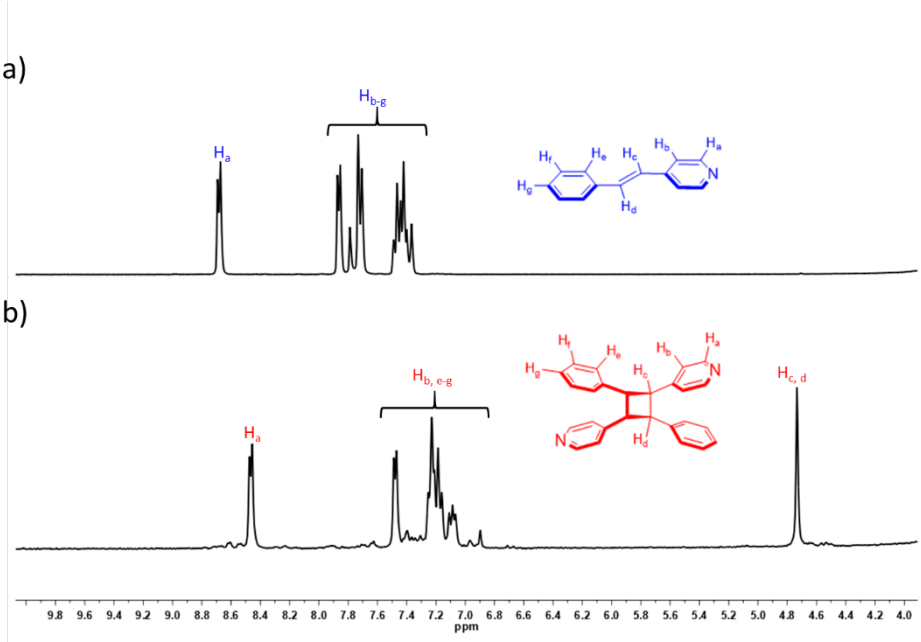


**Fig. S1**. $^1$H NMR spectra of [**4-stilbz**•(**4-stilbzH**$^+$)(**PF**$_6^-$)] before (a) and after UV irradiation for 20 h (b) (300 MHz, DMSO-$d_6$).

## S5. Powder X-ray diffraction data

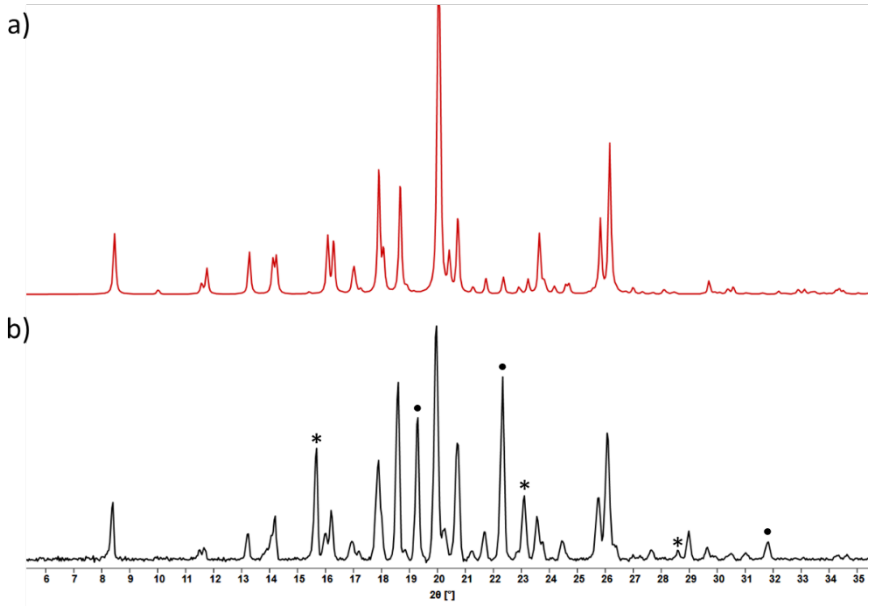


**Fig. S2.** PXRD patterns of [**4-stilbz**•(**4-stilbzH**$^+$)(**PF$_6^-$**)] before UV irradiation: (a) simulated pattern from single crystal X-ray diffraction data; (b) experimental pattern from sample (starting materials: asterisk = 4-stilbazole, dots = $NH_4PF_6$).

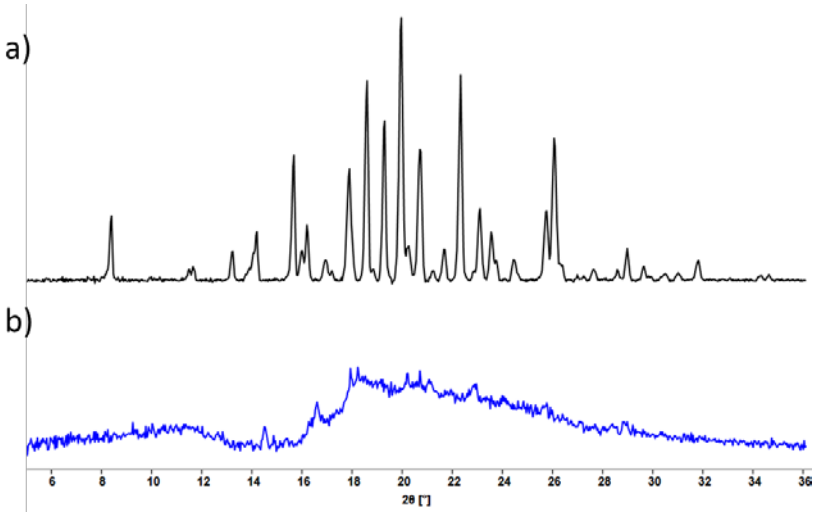


**Fig. S3.** PXRD patterns of [**4-stilbz**•(**4-stilbzH**$^+$)(**PF$_6^-$**)]: (a) before and (b) after 20 h UV irradiation.

## References


1. (a) S. M. N. Efange, R. Michelson, R. P. Remmel, R. Boudreau, A. Dutta and A. Freshler, *J. Med. Chem.*, 1990, **33**, 3133-3138; (b) E. D. Lorance, W. H. Kramer and I. R. Gould, *J. Am. Chem. Soc.*, 2002, **124**, 15225-15238.
2. G. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3-8.
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4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.