

Supporting Information

for

Application of a tetrapyrimidyl cyclobutane synthesized in the organic solid state: a halogen-bonded supramolecular ladder

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1. Materials, General Methods and Synthesis of the Co-crystal	Page 2
2. Single X-ray Diffraction Information and Data Table	Page 2-3
3. ¹ H NMR Spectra	Page 4
4. References	Page 4

1. Materials, General Methods and Synthesis of the Co-crystal

Materials

The solvents ethanol and toluene were both purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received. The halogen bond donor 1,4-diiodoperchlorobenzene ($C_6I_2Cl_4$) was synthesized by a previous reported method.¹ The reactant *trans*-1,2-bis(5'-pyrimidyl)ethylene (**BPmE**) was also synthesized by a previous reported method.² All crystallization studies were performed in 20 mL scintillation vials.

General Methods

The reactant **BPmE** was placed between Pyrex glass plates for irradiation. Upon exposure to UV-radiation from a 450 W medium-pressure mercury lamp in an ACE Glass photochemistry cabinet the solid underwent a [2 + 2] cycloaddition reaction to form the photoproduct *rect*-tetrakis(5'-pyrimidyl)cylcobutane (**TPmCB**) with an overall yield of 95%.²

Synthesis of the Co-crystal

The co-crystal (**TPmCB**)•2($C_6I_2Cl_4$)•(toluene) (**1**) was synthesized by dissolving 25.0 mg of **TPmCB** in 1.0 mL of toluene and 2.0 mL of ethanol, which was then combined with a separate warm 2.0 mL toluene solution of 63.5 mg of $C_6I_2Cl_4$ (1:2 molar equivalent). Each solution was placed in a sonicator till all of the solids dissolved. The resulting solution was allowed to cool and slowly evaporate and after 2 days crystals suitable for X-ray diffraction were realized.

2. Single X-ray Diffraction Information and Data Table

Single-crystal diffraction data for **TPmCB** were collected on a Nonius Kappa CCD single-crystal X-ray diffractometer at room temperatures using MoK_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection, cell refinement, and data reduction were performed using Collect³ and HKL Scalepack/Denzo,⁴ respectively. Single-crystal diffraction data for **1** was collected on a suitable crystal mounted to a MiTeGen cryoloop for data collection. Data collection of **1** was performed using a Bruker Venture Duo Photon-II single crystal X-ray diffractometer equipped with an Oxford Cryostream device and operated at 1500 W (50 kV, 30 mA) to generate graphite-monochromated MoK_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). Apex II and SAINT software packages were used for data collection and integration.⁵ Data collected were corrected for systematic errors using SADABS based on the Laue symmetry using equivalent reflections.⁶ Structure solution and refinement were accomplished using ShelXT⁷ and ShelXL,⁸ respectively, using Olex2⁹ graphical user interface. All non-hydrogen atoms were identified from the difference Fourier map and refined anisotropically. All hydrogen atoms were placed in their calculated positions and were refined using isotropic thermal parameters.

Table S1. X-ray data and refinement data for **TPmCB** and **1**.

	TPmCB	1
CCDC	2010995	2010996
Empirical formula	C ₂₀ H ₁₆ N ₈	C ₃₉ H ₂₄ Cl ₈ I ₄ N ₈
Formula weight	368.41	1395.86
Temperature/K	298	100(2)
Crystal system	monoclinic	triclinic
Space group	C2/c	P $\bar{1}$
a/Å	15.6660(16)	8.9258(5)
b/Å	7.1513(7)	9.1762(6)
c/Å	17.0738(17)	14.6465(8)
α /°	90	82.686(2)
β /°	111.938(5)	74.068(2)
γ /°	90	72.653(2)
Volume/Å ³	1774.3(3)	1099.72(11)
Z	4	1
$\rho_{\text{calc}}/\text{gcm}^{-3}$	1.379	2.108
μ/mm^{-1}	0.089	3.361
F(000)	768.0	662.0
Crystal size/mm ³	0.48 × 0.42 × 0.14	0.172 × 0.115 × 0.078
Radiation	Mo K α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	6.03 to 50.724	4.656 to 54.974
Index ranges	-16 ≤ h ≤ 18, -8 ≤ k ≤ 8, -20 ≤ l ≤ 20	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -19 ≤ l ≤ 18
Reflections collected	5586	13882
Independent reflections	1618 [R _{int} = 0.0422, R _{sigma} = 0.0287]	4990 [R _{int} = 0.0332, R _{sigma} = 0.0359]
Data/restraints/parameters	1618/1/146	4990/136/299
Goodness-of-fit on F ²	1.119	1.048
Final R indexes [I >= 2 σ (I)]	R ₁ = 0.0577, wR ₂ = 0.1333	R ₁ = 0.0225, wR ₂ = 0.0480
Final R indexes [all data]	R ₁ = 0.0677, wR ₂ = 0.1400	R ₁ = 0.0283, wR ₂ = 0.0499
Largest diff. peak/hole / e Å ⁻³	0.24/-0.19	0.55/-0.46

3. ^1H NMR Spectra

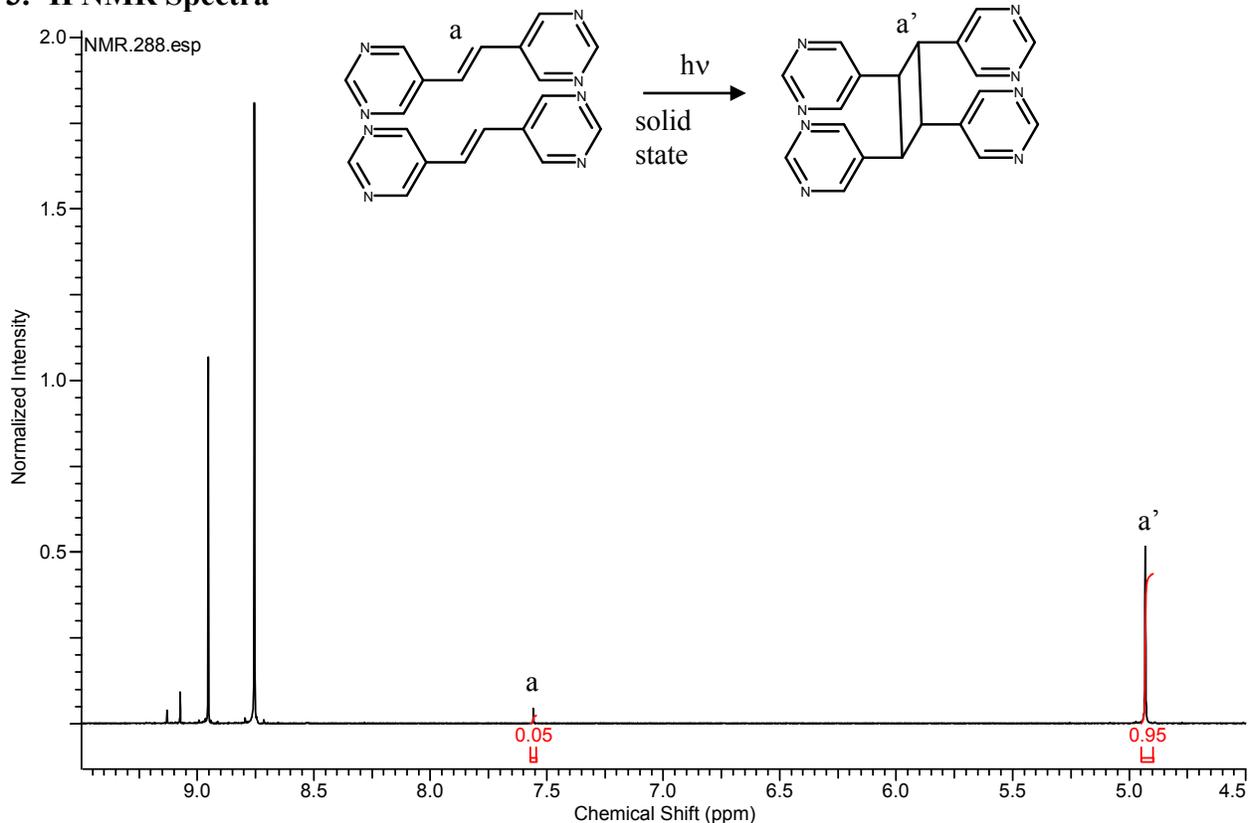


Figure S1: ^1H NMR spectrum of **BPmE** after 20 hours of UV irradiation as it converts to **TPmCB** via the [2 + 2] cycloaddition reaction with an overall yield of 95% (400 MHz, $\text{DMSO-}d_6$).

4. References

1. C. M. Reddy, M. T. Kirchner, R. C. Gundakaram, K. A. Padmanabhan and G. R. Desiraju, *Chem. Eur.*, **2006**, *12*, 2222.
2. E. Bosch, J. M. Matheny and N. P. Rath, *Synth. Commun.*, **2007**, *37*, 3835.
3. R. W. W. Hooft, COLLECT. Nonius BV, Delft, The Netherlands, (1998).
4. Z. Otwinowski and W. Minor, (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr. & R. M. Sweet, pp. 307-326. New York: Academic Press.
5. Bruker (2012). Bruker AXS Inc., Madison, Wisconsin, USA.
6. Bruker (2001). Bruker AXS Inc., Madison, Wisconsin, USA.
7. G. Sheldrick, *Acta Crystallogr. Sect. A*, **2015**, *71*, 3.
8. G. Sheldrick, *Acta Crystallogr. Sect. C*, **2015**, *71*, 3.
9. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.