

Supporting Information

for

**Covalent bond formation via a [2+2] cycloaddition reaction as a tool
to alter thermal expansion parameters of organic co-crystals**

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1. Materials and Synthesis of the Photoproduct Co-crystal

Materials

Resorcinol (**res**), *trans*-1,2-bis(4-pyridyl)ethylene (**4,4'-BPE**), and ethanol (95% pure) were all purchased from Sigma–Aldrich Chemical (St. Louis, MO, USA) and were used as received.

Preparation of the Photoproduct Co-crystal

The synthesis and photoreactivity of the co-crystal 2(**res**)•2(**4,4'-BPE**) has been previously reported.¹ In the present study, 50 mg of **4,4'-BPE** was dissolved in 3 mL of ethanol and was combined with a second 2 mL ethanol solution of 30 mg of **res** (1:1 molar ratio). Within one day, crystals suitable for X-ray diffraction were realized. The crystals were crushed between two glass plates and placed in a photoreactor containing a 450 W medium pressure mercury light bulb. The sample was exposed to 50 hours of UV light to achieve a quantitative yield for the photoreaction as determined by ¹H NMR spectroscopy (Figure S1).

2. ^1H NMR Spectrum of the Photoproduct

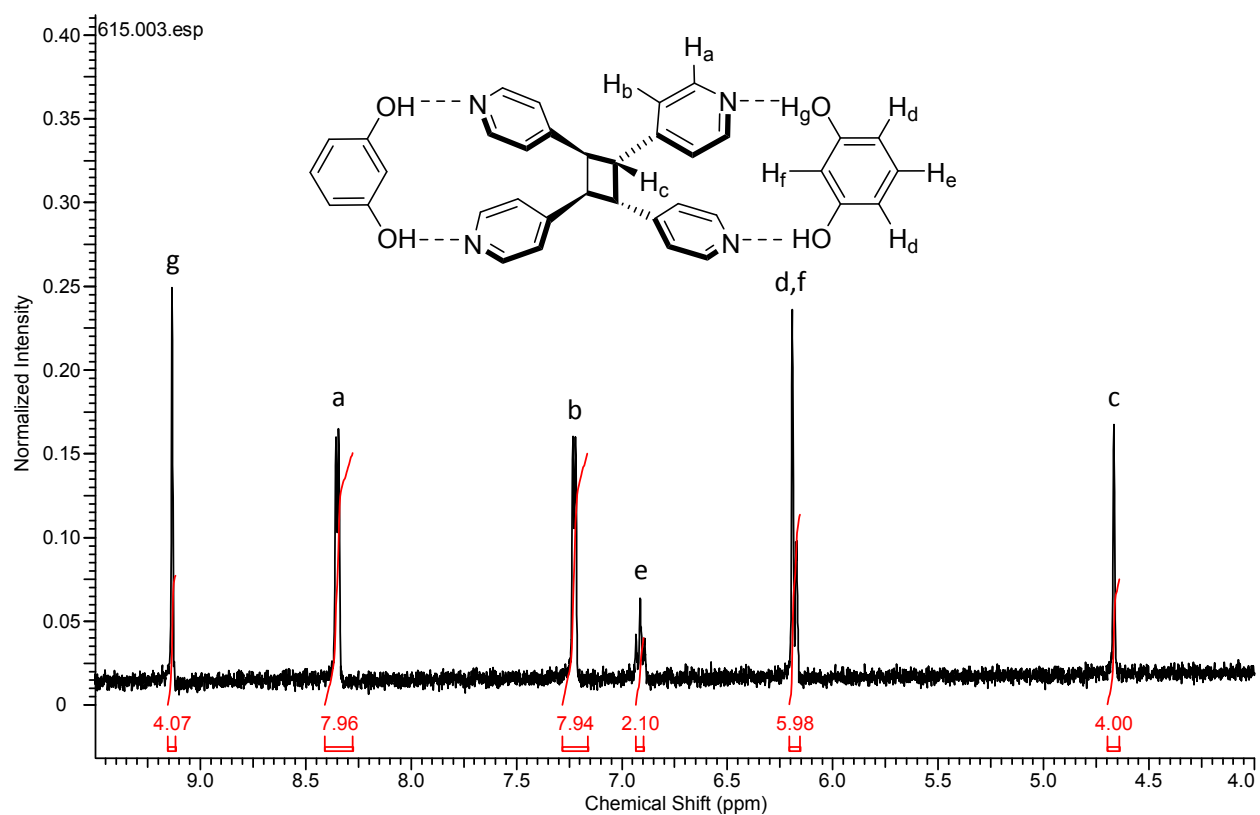


Figure S1. ^1H NMR spectrum of $2(\text{res})\cdot(\text{TPCB})$ following 50 hours of UV irradiation indicating a quantitative yield for the [2+2] cycloaddition reaction (400 MHz, $\text{DMSO}-d_6$).

3. X-ray Diffraction Information and Data Tables

A suitable single crystal of $2(\text{res})\cdot(\text{TPCB})$ was secured to Mitegen magnetic mount using Paratone oil and was placed on Bruker APEX II Kappa Diffractometer equipped with an Oxford Cryostream low temperature device using Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). All of the diffraction data was collected on the same crystal. Data collection strategies to ensure maximum data redundancy and completeness were calculated using Apex II. Data collection, initial indexing, frame integration, Lorentz-polarization corrections and final cell parameter calculations were carried out again using Apex II. Multi-scan absorption corrections were performed using *SADABS*.² The *SHELXL-2014*³, series of programs were used for the solution and refinement of the crystal structure. All non-hydrogen atoms were refined anisotropically and hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. Crystallographic and refinement data for $2(\text{res})\cdot(\text{TPCB})$ at each temperature is summarized in Table S1.

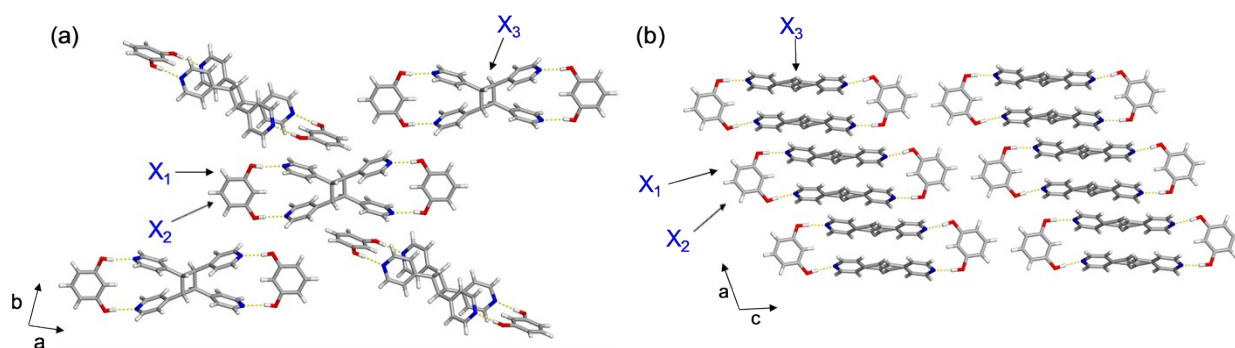


Figure S2. X-ray crystal structures of: (a) $2(\text{res})\cdot(\text{TPCB})$ and (b) $2(\text{res})\cdot 2(4,4'\text{-BPE})_4$ highlighting X_1 , X_2 , and X_3 axes. The O-H...N hydrogen bonds are shown with yellow dotted lines.

Table S1. X-ray crystallographic and refinement data for 2(res)•(TPCB) at various temperatures.

compound formula	C ₃₆ H ₃₂ N ₄ O ₄	C ₃₆ H ₃₂ N ₄ O ₄	C ₃₆ H ₃₂ N ₄ O ₄
formula mass	584.65	584.65	584.65
crystal system	monoclinic	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n
a/Å	11.3117(10)	11.3142(10)	11.3139(9)
b/Å	9.8022(5)	9.7891(6)	9.7762(5)
c/Å	14.2920(13)	14.2833(13)	14.2685(12)
α/°	90	90	90
β/°	111.539(4)	111.607(4)	111.658(4)
γ/°	90	90	90
V/Å ³	1474.0(2)	1470.8(2)	1466.78(19)
ρ _{calc} /g cm ⁻³	1.317	1.320	1.324
T/K	290	270	250
Z	2	2	2
radiation type	Mo Kα	Mo Kα	Mo Kα
absorption coefficient, μ/mm ⁻¹	0.087	0.087	0.088
no. of reflections measured	7800	7746	7726
no. of independent reflections	3395	3381	3383
no of reflection (I > 2σ(I))	1634	2035	2088
R _{int}	0.0506	0.392	0.0380
R ₁ (I > 2σ(I))	0.0425	0.0499	0.0486
wR(F ²) (I > 2σ(I))	0.0737	0.1012	0.1021
R ₁ (all data)	0.1060	0.0967	0.0933
wR(F ²) (all data)	0.0877	0.1209	0.1213
Goodness-of-fit	0.800	1.011	1.015
CCDC deposition number	1859283	1859282	1859281

compound formula	C ₃₆ H ₃₂ N ₄ O ₄	C ₃₆ H ₃₂ N ₄ O ₄	C ₃₆ H ₃₂ N ₄ O ₄
formula mass	584.65	584.65	584.65
crystal system	monoclinic	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n
a/Å	11.3216(8)	11.3155(9)	11.3235(6)
b/Å	9.7698(4)	9.7527(5)	9.7491(3)
c/Å	14.2672(10)	14.2477(11)	14.2452(8)
α/°	90	90	90
β/°	111.713(3)	111.746(3)	111.822(2)
γ/°	90	90	90
V/Å ³	1466.12(16)	1460.43(18)	1459.90(12)
ρ _{calc} /g cm ⁻³	1.324	1.330	1.330
T/K	230	210	190
Z	2	2	2
radiation type	Mo Kα	Mo Kα	Mo Kα
absorption coefficient, μ/mm ⁻¹	0.088	0.088	0.088
no. of reflections measured	7748	7750	7726
no. of independent reflections	3372	3364	3356
no of reflection (I > 2σ(I))	2135	2225	2300
R _{int}	0.0362	0.0384	0.0371
R ₁ (I > 2σ(I))	0.0461	0.0462	0.0463
wR(F ²) (I > 2σ(I))	0.0978	0.0979	0.0992
R ₁ (all data)	0.0874	0.0809	0.0780
wR(F ²) (all data)	0.1174	0.1136	0.1150
Goodness-of-fit	1.006	1.016	1.009
CCDC deposition number	1859280	1859279	1859278

4. Thermal Expansion Data and Intermolecular Interaction Distances

The thermal expansion coefficients were calculated using the PASCAL program.⁵ The crystallographic data sets were collected at 290, 270, 250, 230, 210, and 190 K and used for the thermal expansion calculations.

Table S2. Thermal expansion coefficients for the co-crystal 2(res)•(TPCB). Errors denoted in parentheses and approximate crystallographic axis denoted in brackets.

Co-crystal	α_{x_1} (MK ⁻¹) [axis]	α_{x_2} (MK ⁻¹) [axis]	α_{x_3} (MK ⁻¹) [axis]	α_V (MK ⁻¹)
2(res)•(TPCB)	-12(2) [4 0 -1]	56(3) [0 1 0]	56(1) [1 0 1]	104(7)

Table S3. Intermolecular interaction distances that contribute to the thermal expansion parameters.

Co-crystal	O-H···N hydrogen bond (Å) 290 K	O-H···N hydrogen bond (Å) 190 K	Change (Å)
2(res)•(TPCB)	2.7207	2.7125	0.0082
	2.7839	2.7840	-0.0001
	C-H···O hydrogen bond (Å) 290 K	C-H···O hydrogen bond (Å) 190 K	Change (Å)
	3.325	3.292	0.033
	3.329	3.273	0.056
	3.510	3.471	0.039
	C-H··· π distances (Å) 290 K	C-H··· π distances (Å) 190 K	Change (Å)
	3.566	3.544	0.022
	3.735	3.714	0.021
	3.679	3.651	0.028
3.817	3.790	0.027	
C-H(pyr)···C-H(pyr) distances (Å) 290 K	C-H(pyr)···C-H(pyr) distances (Å) 190 K	Change (Å)	
3.883	3.848	0.035	

References

1. L. R. MacGillivray, J. L. Reid and J. A. Ripmeester, *J. Am. Chem. Soc.*, 2000, **122**, 7817.
2. Krause *et al.*, (2015) SADABS v 2016/2.
3. G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3.
4. K. M. Hutchins, D. K. Unruh, F. A. Verdu and R. H. Groeneman, *Cryst. Growth Des.*, 2018, **18**, 566.
5. M. J. Cliffe and A. L. Goodwin, *J. Appl. Crystallogr.*, 2012, **45**, 1321.