Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

for

Regioselective [2 + 2] cycloaddition reaction within a pair of polymorphic co-crystals based upon halogen bonding interactions

Eric Bosch, Samantha J. Kruse, Eric W. Reinheimer, Nigam P. Rath, and Ryan H. Groeneman

Department of Chemistry, Missouri State University, 901 South National Ave. Springfield, MO 65897, USA

Department of Biological Sciences, Webster University, 470 E. Lockwood Ave., St. Louis, MO, 63119, USA

Rigaku Corporation, 9009 New Trails Dr. The Woodlands, TX 77381, USA

Department of Chemistry and Biochemistry and the Center for Nanoscience, University of Missouri-St. Louis, 1 University Blvd., St. Louis, MO 63121, USA

1. Materials, General Methods and Synthesis of the Polymorphs

Materials

4-Stilbazole (**4-SB**) as well as the solvent 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] All crystallization studies were performed in 20 mL scintillation vials.

General Methods

Photoreactions were conducted using UV-radiation from a 450 W medium-pressure mercury lamp in an ACE Glass photochemistry cabinet. Both polymorphic forms of the co-crystal (**$C_6I_2Cl_4$**)•2(**4-SB**) were placed between a pair of Pyrex glass plates for irradiation. The photoreactivity of (**$C_6I_2Cl_4$**)•2(**4-SB**) was determined by using ^{1}H NMR spectroscopy. ^{1}H NMR spectrum was collected using a Bruker Avance 400 MHz spectrometer using DMSO-d_6 as a solvent. Powder X-ray diffraction data was collected at room temperature on a Rigaku Ultima IV X-ray diffractometer using Cu $K_\alpha 1$ radiation (λ = 1.54056 Å) between 5° to 40° two-theta.

Synthesis of Form I and Form II of (**$C_6I_2Cl_4$**)•2(**4-SB**)

Co-crystals of (**$C_6I_2Cl_4$**)•2(**4-SB**) in both forms were synthesized by dissolving 25.0 mg of **$C_6I_2Cl_4$** in 2.0 mL of toluene, which was then combined with a separate 2.0 mL toluene solution containing 19.4 mg of **4-SB** (1:2 molar equivalent). Form I was achieved by removing the cap of the 20 mL scintillation vial while Form II was formed by covering the vial with a folded Kimwipe or placing cotton in the opening. The rate of solvent evaporation is attributed to the formation of the particular polymorph. In both cases, after most of the solvent is evaporated single crystals suitable for X-ray diffraction were realized ranging from two days for Form I and up to three days for Form II.

2. Single X-ray Diffraction Information and Data Tables

Crystals were mounted on a MiTeGen cryoloop in random orientations for data collection. Data collections were performed using a Bruker Venture Duo Photon-II single crystal X-Ray diffractometer equipped with an Oxford Cryostream device. Apex II and SAINT software packages were used for data collection and integration. Data collected were corrected for systematic errors using SADABS[2] based on the Laue symmetry using equivalent reflections. Structure solution and refinement were carried out using the SHELXTL-PLUS[3] software package. All structures were solved by direct methods with a full matrix least-squares refinement. Non-hydrogen atoms were refined anisotropically to convergence. All hydrogen atoms were treated using an appropriate riding model (AFIX m3).

Table S1. X-ray data for Form I of **($C_6I_2Cl_4$)**•2(**4-SB**) and the partial photoproduct.

polymorphic form	Form I	Form I	Partial Photoproduct
chemical formula	$C_{16}H_{11}Cl_2IN$	$C_{16}H_{11}Cl_2IN$	$C_{16}H_{11}Cl_2IN$
formula mass	415.06	415.06	415.06
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	5.7320(3)	5.7219(2)	5.6832(2)
b/Å	11.2839(6)	11.2301(4)	11.0865(4)
c/Å	12.3090(7)	12.2908(4)	12.2076(5)
α/°	83.794(2)	83.6745(16)	82.9822(14)
β/°	82.313(2)	82.3392(14)	82.3948(12)
γ/°	77.034(2)	77.1630(14)	77.3857(12)
V/Å^3	766.35(7)	760.51(5)	740.53(5)
ρ_{calc} /g cm^{-3}	1.799	1.813	1.861
T/K	290	250	100
Z	2	2	2
radiation type	Mo Kα	Mo Kα	Mo Kα
absorption coefficient, μ/mm^{-1}	2.426	2.445	2.511
no. of reflections measured	9405	9468	12920
no. of independent reflections	3487	3477	2996
R_{int}	0.0460	0.0430	0.0210
R_1 ($I > 2\sigma(I)$)	0.0370	0.0361	0.0157
$wR(F^2)$ ($I > 2\sigma(I)$)	0.0660	0.0646	0.0387
R_1 (all data)	0.0638	0.0539	0.0162
$wR(F^2)$ (all data)	0.0850	0.0796	0.0390
Goodness-of-fit	1.053	1.061	0.985
CCDC deposition number	1947988	1947989	1947991

Table S2. X-ray data for Form II of **($C_6I_2Cl_4$)**•2(**4-SB**).

polymorphic form	Form II	Form II
chemical formula	$C_{16}H_{11}Cl_2IN$	$C_{16}H_{11}Cl_2IN$
formula mass	415.06	415.06
crystal system	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/c$
a/Å	10.9466(5)	10.9007(3)
b/Å	16.4851(7)	16.4319(4)
c/Å	8.6575(3)	8.6457(2)
α/°	90	90
β/°	96.0062(19)	96.2379(10)
γ/°	90	90
V/Å^3	1553.72(11)	1539.44(7)
ρ_{calc} /g cm^{-3}	1.774	1.791
T/K	290	250
Z	4	4
radiation type	Mo Kα	Mo Kα
absorption coefficient, μ/mm^{-1}	2.393	2.416
no. of reflections measured	43120	29690
no. of independent reflections	4692	4634
R_{int}	0.0970	0.0490
R_1 ($I > 2\sigma(I)$)	0.0662	0.0328
wR(F^2) ($I > 2\sigma(I)$)	0.0704	0.0638
R_1 (all data)	0.1405	0.0554
wR(F^2) (all data)	0.0794	0.0762
Goodness-of-fit	1.082	1.141
CCDC deposition number	1947992	1947993

3. ^{1}H NMR Spectroscopic Data

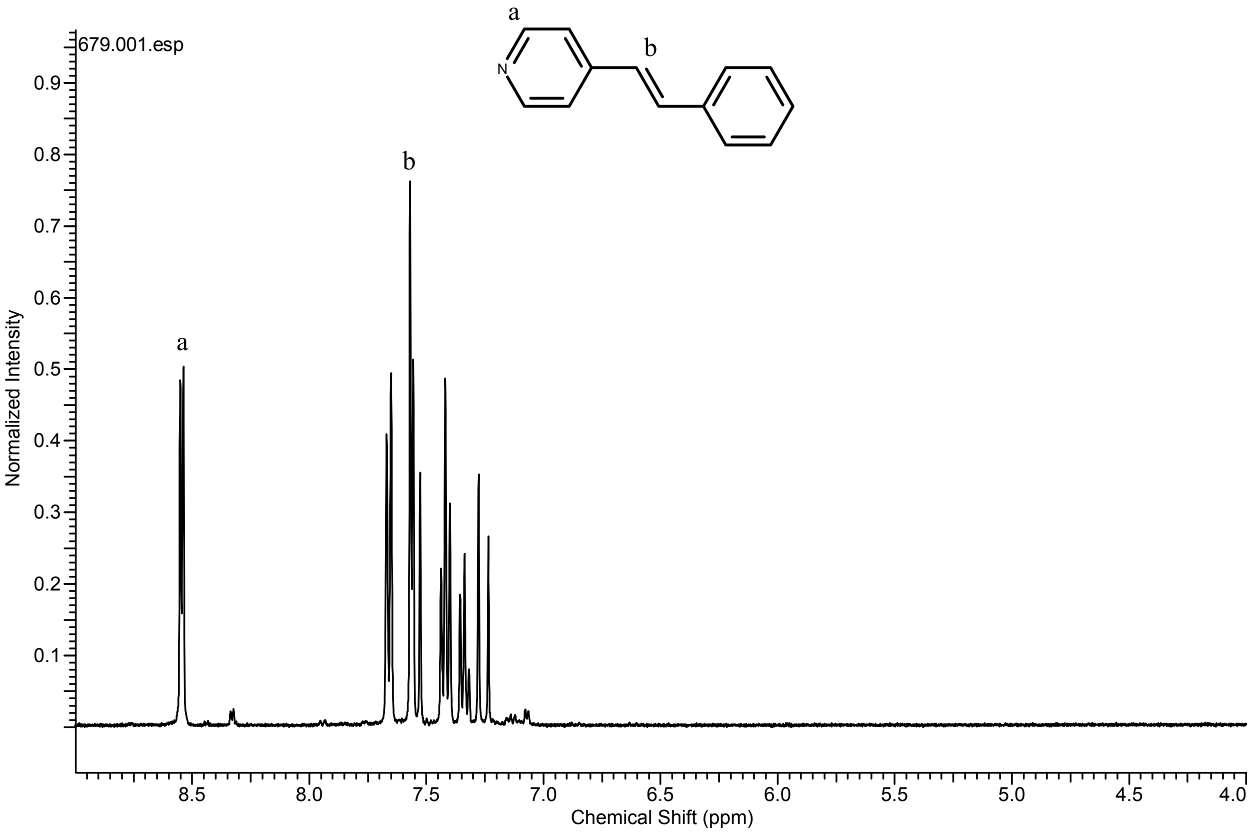

Figure S1: ^{1}H NMR spectrum of **4-SB** before UV irradiation (400 MHz, DMSO-d_6).

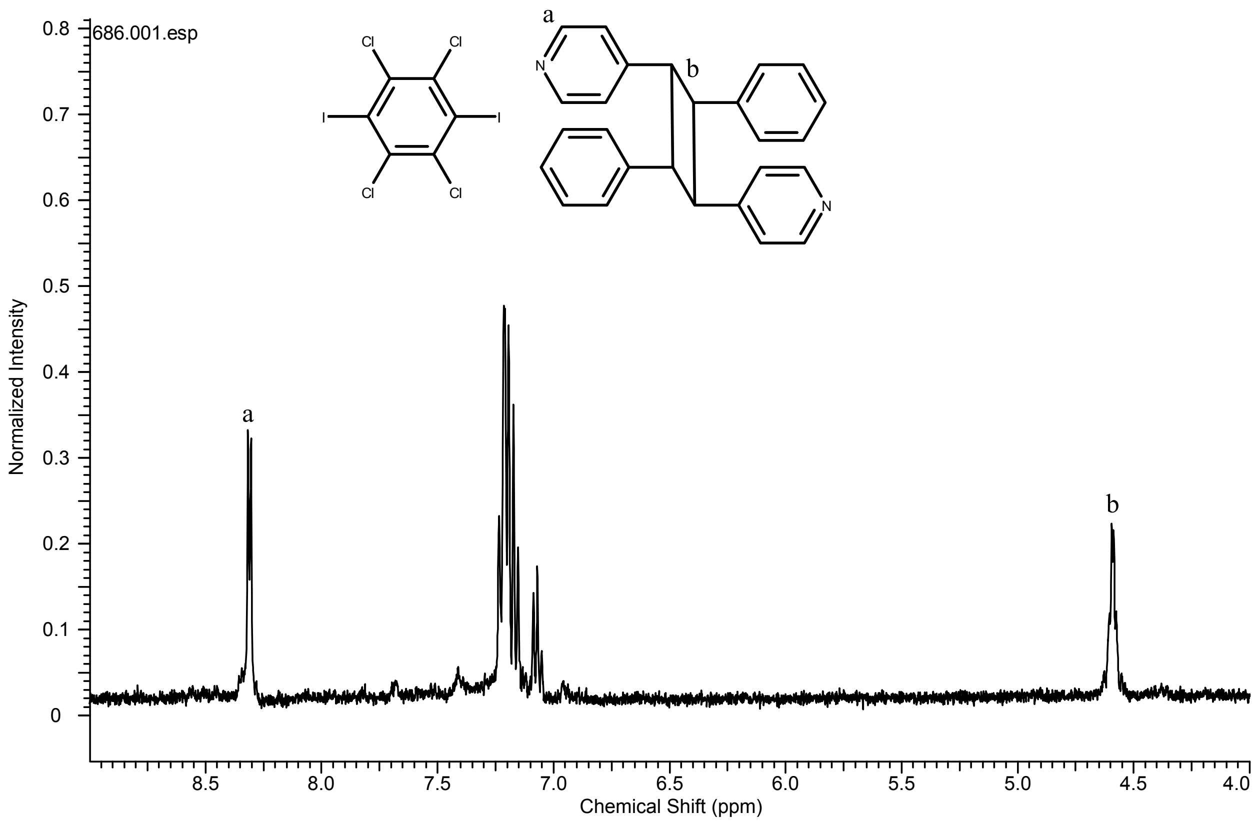

Figure S2: ^{1}H NMR spectrum of Form I of the co-crystal (**$C_6I_2Cl_4$**)•2(**4-SB**) after 30 hours of UV irradiation reaching a quantitative yield for the [2+2] cycloaddition reaction (400 MHz, DMSO-d_6).

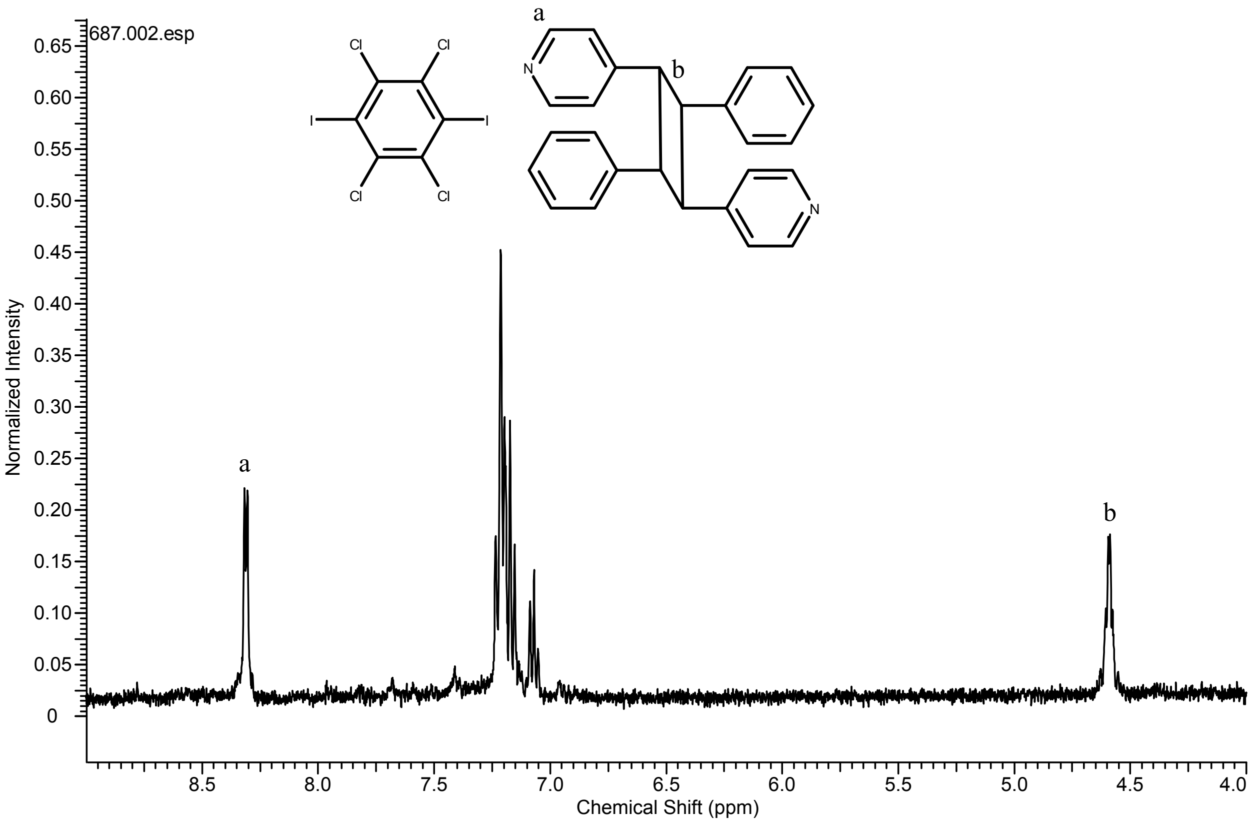

Figure S3: ^{1}H NMR spectrum of Form II of the co-crystal ($\mathbf{C_6I_2Cl_4}$)•2(**4-SB**) after 30 hours of UV irradiation reaching a quantitative yield for the [2+2] cycloaddition reaction (400 MHz, DMSO-d_6).

4. Powder X-ray Diffractograms

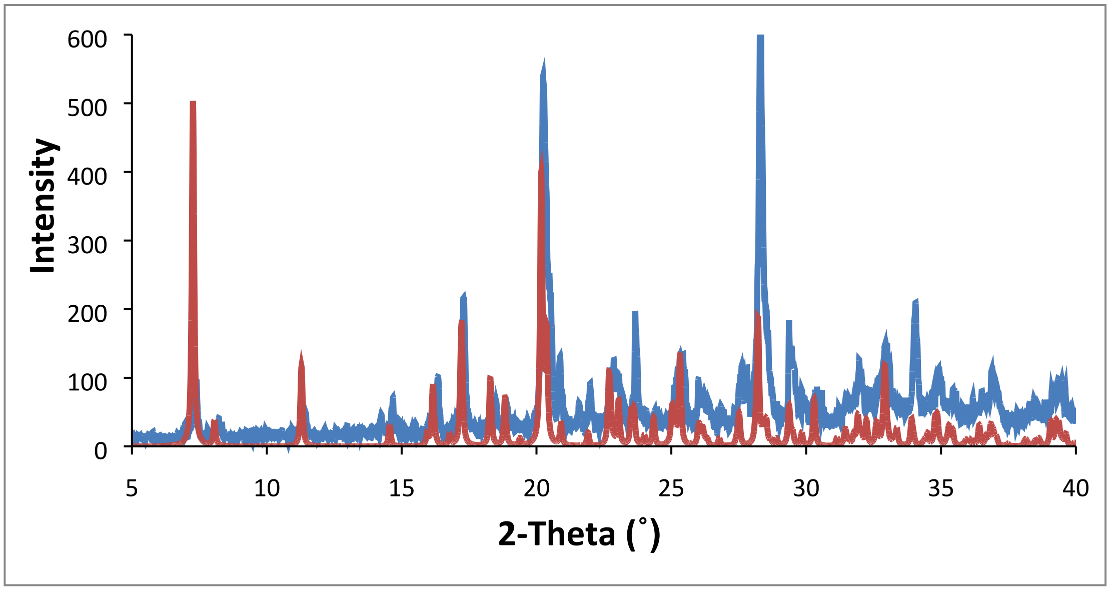

Figure S4: Powder X-ray diffraction data for the co-crystal (**$C_6I_2Cl_4$**)•2(**4-SB**) based upon the fast evaporation method. Color scheme the observed pattern (blue) and the calculated powder pattern for Form I (red).

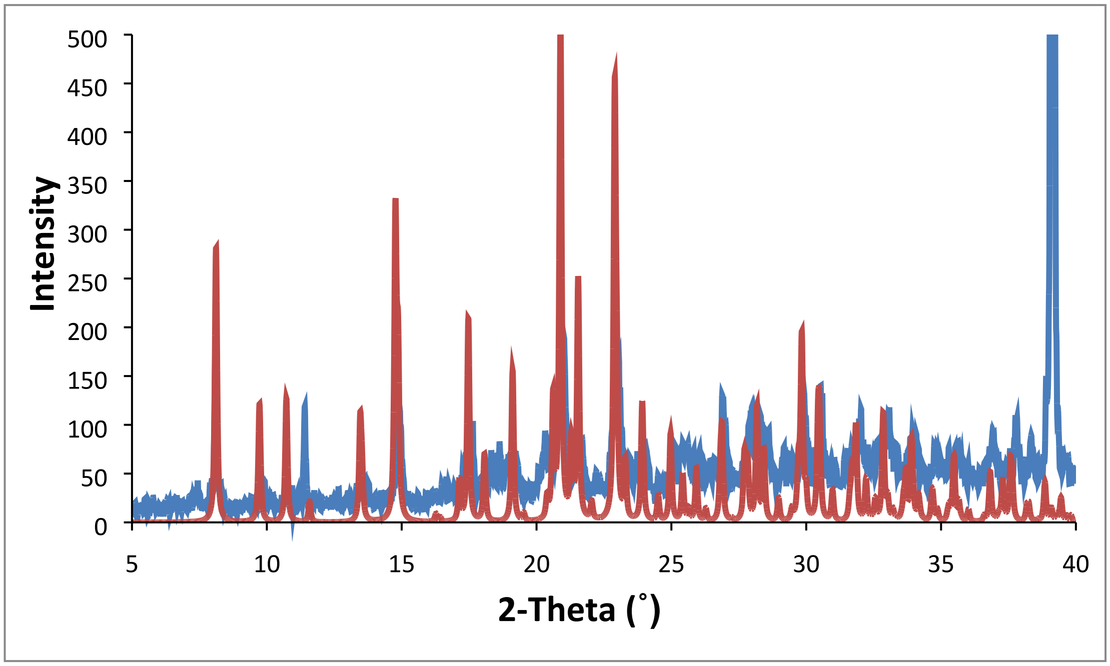

Figure S5: Powder X-ray diffraction data for the co-crystal (**$C_6I_2Cl_4$**)•2(**4-SB**) based upon the slow evaporation method. Color scheme is the observed pattern (blue) and the calculated powder pattern for Form II (red).

References

1. Reddy, C. M.; Kirchner, M. T.; Gundakaram, R. C.; Padmanabhan, K. A.; Desiraju, G. R. *Chem. Eur. J*. **2006**, *12*, 2222.

2. Krause *et al.*, (2015) SADABS v 2016/2.

3. Sheldrick, G. M. *Acta Crystallogr*., **2015**, *C71*, 3.