Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

for

Iodoperchlorobenzene acts as a dual halogen-bond donor to template a [2 + 2] cycloaddition reaction within an organic co-crystal

Nicole M. Shapiro, Eric Bosch, Daniel K. Unruh, Herman R. Krueger, Jr.,
and Ryan H. Groeneman

Department of Chemistry, Missouri State University, Springfield, MO 65804, USA

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX, 79409, USA

Department of Biological Sciences, Webster University, St. Louis, MO, 63119, USA

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

Materials

trans-1,2-bis(4-pyridyl)ethylene (**BPE**) and 4,4'-azopyridine (**AP**) as well as the solvent toluene were all purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received. 1,2-bis(4-pyridyl)acetylene (**BPA**) was purchased from Synquest Laboratories (Alachua, FL, USA) and used as received. The halogen bond donor iodoperchlorobenzene (**C_6ICl_5**) 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. The co-crystal (**C_6ICl_5**)•(**BPE**) was placed between a pair of Pyrex glass plates for irradiation. The photoreactivity of (**C_6ICl_5**)•(**BPE**) was determined after 40 hours of UV exposure by using ^1H NMR spectroscopy. ^1H 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 III X-ray diffractometer using Cu $K_\alpha 1$ radiation (λ = 1.54056 Å) between 5° to 50° two-theta.

Synthesis of (C_6ICl_5)•(BPE)

Co-crystals of (**C_6ICl_5**)•(**BPE**) was synthesized by dissolving 25.0 mg of **C_6ICl_5** in 2.0 mL of toluene, which was then combined with a separate 2.0 mL toluene solution containing 12.1 mg of **BPE** (1:1 molar equivalent). The combined solution was mixed and then the cap was removed to allow for slow evaporation. After three days and significant loss of solvent single crystals suitable for X-ray diffraction formed.

Synthesis of (C_6ICl_5)•(BPA)

In a similar manner as before, co-crystals of (**C_6ICl_5**)•(**BPA**) was synthesized by dissolving 25.0 mg of **C_6ICl_5** in 2.0 mL of toluene, which was then combined with a separate 2.0 mL toluene solution containing 12.0 mg of **BPA** (1:1 molar equivalent). The resulting solution was mixed and the cap was removed to allow for slow evaporation. After three days with loss of solvent single crystals suitable for X-ray diffraction formed.

Synthesis of (C_6ICl_5)•(AP)

In a similar way as before, co-crystals of (**C_6ICl_5**)•(**AP**) was synthesized by dissolving 25.0 mg of **C_6ICl_5** in 2.0 mL of toluene, which was then combined with a separate 2.0 mL toluene solution containing 12.2 mg of **AP** (1:1 molar equivalent). As before, the combined solution was mixed with the cap removed to allow for slow evaporation. Within three days and loss of solvent single crystals suitable for X-ray diffraction were realized.

2. Electronic Structure Calculations

To obtain binding energies, Density Functional Theory calculations were performed using the M06-2X density functional as implemented in the Gaussian 16 program.[2] An aug-cc-pVTZ basis set was used on all atoms, with the exception of iodine, using the basis sets stored internally in the Gaussian program. For iodine, the basis set, which included a core potential replacing the inner 28 electrons, was obtained from the EMSL Basis Set Exchange Library.[3] The energies were computed using the counterpoise method as implemented in Gaussian. This procedure computes the energy as the difference between the energy of the pair and the energies of the separated molecules. In the case of the separated fragments, the energies are computed using the entire set of orbitals for the molecular pair. For all calculations, the counterpoise correction was rather modest, comprising about 10% of the computed value.

3. Electrostatic potential calculations.

The geometry of $\mathbf{C_6ICl_5}$ was minimized and the electrostatic potential energy surface calculated using the Spartan'10 molecular modelling program with density functional theory (DFT) at the B3LYP/6- 311++G** level.[4]

4. Single X-ray Diffraction Information and Data Tables

Data were collected on a Rigaku XtaLAB Synergy-*i*Kappa diffractometer equipped with a PhotonJet-*i* X-ray source operated at 50 W (50kV, 1 mA) to generate Cu Kα radiation (λ = 1.54178 Å) and a HyPix-6000HE HPC (hybrid photon counting) detector. Crystals were transferred from the vial and placed on a glass slide in type NVH immersion oil by Cargille. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The crystal and a small amount of the oil were collected on a Hampton Research 20 micron cryoloop and transferred to the instrument where it was placed under a cold nitrogen stream (Oxford). The sample was optically centered with the aid of a video camera to insure that no translations were observed as the crystal was rotated through all positions. The crystal was measured for size, morphology, and color.

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects using *CrysAlis^{Pro}*.[5] A numerical absorption correction was applied based on a Gaussian integration over a multifaceted crystal and followed by a semi-empirical correction for adsorption applied using the program *SCALE3 ABSPACK*.[6] The *SHELX-2014*,[7] series of programs was used for the solution and refinement of the crystal structures. Hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

Table S1. X-ray data for **(C_6ICl_5)**, **(C_6ICl_5)•(BPE)**, **(C_6ICl_5)•(BPA)**, and **(C_6ICl_5)•(AP)**.

crystal	**(C_6ICl_5)**	**(C_6ICl_5)•(BPE)**	**(C_6ICl_5)•(BPA)**	**(C_6ICl_5)•(AP)**
chemical formula	C_6Cl_5I	$C_{18}H_{10}Cl_5IN_2$	$C_{18}H_8Cl_5IN_2$	$C_{18}H_8Cl_5IN_4$
formula mass	376.21	558.43	556.41	560.41
crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.1229(2)	3.9746(1)	3.9516(1)	3.9144(1)
b/Å	3.9138(1)	10.7984(2)	11.1045(2)	10.6909(1)
c/Å	15.0718(4)	12.4426(3)	12.2703(3)	12.4925(2)
α/°	90	111.056(2)	112.085(2)	111.510(1)
β/°	92.013(2)	93.327(2)	91.110(2)	93.205(1)
γ/°	90	93.491(2)	96.392(2)	91.807(1)
V/Å^3	478.86(2)	495.61(2)	494.72(2)	484.858(16)
ρ_{calc} /g cm^{-3}	2.609	1.871	1.868	1.919
T/K	100	290	290	290
Z	2	1	1	1
radiation type	Cu Kα	Cu Kα	Cu Kα	Cu Kα
absorption coefficient, μ/mm^{-1}	38.608	18.940	18.974	19.394
no. of reflections measured	6562	11021	10654	10832
no. of independent reflections	946	1952	1944	1902
R_{int}	0.0437	0.0525	0.0479	0.0490
R_1 ($I > 2\sigma(I)$)	0.0260	0.0281	0.0252	0.0272
wR(F^2) ($I > 2\sigma(I)$)	0.0663	0.0724	0.0634	0.0751
R_1 (all data)	0.0280	0.0298	0.0268	0.0281
wR(F^2) (all data)	0.0674	0.0740	0.0643	0.0758
Goodness-of-fit	1.112	1.056	1.074	1.076
CCDC deposition number	2106689	2106690	2106691	2106692

5. Powder X-ray Diffractograms

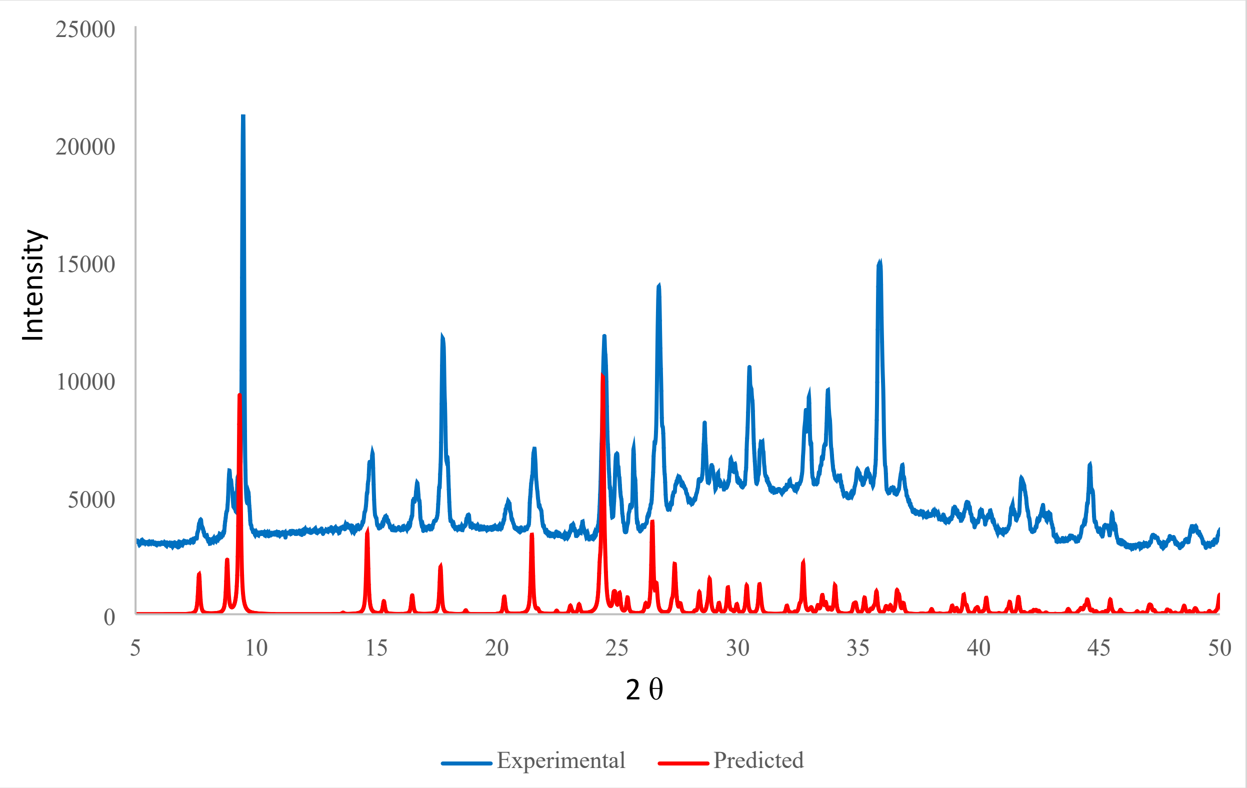

Figure S1: Powder X-ray diffraction data for the co-crystal (**C_6ICl_5**)•(**BPE**). Color scheme is the observed pattern (blue) and the calculated powder pattern (red).

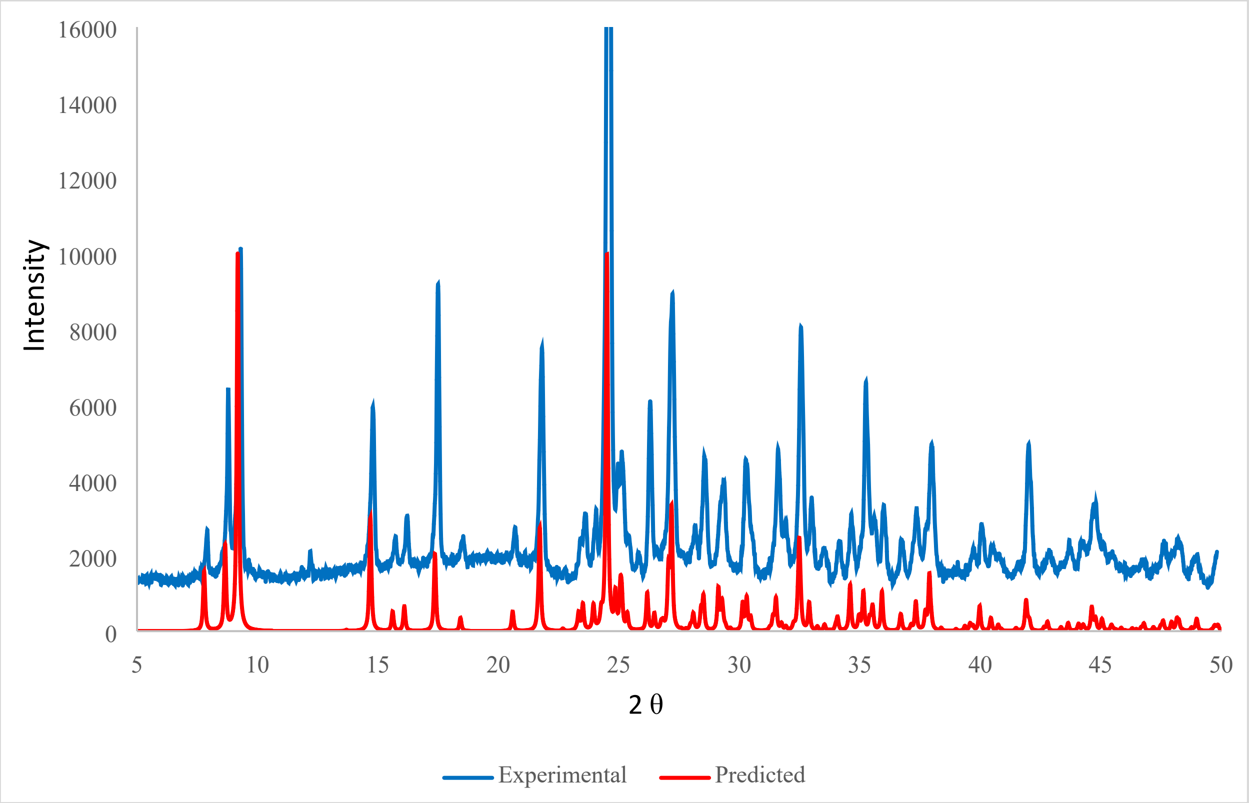

Figure S2: Powder X-ray diffraction data for the co-crystal (**C_6ICl_5**)•(**BPA**). Color scheme is the observed pattern (blue) and the calculated powder pattern (red).

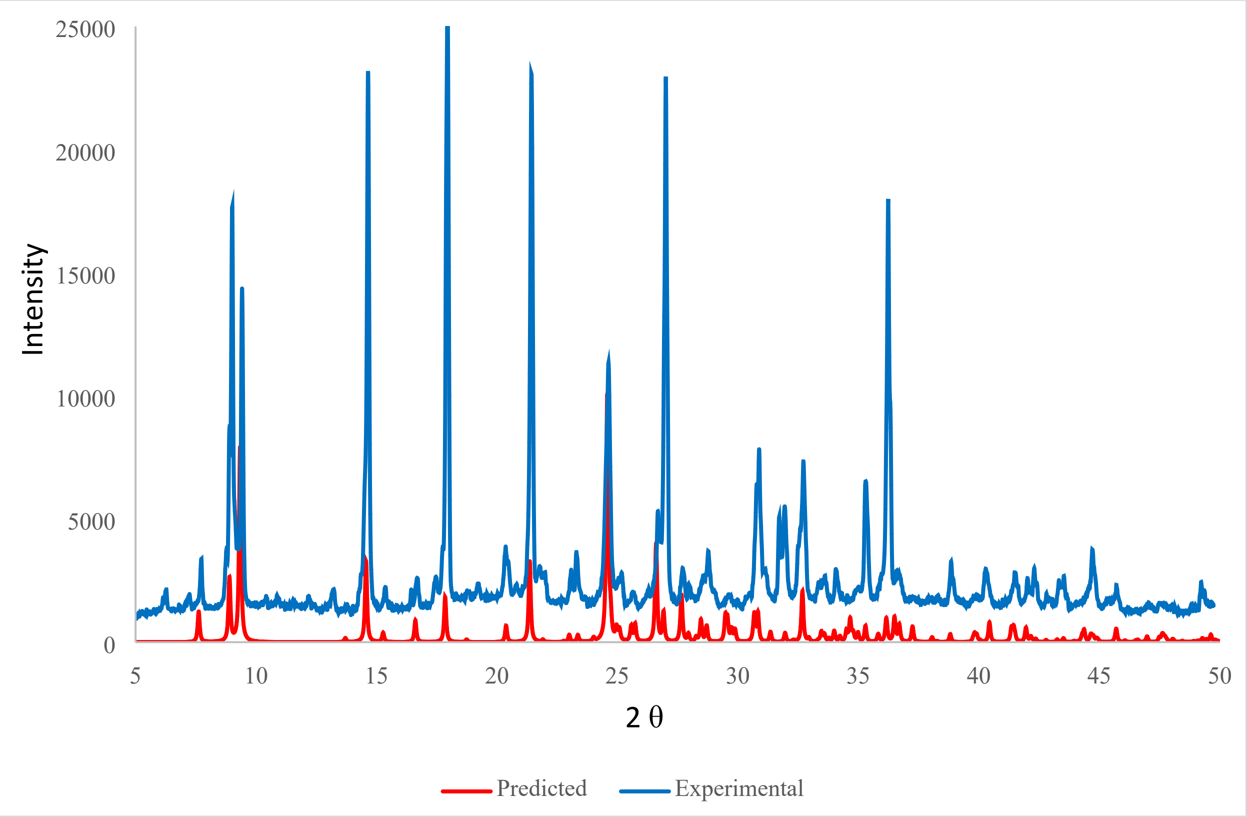

Figure S3: Powder X-ray diffraction data for the co-crystal (**C_6ICl_5**)•(**AP**). Color scheme is the observed pattern (blue) and the calculated powder pattern (red).

6. ^{1}H NMR Spectroscopic Data

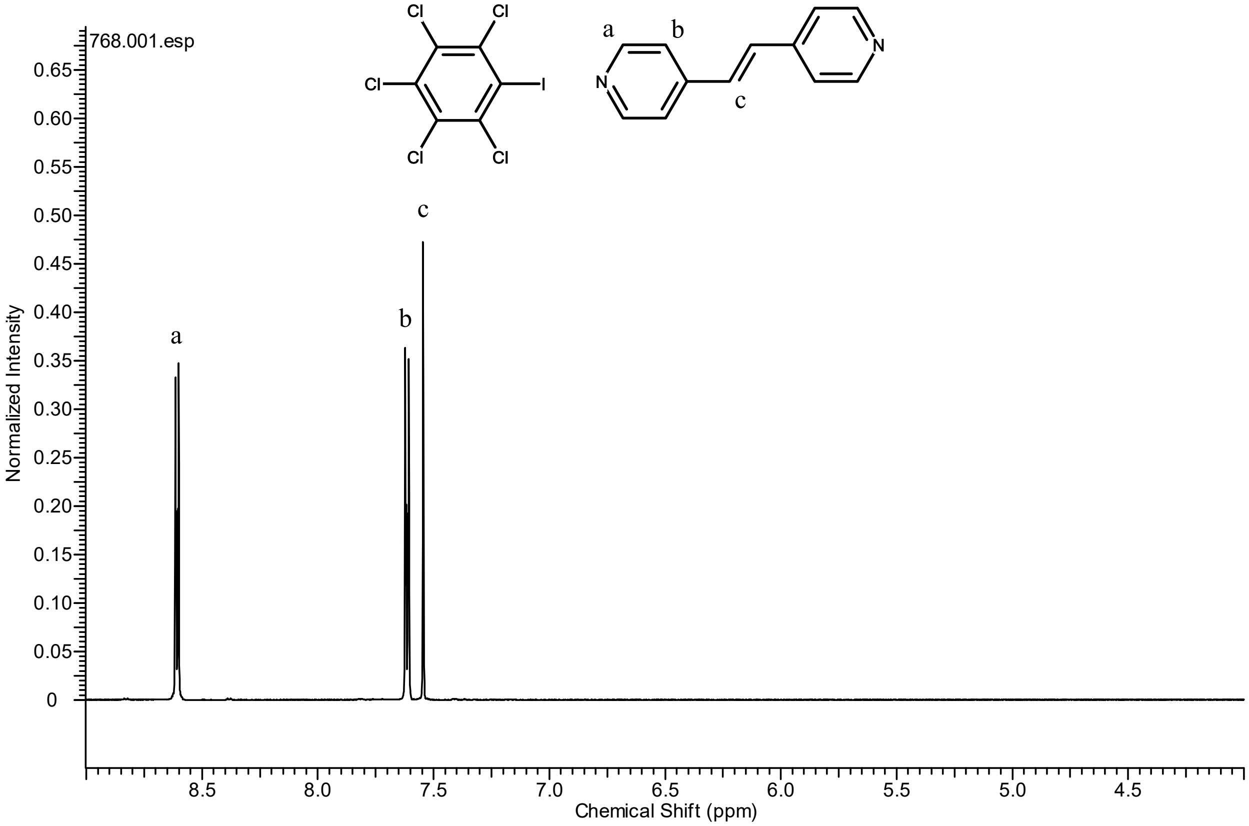

Figure S4: ^{1}H NMR spectrum of the co-crystal (**C_6ICl_5**)•(**BPE**) before UV irradiation (400 MHz, DMSO-d_6).

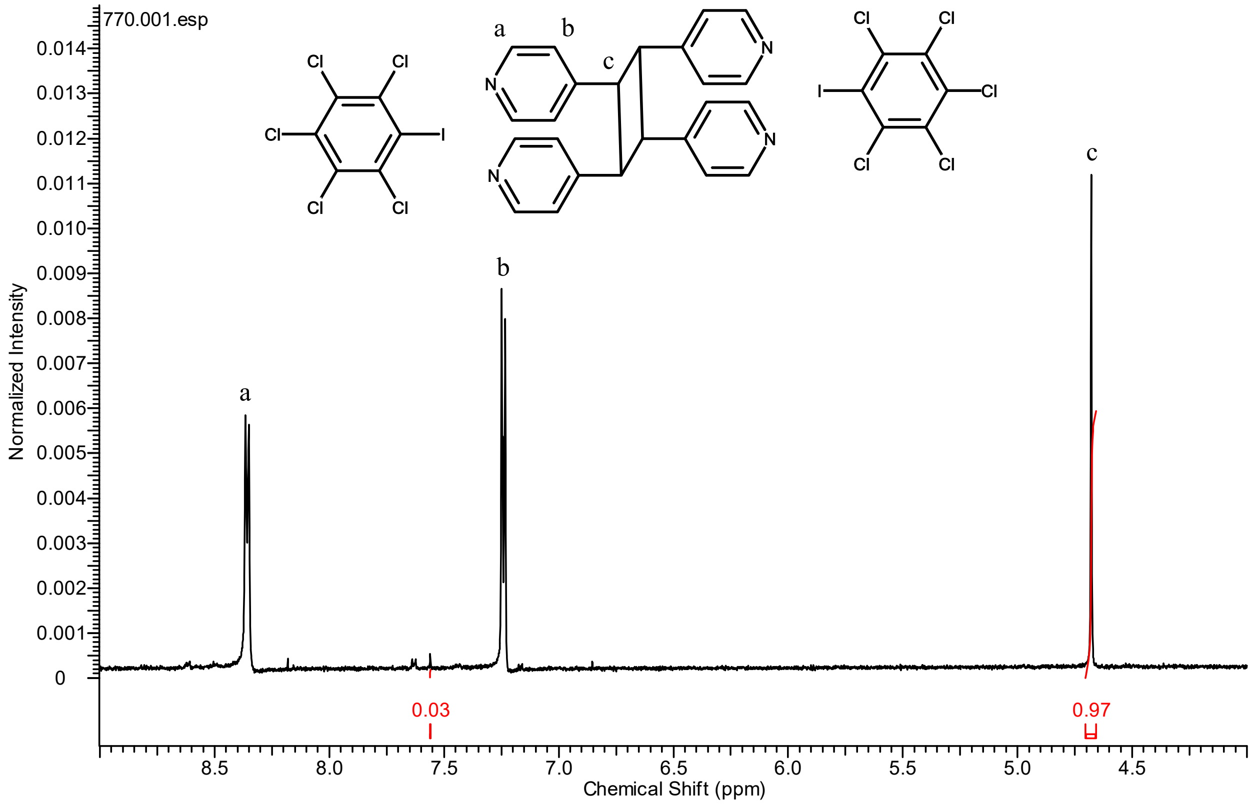

Figure S5: ^{1}H NMR spectrum of ($\mathbf{C_6ICl_5}$)•(**TPCB**) after 40 hours of UV irradiation reaching a yield of 97% for the [2+2] cycloaddition reaction (400 MHz, DMSO-d_6).

References

1. H.-Q. Do and O. Dauglis, *Org. Lett.*, 2009, **11**, 421.

2. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

3. EMSL Basis Set Exchange Library. https://bse.pnl.gov/bse/portal.

4. *Spartan'10*, Version 1.0.1, Wavefunction, Inc. Irvine, CA, USA.

5. CrysAlis^{Pro} (2018) Oxford Diffraction Ltd.

6. SCALE3 ABSPACK (2005) Oxford Diffraction Ltd.

7. (a) G. M. Sheldrick, *Acta. Cryst*. **2015**, *A71*, 3; (b) G. M. Sheldrick, *Acta. Cryst*. **2015**, *C71*, 3.