Supporting Information

for

Cooperative non-covalent interactions and synthetic feed as driving forces to structural diversity within organic co-crystals containing isosteric perhalobenzenes

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1. Materials and Synthesis of the Co-crystals

Materials

The halogen-bond donor 1,4-diiodoperfluorobenzene (**$C_6I_2F_4$**) as well as the solvent toluene were both purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received. The other halogen-bond donor 1,4-diiodoperchlorobenzene (**$C_6I_2Cl_4$**)[1] and the ester, namely *trans*-1-(4-methylbenzoate)-2-(4-pyridyl)ethylene (**4-PEBE**)[2] were synthesized by previous reported methods. All crystallization studies were performed in 20 mL scintillation vials.

Synthesis of (**$C_6I_2F_4$**)•(**4-PEBE**)

Co-crystals of (**$C_6I_2F_4$**)•(**4-PEBE**) was synthesized by dissolving 25.0 mg of **$C_6I_2F_4$** in 2.0 mL of toluene, which was then combined with a separate 2.0 mL toluene solution containing 14.9 mg of **4-PEBE** (1:1 molar equivalent). The solution was then allowed to slowly evaporate and within two days, crystals suitable for X-ray diffraction formed.

Synthesis of (**$C_6I_2F_4$**)•2(**4-PEBE**)

Co-crystals of (**$C_6I_2F_4$**)•2(**4-PEBE**) was synthesized by dissolving 25.0 mg of **$C_6I_2F_4$** in 2.0 mL of toluene, which was then combined with a separate 2.0 mL toluene solution containing 29.8 mg of **4-PEBE** (1:2 molar equivalent). The solution was then allowed to slowly evaporate and within two days, crystals suitable for X-ray diffraction formed.

Synthesis of (**$C_6I_2Cl_4$**)•2(**4-PEBE**)

In a similar way as before, co-crystals of (**$C_6I_2Cl_4$**)•2(**4-PEBE**) was synthesized by dissolving 25.0 mg of **$C_6I_2Cl_4$** in 2.0 mL of toluene, which was then combined with either a 2.0 mL toluene solution containing 12.8 mg of **4-PEBE** (1:1 molar equivalent) or a 25.6 mg of **4-PEBE** (1:2 molar equivalent). Both solutions were then allowed to slowly evaporate and within two days, crystals suitable for X-ray diffraction formed. Crystals were removed before all solvent was evaporated. Both ratios yielded only one type of co-crystal.

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.[3] An aug-cc-pVTZ basis set was used on all atoms. With the exception of iodine, the basis sets employed were those 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.[4] 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 fragments. 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 **4-PEBE** were 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.[5]

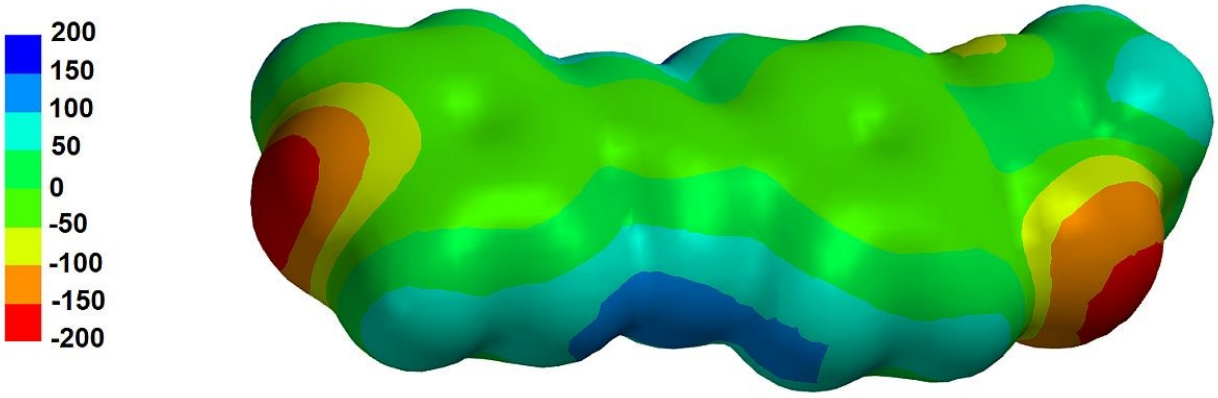

Figure S1. Molecular electrostatic potential plot for **4-PEBE**. The units of the scale are in kJ/mol.

4. Single X-ray Diffraction Information and Data Tables

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.

Table S1. X-ray crystallographic and refinement data for (**$C_6I_2F_4$**)•(**4-PEBE**), (**$C_6I_2F_4$**)•2(**4-PEBE**), and (**$C_6I_2Cl_4$**)•2(**4-PEBE**).

compound name	(**$C_6I_2F_4$**)•(**4-PEBE**)	(**$C_6I_2F_4$**)•2(**4-PEBE**)	(**$C_6I_2Cl_4$**)•2(**4-PEBE**)
chemical formula	$C_{21}H_{13}F_4I_2NO_2$	$C_{36}H_{26}F_4I_2N_2O_4$	$C_{18}H_{13}Cl_2INO_2$
formula mass	641.12	880.39	473.09
crystal system	Monoclinic	Triclinic	Triclinic
space group	*C*2/*c*	*P*$\bar{1}$	*P*$\bar{1}$
a/Å	16.3940(10)	6.2670(1)	8.2756(2)
b/Å	6.4768(4)	11.0627(2)	10.2186(3)
c/Å	38.606(2)	12.1817(3)	11.8757(4)
α/°	90	76.276(2)	114.5720(10)
β/°	93.249(3)	83.834(2)	92.194(2)
γ/°	90	83.200(2)	107.358(2)
V/Å^3	4092.6(4)	811.91(3)	856.35(4)
ρ_{calc}/g cm^{-3}	2.081	1.801	1.835
T/K	100(2)	100(2)	100(2)
Z	8	1	2
radiation type	MoK_α	CuKα	MoK_α
absorption coefficient, μ/mm^{-1}	3.128	15.791	2.192
no. of reflections measured	51577	15382	32790
no. of independent reflections	5403	3231	6056
no. of reflections ($I > 2\sigma(I)$)	4397	3062	5711
R_{int}	0.0574	0.0664	0.0176
R_1 ($I > 2\sigma(I)$)	0.0261	0.0303	0.0162
$wR(F^2)$ ($I > 2\sigma(I)$)	0.0447	0.0712	0.0377
R_1 (all data)	0.0396	0.0328	0.0185
$wR(F^2)$ (all data)	0.0477	0.0737	0.0388
Goodness-of-fit	1.019	1.045	1.110
CCDC deposition number	2156801	2168646	2156802

5. Powder X-ray Diffractograms

Powder X-ray diffraction data was collected at room temperature on a Rigaku MiniFlexII X-ray diffractometer using Cu $K_\alpha 1$ radiation (λ = 1.54056 Å) between 5˚ to 50˚ two-theta.

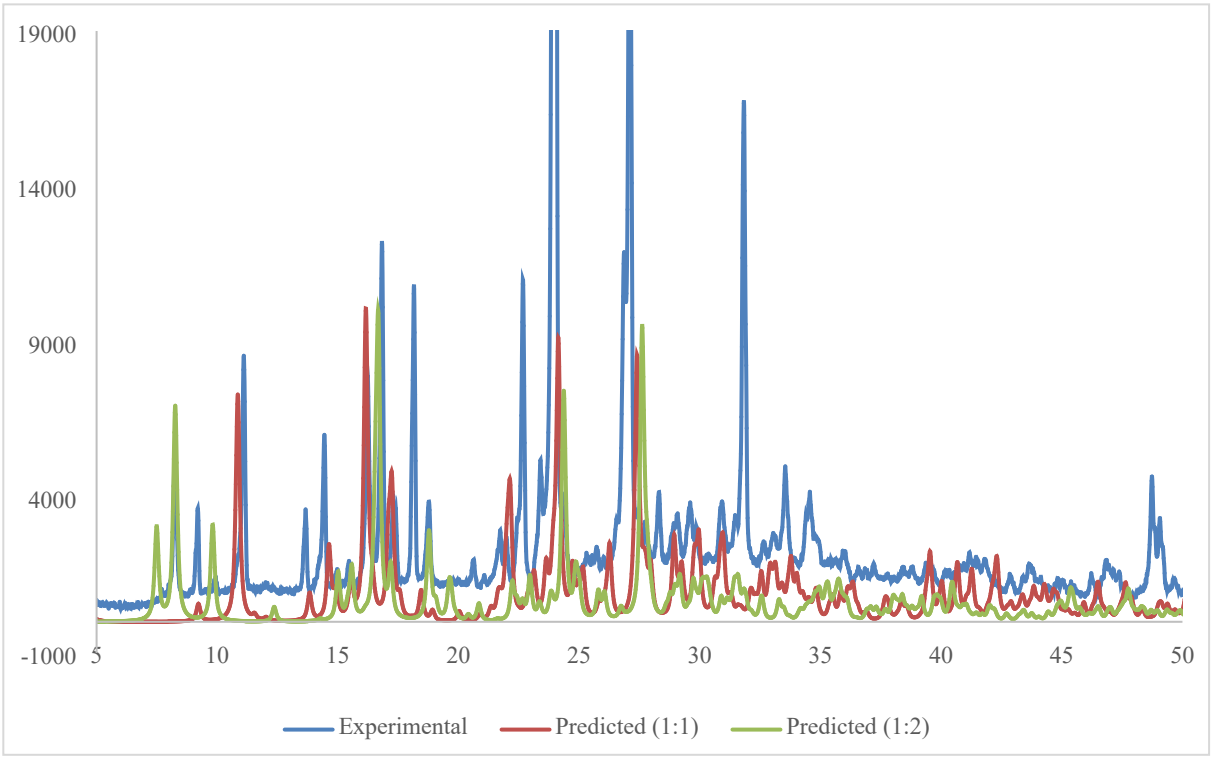

Figure S2: Powder X-ray diffraction data for the solution containing both co-crystals (**$C_6I_2F_4$**)•(**4-PEBE**) and (**$C_6I_2F_4$**)•2(**4-PEBE**). Color scheme is the observed pattern (blue) and the calculated powder pattern for (**$C_6I_2F_4$**)•(**4-PEBE**) (red) and (**$C_6I_2F_4$**)•2(**4-PEBE**) (green).

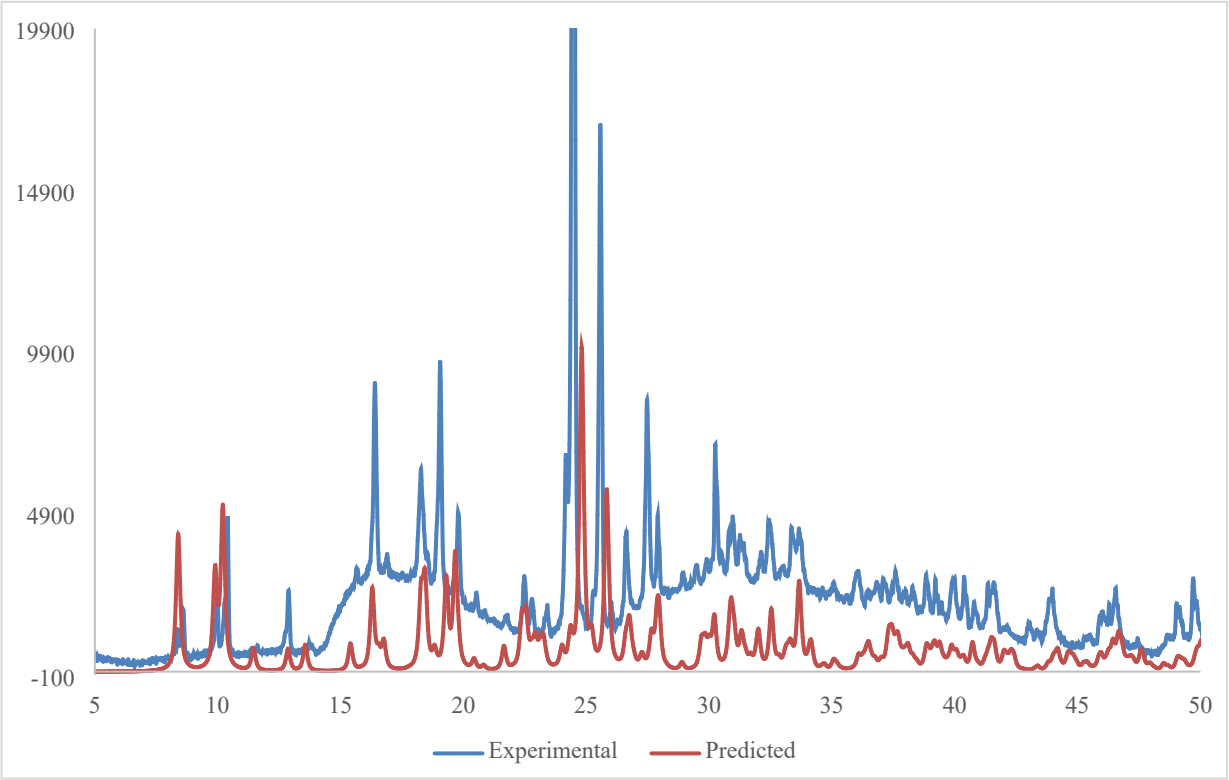

Figure S3: Powder X-ray diffraction data for the co-crystal ($C_6I_2Cl_4$)•2(**4-PEBE**). Color scheme is the observed pattern (blue) and the calculated powder pattern (red).

6. References

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

2. M. L. Boillot, C. Roux, J. P. Audière, A. Dausse, J. Zarembowitch, *Inorg. Chem*., 1996, **35**, 3975.

3. 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.

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

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