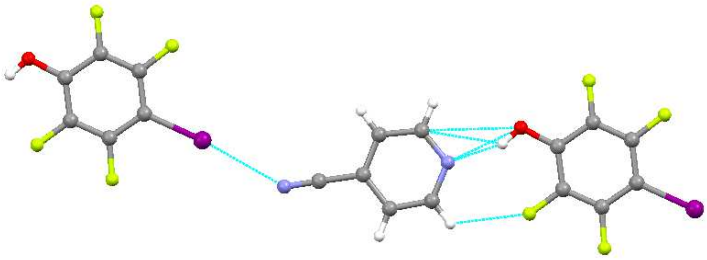
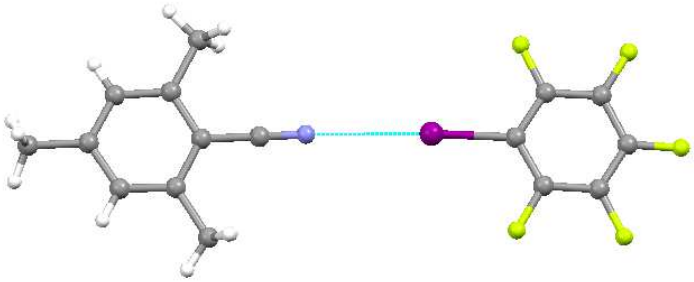
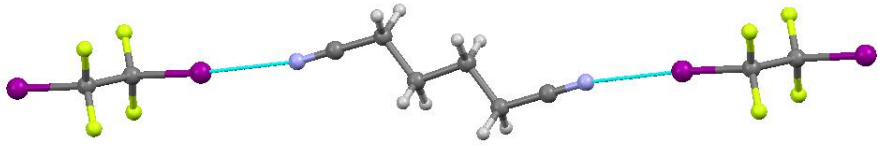
Electronic
Supplementary
Information

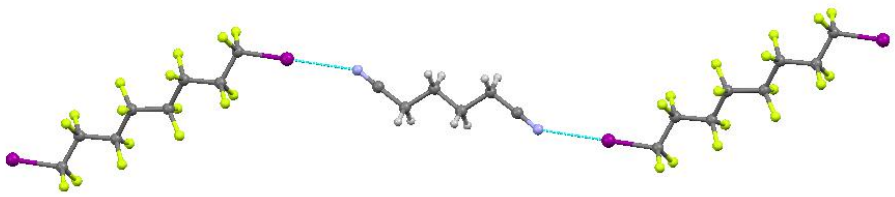
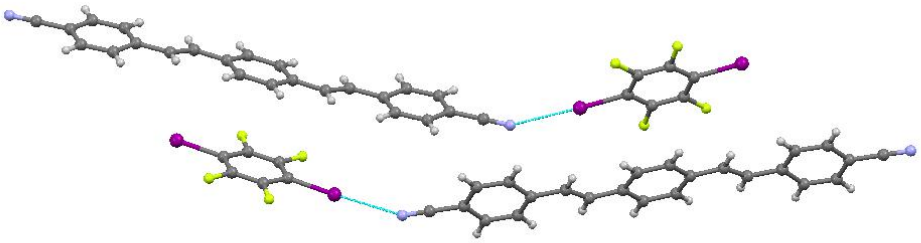
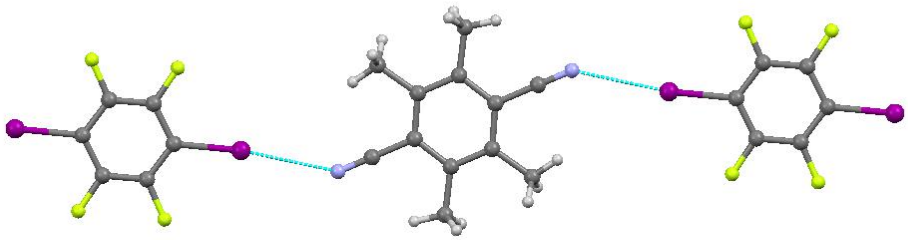
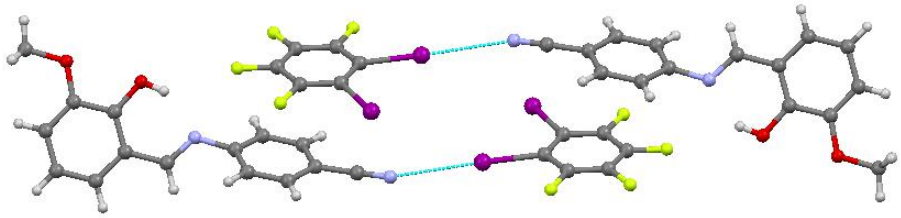
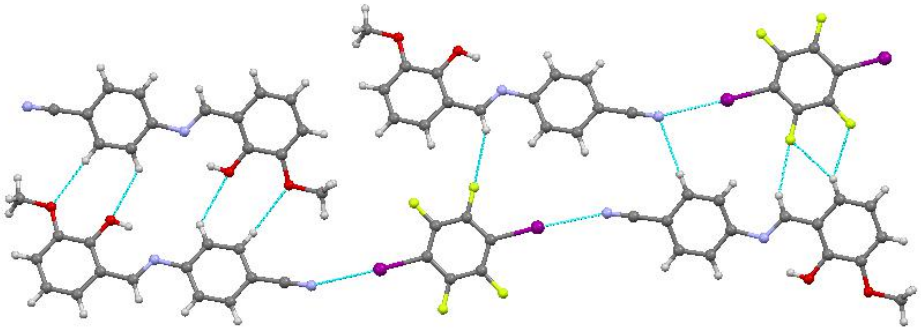
The Energy Frameworks of Aufbau Synthon Modules in 4-Cyanopyridine Co-crystals.

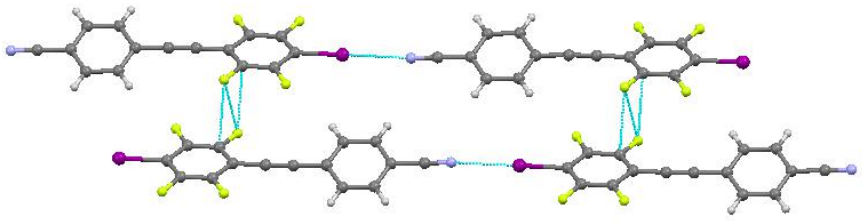
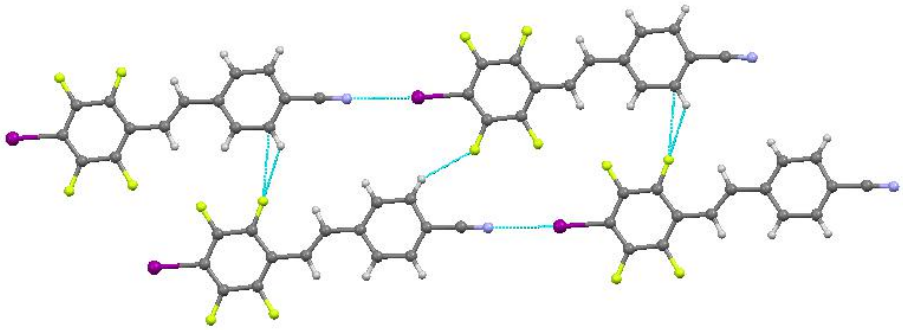
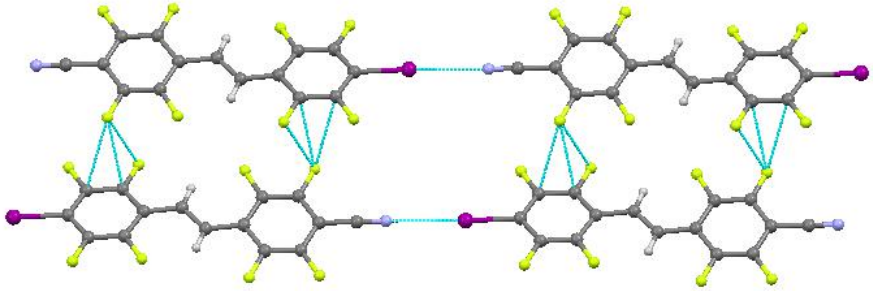
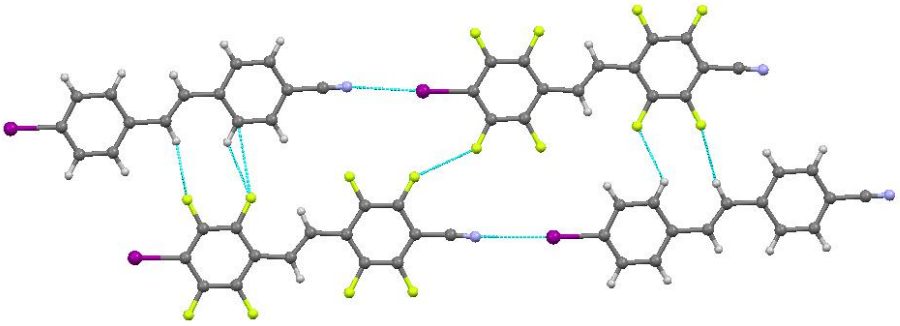
Y. V. Torubaev, I. V. Skabitsky.

Table S1. Selected examples of intermolecular CN---I-R_f[1]bonding in the co-crystals (from the Cambridge Structural Database [2])

	CSD Identifier	Structure	Rederence
1	BUNJEB		C.B.Aakeroy, C.L.Spartz, S.Dembowski, S.Dwyre, J.Desper, *IUCrJ* (2015), **2**, 498
2	EBIHEF		A.Wasilewska, M.Gdaniec, T.Polonski, *CSD Communication* (2016)
3	EBIHIH		P.Metrangolo, T.Pilati, G.Resnati, A.Stevenazzi, *Chem.Commun.* (2004), 1492

[1]. R_f – perfluorinated aryl or alkyl group
[2]The Cambridge Structural Database C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, ActaCryst. (2016). B72, 171-179 ; DOI: 10.1107/S2052520616003954

4	EBIHON		P.Metrangolo, T.Pilati, G.Resnati, A.Stevenazzi, *Chem.Commun.* (2004), 1492
5	FAKFII		Dongpeng Yan, A.Delori, G.O.Lloyd, T.Friscic, G.M.Day, W.Jones, Jun Lu, Min Wei, D.G.Evans, XueDuan, *Angew.Chem.,Int.Ed.* (2011), **50**, 12483
6	HUMLOQ		D.Britton, W.B.Gleason, *ActaCrystallogr.,Sect.E:Struct.Rep.Online* (2002), **58**, o1375
7	IWONAL		M.Zbacnik, M.Vitkovic, V.Vulic, I.Nogalo, D.Cincic, *Cryst.Growth Des.* (2016), **16**, 6381
8	IWONOZ		M.Zbacnik, M.Vitkovic, V.Vulic, I.Nogalo, D.Cincic, *Cryst.Growth Des.* (2016), **16**, 6381

9	NUHDEB		F.Frausto, Z.C.Smith, T.E.Haas, S.W.Thomas III, *Chem.Commun.* (2015), **51**, 8825
10	QORZUT		R.Mariaca, G.Labat, N.-R.Behrnd, M.Bonin, F.Helbling, P.Eggli, G.Couderc, A.Neels, H.Stoeckli-Evans, J.Hulliger, *J.Fluorine Chem.* (2009), **130**, 175
11	QOSCAD		R.Mariaca, G.Labat, N.-R.Behrnd, M.Bonin, F.Helbling, P.Eggli, G.Couderc, A.Neels, H.Stoeckli-Evans, J.Hulliger, *J.Fluorine Chem.* (2009), **130**, 175
12	QOSCOR		R.Mariaca, G.Labat, N.-R.Behrnd, M.Bonin, F.Helbling, P.Eggli, G.Couderc, A.Neels, H.Stoeckli-Evans, J.Hulliger, *J.Fluorine Chem.* (2009), **130**, 175

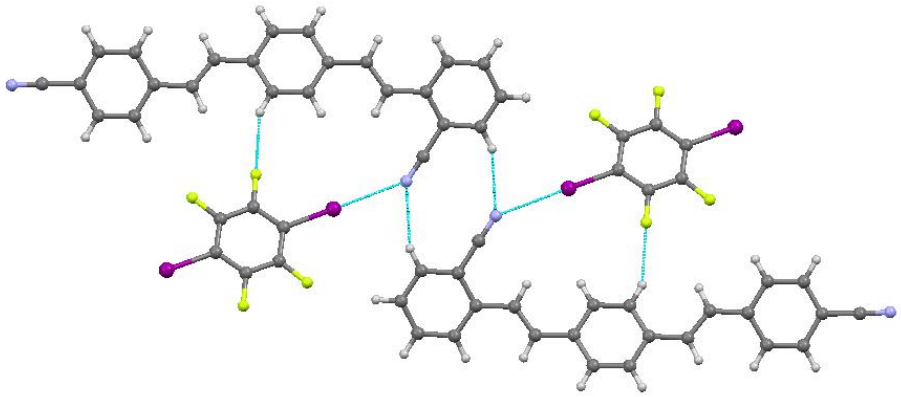
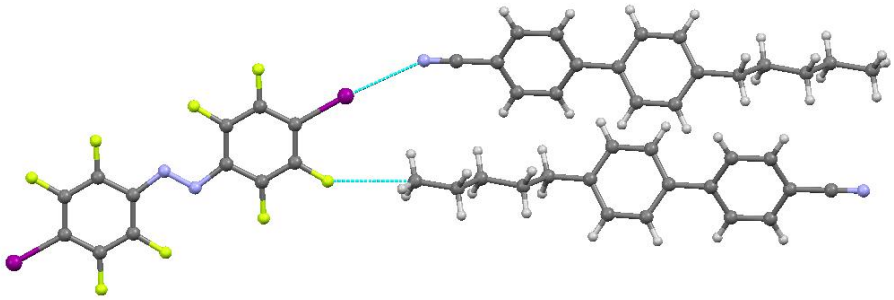
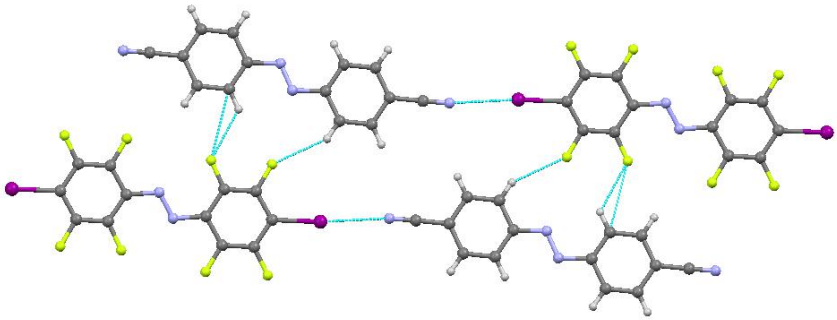
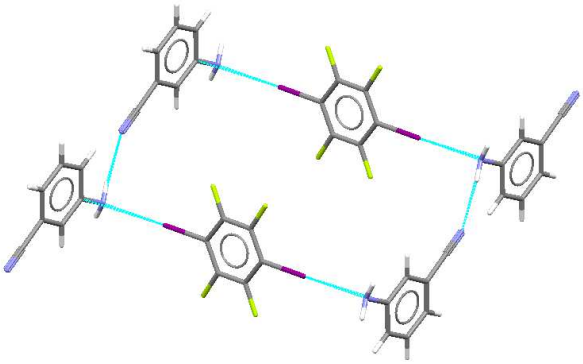
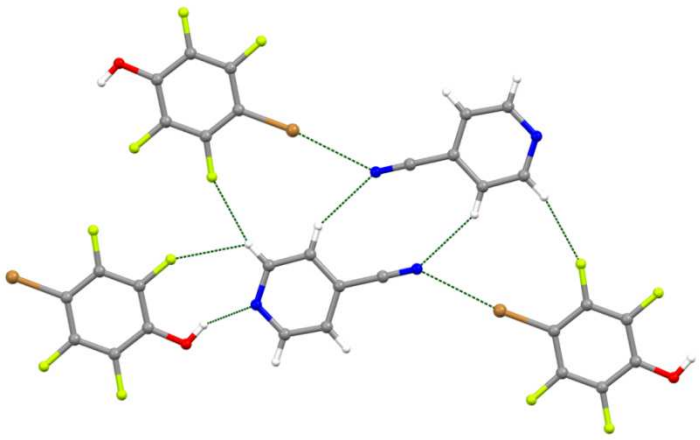
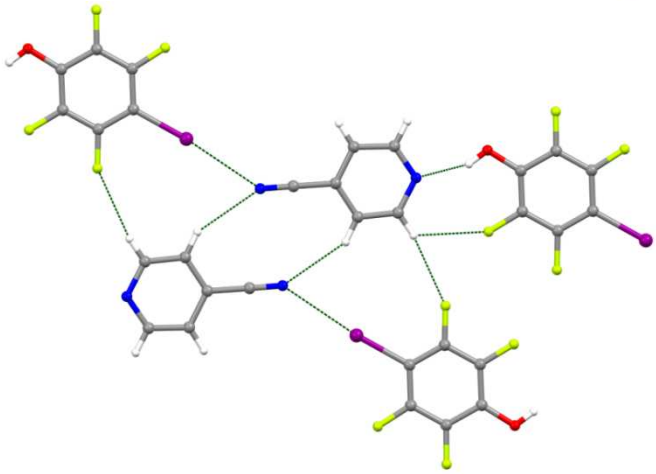
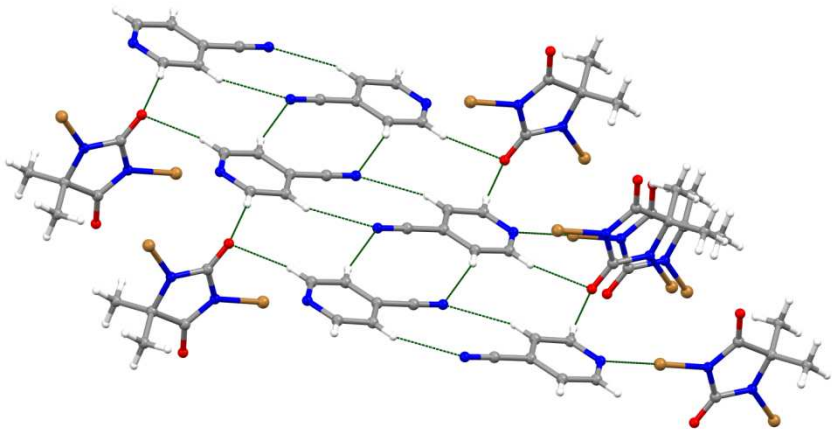
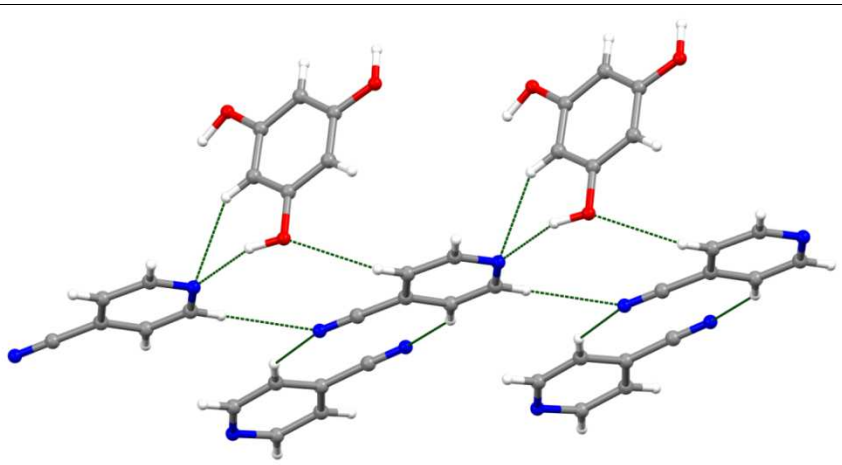
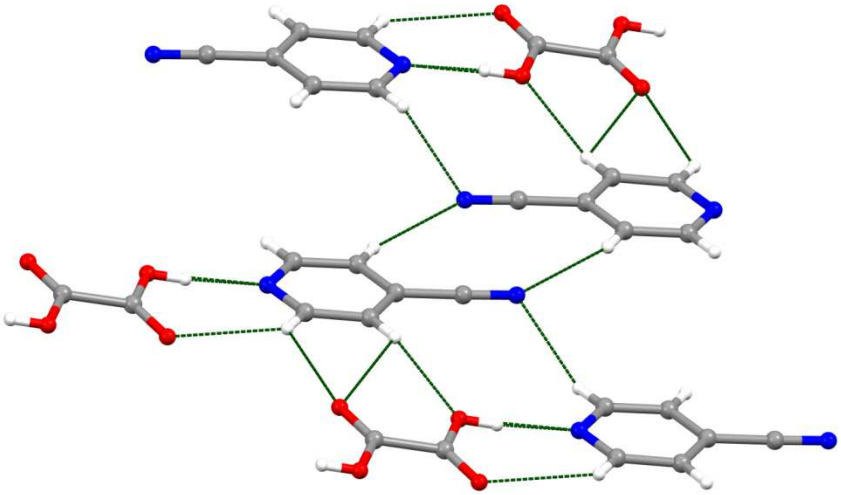
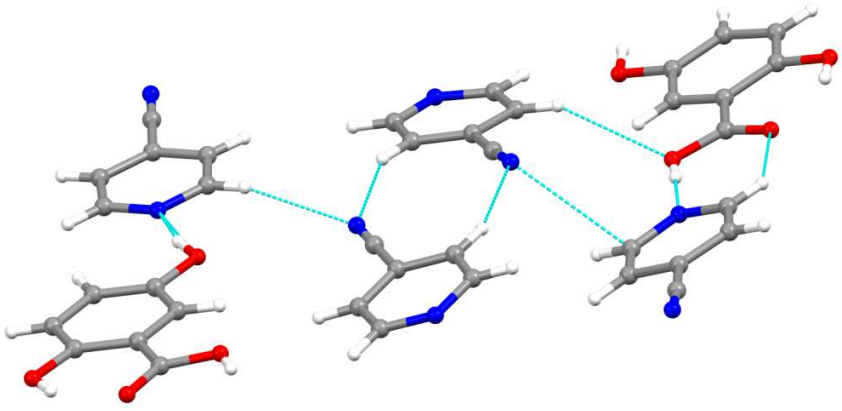
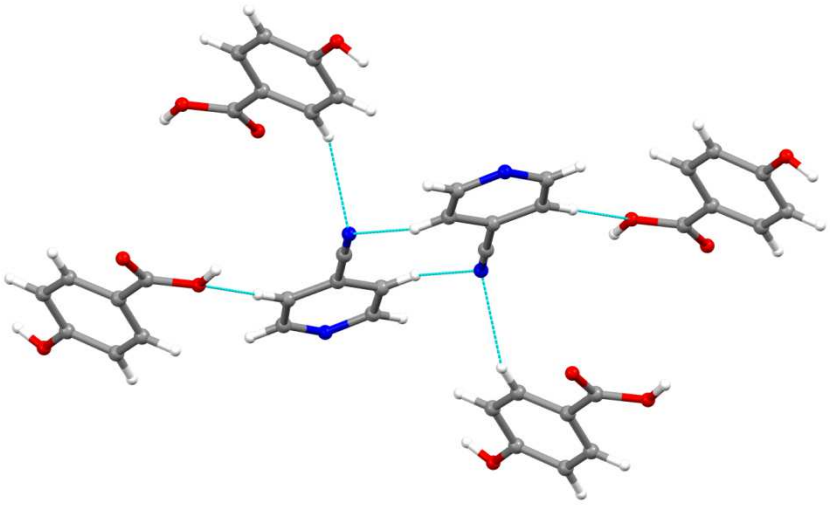
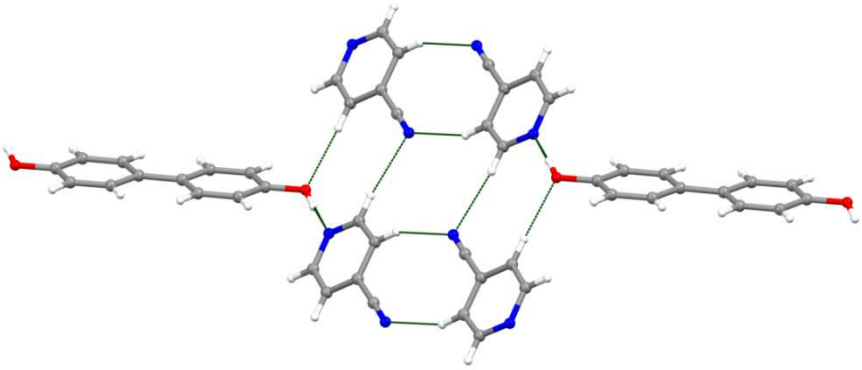
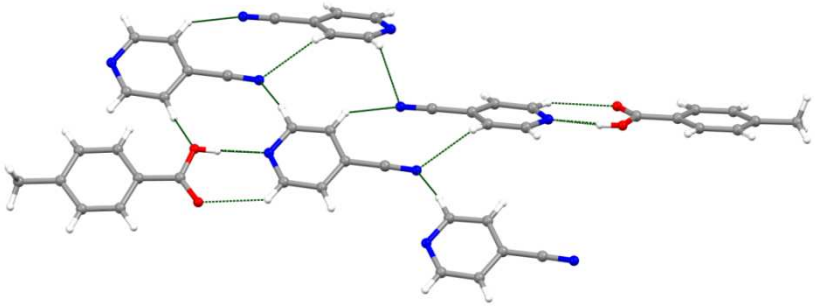
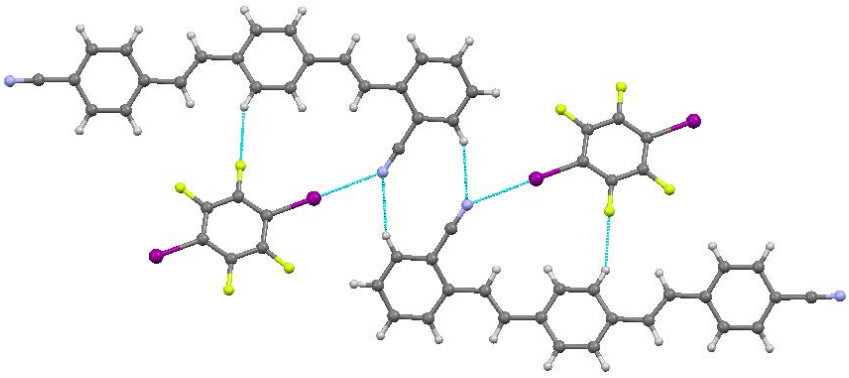
13	SAHJAP		Guoling Fan, Dongpeng Yan, *Scientific Reports* (2014), **4**, 4933
14	ZABLOG		O.S.Bushuyev, T.Friscic, C.J.Barrett, *Cryst.Growth Des.* (2016), **16**, 541
15	ZABLUM		O.S.Bushuyev, T.Friscic, C.J.Barrett, *Cryst.Growth Des.* (2016), **16**, 541
16	JEHZUU		V.Nemec, D.Cincic, CrystEngComm (2016), 18, 7425, doi:10.1039/C6CE01703G

Table S2. Selected examples of intermolecular CN---H- hydrogen bonded 4-cyanopyridine associates in binary co-crystals (from the Cambridge Structural Database [2])

	CSD Identifier		
1	BULVAH		C.B.Aakeroy, C.L.Spartz, S.Dembowski, S.Dwyre, J.Desper, *IUCrJ* (2015), **2**, 498
2	BUNJEB		C.B.Aakeroy, C.L.Spartz, S.Dembowski, S.Dwyre, J.Desper, *IUCrJ* (2015), **2**, 498
3	EZIBIA		I.Nicolas, O.Jeannin, D.Pichon, M.Fourmigue, *CrystEngComm* (2016), **18**, 9325

4	KIHZEH		J.A.Bis, P.Vishweshwar, D.Weyna, M.J.Zaworotko, *Mol.Pharmaceutics* (2007), **4**, 401
5	PAVGOK		Wen-Ni Zheng, *ActaCrystallogr.,Sect.E Struct.Rep.Online* 2012), **68**, o1625
6	PEKTAC		V.Stilinovic, B.Kaitner, *Cryst.Growth Des.* (2012), **12**, 5763

7	SOLFEG		A.Mukherjee, G.R.Desiraju, *Cryst.Growth Des.* (2014), **14**, 1375
8	TEHNAW		J.A.Bis, P.Vishweshwar, R.A.Middleton, M.J.Zaworotko, *Cryst.Growth Des.* (2006), **6**, 1048
9	USOBOU		Xing-Wei Cai, Hong-Fei Lu, *ActaCrystallogr.,Sect. E:Struct.Rep.Online* (2011), **67**, o1555
10	SAHJAP		Guoling Fan, Dongpeng Yan, *Scientific Reports* (2014), **4**, 4933

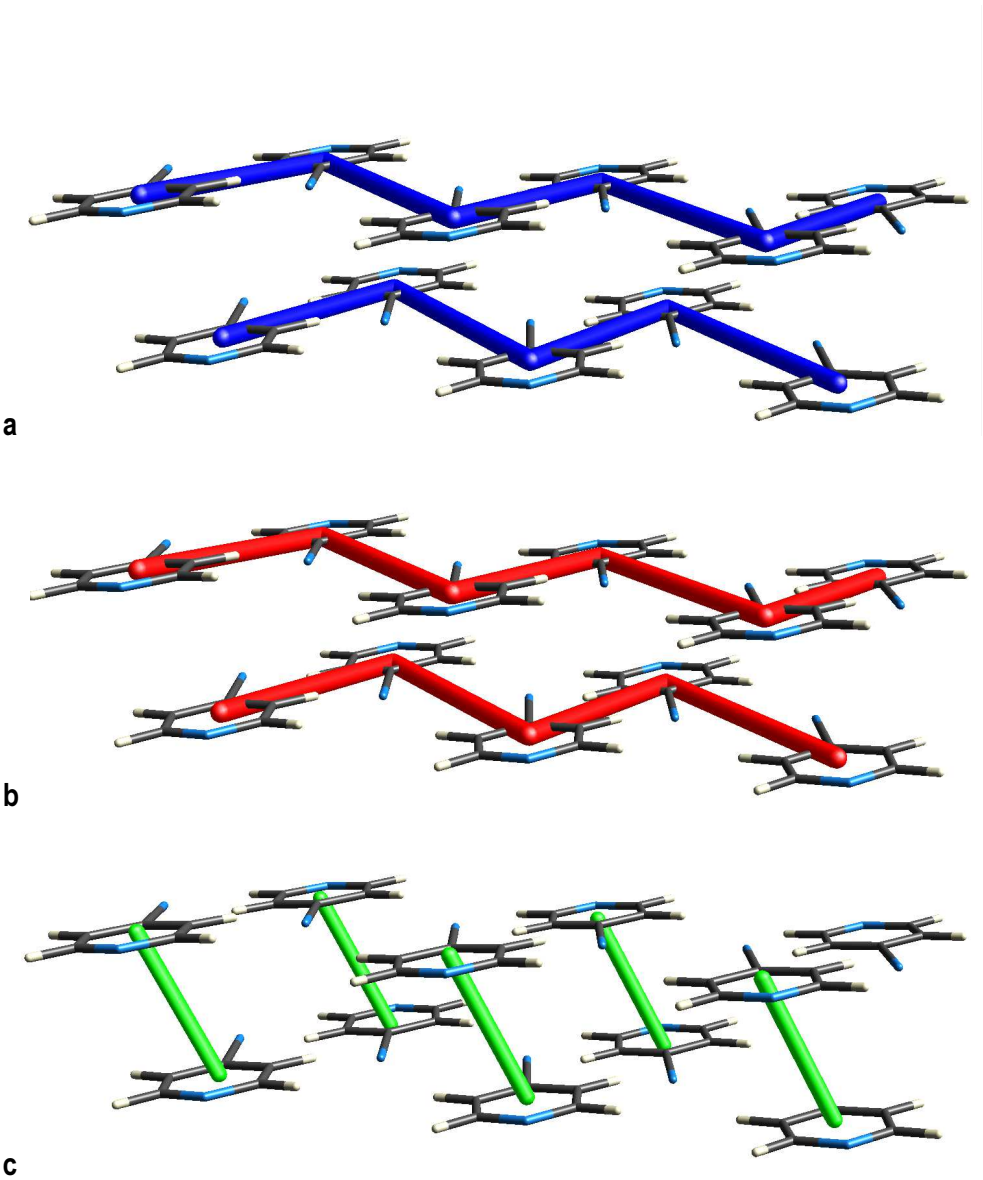
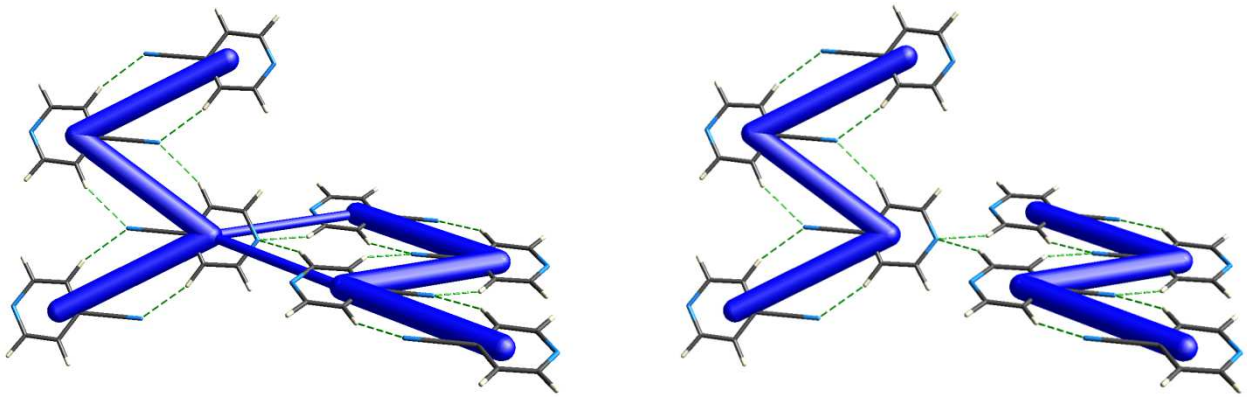


Figure S1. Energy frameworks in **4CNpy**. **a) total energy , b) electrostatic c) dispersion**(15 kJ/mol cut-off).

Note that total energy is the sum of the four energy components, **scaled** using the scale factors below:

Energy Model	k_ele	k_pol	k_disp	k_rep
B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618



a **b**

Figure S2. Fragment of 4-CNpy crystal packing, showing paralel *zig-zag* energy frameworks at 10 kJ/mol) (**a**) and 12 kJ/mol (**b**) cut-off.

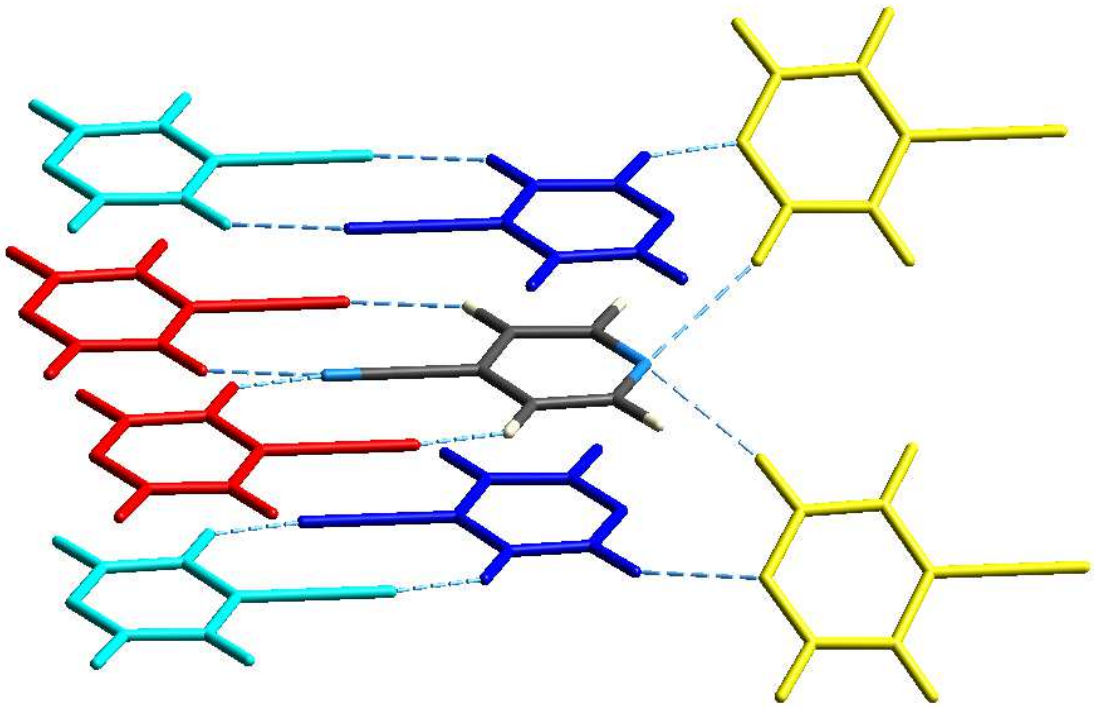


Figure S3 (for Table S3). Intermolecular interactions in 4CNpy.

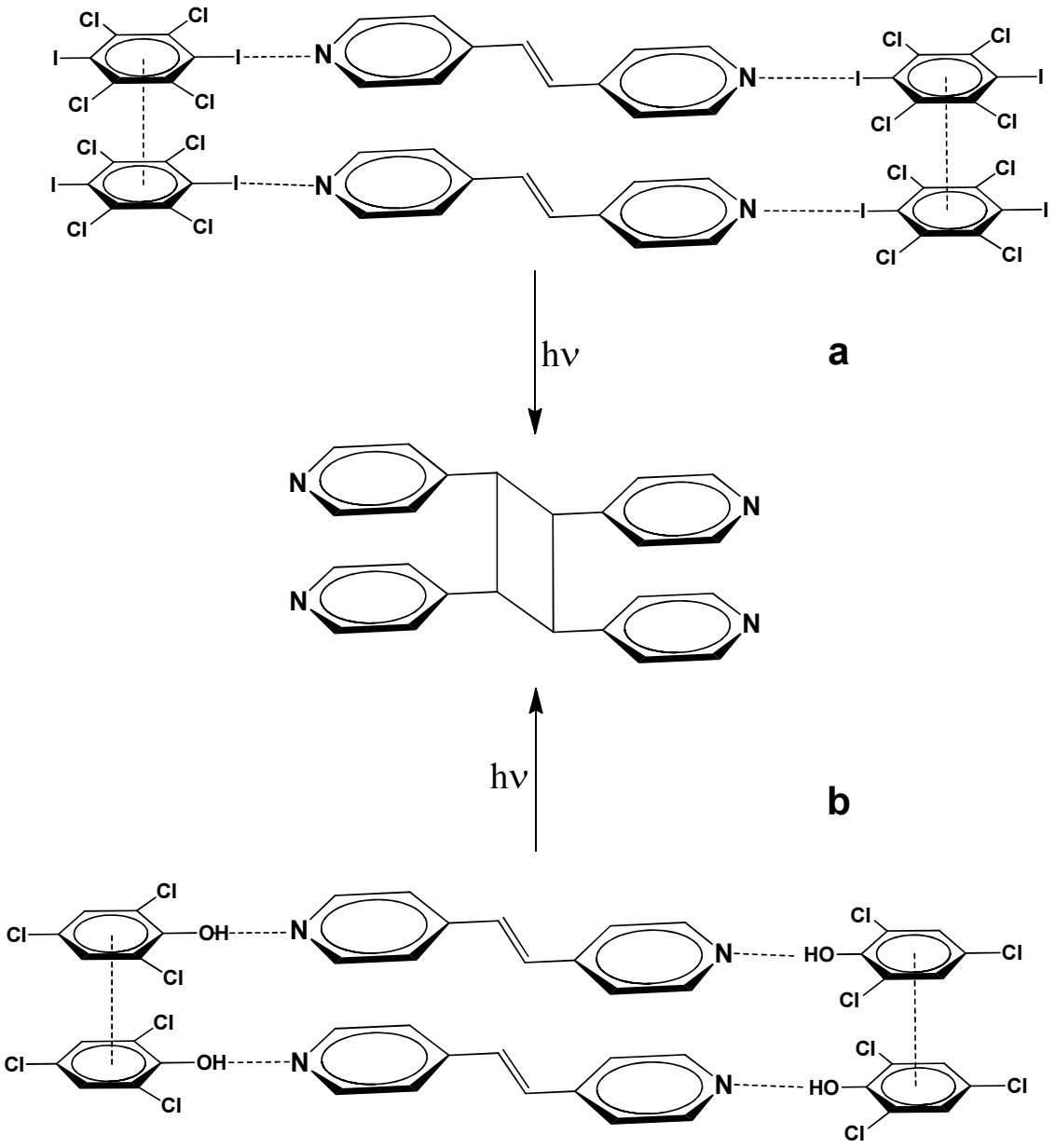
Table S3. Interaction Energies (kJ/mol) in 4CNpy.

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot

	2	-x, -y, -z	6.47	B3LYP/6-31G(d,p)	-24.2	-4.4	-10.5	22.1	-24.3
				B3LYP/DGDZVP	-27.3	-4.5	-10.5	25.6	-25.5
	4	x+1/2, -y, -z+1/2	7.21	B3LYP/6-31G(d,p)	-7.9	-1.2	-7.1	8.1	-10.5
				B3LYP/DGDZVP	-9.9	-1.4	-7.1	10.0	-11.6
	2	-x, -y, -z	6.47	B3LYP/6-31G(d,p)	-7.1	-1.5	-6.9	2.8	-12.9
				B3LYP/DGDZVP	-8.1	-1.6	-6.9	4.7	-12.8
	2	x, y, z	3.82	B3LYP/6-31G(d,p)	5.0	-0.7	-22.4	10.1	-8.5
				B3LYP/DGDZVP	0.6	-0.7	-22.4	18.4	-8.0

Table S4. Intermolecular interaction energy (TONTO CE-B3LYP / DGDZVP)

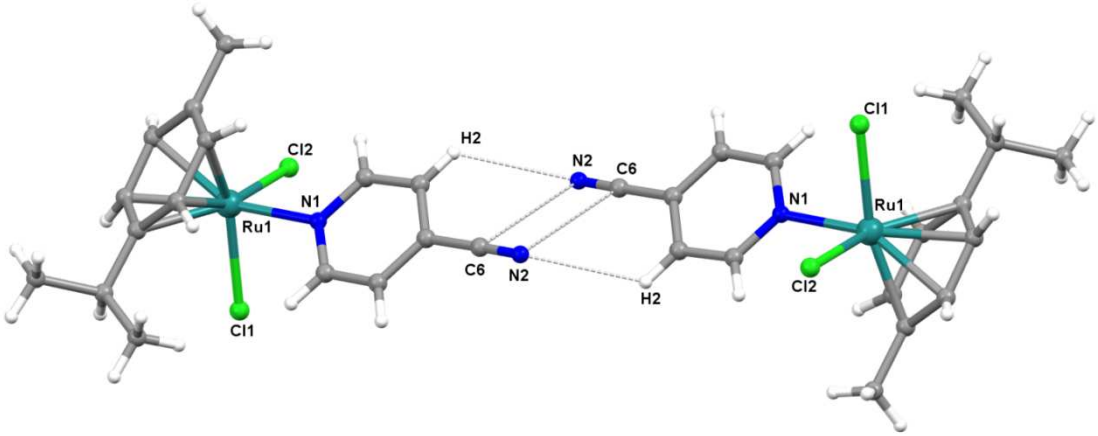
Intermol. interaction energy, -kJ/mol	**4CNpy**	**Co-crystal 1**	**Co-crystal 2**	**Co-crystal 3**	**Co-crystal 4**
I---N_{py} bonded	n/a	19.4	22.4	19.6	19.6
I---N_{CN} bonded	n/a	n/a	n/a	12.3	11.6
$[4CNpy]_2$ dimers	25.5	26	n/a	n/a	20
4CNpy stacking	8.0	11	10.0	10.9	9.0
Acceptor-acceptor stacking	n/a	21	10.7	32.2 – 32.7	29.1



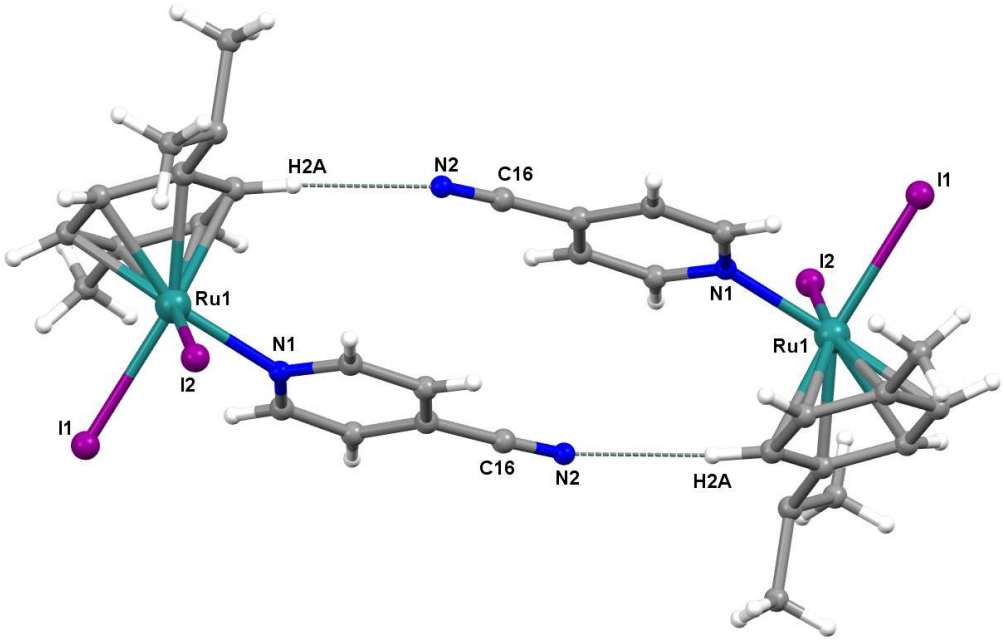
Scheme S1. Solid state photochemical [2+2] cycloaddition of trans-1,2-bis(4-pyridyl)ethylene templated by π-π stacked columnar modules of XB (**a**) [3] and HB (**b**) [4]donor co-formers.

3. E. Bosch, S. J. Kruse, H. R. Krueger, and R. H. Groeneman, Crystal Growth & Design, vol. 19, no. 6, pp. 3092–3096, Apr. 2019. DOI: 10.1021/acs.cgd.9b00275.

4. G. Campillo-Alvarado, C. Li, D. C. Swenson, and L. R. MacGillivray, Crystal Growth & Design, vol. 19, no. 5, pp. 2511–2518, Mar. 2019. DOI: 10.1021/acs.cgd.9b00035



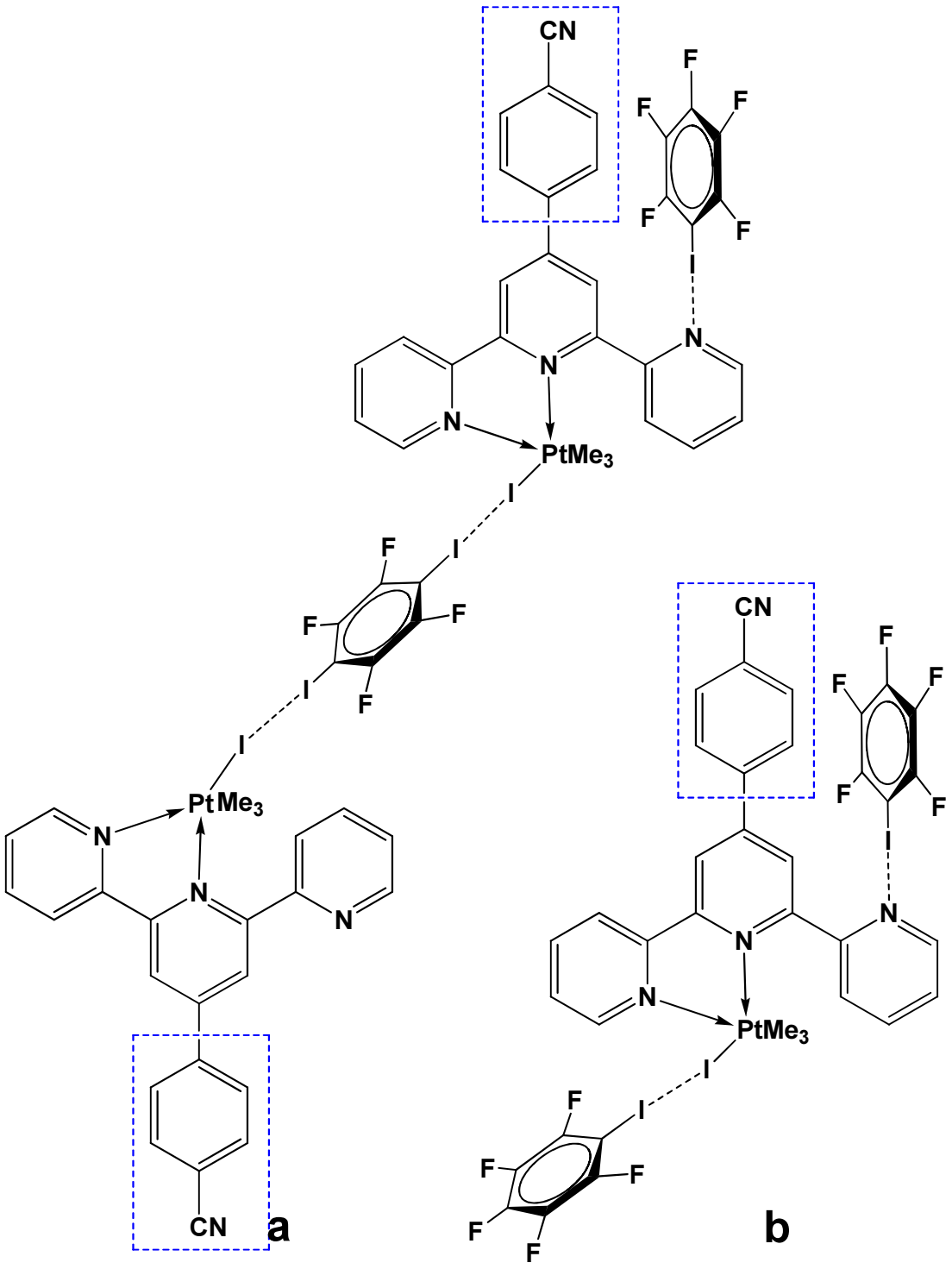
a



b

Figure S4. Fragment or crystal packing of **CymRuX$_2$(4CNpy)** (X=**Cl** (CIDFIE [5]), **I** (**5,** disorder of*i*-Pr group is omitted for clarity)),
Selected distances (Å):
CymRuCl$_2$(4CNpy) (CIDFIE)
N(2)-H(2) 2.70,
C(6)-N(2) 3.16(1);
CymRuI$_2$(4CNpy)
Ru(1)-I(1) 2.741(8)
Ru(1)-I2 2.728(1)
Ru(1)-N(1) 2.135(4)

5. D.K.Gupta, A.N.Sahay, D.S.Pandey, N.K.Jha, P.Sharma, G.Espinosa, A.Cabrera, M.C.Puerta, P.Valerga, *J.Organomet.Chem.* (1998), **568**, 13



Scheme S2 Preference for I---N_{py} and I---I-Pt XBs in (4'-(4-cyanophenyl)-2,2':6',2"-terpyridine) trimethyl platinum(IV) iodide / p-$C_6F_4I_2$ (**a**) and C_6F_5I (**b**)co-crystals [6].

6. B.N. Ghosh, M. Lahtinen, E. Kalenius, P. Mal, K. Rissanen, *Cryst. Growth Des*. 16 (2016) 2527

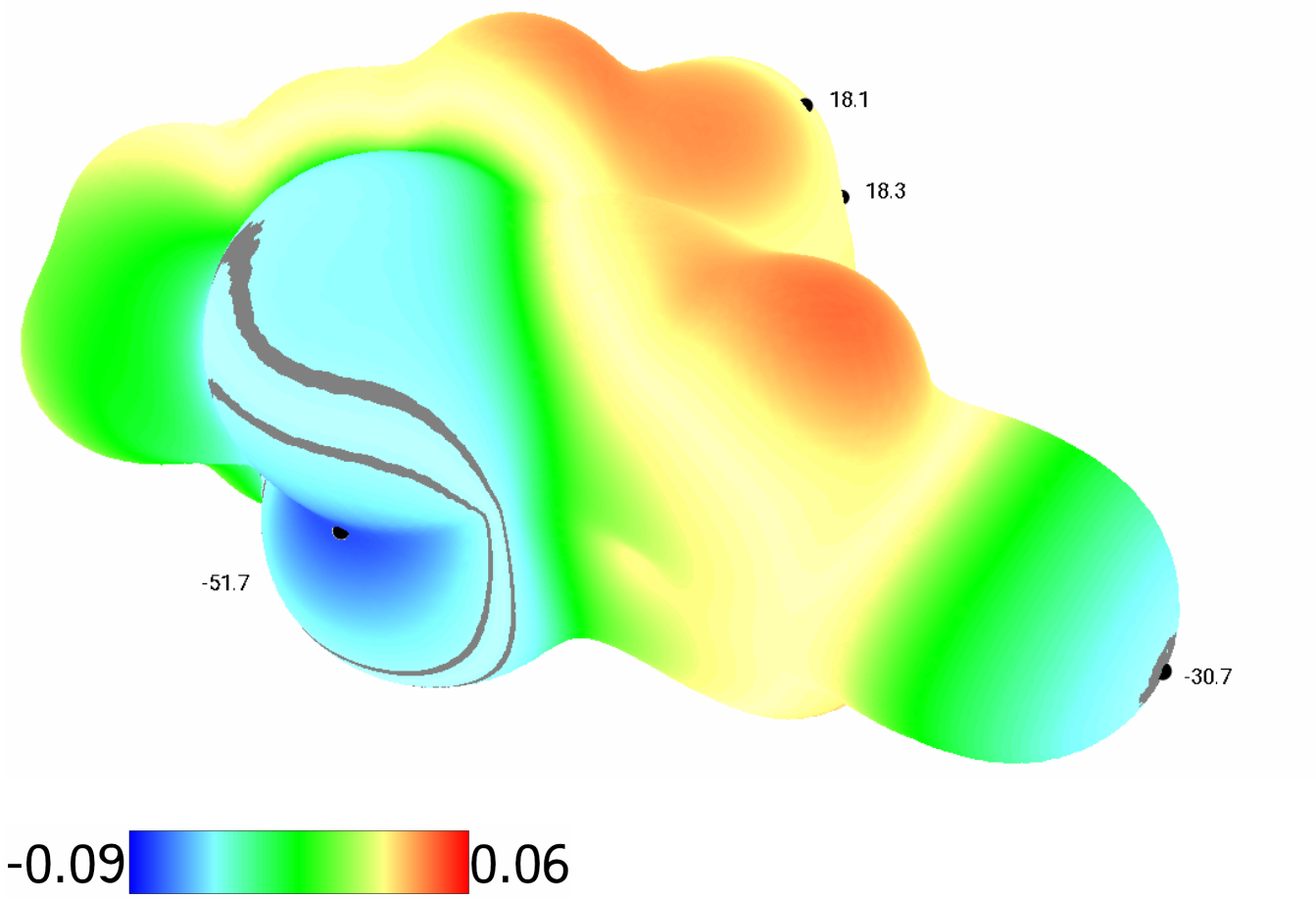


Figure S5. Molecular electrostatic potential map for **CymRuCl$_2$(4CNpy)**, (0.001 e/A^3 electron density isosurface), showing the iso-potential areas for Cl and V_{max}on CN group (colored in gray).

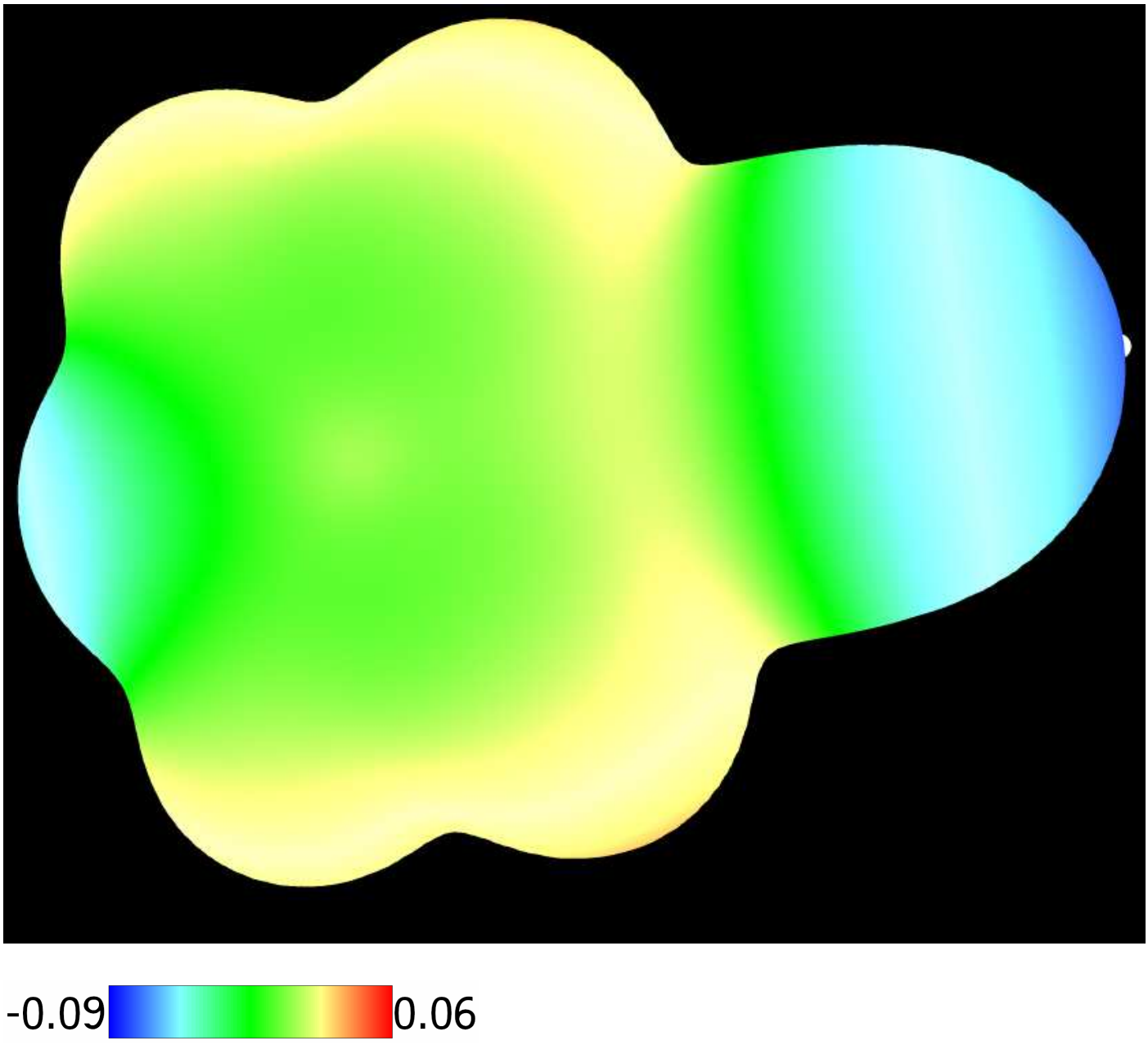
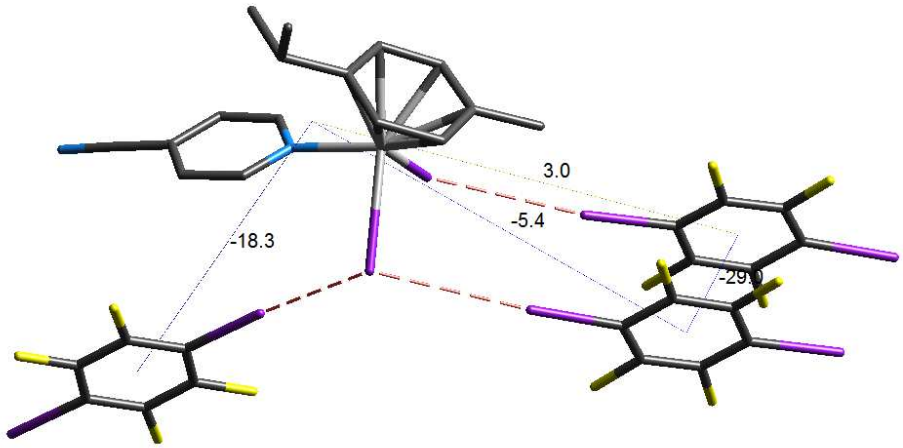
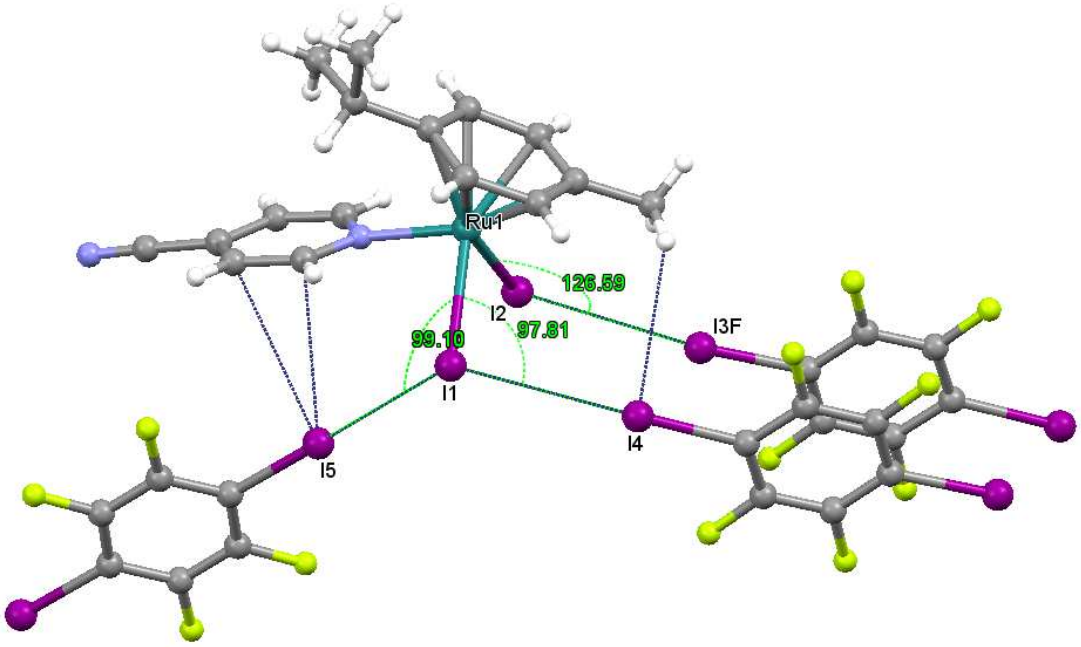


Figure S6. Molecular electrostatic potential map for **4CNpy**$_{\perp}$(0.001 e/A^3 electron density isosurface), showing V_{max} on CN group (-33.3 kcal/mol). Compare with N_{py} (-26.6 kcal/mol)



a



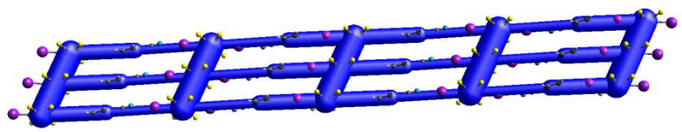
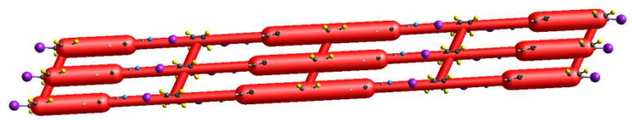
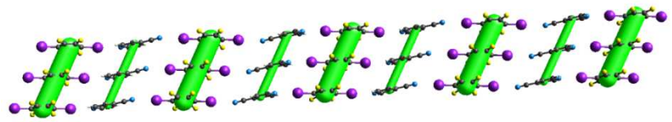
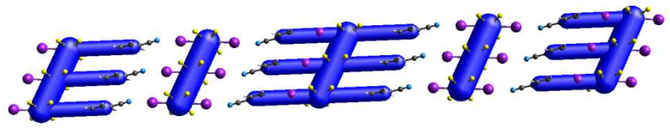
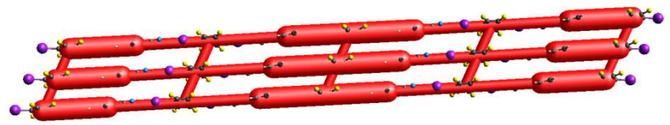
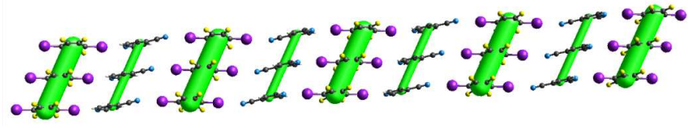
b

Figure S7. Fragment or crystal packing of **CymRuI$_2$(4CNpy)p-DITFB**, showing (**a**) intermolecular interaction energies (Crystal Explorer 17.5 TONTO B3LYP-DGDZVP , kJ/mol) and (**b**) I----I halogen bond angles (I---I-Ru).

Table S5. Energy frameworks in **2**. .**a) total energy , b) electrostatic c) dispersion** at different cut-off levels.

Note that **total energy** is the sum of the four energy components, **scaled** using the scale factors below:

Energy Model	k_ele	k_pol	k_disp	k_rep
B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

Cutoff (kJ/mol)	Full energy framework	Electrostatic	Dispersion
-12			
-17			
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