Electronic Supplementary Material (ESI) for CrystEngComm.
This journal is © The Royal Society of Chemistry 2020

Exploring the Structural Landscape of Triptycene in Cocrystallization with Ferrocene

Ajeet Singh,[a] Yury Torubaev,[d] Shagufi N. Ansari,[a] Sandip K. Singh[a], Shaikh M. Mobin,[a,b,c] and Pradeep Mathur*[a]*

[a]Discipline of Chemistry, School of Basic Sciences, [b]Centre for Biosciences and Biomedical Engineering, [c]Discipline of Metallurgical Engineering and Materials Science, Indian Institute of Technology Indore, Simrol-453552, India.

[d]N.S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russia

*Email: xray@iiti.ac.in, dorector@iiti.ac.in

Contents:

EXPERIMENTAL

TripH, Fc-C≡C-H, FcH and its derivative were purchased from Sigma-Aldrich and were used without additional purification. $(C_{10}H_9)_2Fe_2$ or DiFc (Fc_2) is prepared by the literature method[1] (Note: n-butyl lithium should be handled with care). HPLC grade hexane, chloroform, and DCM were used without additional purification. Crystals were grown with the minor variation in the solvent according to the solubility of the molecules **1**–**5**.

Preparation of PCP-C≡C- Fc

The synthesis of PCP-C≡C- Fc is carried out exactly as reported in our previous report.[2] Please see compound **6**.

Preparation of Fc-C≡C-C≡C-Fc

The synthesis of compound Fc-C≡C-C≡C-Fc by the Palladium-Catalyzed Homocoupling Reactions of Ethynylferrocene with modified literature procedure.[3] A mixture of Ethynylferrocene (1 mmol), $Pd(OAc)_2$ (2.0 mol %), CuI (2.0 mol %), DABCO (3 equiv), and MeCN (10 mL) was stirred under argon at room temperature for 6h. After the completion of reaction, the mixture was evaporated, the residue was purified by flash column chromatography (hexane/ethyl acetate in 95:5 ratio) to afford the desired Fc-C≡C-C≡C-Fc. Crystallization is done using hexane/$CHCl_3$ with 9:1 ratio. MP 244-246 °C. The unreacted ferrocene can also be easily removed by filtration using warm hexane.

Preparation of FcH/TripH (1)

37.2 mg (~0.2 mmol) of FcH and 51 mg (~0.2 mmol) of TripH were dissolved in a mixture of 1mL of hexane and 1 mL of chloroform in a 2.5 mL tube under modest heating to ensure complete solubility of the starting materials. Then sonication was done for 5 min. The clear solution was covered using parafilm, and then left at room temperature for 24 h producing **1** as long orange crystals. Crystals were separated, and less un-crystallized white coloured TripH was removed manually, the crystals were not washed and using paraffin oil XRD measurement was performed, and other physical measurements have been carried out without additional purification. Yield: 79 mg (~90%)

Preparation of Cp_2FeCHO / TripH (2)

42.8 mg (~0.2 mmol) of Fc-carboxaldehyde (FcCHO) and 51 mg (~0.2 mmol) of TripH were dissolved in 1 mL of hexane and 1 mL of chloroform in a 2.5 mL tube under modest heating to ensure complete solubility of the starting materials. Then sonication was done for 5 min. The clear solution was covered with parafilm and then left at room temperature for 2 days producing **2** as dark red crystals. Crystals were separated, SC-XRD was done. Yield: 47 mg (50%)

Preparation of $CpFeC_5H_4$-C ≡C-C≡C-C_5H_4FeCp/ TripH (3)

4.2 mg (~0.01 mmol) of Fc-C_2-C_2-Fc and 5.0 mg (~0.02 mmol) of TripH were dissolved in 0.5 ml of chloroform in a 1mL eppendorf and shake well to ensure complete solubility of the starting materials. The obtained orange solution was left at room temperature for two days in a closed eppendorf. Good quality orange crystalline molecules were separated and used for X-ray diffraction measurement without additional purification. Yield: 6 mg (65%)

Preparation of PCP-C≡C- Cp_2Fe/TripH (4)

8.3 mg (~0.02 mmol) of PCP-C≡C- Cp_2Fe and 5.1 mg (~0.02 mmol) of TripH were dissolved in 0.5 mL of hexane and 0.5 mL of chloroform in a 2.5 mL tube under average heating to ensure complete solubility of the starting materials. Then sonication was done for 5 min. The obtained clear solution was closed with a lid with one small hole and then left at room temperature for two days giving **4** as orange crystals. Crystals were separated, SC-XRD measurement was carried out. Yield: 8 mg (~60%)

Preparation of $CpFeC_5H_4$-C_5H_4FeCp/ TripH (5)

3.7mg (~0.01mmol) of diFc and 2.5 mg (~0.01mmol) of TripH were dissolved in 0.5ml of chloroform in a 1mL eppendorf and shake well to ensure complete mixing and solubility of the starting materials. The orange solution produced, was left at room temperature for two days with one pin hole on eppendorf. Orange crystalline molecules (**5**) were separated, followed by washing with 0.5 mL of cold hexane quickly, and used for X-ray measurement without purification. Yield: 3 mg (~48%)

Computations

Intermolecular interactions energy and energy frameworks were calculated in CrystalExplorer 17.5 [TONTO, HF/3-21G, B3LYP/6-31G(d,p)][4, 5] for all unique molecular pairs in the first coordination sphere of a molecule (~3.8 Å), using experimental crystal geometries. For the cocrystals, the above procedure has been performed for each conformer molecule centered cluster.[6]

Electrical conductivity measurements

The electrical conductivity was studied on a Z2000 impedance meter (LTD "Elins") (operating frequencies range; 2 MHz–1 Hz) using C/solid electrolyte/C symmetrical cells. The external alternating signal amplitude has been 50–70 mV, which depends on the impedance of the sample without any direct current polarization. The resistance frequency dependence has been analyzed by the graphical-analytical method. The samples have been prepared by pressing (10 atm) which produced the pellets of 0.7–1.2 mm thickness and 5 mm diameter and placed in the cells with nitrogen-atmosphere.

Crystal structure determination

Data were collected at 293 K using graphite-monochromated MoKα radiation (λ = 0.71070 Å) and CuKα radiation (λ = 1.54184 Å). The data collection strategy was interpreted by employing the CrysAlisPro software for **1–5**. The data have been collected through the standard omega scan technique and reduced by the SHELXL-97 software. Structures were solved by direct methods and refinement was carried out by full-matrix least squares against F^2 utilizing the SHELXL-97 software.[7] Non-hydrogen atoms have been refined with anisotropic thermal parameters. All hydrogen atoms have been geometrically fixed, and a riding model refinement is carried out. Olex2 software[8] was also used for labelling and refining of **1–5**.

Table S1 Crystal information table for **1–5**

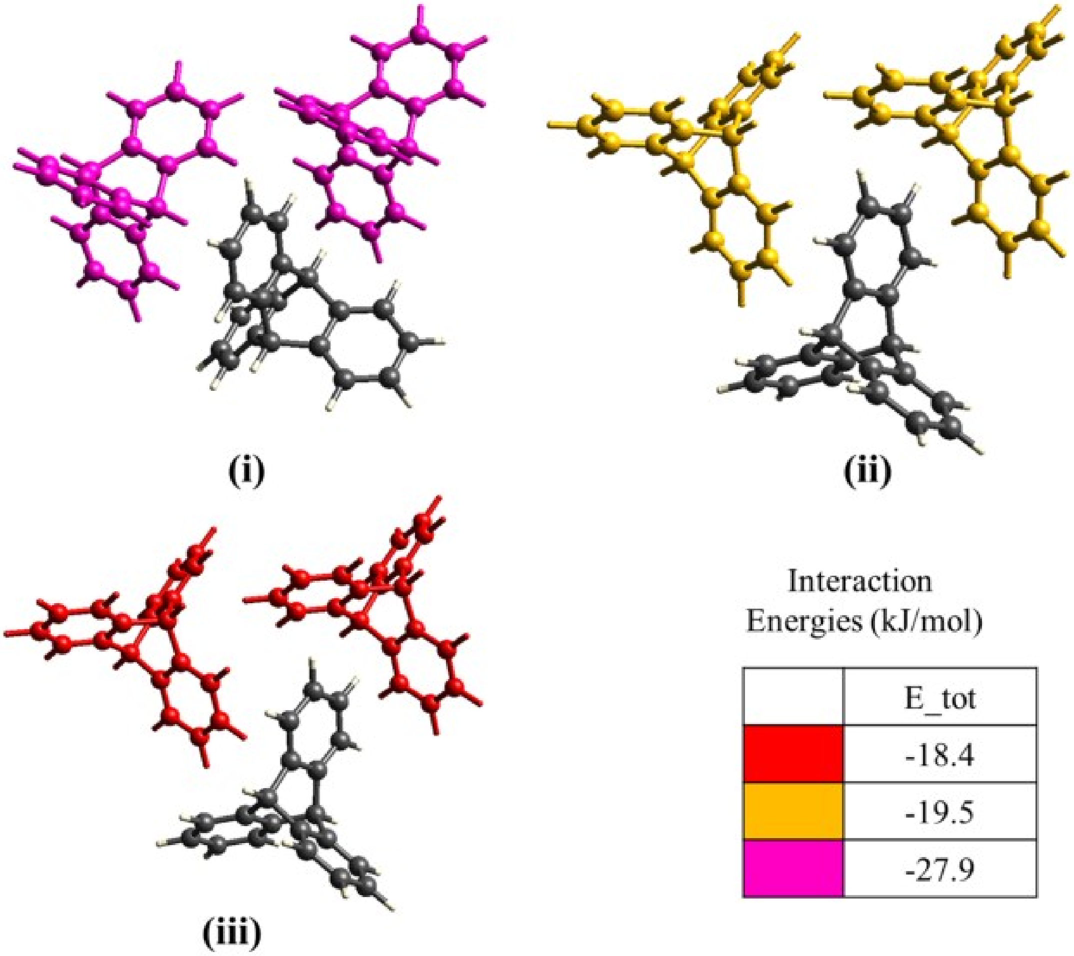
Identification code	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{30}H_{24}Fe$	$C_{31}H_{24}FeO$	$C_{64}H_{46}Fe_2$	$C_{48}H_{38}Fe$	$C_{60}H_{46}Fe_2$
Formula weight	440.34	468.35	926.71	670.63	878.67
Temperature/K	293	293(2)	298	293(2)	293(2)
Crystal system	**triclinic**	**triclinic**	**triclinic**	**monoclinic**	**monoclinic**
Space group	*P*-1	*P*-1	*P*-1	$P2_1/c$	$P2_1/n$
a/Å	9.4217(5)	9.6767(12)	13.3320(15)	7.9500(4)	8.93360(10)
b/Å	10.3198(6)	10.3972(12)	13.4018(12)	28.507(2)	8.41050(10)
c/Å	13.0913(6)	12.9455(15)	16.138(2)	15.5007(8)	28.5683(4)
α/°	67.835(5)	70.641(10)	95.029(9)	90	90
β/°	71.685(5)	71.847(11)	105.145(11)	104.262(5)	93.5820(10)
γ/°	86.556(5)	89.794(10)	119.521(10)	90	90
Volume/Å^3	1116.62(11)	1160.4(3)	2340.2(5)	3404.6(4)	2142.31(5)
Z	2	2	2	4	2
ρcalcg/cm^3	1.31	1.34	1.315	1.308	1.362
μ/mm-1	0.69	0.671	0.662	3.8	5.734
F(000)	460	488	964	1408	916
Crystal size/mm^3	0.45 × 0.38 × 0.30	0.38 × 0.36 × 0.29	0.34 × 0.32 × 0.28	0.4 × 0.34 × 0.32	0.38 × 0.33 × 0.28
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.042 to 64.426	6.342 to 64.606	6.07 to 50	11.018 to 144.248	6.2 to 142.574
Index ranges	-11 ≤ h ≤ 14, -15 ≤ k ≤ 15, -18 ≤ l ≤ 19	-14 ≤ h ≤ 13, -14 ≤ k ≤ 15, -15 ≤ l ≤ 19	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -19 ≤ l ≤ 19	-7 ≤ h ≤ 9, -34 ≤ k ≤ 34, -19 ≤ l ≤ 18	-10 ≤ h ≤ 10, -10 ≤ k ≤ 7, -35 ≤ l ≤ 33
Reflections collected	13361	15015	21024	23737	13762
Independent reflections	7220 [R_{int} = 0.0331, R_{sigma} = 0.0422]	7481 [R_{int} = 0.1015, R_{sigma} = 0.1430]	8192 [Rint = 0.1238, Rsigma = 0.1770]	6536 [Rint = 0.0946, Rsigma = 0.0811]	4112 [Rint = 0.0347, Rsigma = 0.0245]
Data/restraints/parameters	7220/0/280	7481/0/298	8192/0/595	6536/0/442	4112/0/280
Goodness-of-fit on F^2	1.028	0.961	1.021	1.027	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0538, wR_2 = 0.1391	R_1 = 0.1203, wR_2 = 0.3157	R_1 = 0.0914, wR_2 = 0.1986	R_1 = 0.1158, wR_2 = 0.3075	R_1 = 0.0438, wR_2 = 0.1287
Final R indexes [all	R1 = 0.0733,	R_1 = 0.2121,	R_1 = 0.2107,	R_1 = 0.1747,	R_1 = 0.0497,

data]	wR2 = 0.1533	wR_2 = 0.3924	wR_2 = 0.2736	wR_2 = 0.3614	wR_2 = 0.1397
Largest diff. peak/hole / e Å^{-3}	0.36/-0.52	1.47/-0.81	0.73/-0.38	1.03/-0.59	0.35/-0.54
CCDC No.	1586854	1586855	1839843	1586856	1586857

Table S2 Interactions present in cocrystals **1–5** with bond distances and contact atoms

Cocrystal	**Interaction**	**Contact atoms**	**distance**
1	$H_{bridgehead}$---π_{cp}	H11-C1	2.882 Å
	$H_{bridgehead}$---π_{cp}	H12- C9	2.885 Å
	π_{Htrip}---π_{Ctrip}	H27-C21	2.884 Å
2	$H_{bridgehead}$---π_{cp}	H12-C8	2.966 Å
	$H_{bridgehead}$---π_{cp}	H11-C5	2.927 Å
	O---$H_{aromatic}$	O1-H23	2.713 Å
	π_{cp} ---π_{cp}	C20-C22	3.508 Å
3	π_{H}---π_{cp}	H49-C20	2.909 Å
	$H_{bridgehead}$---π_{cp}	H48-C22	2.801 Å
	π_{trip}---π_{trip}	C42-C50	3.420 Å
4	$H_{bridgehead}$---π_{cp}	H12-C34	2.731 Å
	π_{H}---π_{pcp}	H29- C38	2.878 Å
	π_{H}---π_{cp}	H20- C8	2.824 Å
5	π_{H}---π_{cp}	H23-C9	2.961 Å
	$H_{bridgehead}$---π_{cp}	H11-C10	2.944 Å
	π_{H}---π_{cp}	H29-C16	2.834 Å
	π_{cpH}---π_{trip}	H4-C21	3.061 Å

Figure S1. Values of total energy calculated by B3LYP/6-31G(d,p) in Triptycene


(i)

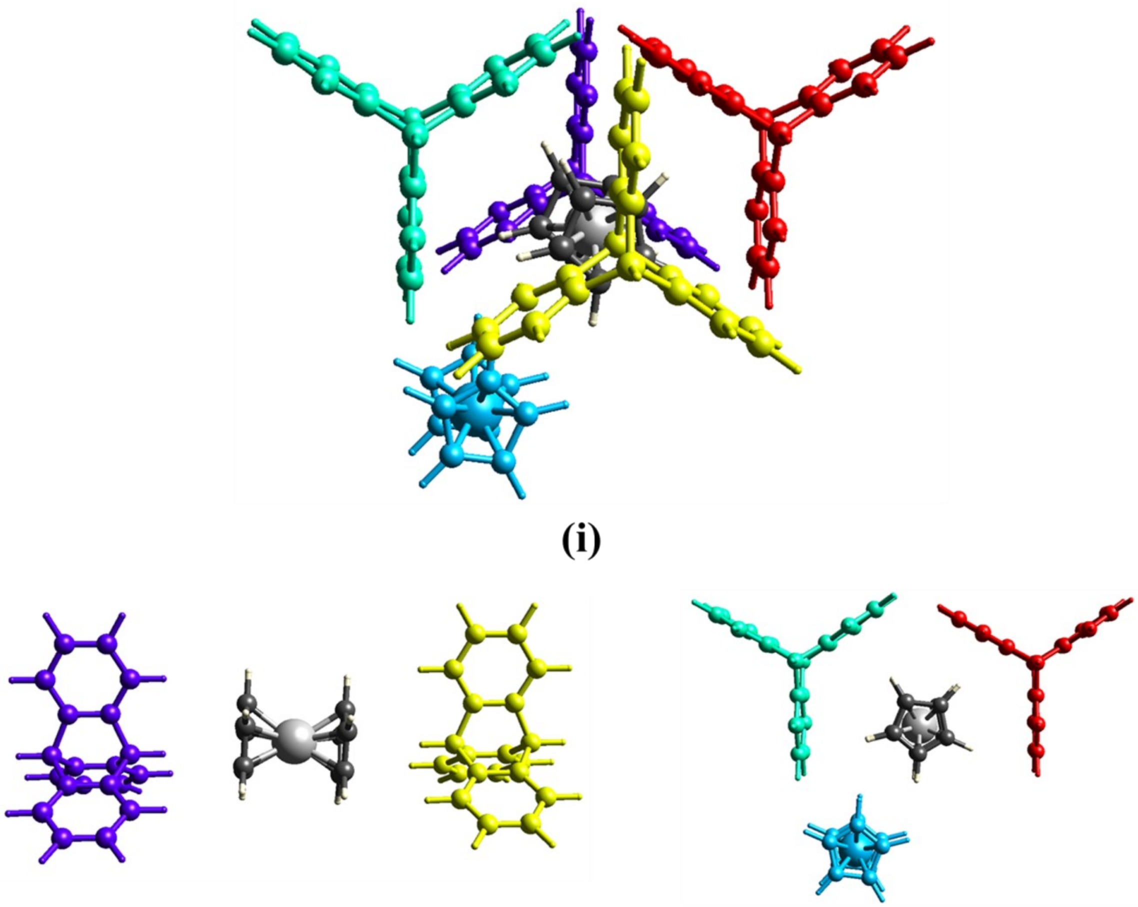
(ii)

(iii)

Interaction Energies (kJ/mol)

	E_tot
🟥	-18.4
🟧	-19.5
🟪	-27.9

Figure S2. Values of total energy calculated by B3LYP/6-31G(d,p) in Cocrystal **1**



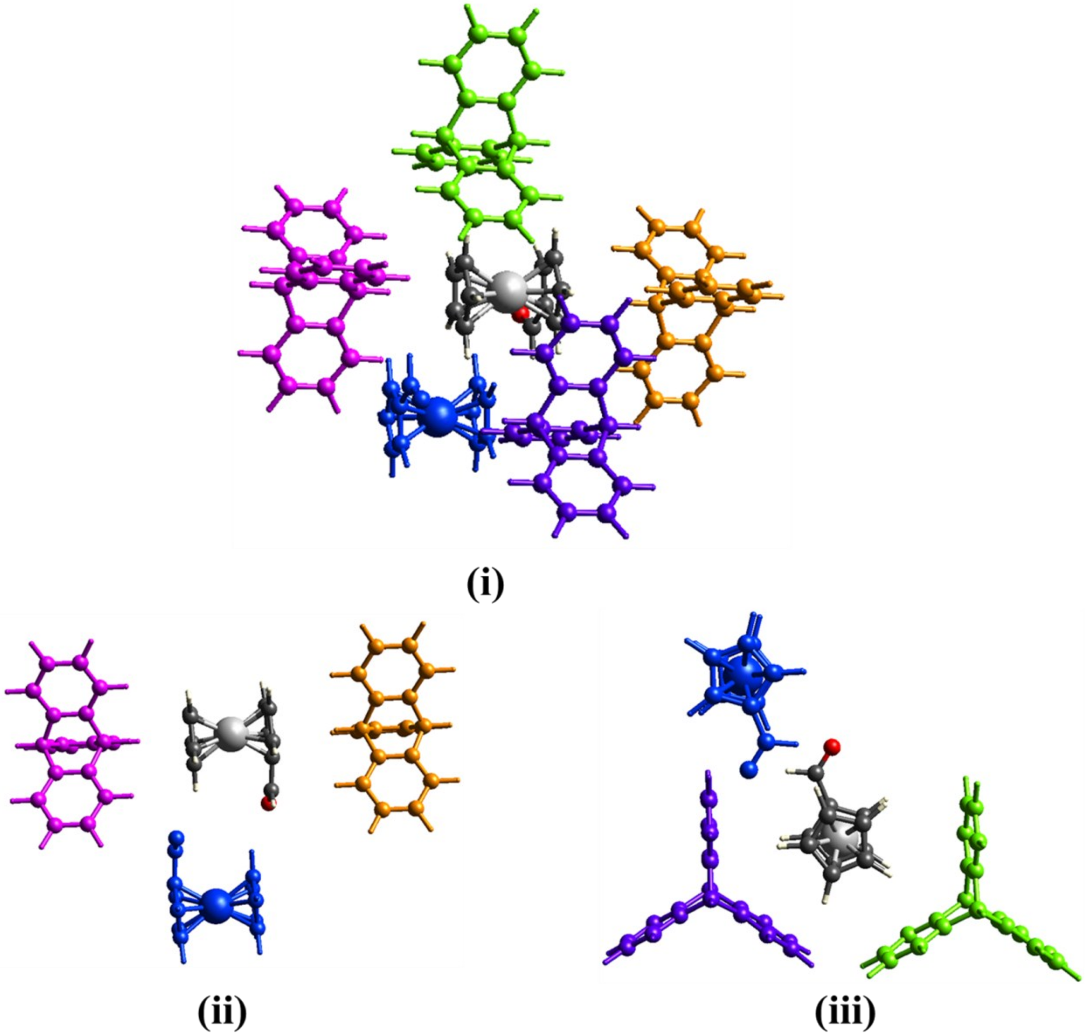
(i)

(ii) **(iii)**

	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
🟥	5.82	B3LYP/6-31G(d,p)	-5.2	-1.2	-33.0	15.2	-25.7
🟨	6.77	B3LYP/6-31G(d,p)	-6.0	-1.0	-23.2	14.6	-18.3
🟩	5.85	B3LYP/6-31G(d,p)	-5.3	-1.2	-31.3	14.1	-25.0
🟦	6.21	B3LYP/6-31G(d,p)	-1.5	-0.1	-14.5	3.4	-12.2
🟪	6.77	B3LYP/6-31G(d,p)	-6.0	-1.2	-22.8	13.7	-18.6

Where, Interaction Energies (kJ/mol), R is the distance between molecular centroids (mean atomic position) in Å. Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled [5]

Figure S3. Values of total energy calculated by B3LYP/6-31G(d,p) in Cocrystal **2**



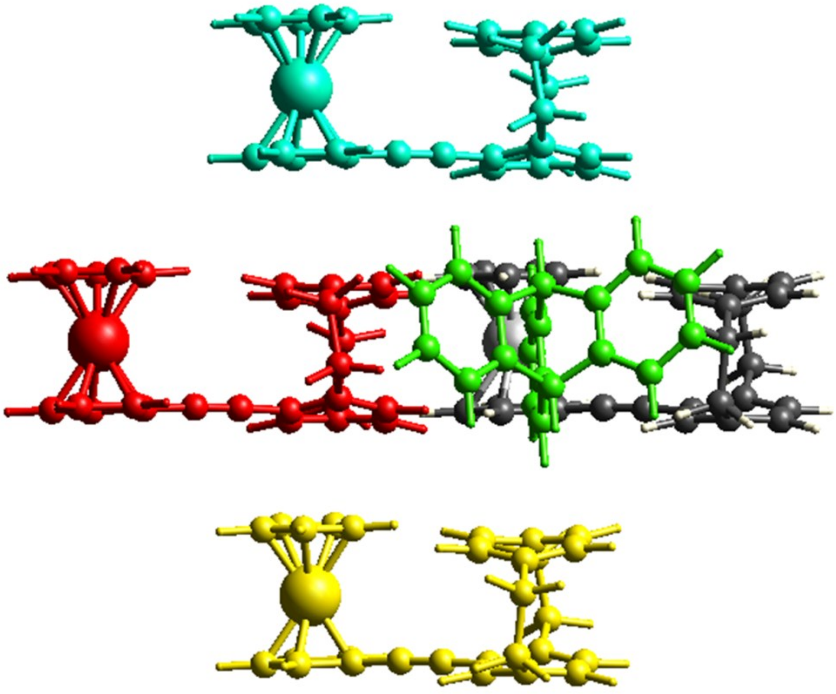
(i)

(ii) **(iii)**

	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
🟧	6.66	B3LYP/6-31G(d,p)	-3.2	-0.8	-23.1	11.3	-17.1
🟩	5.99	B3LYP/6-31G(d,p)	-6.3	-1.8	-36.8	15.9	-30.3
🟦	6.74	B3LYP/6-31G(d,p)	-8.1	-3.1	-17.4	12.2	-18.5
🟪	5.84	B3LYP/6-31G(d,p)	-8.3	-2.0	-36.0	18.6	-30.1
🟪	6.90	B3LYP/6-31G(d,p)	-5.4	-0.7	-25.5	16.3	-18.3

Where, Interaction Energies (kJ/mol), R is the distance between molecular centroids (mean atomic position) in Å. Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled [5]

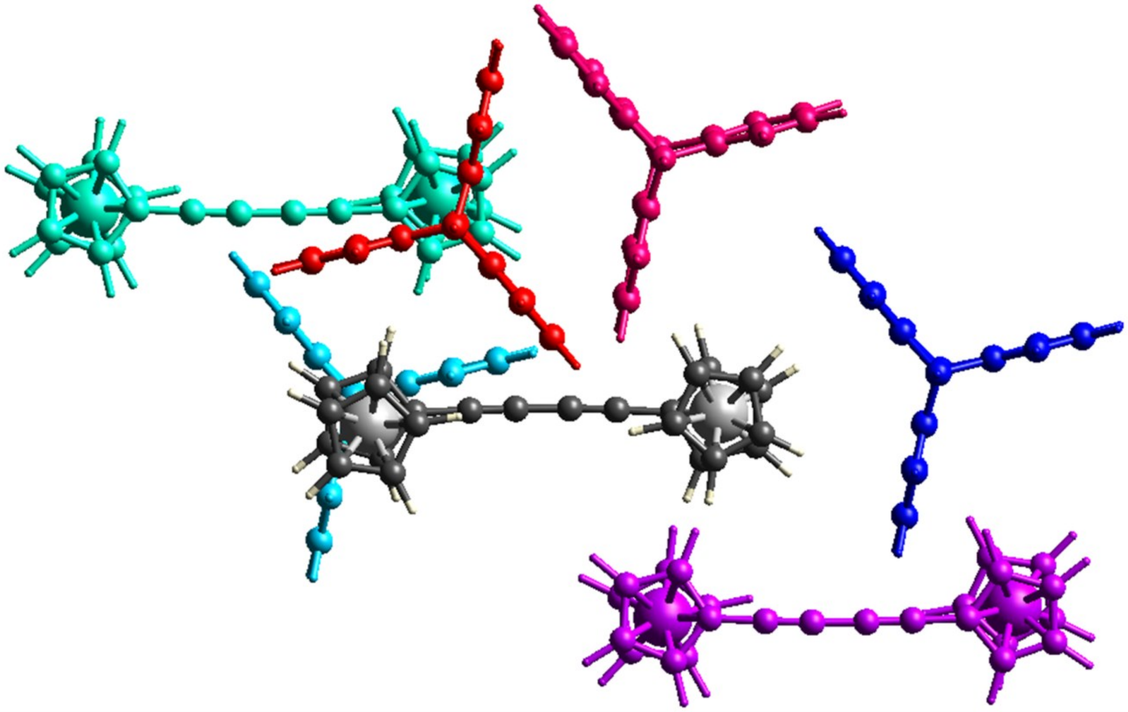
Figure S4. Values of total energy calculated by HF in Cocrystal **3**



	N	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
🟥	1	11.03	HF/3-21G	1.0	-0.7	-20.1	7.4	-11.6
🟩	0	10.08	HF/3-21G	-5.6	-1.2	-19.6	5.8	-19.5
🟩	0	6.79	HF/3-21G	-7.3	-3.4	-34.3	10.3	-32.3
🟦	1	9.42	HF/3-21G	-5.6	-1.2	-19.6	5.8	-19.5

Where, Interaction Energies (kJ/mol), R is the distance between molecular centroids (mean atomic position) in Å. Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled [5]

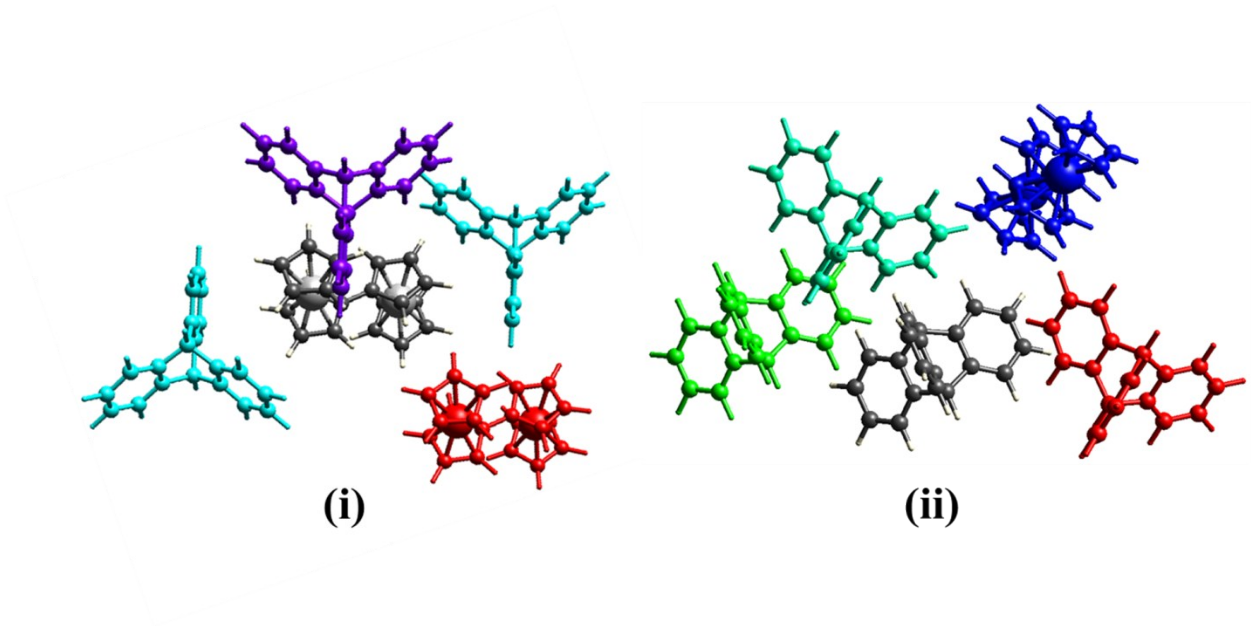
Figure S5. Values of total energy calculated by HF in Cocrystal **4**



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
🟥	1	-	5.90	HF/3-21G	-13.3	-4.5	-57.2	25.9	-47.0
🟩	1	-x, -y, -z	9.89	HF/3-21G	-6.9	-1.3	-13.0	4.3	-16.1
🟦	1	-	8.02	HF/3-21G	-9.5	-3.0	-29.6	15.4	-25.8
🟦	1	-	10.23	HF/3-21G	-12.3	-3.9	-31.3	12.4	-33.2
🟪	1	-x, -y, -z	10.55	HF/3-21G	-7.0	-1.0	-10.1	3.1	-14.5
🟥	1	-	8.85	HF/3-21G	-6.9	-1.3	-13.0	4.3	-16.1

Where, Interaction Energies (kJ/mol), R is the distance between molecular centroids (mean atomic position) in Å. Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled [5]

Figure S6. Values of total energy calculated by B3LYP/6-31G(d,p) in Cocrystal **5**


(i) (ii)

	N	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
🟥	1	8.41	B3LYP/6-31G(d,p)	-5.7	-0.4	-28.5	13.1	-23.1
🟦	1	7.71	B3LYP/6-31G(d,p)	-5.7	-0.4	-28.5	13.1	-23.1
🟪	1	8.50	B3LYP/6-31G(d,p)	-0.6	-0.2	-11.8	1.6	-10.0
🟪	1	12.27	B3LYP/6-31G(d,p)	-3.7	-0.7	-13.5	9.8	-10.1

	N	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
🟥	2	8.23	B3LYP/6-31G(d,p)	-3.5	-0.9	-23.3	11.7	-17.4
🟩	1	8.41	B3LYP/6-31G(d,p)	-1.6	-0.4	-14.3	5.8	-10.9
🟩	1	6.30	B3LYP/6-31G(d,p)	-7.8	-1.7	-37.5	22.7	-28.1
🟦	1	9.07	B3LYP/6-31G(d,p)	-3.5	-0.9	-23.3	11.7	-17.4

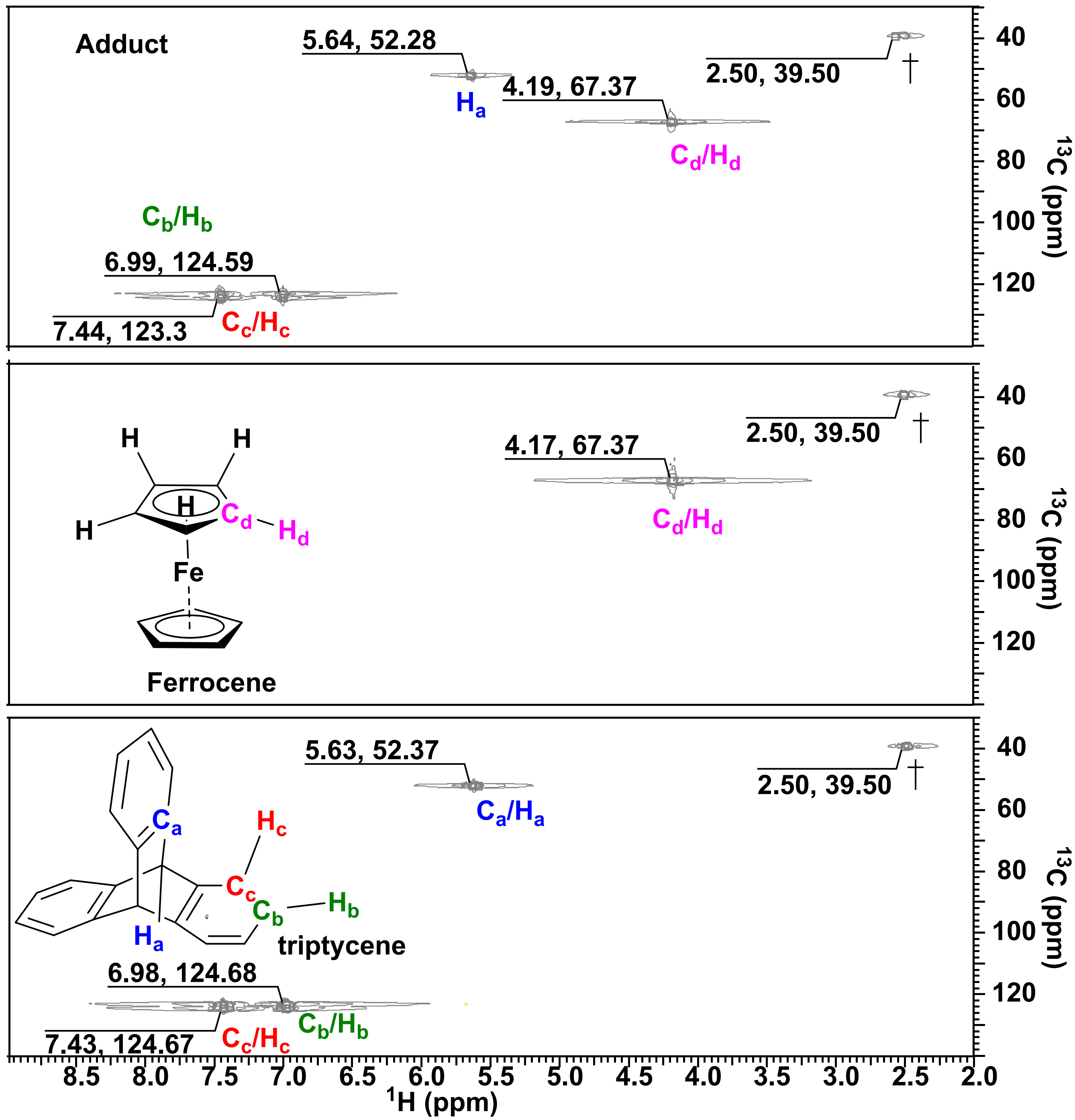


Figure S7. 2D HSQC NMR spectra of (a) triptycene, (b) ferrocene and (c) adduct triptycene-ferrocene. †signals indicate for the DMSO-d6 solvent. All the spectra were recorded after dissolving ca. 1.0 mol samples in 0.7 mL deuterated DMSO solvent.

2D ($^{13}C/^{1}H$ HSQC) NMR

The role of solvent is significant for non-covalent assemblies than for covalent molecules. The balance between enthalpy and entropy is close in these cocrystals. Small perturbations from solvation would, therefore, be expected to be much more critical for them than for covalent compound.[9] To get the explanation; if these cocrystal are forming in the solvent or not? An advanced 2D heteronuclear single quantum correlation ($^{13}C/^{1}$ H HSQC) NMR was studied.

And the observations indicate that the solvent did not allow forming the cocrystal lattice because of the perturbation created by the solvent as they are capable of competitive hydrogen bonding in the molecule (DMSO-d6). The chemical shift values did not shift significantly in cocrystal **1**. The difference in chemical shift value Δδ= $^{13}C/^{1}H$ (ppm) was only 0.09 and 0.01 respectively that is not due to interaction but likely due to solvent **(**Table S8 and Figure S2**)**. This non-significant difference proves that the FcH and TripH were not interacting in the presence of DMSO solvent.

Table S8. HSQC NMR study of cocrystal **1**

Entry No.	**Assignment $^{13}C/^{1}H$**	**TripH $^{13}C/^{1}H$ (ppm)**	**FcH $^{13}C/^{1}H$ (ppm)**	**Adduct $^{13}C/^{1}H$ (ppm)**	**Δδ= $^{13}C/^{1}H$ (ppm)**
1	C_a/H_a	52.37/5.63	-	52.28/5.64	0.09/0.01
2	C_b/H_b	124.68/6.98	-	124.59/6.99	0.09/0.01
3	C_c/H_c	124.67/7.43	-	124.59/7.44	0.08/0.01
4	C_d/H_d	-	67.37/4.17	67.37/4.19	0/0.02
Note: NMRs were recorded in DMSO-d^6					

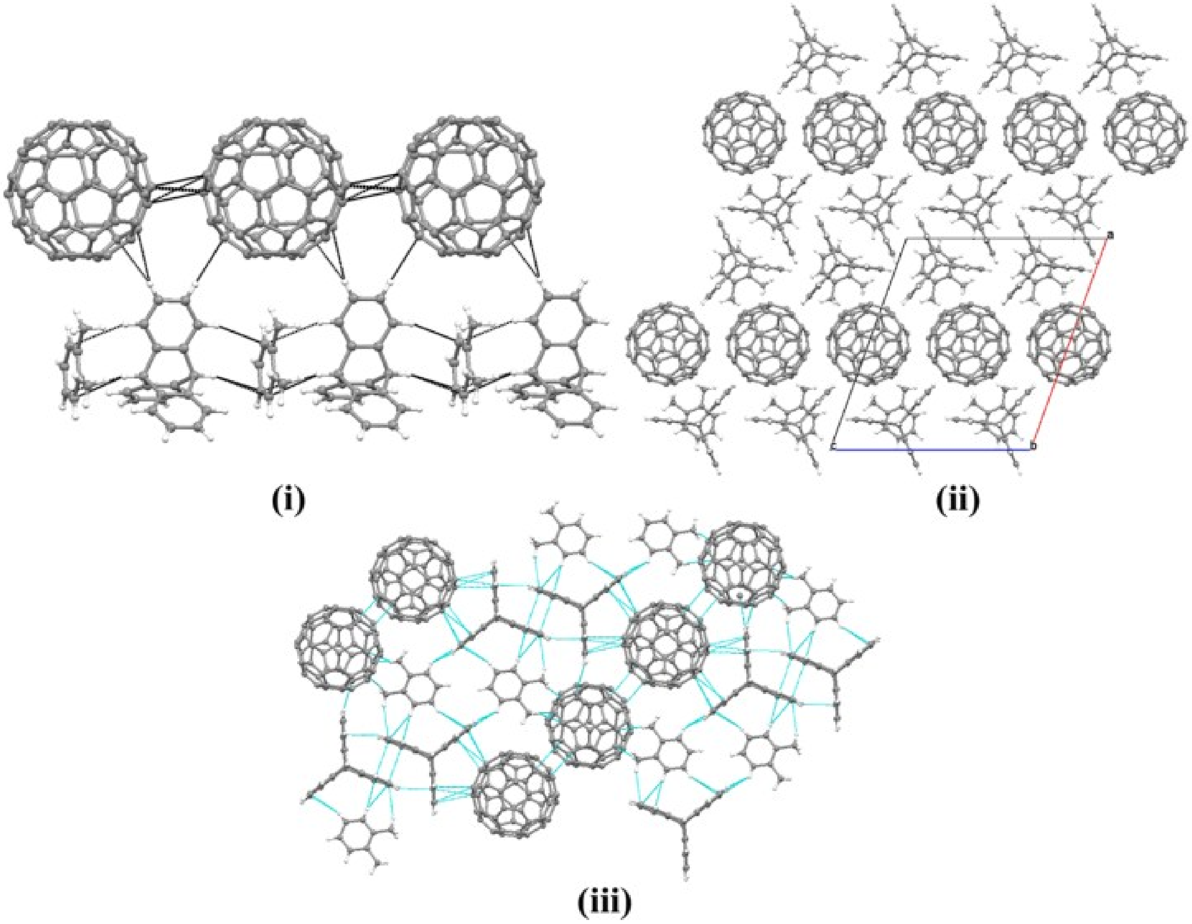
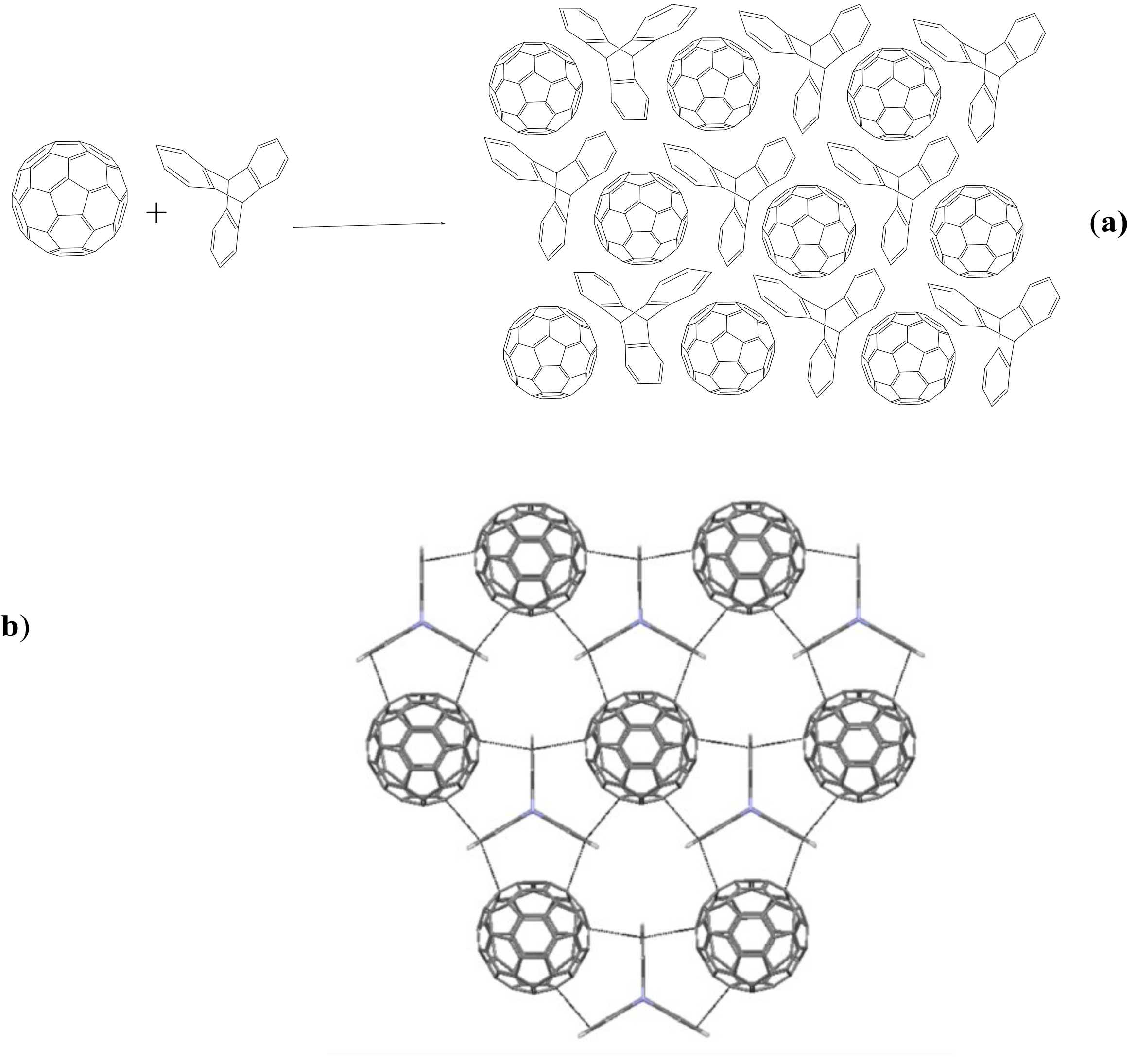


Figure S8. Chains and sheets C_{60}-TripH-*o*-xylene sheets in CEMNUD, Compare with TripH-FcH chains (see **Figure 4**) and FcC_2C_2Fc-TripH sheets (see **Figure 9**)

Notably, the packing observed in **1** (see **Figure 4**), resembles the pattern envisioned by Feringa *et et al.*[10] for TripH – fullerene co-crystal *(see* **Scheme S1***)*. We can speculate, that apart from an enhanced electrostatic interaction between aza-Trip and C_{60} mentioned in the aforementioned report,[10] the main reason for cocrystallization of azaTrip-C_{60} and TripH-$C_{60,}$ was the incorporation of xylene solvent molecules in TripH system represented by the ditopic C_{sp3}-H structure of TripH (ESI **Scheme S1 a,b**). Aza- Trip, in contrast, has only one C_{sp3}-H fragment capable of forming C_{sp3}-H---$\pi_{(xylene)}$ contacts and therefore has no possibility for 1D chain extension. This observation may mean that C_{sp3}-

H---$\pi_{(\text{arene, cp})}$ is a strong heterosynthon in the structural chemistry and cocrystal design of triptycenes.



Scheme S1. a) TripH-C_{60} packing pattern expected in work[10] **b)** packing pattern of aza-TripH---C_{60} sheets [10]

Similarly, the C_{sp3}-H---$\pi_{(\text{arene, cp})}$ is a strong heterosynthon in the cocrystals **1–5** designed by the utilization of triptycenes

References

1. A. R. Koray, M. Ertas and Ö. Bekaroğlu, *J. Organomet. Chem.*, 1987, **319**, 99-101.
2. Y. V. Torubaev, K. A. Lyssenko, P. Y. Barzilovich, G. A. Saratov, M. M. Shaikh, A. Singh and P. Mathur, *CrystEngComm*, 2017, **19**, 5114-5121.
3. J.-H. Li, Y. Liang and Y.-X. Xie, *J. Org. Chem.*, 2005, **70**, 4393-4396.
4. C. B. Aakeroy and D. J. Salmon, *CrystEngComm*, 2005, **7**, 439-448.
5. Campbell F Mackenzie ., Peter R. Spackman , Dylan Jayatilakaa and M. A. Spackman, *IUCrJ*, 2017, **4**, 575-587.
6. B. Aakeröy Christer, J. Desper, E. Elisabeth, A. Helfrich Brian, B. Levin and F. Urbina Joaquin, *Journal*, 2005, **220**, 325.
7. G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3-8.
8. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
9. G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. Chin, M. Mammen and D. M. Gordon, *Acc. Chem. Res.*, 1995, **28**, 37-44.
10. E. Marc Veen, B. L. Feringa, P. M. Postma, H. T. Jonkman and A. L. Spek, *Chem. Commun.*, 1999, DOI: 10.1039/A904457D, 1709-1710.