Electronic Supporting Information

Self-Assembly of *fac*-$Mn(CO)_3$-Core Containing Dinuclear Metallacycles Using Flexible Ditopic Linkers

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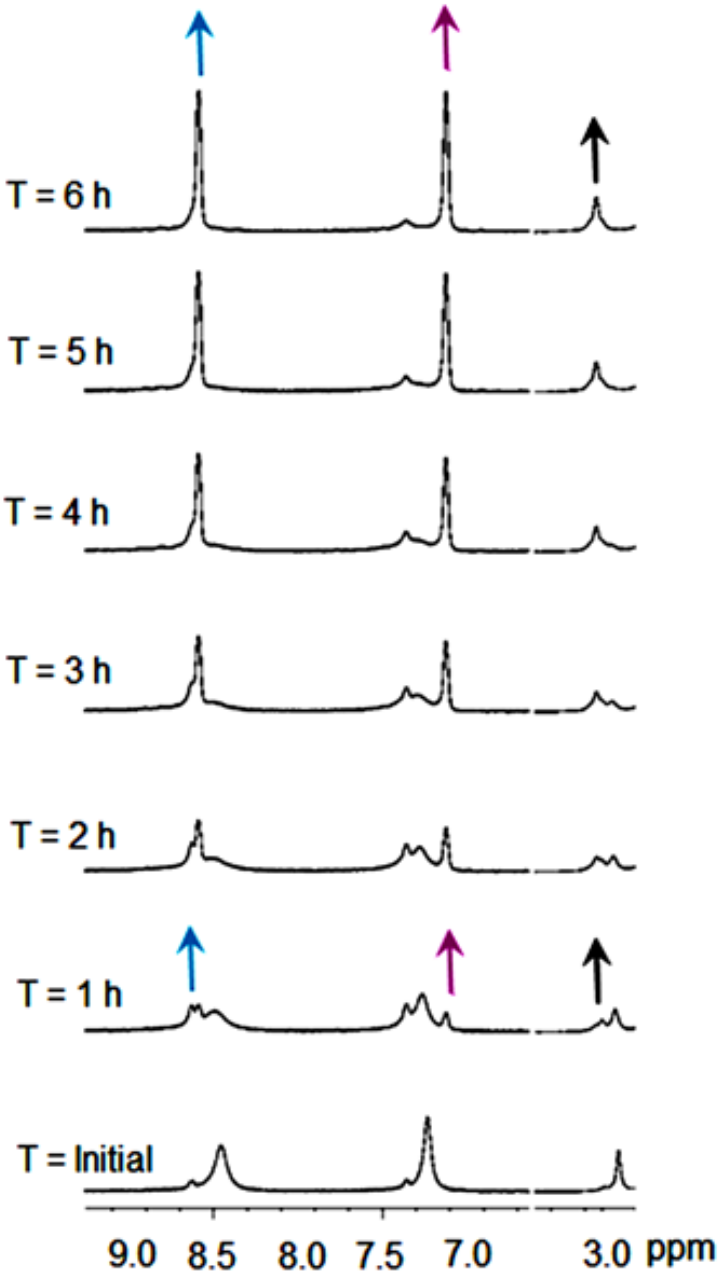


Fig. S1 Stack plot of time-dependent ^{1}H NMR spectra showing self-assembly of $[Mn(CO)_3Br(\mu\text{-bpa})]_2$ (**1**).

***In situ* ^{1}H NMR analysis of 3.**

The dinuclear metallacyclophane **3** was obtained as a single product via a self-assembly process. To evidence this, the self-assembly of manganese(I) dinuclear metallacyclophane $[Mn(CO)_3Br(\mu\text{-edp})]_2$ (**3**) was monitored by *in situ* ^{1}H NMR spectroscopy.[1] Reaction between $Mn(CO)_5Br$ and 1,2-ethanediyldi-4-pyridinecarboxylate was conducted in an NMR tube in chloroform-*d* at 25 °C. The course of the reaction was monitored by recording ^{1}H NMR spectra of reaction mixture at one-hour intervals. Initially the signals of H^2, H^3 (pyridyl) and methylene protons of 1,2-ethanediyldi-4-pyridinecarboxylate ligand appeared at δ 8.79, 7.85 and 4.71 ppm respectively. After one hour, the proton signals corresponding to the manganese(I) dinuclear metallacyclophane **3** started appearing at δ 8.98, 7.80 and 4.71 ppm. The intensities of free ligand signals were found to decrease, while those of dinuclear metallacyclophane **3** were found to increase, indicating product formation. The self-assembly process was nearly completed in thirty six hours, at which time free 1,2-ethanediyldi-4-pyridinecarboxylate proton signals had disappeared completely. At the end of the experiment the methylene protons signals displayed a triplet of doublet at δ 4.71 ppm, due to vicinal coupling between methylene protons. The stack plot of time-dependent ^{1}H NMR spectra is given in Figure S2. An *in situ* ^{1}H NMR spectral study supports the formation of exclusively single product from the self-assembly of four components.

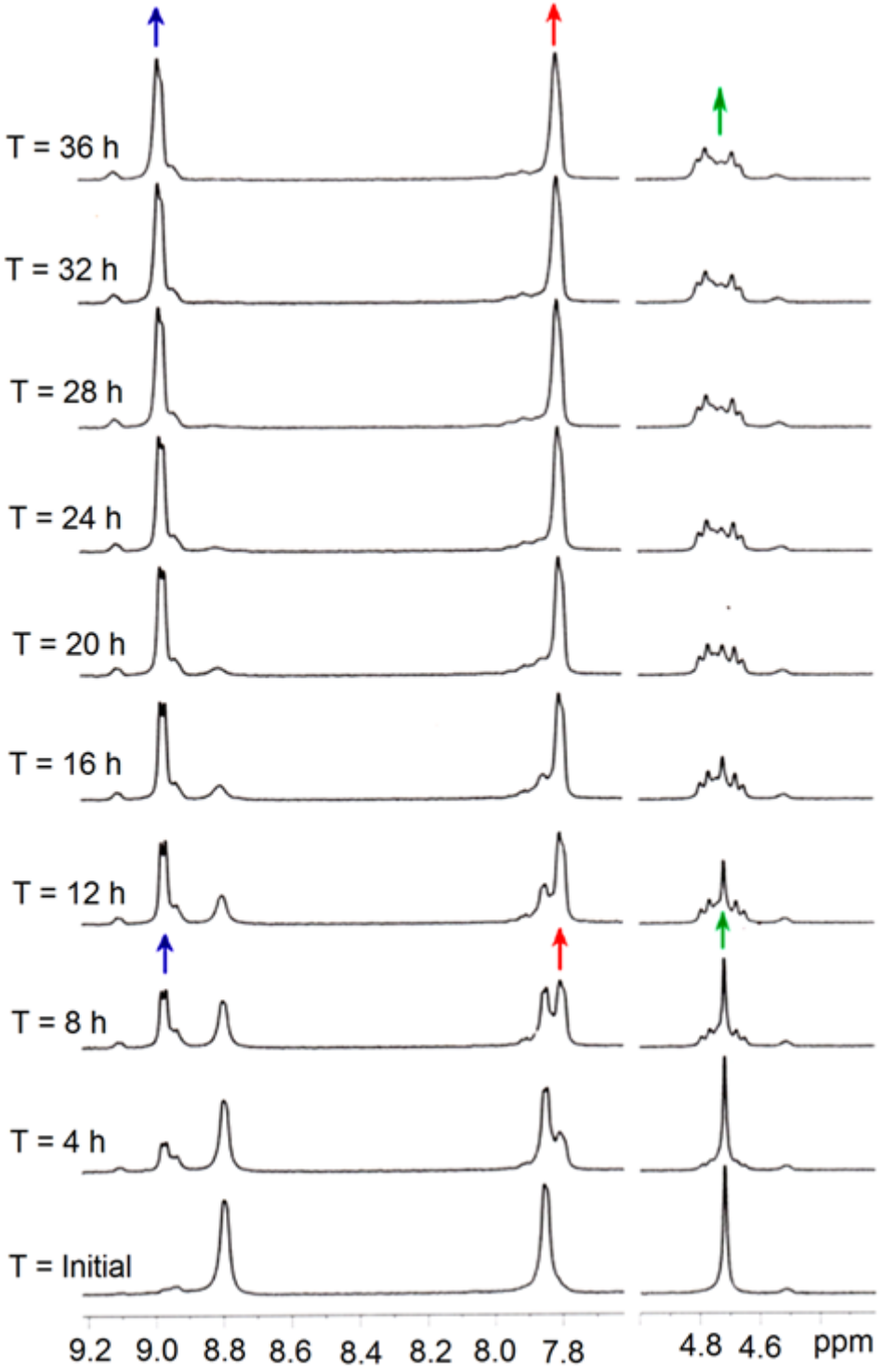


Fig. S2 Stack plot of time-dependent ^{1}H NMR spectra showing self-assembly of $[Mn(CO)_3Br(\mu\text{-edp})]_2$ (**3**).

Table S1 Crystallographic Data and Structure Refinement of **2a**, **3a** and **3b**

	2a	**3a**	**3b**
Formula	$C_{37}H_{32}N_2BrO_4Mn$	$C_{38}H_{29}N_4Br_2O_{14}Cl_8Mn_2$	$C_{70}H_{60}N_4Br_2O_{14}Mn_2$
Formula Weight	1406.97	1318.95	1450.92
Crystal System	monoclinic	monoclinic	triclinic
Temperature (K)	150(2)	150(2)	150(2)
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a/Å	14.3438(10)	12.5491(4)	9.8813(3)
b/Å	10.1990(8)	13.3073(7)	12.6032(7)
c/Å	22.1532(10)	15.8423(6)	14.2018(7)
α/°	90	90	99.250(4)
β/°	95.416(4)	107.932(4)	102.363(4)
γ°	90	90	94.534(4)
Unit Cell volume/Å^3	3226.4(4)	2517.06(18)	1693.31(14)
Z	2	2	1
F(000)	1440	1306	740
D_{calc} (mg mm^{-3})	1.448	1.740	1.423
Absorption Coefficient (mm^{-1})	1.690	2.579	1.619
Theta range for data collection (deg)	3.15 to 25.00	2.72 to 24.99	2.82 to 25.00
Crystal size (mm)	0.38 × 0.36 × 0.36	0.20 × 0.20 × 0.10	0.30 × 0.30 × 0.20
No. of reflns collected/unique	17497/5593	10527/4417	11204/5953
R_{int}	0.03771	0.0393	0.0426
data/restraints/params	5593/0/408	4417/9/319	5953/4/396
goodness-of-fit on F^2	1.206	1.108	0.827
final R indices [I > 2σ(I)]	R_1 = 0.0564, wR_2 = 0.1343	R_1 = 0.0598, wR_2 = 0.1611	R_1 = 0.0402, wR_2 = 0.0666
R indices (all data)	R_1 = 0.0764, wR_2 = 0.1411	R_1 = 0.0788, wR_2 = 0.1674	R_1 = 0.0893, wR_2 = 0.0717
largest diff peak and hole (e Å^3)	0.645 and –0.523	1.49 and –1.51	0.41 and –0.35
CCDC Number	1057206	1057207	1057205

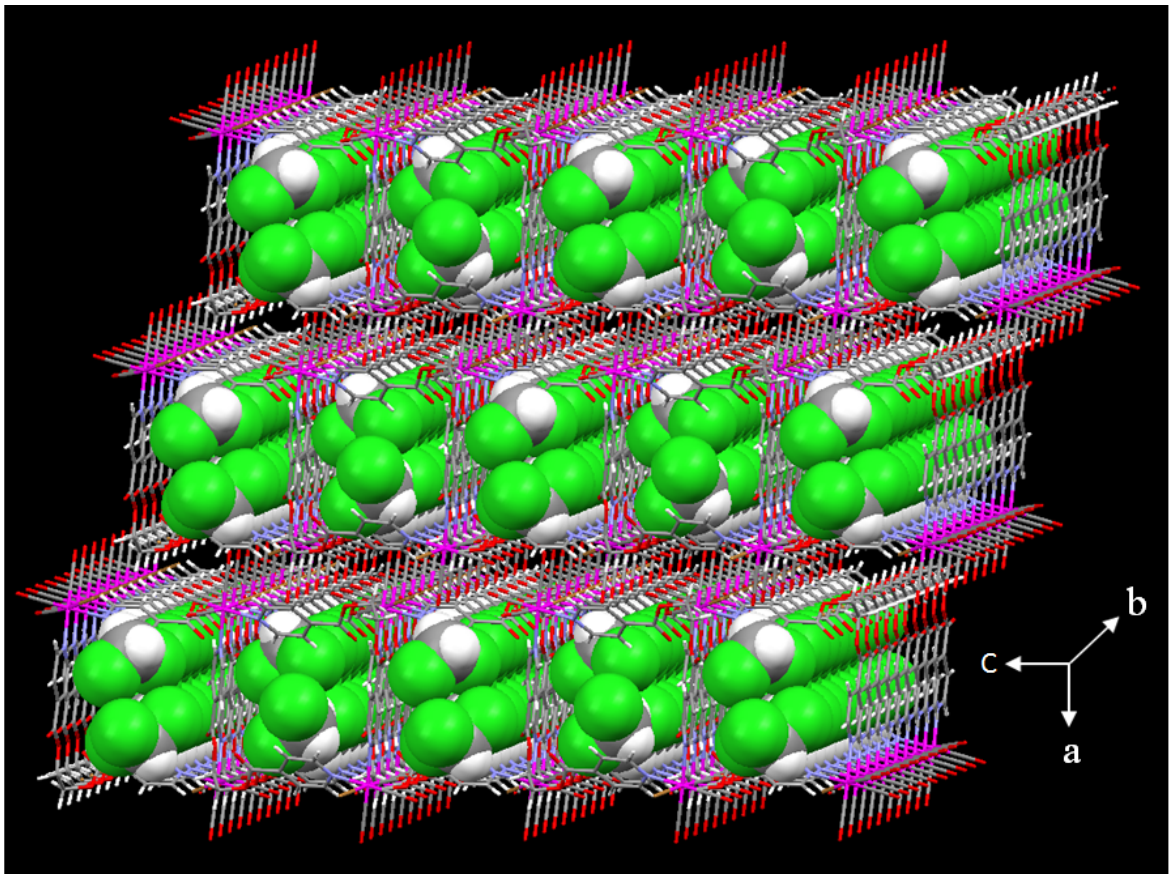


Fig. S3 Packing diagram of **3a** along the *b* axis showing infinite channels with dichloromethane molecules entrapped into the channels.

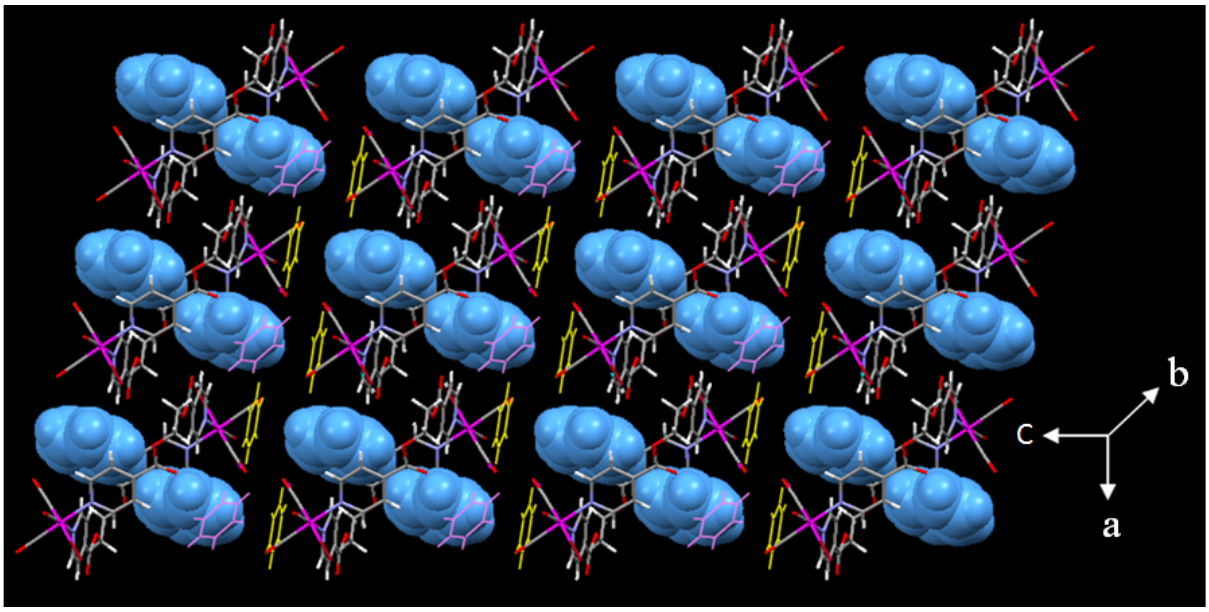


Fig. S4 Packing diagram of host **3b** along the *ac* plane is viewed with benzene molecules oriented towards the host cavity.

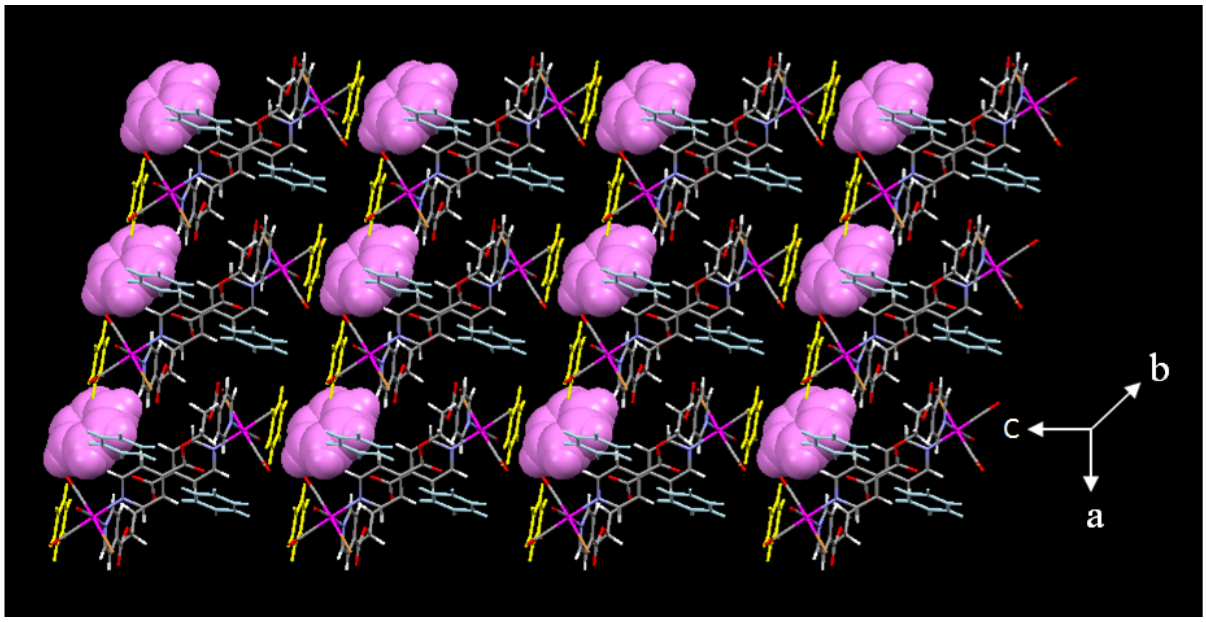
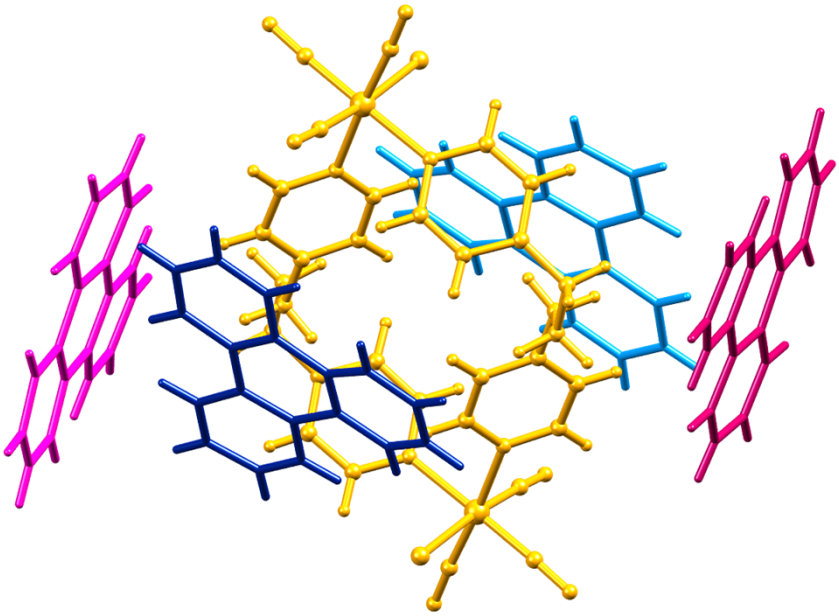
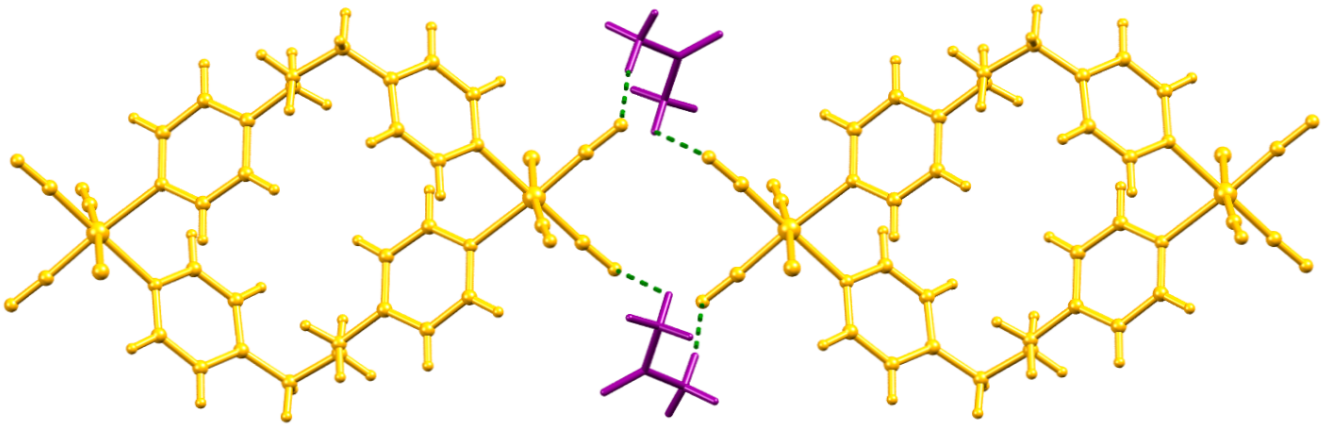


Fig. S5 Packing diagram of **3b** along the *ac* plane is viewed with benzene molecules in the interstitial positions.



(a)



(b)

Fig. S6 (a) Packing arrangement of **2a** showing four triphenylene guests (blue and pink color) sandwiching a host molecule (orange color). (b) Two host molecules (**2a**, orange color) bridged by acetone molecules (purple color) via C–H···O hydrogen bonding interactions.

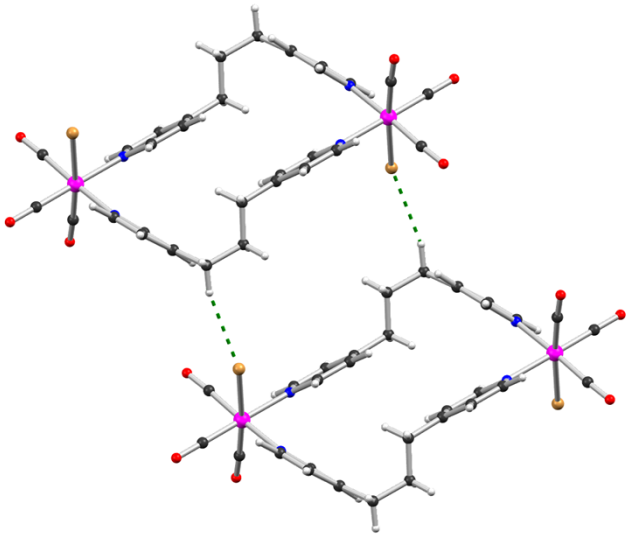


Fig. S7 Intermolecular C–H···Br interactions between adjacent hosts **2a**.

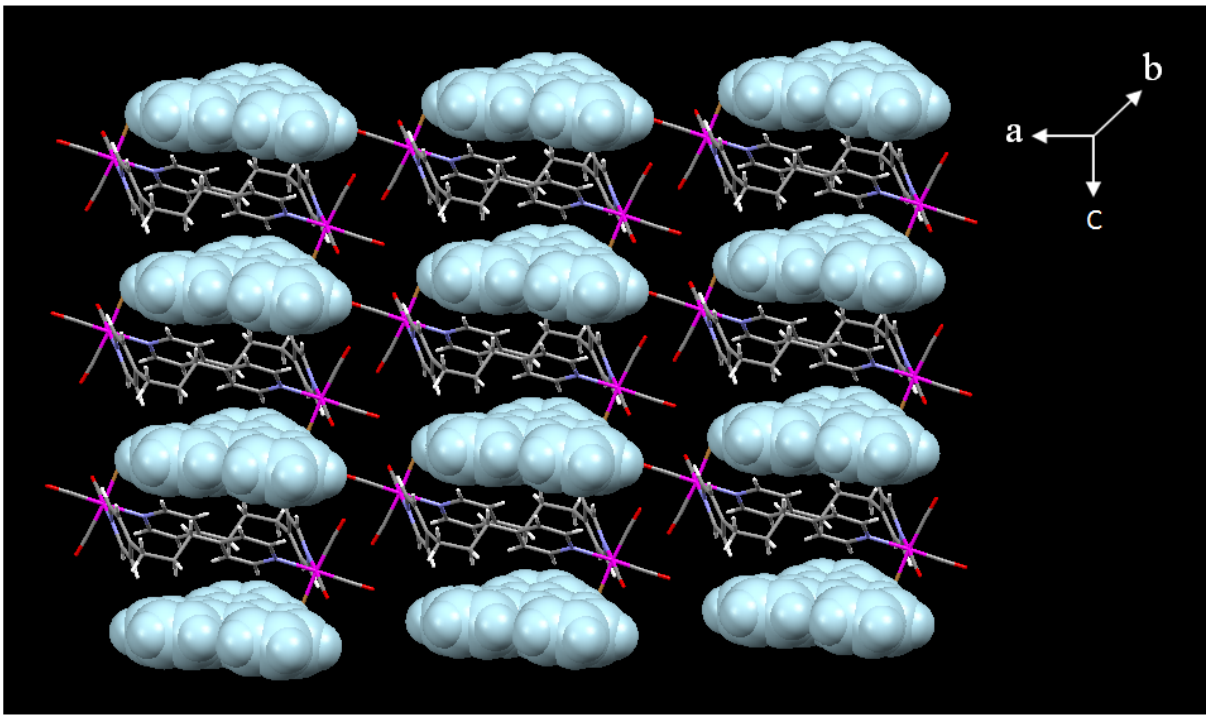


Fig. S8 Packing diagram of **2a** showing one-to-one host -guest interactions (triphenylene guest - space filling representation).