Supplementary Information for manuscript

Supramolecular Synthons: Will Giant Rigid Superspheres Do?

by

Eugenia Peresypkina,[§,†*] Alexander Virovets[§,†] and Manfred Scheer[§*]

§ Institut für Anorganische Chemie, Universität Regensburg, Universitätsstr. 31, Regensburg 93053, Germany
† Nikolaev Institute of Inorganic Chemistry SB RAS, Ak. Lavrentiev prosp. 3, Novosibirsk 630090, Russia

Content:

1. Pentaphosphaferrocene-based supramolecules

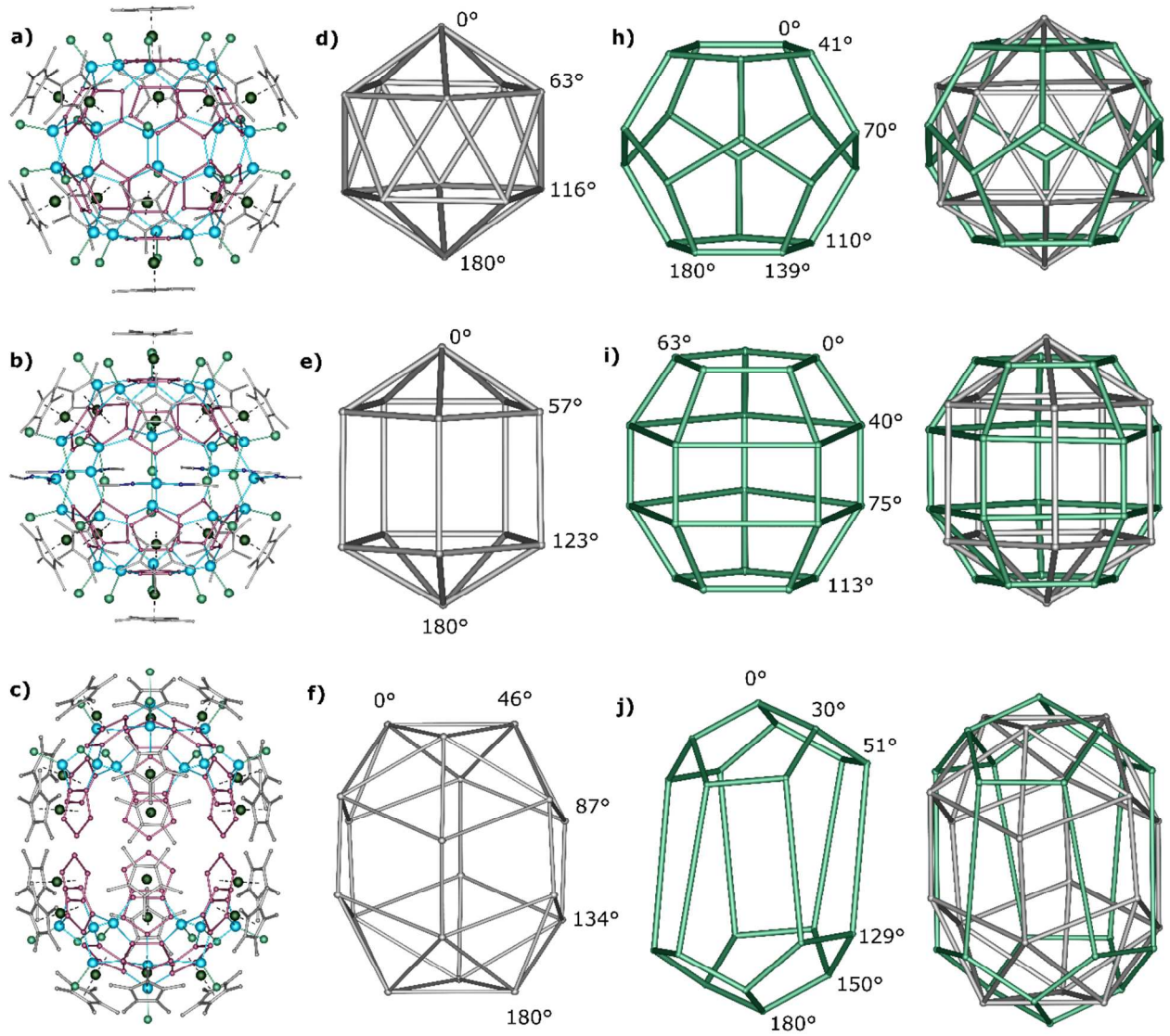


Figure S1. Spatial arrangement of Cp* (gray, d-f) and X functional groups (green, h-j) and their combination in superspheres (a) **2**, (b) **3** and (c) **4**.

2. Superspheres as potential synthons. Specific interactions and their geometric requirements.

Table S1. Some angles between the functional groups in 2-5

	$\tau_{Cp\text{-}Cp}$,°	$\tau_{X\text{-}X}$, °	$\tau_{X\text{-}Cp}$, °
2	63, 116, 180	41, 70, 109, 139, 180	38, 79, 100, 143,
3	57, 105, 123, 180	38, 63, 75, 96, 113, 127, 160	33, 61, 72, 94, 108, 146, 156
4	46, 87, 93, 134, 180	30, 51, 129, 150, 180	26, 57, 74, 107, 122, 153
5	52, 57, 75, 77, 80, 98, 107, 123	37, 60, 75, 87, 93, 98, 118, 136, 158	32, 56, 84, 88, 93, 106, 112, 122, 133, 147

[a] The angle ($\tau_{Cp\text{-}Cp}$) between the rays 1. and 2. (*cf* Fig. 2); [b] the angle ($\tau_{X\text{-}X}$) between the rays 3. and 4.; [c] the angle ($\tau_{X\text{-}Cp}$) between the rays 2. and 3.

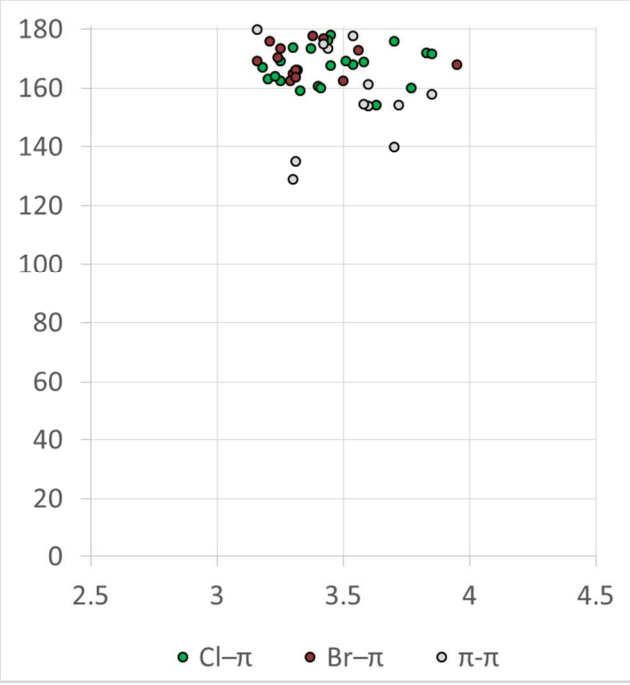


Fig.S2 The d(Å)-ϕ(°) distributions the for the synthons.

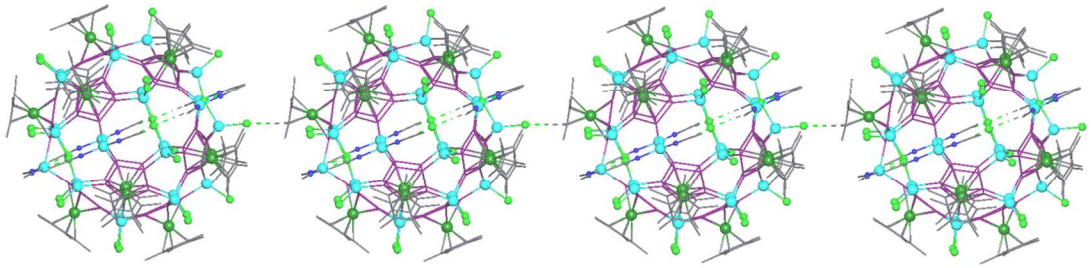
The distribution shows that the geometry of the synthons represented as d_1 vs. φ_1 (for σ–π synthon) or d_2 vs. φ_1 (for π–π synthon) vary in more narrow range for the σ–π synthon.

3. Synthon types in 2-5 and their geometry

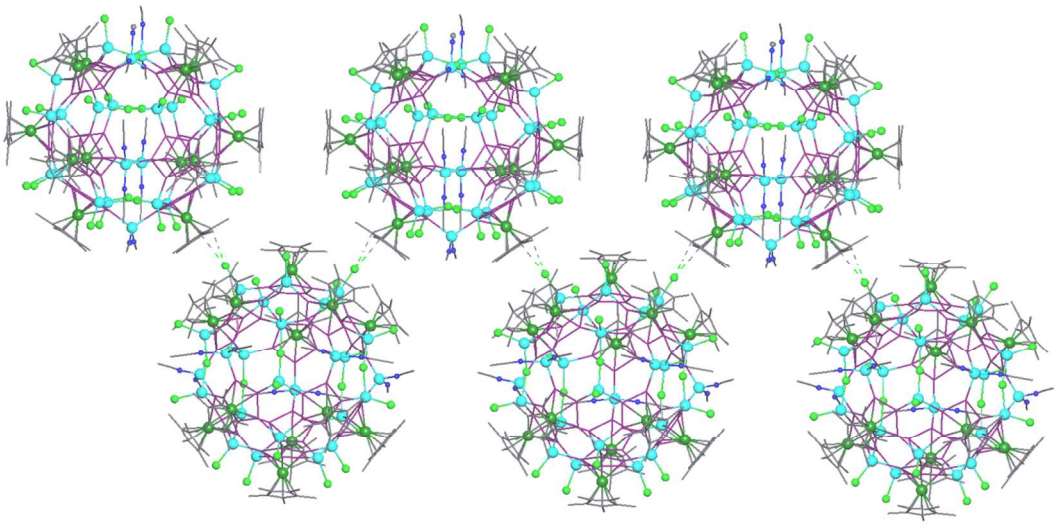
The more detailed information on the synthons in **2-5** and its geometry. In addition, the clickable Reference Codes in CSD are listed to ease access to the structural data. In the column D...A the type and the number of synthons per each crystallographically unique supramolecule are listed. For **3e** the characteristics of the double σ–π synthons are listed in brackets.

Table S2. The structures of **1a**- and **1b**-based supramolecules.

	Compound	σ–π (or double σ–π)			π–π			RefCode [e]
		D···A	d_1, Å [a]	φ_1, ° [b]	D···A	d_2, Å [c]	φ_2, ° [d]	
2a	$(o\text{-}C_2B_{10}H_{12})_{0.5}$@$[(1a)_{12}(CuBr)_{18.8}]$·7.33$C_7H_8$·0.67MeCN	2Cp*+2Br 4Cp* 4Br	3.21–3.39	162.5-175.8	-	-	-	KUCJEZ
2b	$(o\text{-}C_2B_{10}H_{12})_{0.5}$@$[(1a)_{12}(CuBr)_{18.8}]$·3.82$C_7H_8$·2.23MeCN	2Cp*+2Br 4Cp* 4Br	3.24-3.50	162.4-173.3	-	-	-	KUCJAV
2c	Cp_2Fe@$[(1a)_{12}(CuCl)_{20}]$	-	-	-	-	-	-	TATTOZ
2d	$CpCrAs_5$@$[(1a)_{12}(CuCl)_{20}]$	-	-	-	-	-	-	TATTUF
3a	[1a]@$[(1a)_{12}(CuBr)_{25}(MeCN)_{10}]$·2.1$C_6H_4Cl_2$·MeCN	2Cp*+2Br	3.30-3.38	165.0-177.7	-	-	-	GUSLEM
3b	[1a]@$[(1a)_{12}(CuBr)_{25}(MeCN)_{10}]$·10.4$C_7H_8$·0.8MeCN	3Cp*+3Br	3.31-3.42	166.0-176.8	-	-	-	GUSLIQ
3c	[1a]@$[(1a)_{12}(CuBr)_{25}(MeCN)_{10}]$·5$C_7H_8$·17.7MeCN	3Cp*+3Br	3.29-3.95	162.4-168.1	-	-	-	GUSLOW
3d	$[(CpCr)_2(\mu,\eta^5\text{-}As_5)]$@$[(1a)_{12}(CuBr)_{25}(MeCN)_{10}]$·10$C_7H_8$·3MeCN	3Cp*+3Br	3.32-3.44	166.1-176.2	-	-	-	TATVAN
3e	[1b]@$[(1b)_{12}(CuBr)_{25}(MeCN)_{10}]$·2$CH_2Cl_2$·1.5MeCN	7Cp^{Et}+4Br 4Cp^{Et}+7Br	3.51-3.70, (3.83-3.85)	168.0-175.9 (171.6-171.9)	-	-	-	TAXDAY
3f	[1a]@$[(1a)_{12}(CuBr)_{25}(MeCN)_{10}]$·2.9$C_6H_4Cl_2$·3.9MeCN	2Cp*+2Br	3.31-3.56	163.8-172.7	2Cp*	3.72	154.2	GUSLAI
3g	$[1a]_{0.6}$@$[(1a)_{12}Cu_{25}Cl_{24}(MeCN)_9]$ $[(1a)_{12}Cu_{25}Cl_{26}(MeCN)_9]$·12$C_7H_8$·1.5MeCN	4Cp* 4Cl	3.25-3.40	160.5-173.7	3Cp* 2Cp*	3.30-3.60	129.0-153.8	GUSKUB
3h	$[1a]_{0.5}$@$[(1a)_{12}(CuCl)_{25}(MeCN)_{10}]$·6$CH_2Cl_2$·1.5MeCN	2Cp* 2Cl	3.20	163.1	2Cp* 2Cp*	5.26	180.0	GUSKIP
3i	$[1a]_{0.6}$@$[(1a)_{12}(CuCl)_{25}(MeCN)_{10}]$·9.5THF·2MeCN	Cp*+Cl	3.16-3.85	154.6-180	6Cp*	3.58	168.8	GUSKOV
3j	$[Cu(MeCN)_4]^+[\{1a\}_{0.5}$@$(1a)_{12}(CuCl)_{25}(MeCN)_{10}]_3$ $\{1a\}_{0.5}$@$[(1a)_{12}Cu_{24}Cl_{25}(MeCN)_8]^-$·34$CH_2Cl_2$	4Cp*+Cl 2Cp*+5Cl	3.18-3.77	160.0-177.9	2Cp* -	3.44-3.70	140.0-173.4	BAPFOO
4	[1a]@$[(1a)_9\{CuCl\}_{10}]$·2C_7H_8	4Cp*+4Cl	3.33-3.41	159.1-160.1	4Cp*	3.42-3.60	161.3-175.1	OLIWIQ
5	C_{60}@$[(1a)_{13}(CuCl)_{26}(H_2O)_2(MeCN)_9]$·6$C_6H_4Cl_2$·MeCN	2Cp*+2Cl	3.63 [f]	154.1	-	-	-	COVBAR

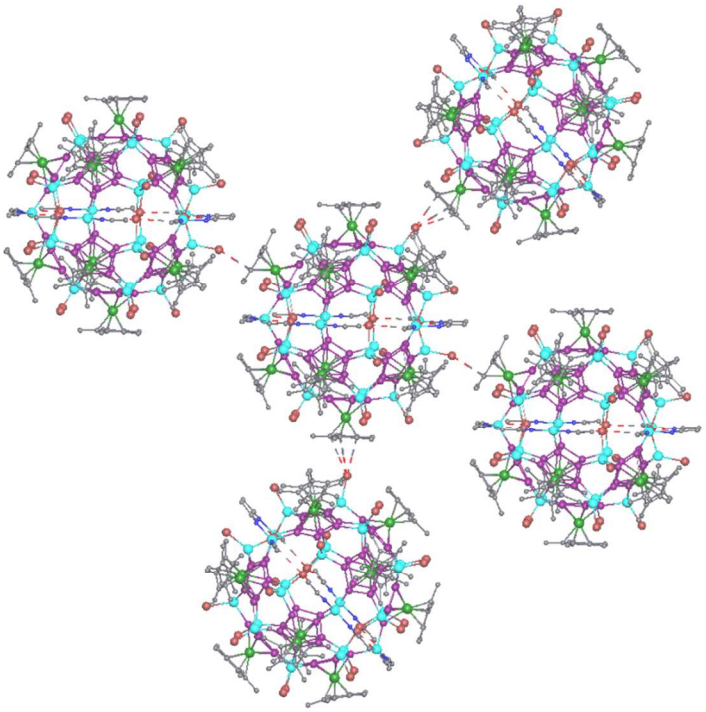


(a)

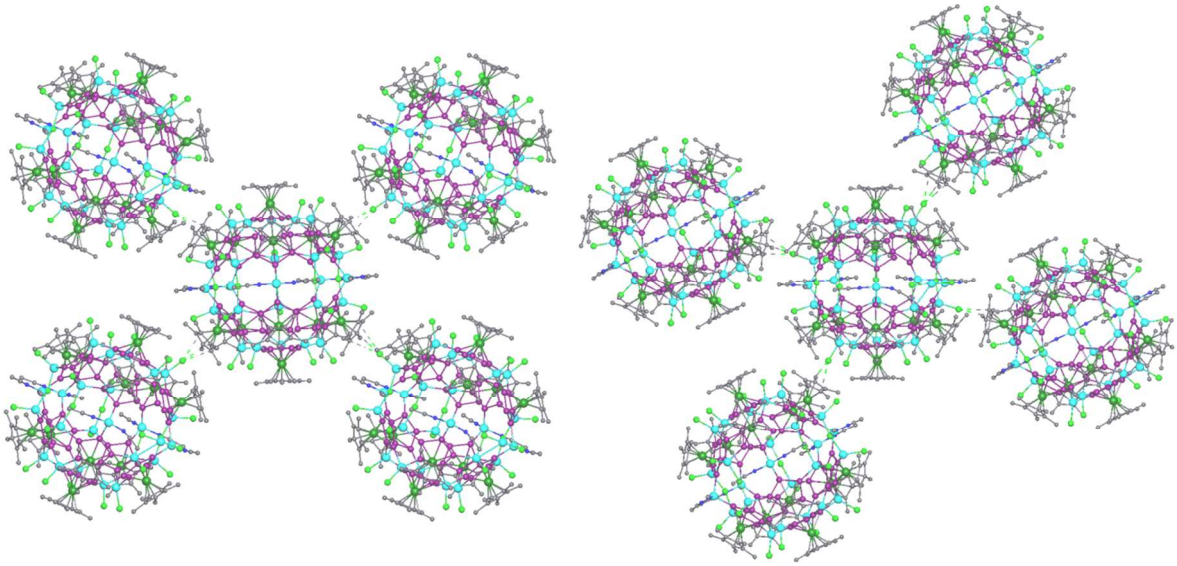


(b)

Fig.S3 The σ–π synthon-based chains in 90-vertex supramolecules: (a) linear chain in **3i** and (b) zigzag chain in **3h**.



(a)



(b) (c)

Fig. S4 The σ–π synthon-based square layers in the supramolecules in monosystem crystal structures (a) **3a** and **3f**, and (b, c) crystal structure **3g,** containing two crystallographically unique supramolecules.

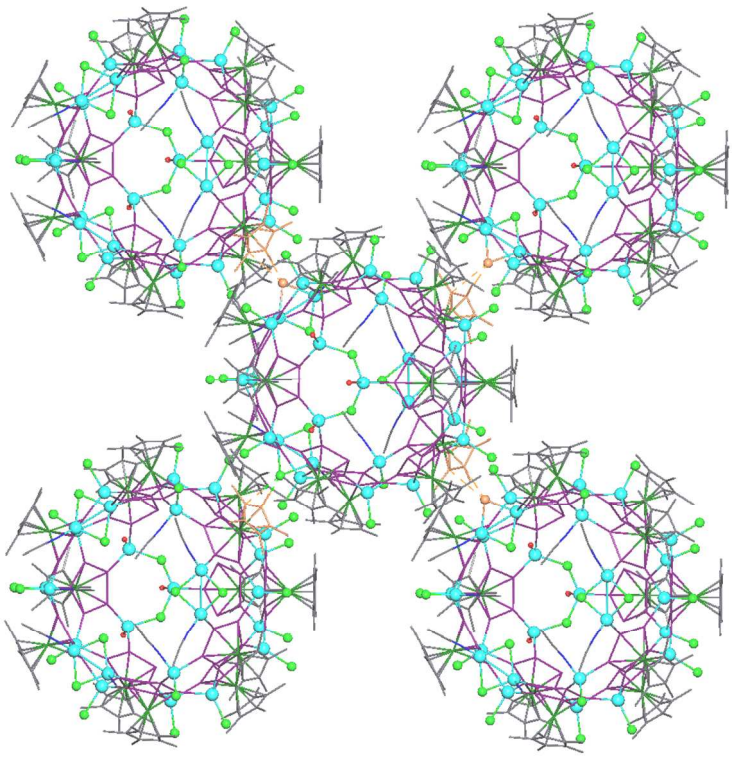


Fig.S5 The σ–π synthon-based square layers for supramolecules in **5** (top view). The synthons are highlighted in orange.

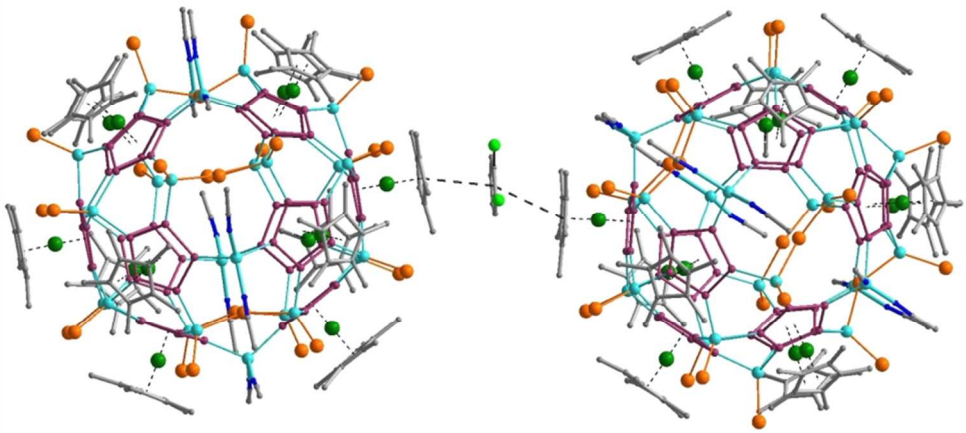


Fig.S6. Solvent-mediated π–π interactions between supramolecules **3** with dichlorobenzene molecule.

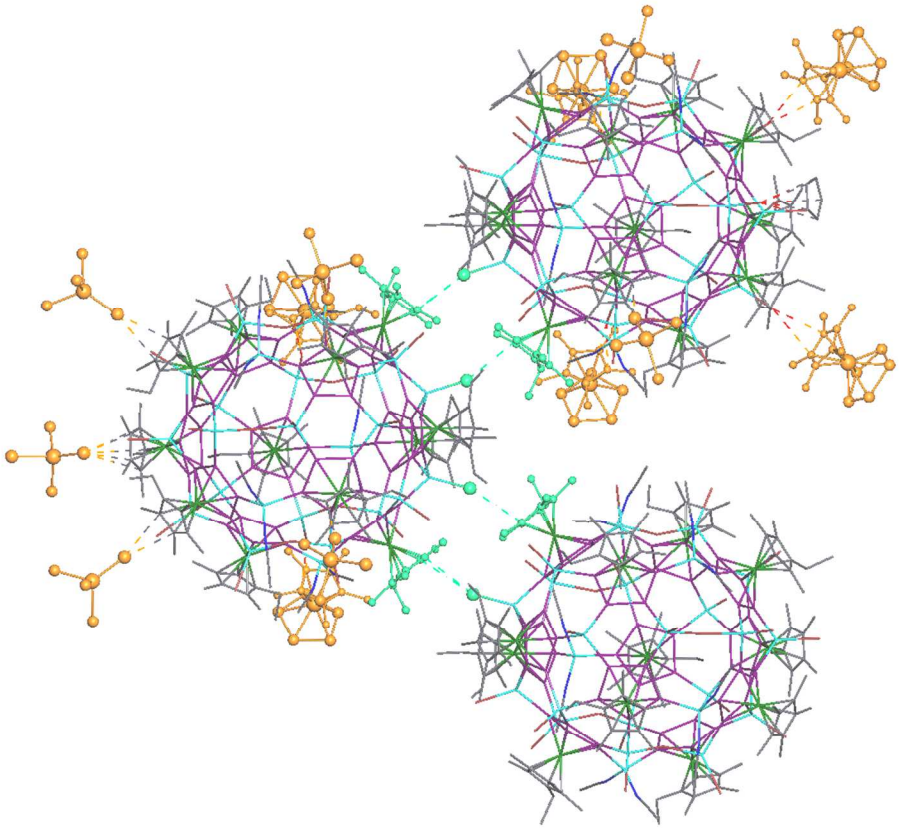
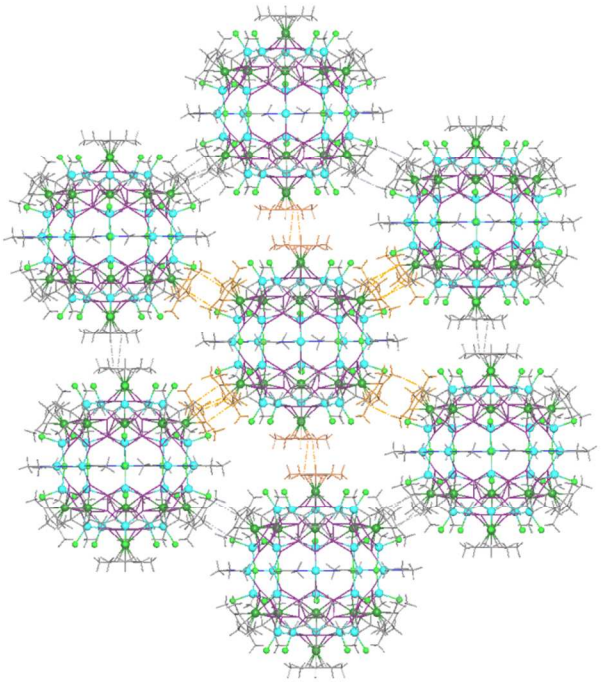
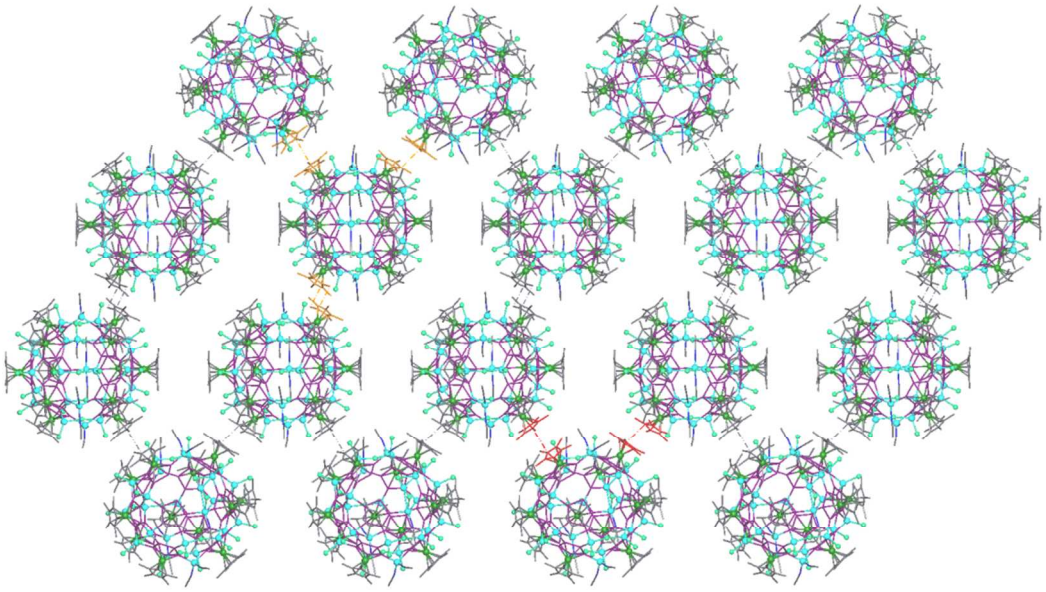


Fig.S7 The realization of the σ–π synthons in the **1b**-derived 90-vertex supramolecule **3e**. The 'single' σ–π synthons are shown as the orange fragments of the neighboring supramolecules; the 'double' synthons are highlighted in green.



(a)



(b)

Fig.S8 The realization of the π–π synthons in the **1a**-derived 90-vertex supramolecules (a) **3i** to give a trigonal layer (The π–π synthons are highlighted in orange) and (b) in **3g** to give a band based on the 3-connected (orange) and 2-connected (red) supramolecules.

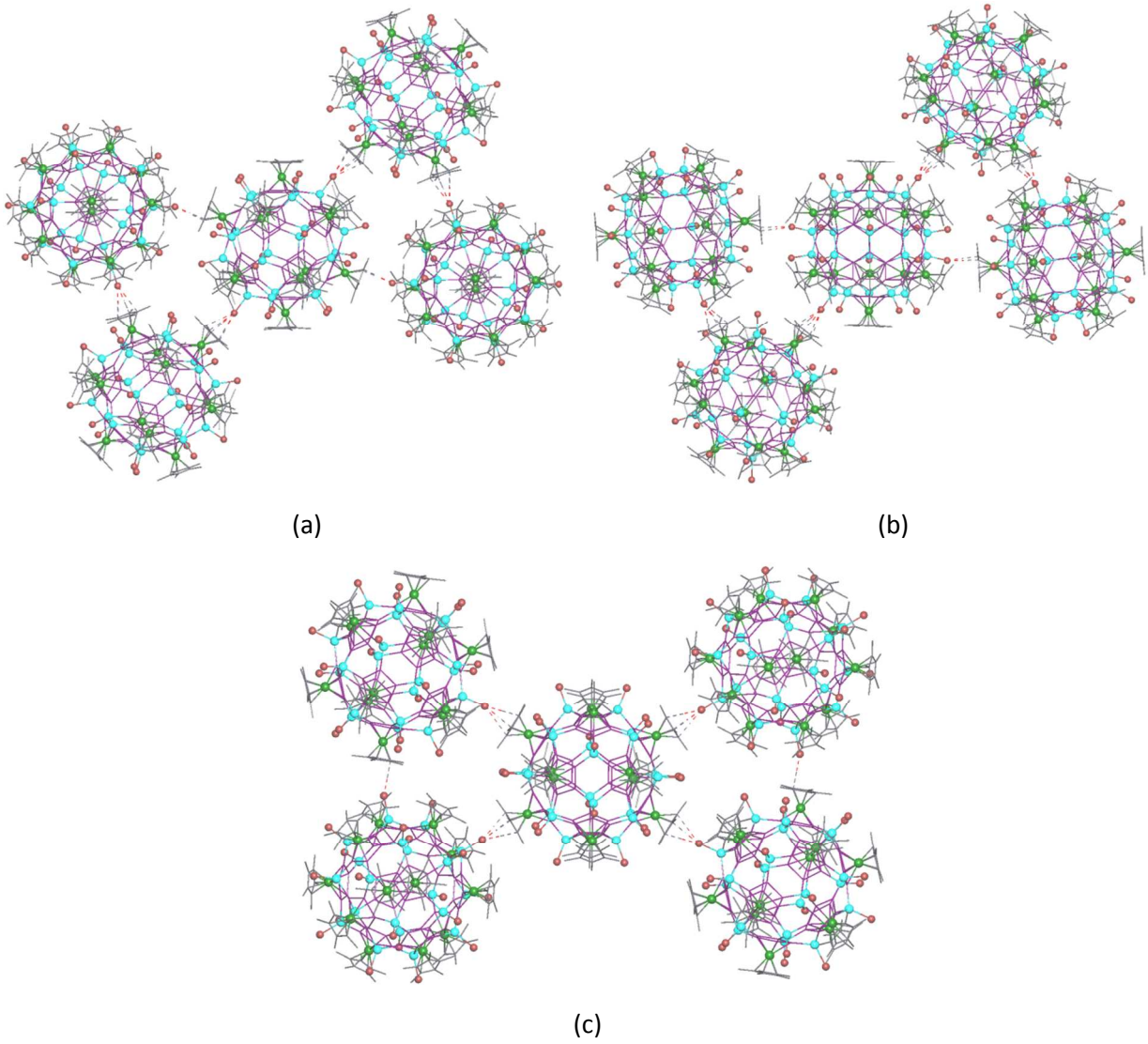


Fig.S9 The formation of Kagome layers in 80-vertex supramolecules **2a** and **2b**. The σ–π synthon-based triangular meshes based on three (a-c) crystallographically unique supramolecules.

To denote a packing, well-known traditional notations are used alongside with symbols of 3D-nets. In these notations, common packings as face-centered cubic (f.c.c.) are also known as fcu net, hexagonal close packing (h.c.p.) as hcp, body-centered cubic as bcu-x type.

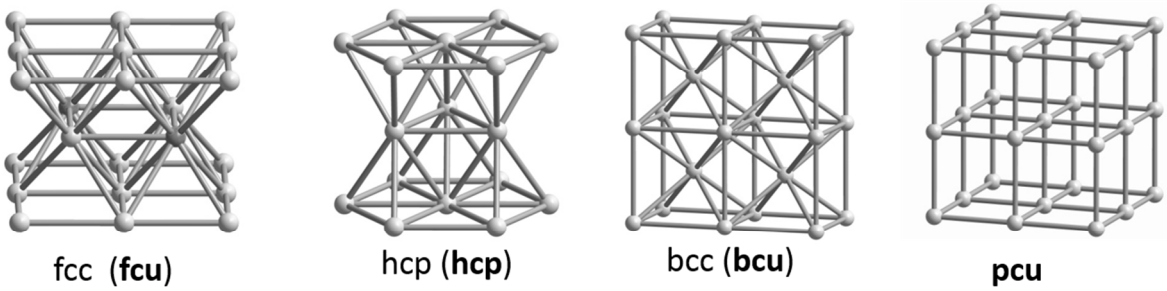


Fig. S10 Idealized nets corresponding to the supramolecular assemblies observed in the structures of supramolecules (*cf* Table 3).

4. Synthons in polymeric structures

The correlation is found between the presence of terminal X atom in the skeleton of the polymeric structure and the presence of the σ–π synthon. The π–π synthon was not found with an exception of the irreproducible interactions with the solvent molecules possessing an aromatic system.

Table S3. The structures of **1a**-based polymers.

D	Formula	Refcode[a]	Type of the intermolecular contact (d_i, Å; φ_i,°)	Role of X
X=Cl				
1D	$(As_4)_{0.75}$@[(Cp*FeP_5)$(CuCl)_2$]	DISDAM	-	bridging
1D	P_4@[(Cp*FeP_5)$(CuCl)_2$]	DISDEQ, DISDEQ01	-	bridging
2D	[(Cp*FeP_5)CuCl]	OLIWOW	Cp*···Cl (3.54; 152.6)	terminal
1D	[(Cp*FeP_5)$(CuCl)_4(MeCN)_2$]·0.4$C_6H_4Cl_2$	TAVCEA	Cp*···Solv	bridging
1D	[(Cp*FeP_5)$_4(CuCl)_4$]·2C_6H_6	TAVBAV	-	bridging
X=Br				
1D	[(Cp*FeP_5)CuBr]·CH_2Cl_2	MOHDOC	-	bridging
2D	[(Cp*FeP_5)CuBr] (2D)	MOHDUI (isostructural OLIWOW)	Cp*···Br (3.62; 151.5)	terminal
2D	[(Cp*FeP_5)(CuBr)]·0.5C_6H_6	TAVBOJ (isostructural TAVBUP)	- (4.66, 149.5)*	terminal
1D	[(Cp*FeP_5)$(CuBr)_4(MeCN)_2$]·0.5$C_6H_4Cl_2$	TAVCIE	-	bridging
X=I				
2D	[(Cp*FeP_5)CuI]	MOHFAQ (substructure of MOHDUI/ OLIWOW)	Cp*···I (3.75; 153.6)	terminal
2D	[(Cp*FeP_5)(CuI)]·0.5C_6H_6	TAVBUP (isostructural TAVBOJ)	- (4.70, 147.7)	terminal
1D	[(Cp*FeP_5)$_2(CuI)_2$]·thf	TAVBEZ	-	bridging
1D	[(Cp*FeP_5)$_4(CuI)_4$]·0.5$C_6H_4Cl_2$	TAVBID	Cp*···Solv	bridging
2D	[(Cp*FeP_5)$(CuI)_3$]·$C_6H_4Cl_2$	TAVCAW	Cp*···Solv	bridging

The shortest X···Cp contact