Coordination polymers with embedded recognition sites: lessons from cyclotriveratrylene-type ligands.

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Supplementary Information

CSD Refcodes for coordination polymers

Composition	Refcode	Reference*
$[Ag(L5)(NC(CH_2)_3CN)]\cdot(NC(CH_2)_3CN)\cdot[Co(C_2B_9H_{11})_2]$	GEGWIZ	11
$[Ag(L5)(NC(CH_2)_3CN)]\cdot2(NC(CH_2)_3CN)\cdot PF_6$	GEGWEV	11
$[Cd(L5)(OAc)_2]\cdot(C_2B_{10}H_{12})\cdot(H_2O)$	PUQKAO	14
$[Ag_9(L16)_7(H_2O)_3]\cdot(L16)\cdot9(SbF_6)$	AVOSEK	15
$[Mn_6(OH)_3(ctc)_4]\cdot Cs_{10}Na_5(H_2O)_n$	TUWWUE	22
$[Eu(L22)(DMF)_2]$	SEMFIC	25
$[Tb(L22)(DMF)_2]$	SEMFOI	25
$[Gd(L22)(DMF)_2]$	SEMFUO	25
$[Eu(L23)(DMF)(H_2O)]\cdot1.5(DMF)(H_2O)$	ZIDHEB	18
$[Cu_2(L1)_2(OTf)_2(NMP)_2(H_2O)_2]\cdot2(OTf)\cdot2NMP$	CUQSOY	20
$[Sm(L17)Cl(DMF)_3]\cdot[SmCl_5(DMF)]\cdot1.5(DMF)$	ZIDHAX	18
$[Cd_2(L9)(NO_3)_3(H_2O)_2(DMA)_2]\cdot(NO_3)\cdot(DMA)$	BAJYAO	16
$[Ag_2(L16)_2]\cdot2(SbF_6)$	AVOSIO	15
$[Yb(L22)(H_2O)(DMF)]$	SEMGAV	25
$[Ag_2(L16)(H_2O)_2]\cdot2(BF_4)\cdot2(MeNO_2)$	AVOSUA	15
$[Ag_2(L16)(CF_3SO_3)_2]$	AVOTAH	15
$[Ag(L16)(CF_3SO_3)]$	AVOTEL	15
$[Cu(L1)(NCMe)]\cdot BF_4\cdot1.5(CH_3CN)\cdot2(H_2O)$	CUQSUE	20
$[Zn_2(OAc)(L20)(DMF)]$	OYOVOP	24
$[Co_2(OAc)(L20)(DMF)]$	OYOVUV	24
$[Cd(L19)(NO_3)_2]\cdot2(DMF)$	REJQAA	17
$[Ag_2(L13)_2]\cdot[Co(C_2B_9H_{11})]_2\cdot1.5(NO_2Me)$	ZOBTOB	19
$[Ag(L14)]\cdot ReO_4\cdot CH_3CN$	WOLSOG	12
$[Ag(L12)]\cdot SbF_6\cdot3(DMF)\cdot H_2O$	WOLSUM	12
$[Ag(L6)(H_2O)]\cdot SbF_6$	GEGVOE	11
$[Co(L7)(NO_3)_2]\cdot4(NMP)$	BAJYIW	16
$[Cd(L18)_2(DMF)_2]\cdot2ClO_4\cdot8(DMF)$	REJQUU	17
$[Cu(L18)_2(DMF)_2]\cdot2ClO_4\cdot8(DMF)$	REJRAB	17
$[Gd(L19)(NO_3)_3]\cdot DMF$	ZIDWAM	18
$[Co(L18)_2(DMF)_2]\cdot2NO_3\cdot4(DMF)\cdot H_2O$	REJREF	17
$[Co_2(L8)_2(NO_3)(H_2O)_5]\cdot3(NO_3)\cdot n(DMF)$	BAJZAP	16
$[Ag_3(L10)_2(CH_3CN)_3Cl]\cdot2BF_4\cdot n(CH_3CN)$	TOHZIA	13
$[Ag_3(L10)_2(CH_3CN)_3Cl]\cdot2AsF_6\cdot n(CH_3CN)$	TOHZOG	13
$[Ag_3(L10)_2(CH_3CN)_3Cl]\cdot2ClO_4\cdot n(CH_3CN)$	TOHZUM	13
$[Cu_3(L3)_4(H_2O)_3]\cdot6(OTf)\cdot n(DMSO)$	CUQSEO	20
$[Zn_6(L21)_4(DMA)_6(H_2O)_5]$	OYOWAC	24
$[\{Re(CO)Br\}_3(L2)_2]\cdot n(CH_3NO_2)$	DIDFEE	21
$[\{Co(H_2O)_2\}_3(L2)_2]\cdot6(NO_3)\cdot n(DMF)$	DIDFOO	21
$[\{Cu(H_2O)_2\}_3(L2)_2]\cdot6(NO_3)\cdot n(DMF)$	DIDFUU	21
$[\{CoCl_2\}_3(L2)_2]\cdot n(DMF)$	DIDGAB	21
$[\{CoBr_2\}_3(L2)_2]\cdot n(DMF)$	DIDGEF	21
$[Co_3I_2(L2)_2]\cdot4I\cdot n(DMF)$	DIDGIJ	21
$[Cu_2(L11)_2Br_2(H_2O)(DMSO)]\cdot2Br\cdot n(DMSO)$	CUQSIS	20
$[Ag_3(NMP)_6(L17)_2]\cdot3(ClO_4)\cdot n(NMP)$	REJPED	17
$[Cu^{I}_4Cu^{II}_{1.5}(L1)_3(CN)_6]\cdot CN\cdot n(DMF)$	CUQSAK	20
$[Cd_3(L15)(BDC)_3]\cdot DMF\cdot6(H_2O)$	MIQTUE	26

$[Zn_3(L15)(BDC)_3]\cdot DMF\cdot 6(H_2O)$	MIQVAM	26
$[Cu_3(L20)_2(EtOH)(PY)_2(H_2O)_2]\cdot 9(DEF)\cdot 8(H_2O)$	FAHGUS	23
$[Ag(L1p)[Co(C_2B_9H_{11})_2]]\cdot 2(DMF)\cdot (H_2O)$	ZOBTIV	19
$[Cd(L1p)(NO_3)_2(H_2O)]\cdot DMF\cdot 2(Et_2O)$	ZOBYAS	19
$[Cu_2(L3)_2Br_3(DMSO)]\cdot Br\cdot n(DMSO)$	CUQTEP	20
$\{[Zn(L17)_2]\cdot 2(BF_4)\cdot n(NMP)\}$	REJPIH	17
$\{[Co(L17)_2]\cdot 2(BF_4)\cdot n(NMP)\}$	REJPON	17
$[Cu(L17)_2]\cdot[Cu(H_2O)(NMP)_4]\cdot 4(BF_4)\cdot 8(NMP)\cdot 2(H_2O)$	REJPUT	17
$[Cu_2(L2)(TFA)_3(INIC)]$	DIDFAA	21
$[Ag(L1)_2]\cdot[Co(C_2B_9H_{11})_2\cdot 9(CH_3CN)$	BIJROC	9
$[Zn(L9)_2(CF_3COO)(H_2O)]\cdot(CF_3COO)\cdot 7(NMP)$	BAJYES	16
$[Ag_2(L2)(DMF)_2]\cdot 2(BF_4)\cdot 2(H_2O)$	DIDDUS	21
$[Cu_5(L19)_2Cl_{10}(NMP)_4]\cdot n(NMP)$	REJQEE	17
$[Cd_2(L9)_2(NO_3)_4(NMP)]\cdot 9(NMP)\cdot 4(H_2O)$	BAJYOC	16
$[Co(L9)(H_2O)_2]\cdot 2(NO_3)\cdot 2(DMF)$	BAJYUI	16
$[Ag_3(L4)_2]\cdot 3(PF_6)$	MASCIT	10
$[Cu_2(L1)_2(NMP)(H_2O)]\cdot 4(BF_4)\cdot 12(NMP)\cdot 1.5(H_2O)$	CUQTAL	20

* Reference numbering is the same as used in the manuscript

Additional Crystal Structure Diagrams

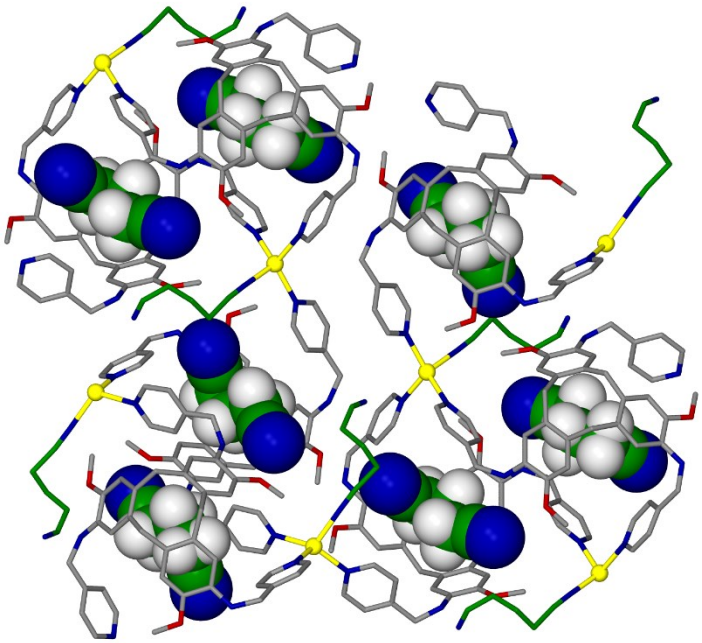


Figure S1. From the crystal structure of $[Ag(L5)(NC(CH_2)_3CN)]\cdot(NC(CH_2)_3CN)\cdot PF_6$, showing **fes** 2D coordination polymer of $Ag(L5)(NC(CH_2)_3CN)]^+$ with guest glutaronitrile in space filling mode.

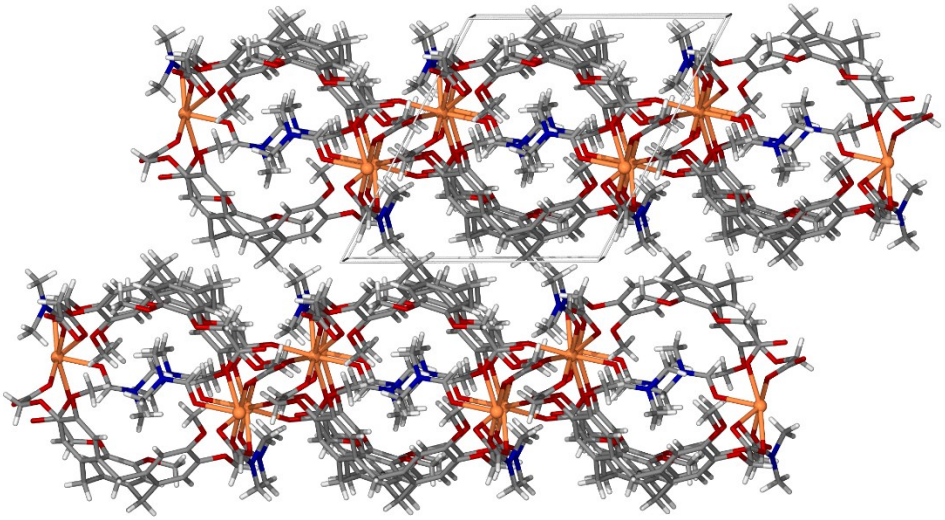


Figure S2. Packing diagram of [Eu(L22)$(DMF)_2$] with unit cell indicated and viewed down the *a* unit cell axis.[25]

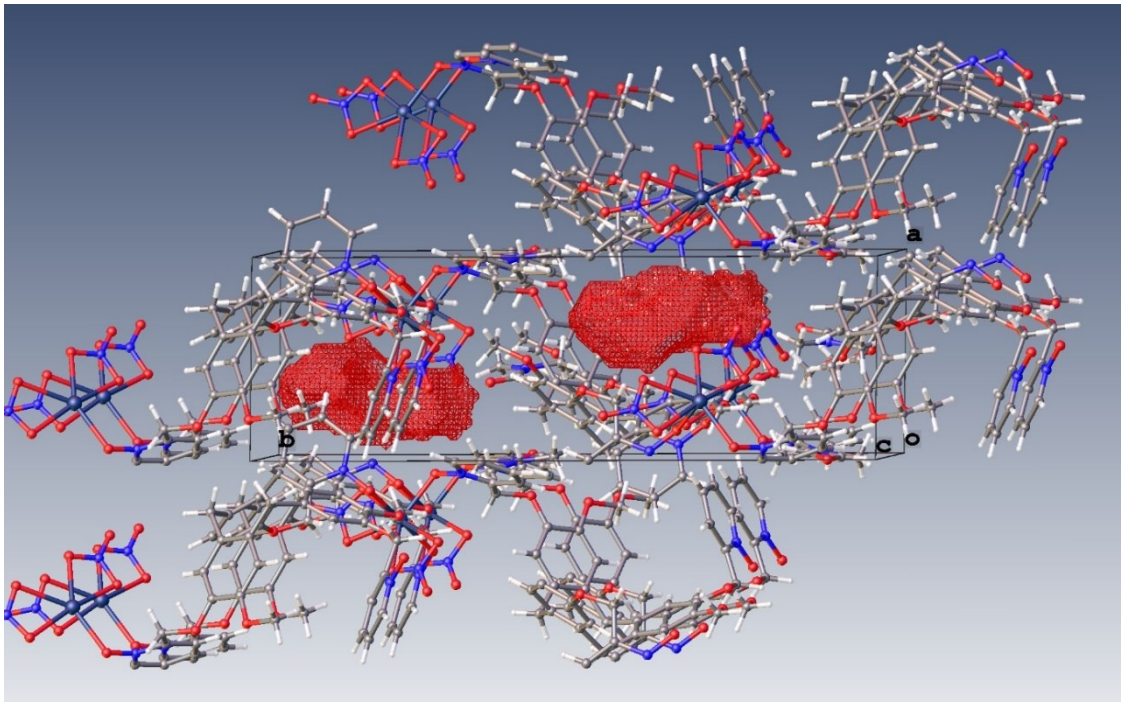


Figure S3. Unit cell diagram of {Cd(L19)$(NO_3)_2$]·2(DMF)} showing small isolated cavities of approximately 44 Å^3 volume (red wireframe) at the L19 bowl.[17]

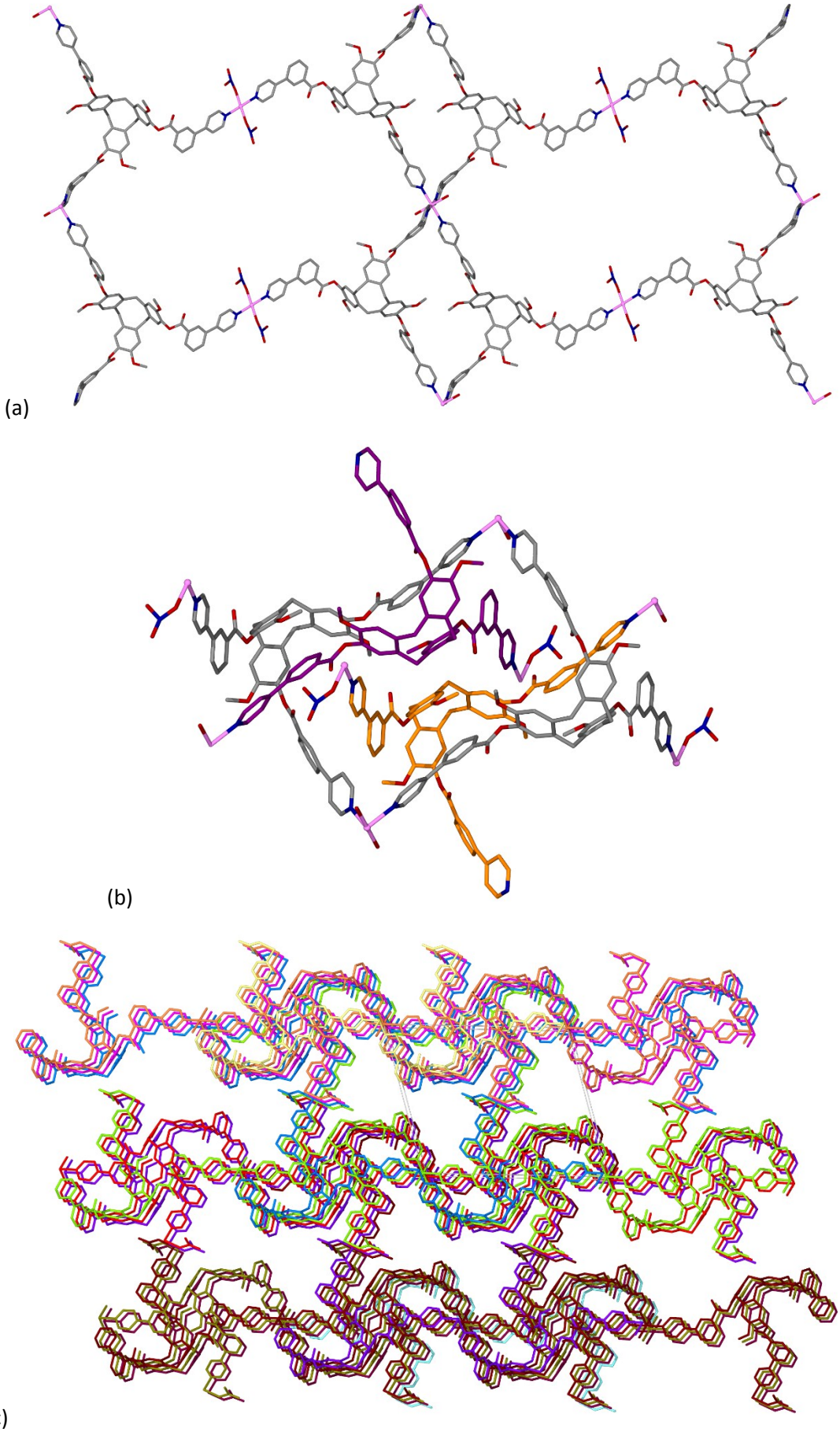


Figure S4. Crystal structure of $[Co_2(L8)_2(NO_3)_2(H_2O)_5]\cdot 2(NO_3)\cdot n(DMF)$. Disordered groups shown in averaged positions throughout. (a) Single **bex** network; (b) hand-shake inclusion between different networks; (c) 2D-to-3D polycatenation with different networks in different colours.[16]

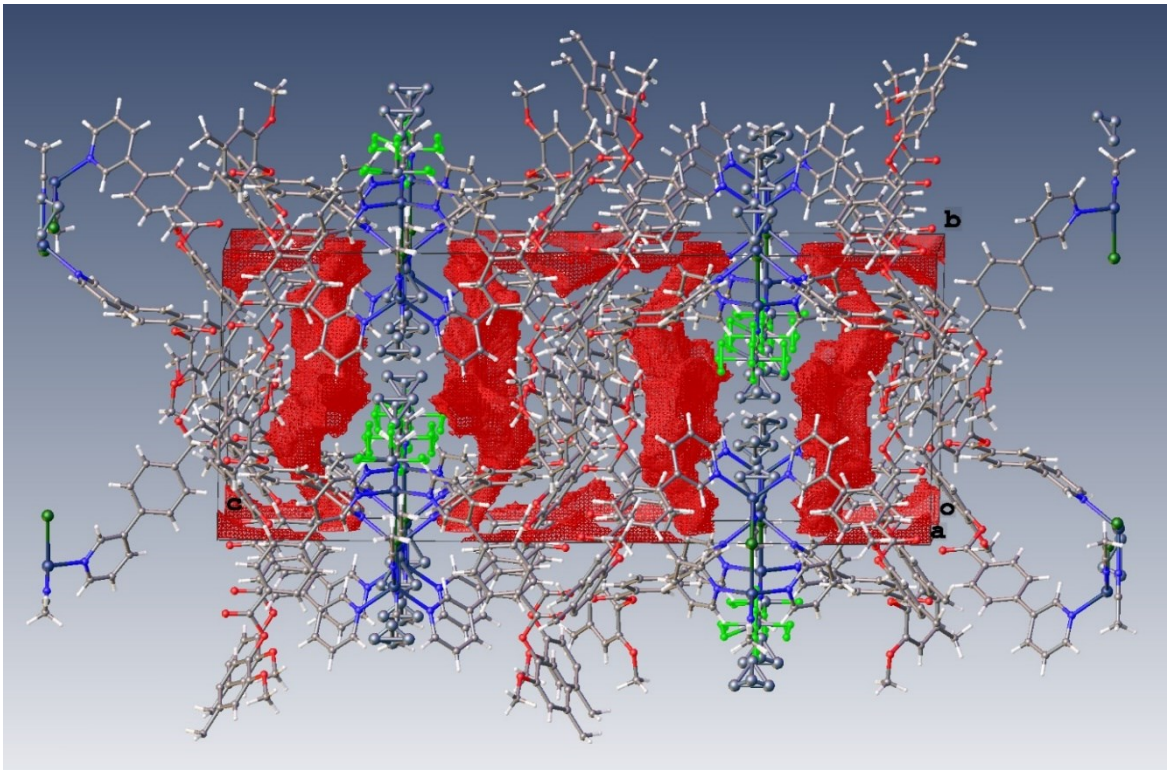


Figure S5. Unit cell diagram of $[Ag_3(L10)_2(CH_3CN)_3Cl].2AsF_6.n(CH_3CN)$ and void space shown in wireframe. The actual void space will be smaller than this appears as F atoms could not be located for one of the disordered AsF_6 sites.

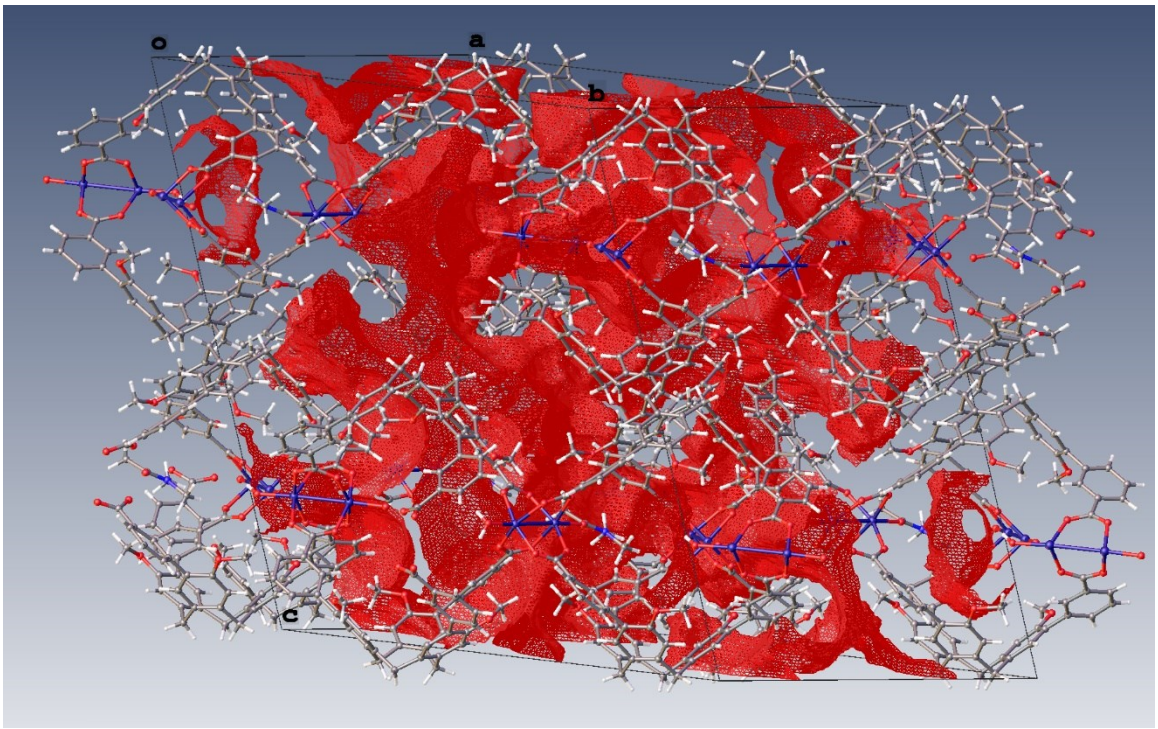


Figure S6. Unit cell diagram of $[Zn_6(L21)_4(DMA)_6(H_2O)_5]$ and void space shown in wireframe. Uncomplexed solvent molecules have been excluded.[24]

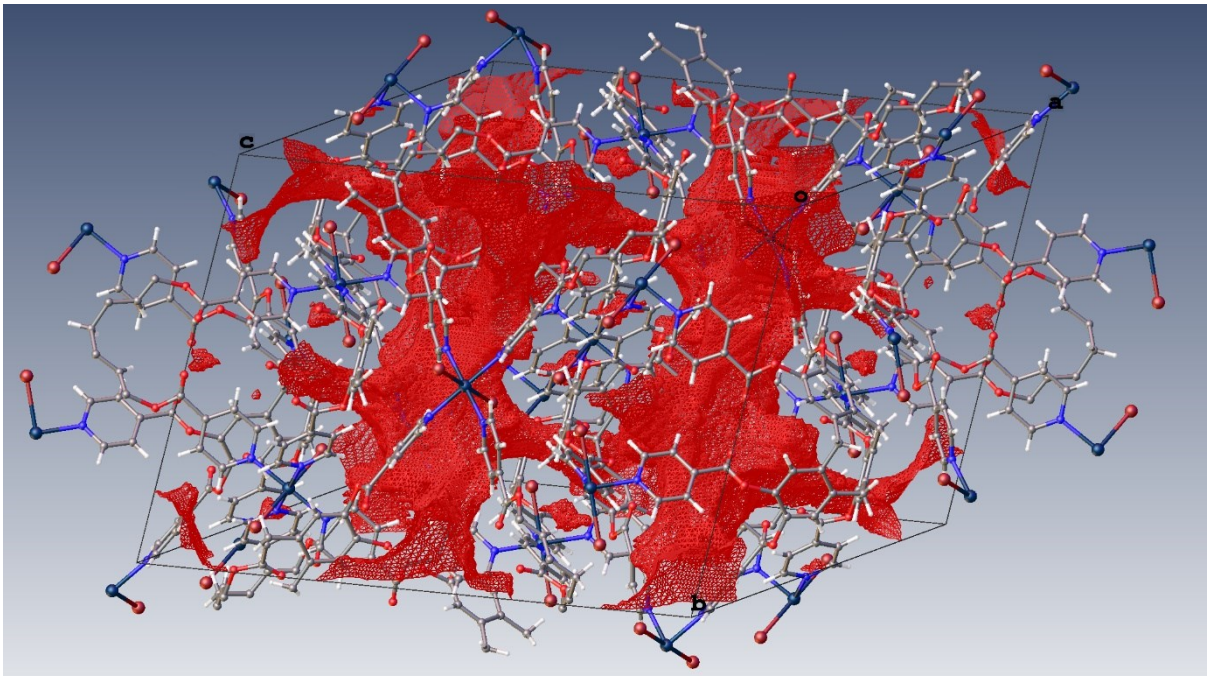


Figure S7. Unit cell diagram of [{Re(CO)Br}$_3$(L2)$_2$] and void space shown in wireframe. Uncomplexed solvent molecules have been excluded.[21]

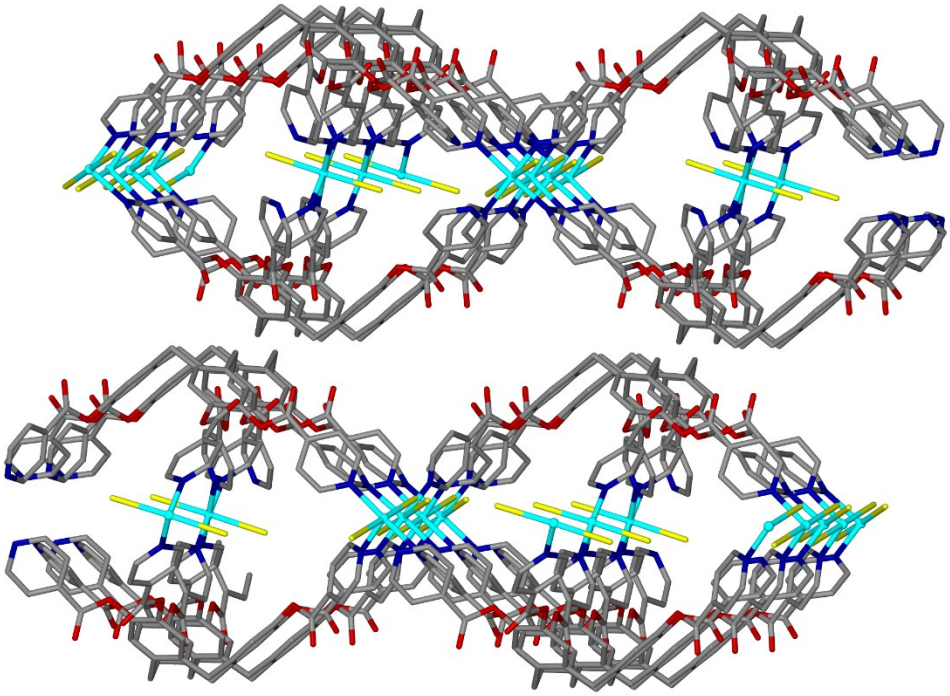
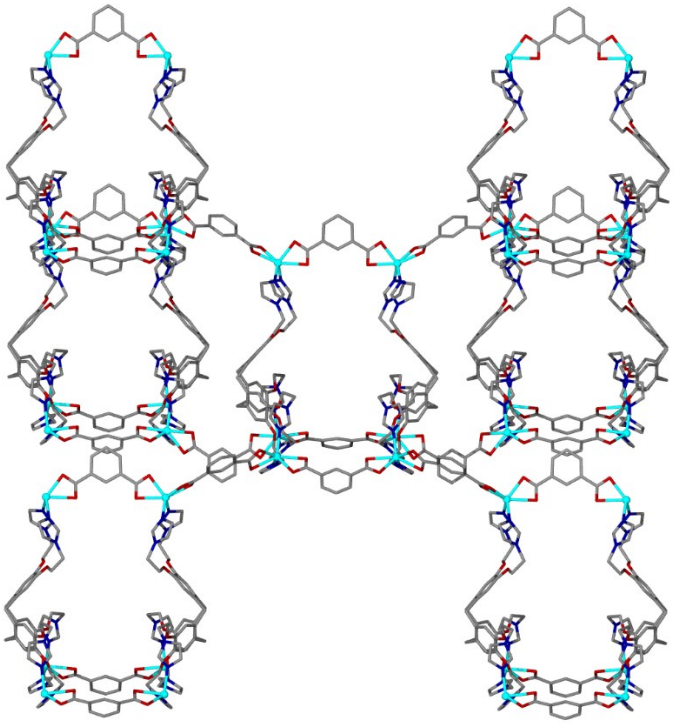
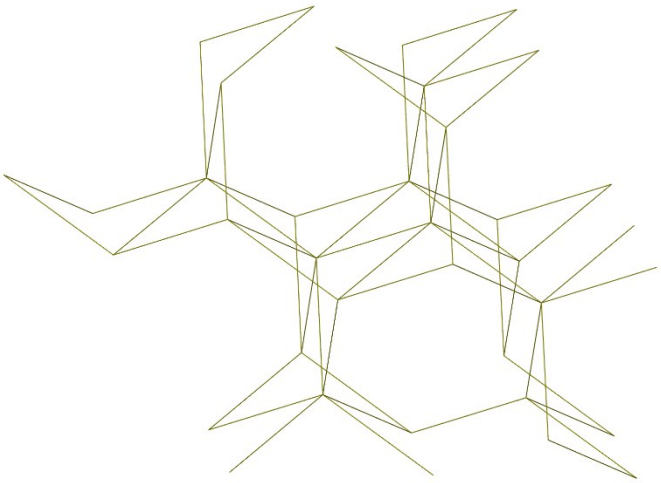


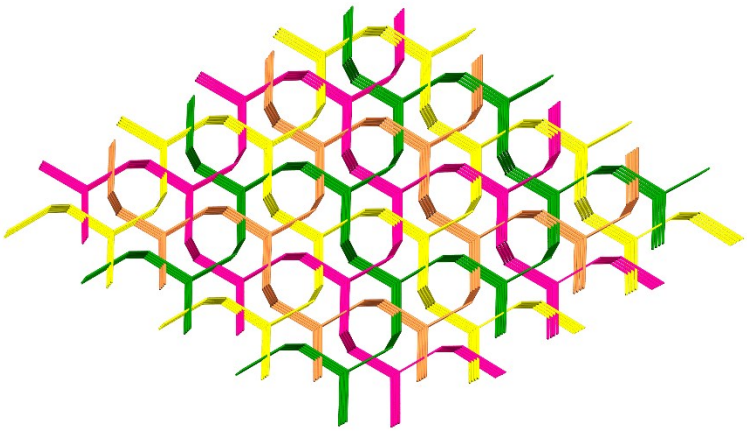
Figure S8. Packing diagram of [{CoBr$_2$}$_3$(L2)$_2$] with solvent excluded.[21]



(a)



(b)



(c)

Figure S9. Crystal structure of $[Cd_3(L15)(BDC)_3]\cdot DMF\cdot 6(H_2O)$. (a) illustration of linkages from one expanded cage (see Figure 11c of manuscript) to six others in a trigonal prismatic fashion via BDC^{2-} ligands; (b) connectivity diagram showing **acs** topology of cages where each connecting centre represents an expanded cage construct; (c) interpenetrating $(6.10^2)_3(6^3)$ nets considering L15 and metal positions as 3-connectors.[26]

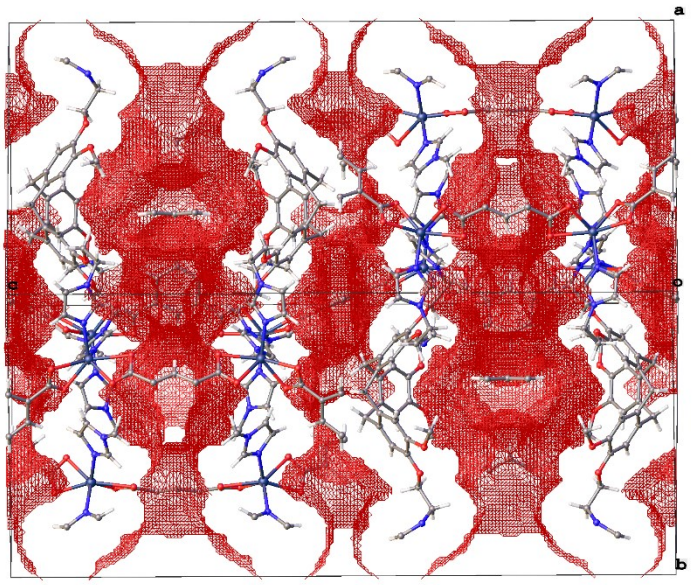


Figure S10. Unit cell diagram of $[Cd_3(L15)(BDC)_3]\cdot DMF\cdot 6(H_2O)$ with voids shown as wireframe and uncomplexed solvent removed.[26]

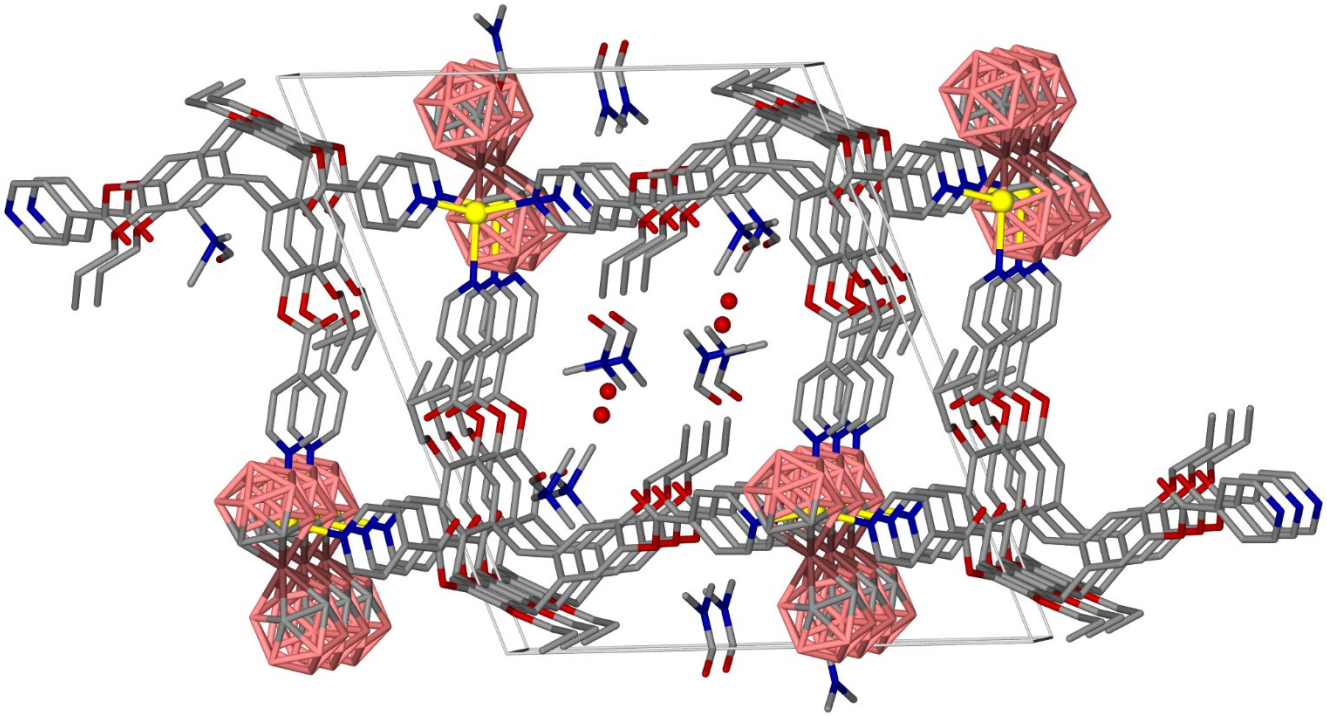
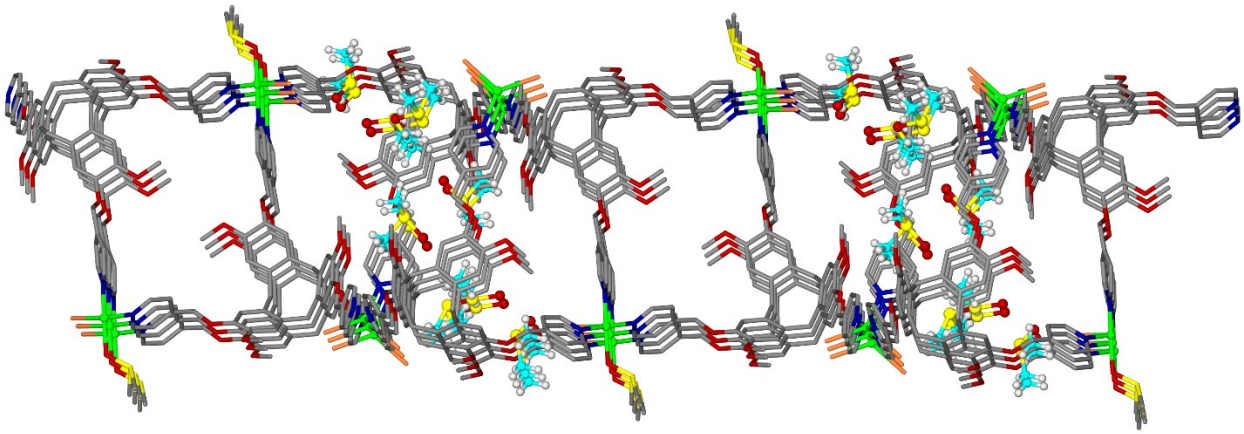
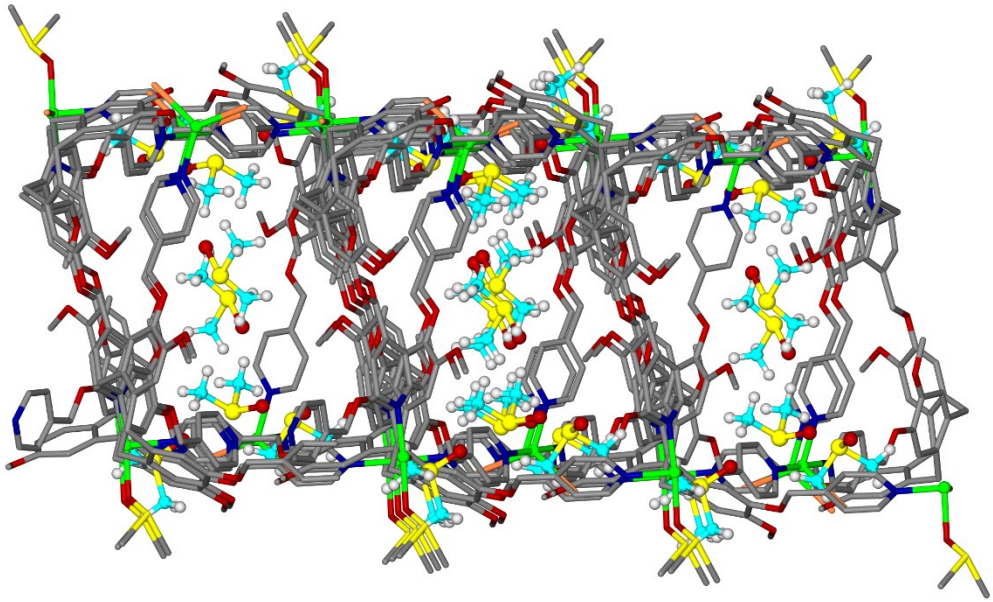


Figure S11. Unit cell of $[Ag(L1p)[Co(C_2B_9H_{11})_2]]\cdot 2(DMF)\cdot(H_2O)$ viewed down the *a* unit cell axis.



(a)



(b)

Figure S12. Two views of the two-tiered **fes** network of $[Cu_2(L3)_2Br_3(DMSO)]\cdot Br\cdot n(DMSO)$. Established guest DMSO positions are shown in ball-and-stick and carbon atoms in light blue. Disordered groups are shown at averaged positions.

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