

Design and synthesis of new luminescent coordination networks of sql topology showing the highest degrees of interpenetration

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SUPPORTING INFORMATION

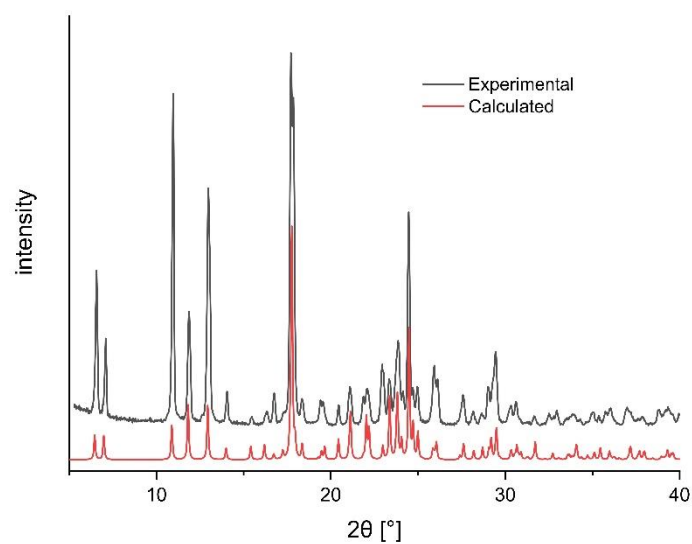


Fig. S1 Comparison between calculated and experimental X-ray powder diffraction patterns for **1**.

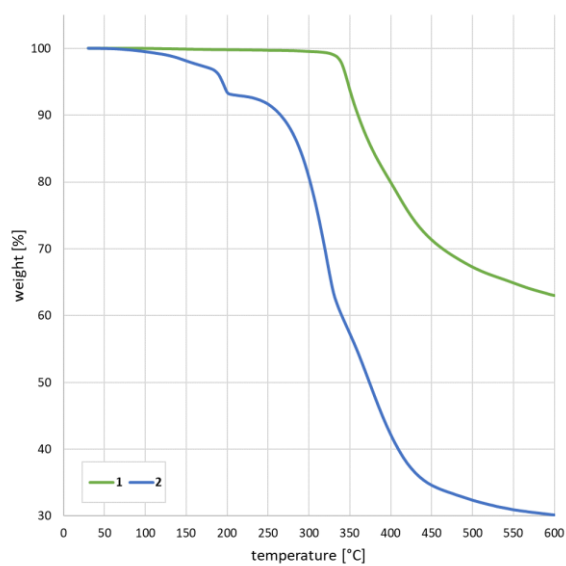


Fig. S2 TGA traces for **1** and **2**.

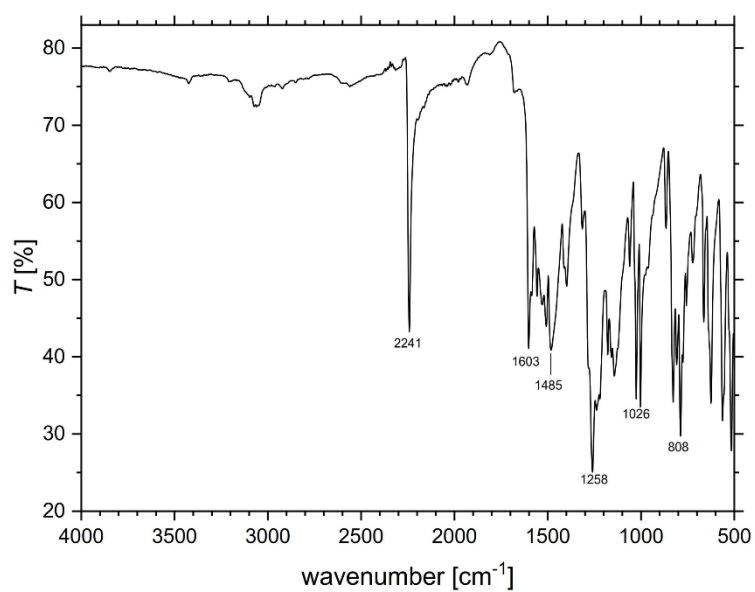


Fig. S3 IR spectrum for **1**.

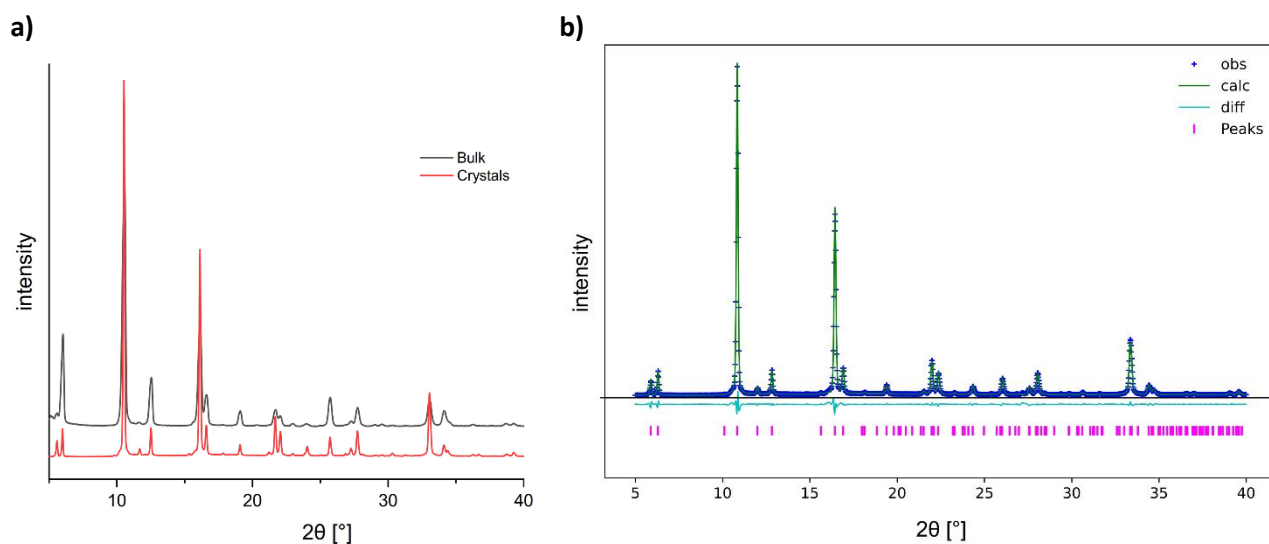


Fig. S4 a) Comparison between the X-ray powder diffraction patterns of a microcrystalline sample and crushed single crystals of **2**. b) Le Bail refinement of the X-ray powder diffraction pattern of a microcrystalline sample of **2**. The blue crosses (I_{obs}), green line (I_{calc}) and cyan line ($I_{\text{obs}} - I_{\text{calc}}$) represent the observed, calculated and difference data, respectively. Cell parameters and reliability factors for the Le Bail-refined compound **2** in *Pban* are $a = 17.154(8)$, $b = 27.171(6)$, $c = 5.178(3)$ Å, $V = 2413.7(2)$ Å³, $R = 0.0410$, $wR = 0.0612$, $S = 4.57$.

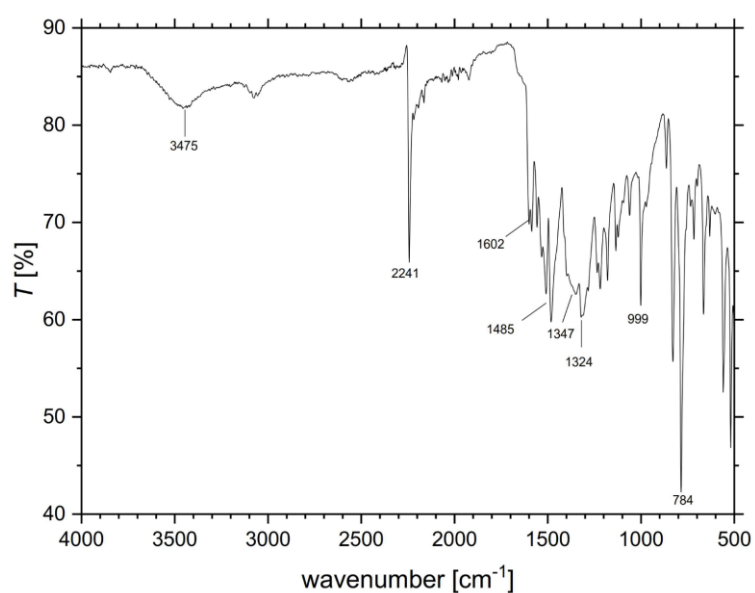


Fig. S5 IR spectrum for **2**.

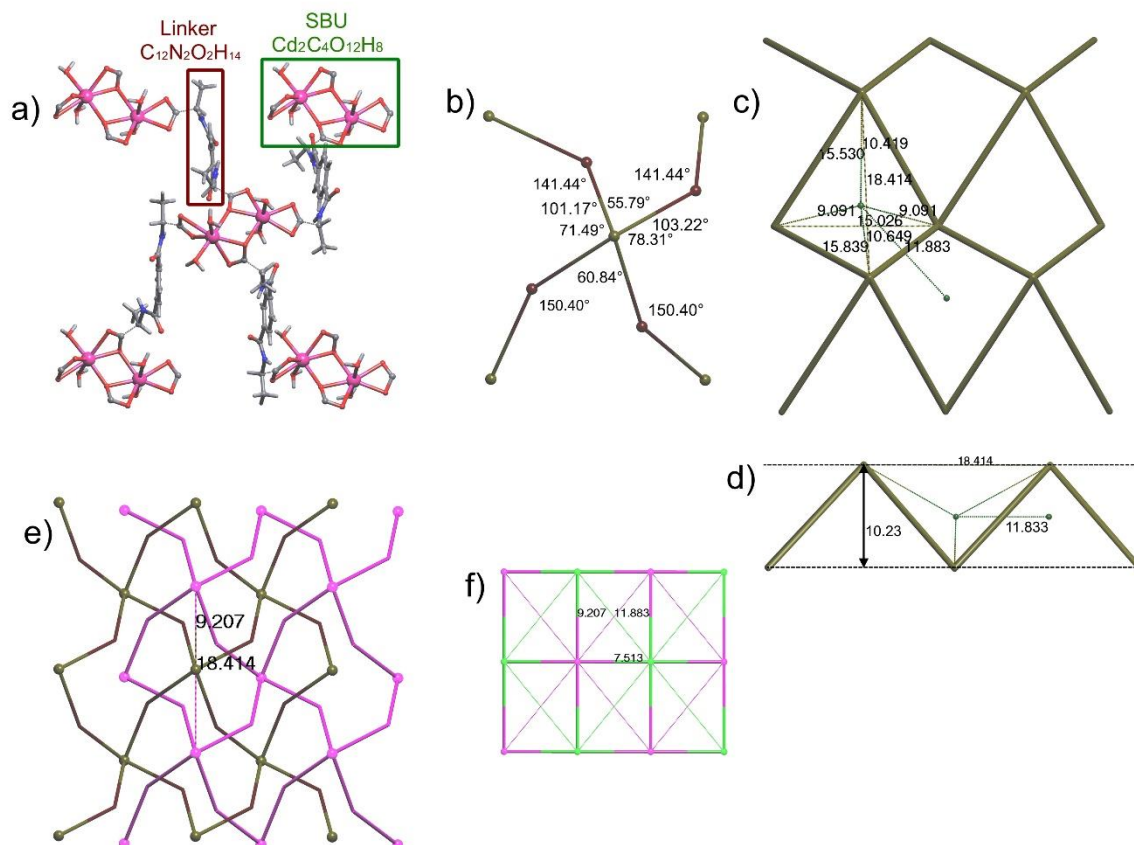


Fig. S6 The calculated descriptors exemplified on the 2-fold interpenetrated network of $[\text{Cd}_2(\text{H}_2\text{O})_4(\text{dbcidp})_2] \cdot 3\text{H}_2\text{O}$ (H_2dbcidp = benzene-1,4-diylbis(carbonylimino)dipropionic acid; CSD RefCode [WINLOX](#)). a) Composition of secondary building unit ($\text{Cd}_2\text{C}_4\text{O}_{12}\text{H}_8$) and linker ($\text{C}_{12}\text{N}_2\text{O}_2\text{H}_{14}$). b) Coordination geometry of secondary building unit (tetragonal pyramid with angles 55.79, 60.84, 71.49, 78.31, 101.17 and 103.22°) and shape of linker (V-type, with angle 141.44 and 150.40°). c) Shape of ring (envelope, with edges of 15.530 and 15.839 Å, diagonals of 15.026 and 18.414 Å, distances from center to vertices of 9.091, 10.419 and 10.649 Å). d) Type of underlying net geometry (undulated with neighboring nodes on different sides), its thickness (10.23 Å), and distance between centers of rings (11.883 Å). The projection on plane (010) is shown. e) Number of catenations of a ring (4), number of interpenetrating nets in the array (2), interpenetration mode (diagonal). f) Hopf ring net (4-c **sql** in ball and stick) and extended ring net (8-c (4,4)IV in ball and stick and dashed lines).

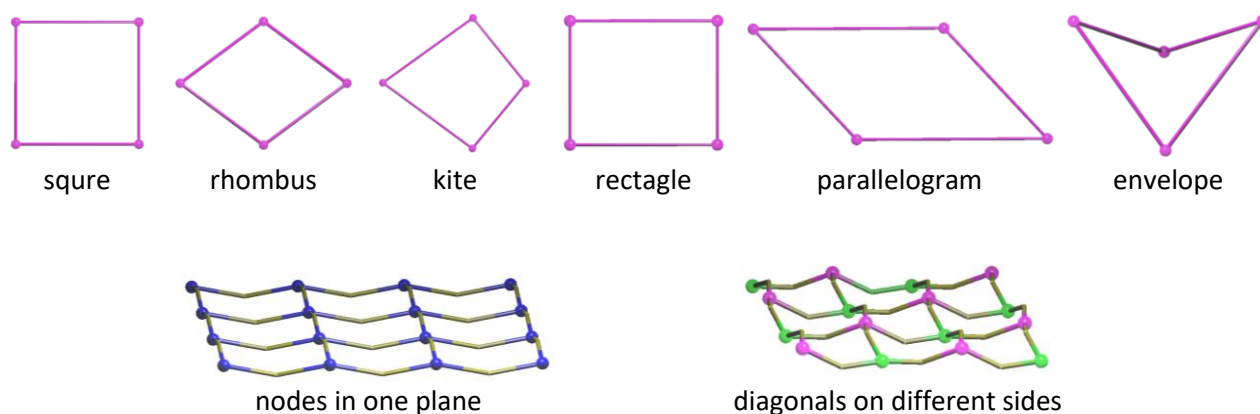


Fig. S7 The shapes of 4-rings and the geometries of 2D **sql** nets.

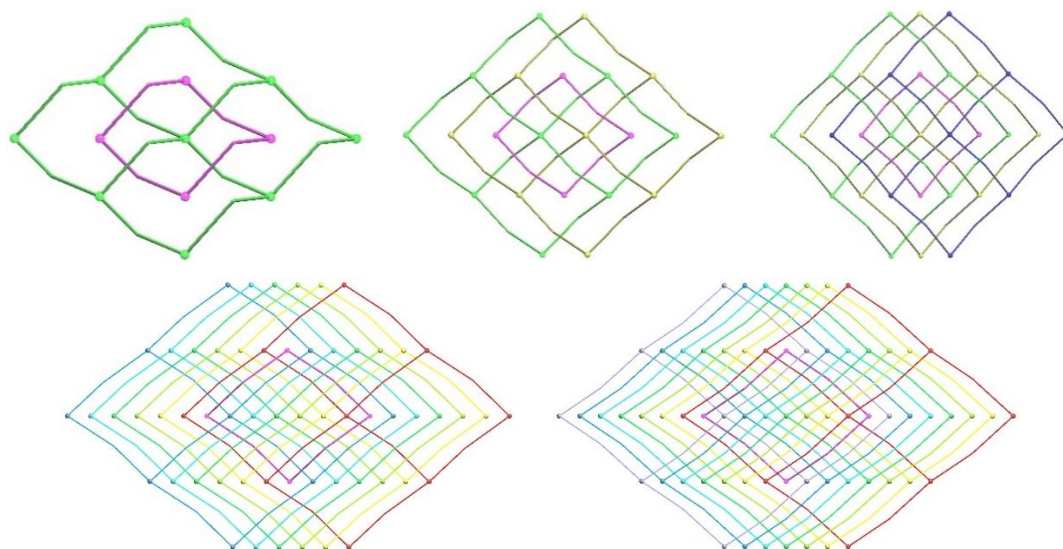


Fig. S8 Catenation of a ring (in magenta) with 4, 8, 12, 24 and 28 rings in the interpenetrating arrays with $Z = 2$ ([QEYZAY](#)), 3 ([VABNIW](#)), 4 ([MAVNOO](#)), 7 (compound **1**) and 8 (compound **2**).

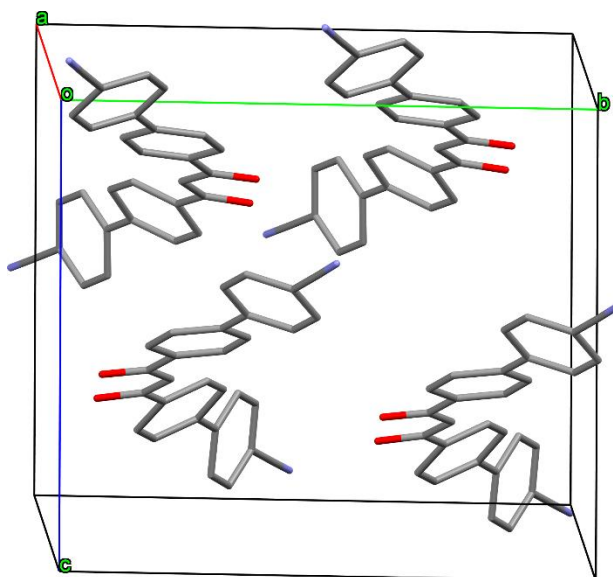


Fig. S9 View of molecular packing in the crystal structure of the ligand **HL** showing the helical arrangement of the molecules. Hydrogen atoms are omitted for clarity.

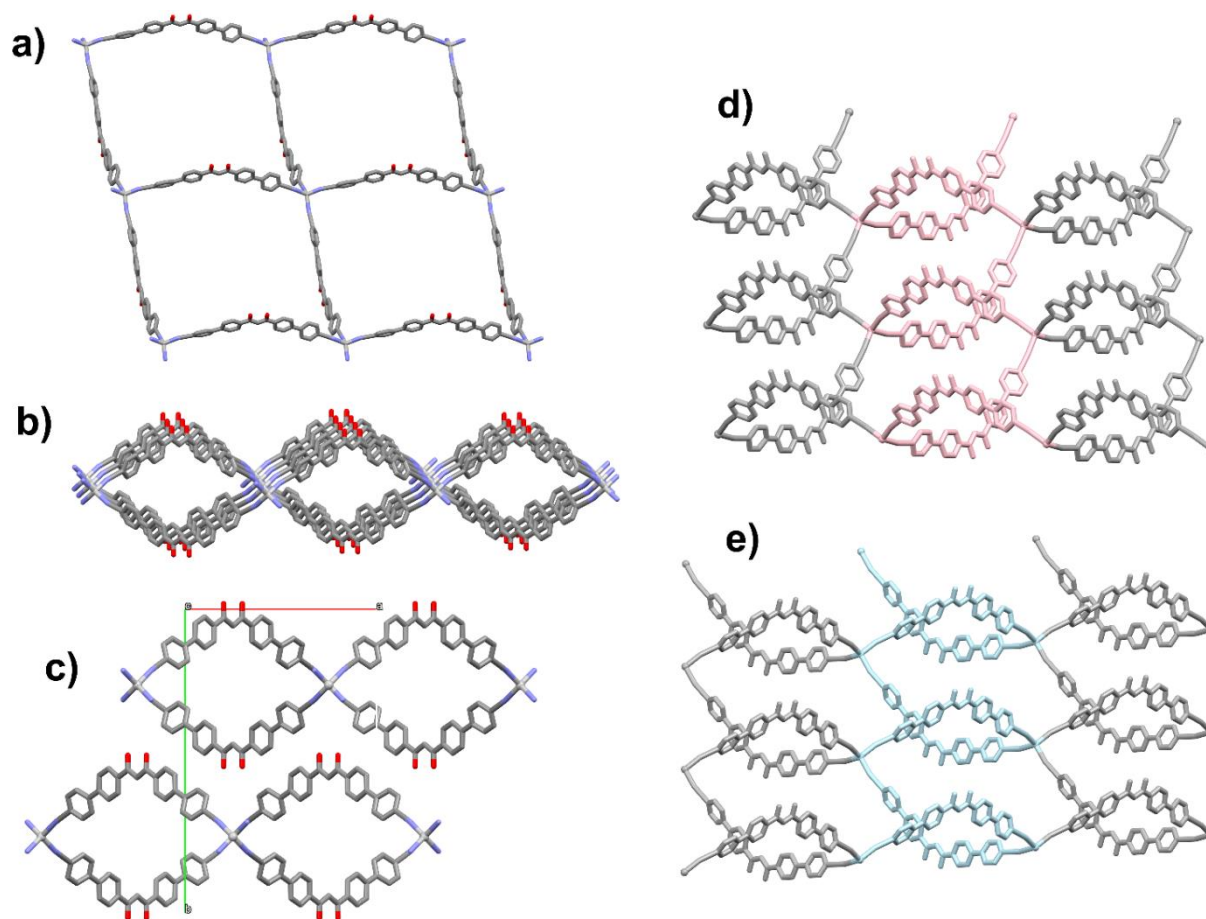


Fig. S10 Crystal structure of **2**: a single molecular layer showing four square windows (a); lateral view of a single molecular layer (b); view down **c** showing the packing of the 8-fold interpenetrated layers (c); helical arrangement of the ligand **HL** within two single layers belonging to two adjacent 8-fold layers and showing opposite helicity (d and f).

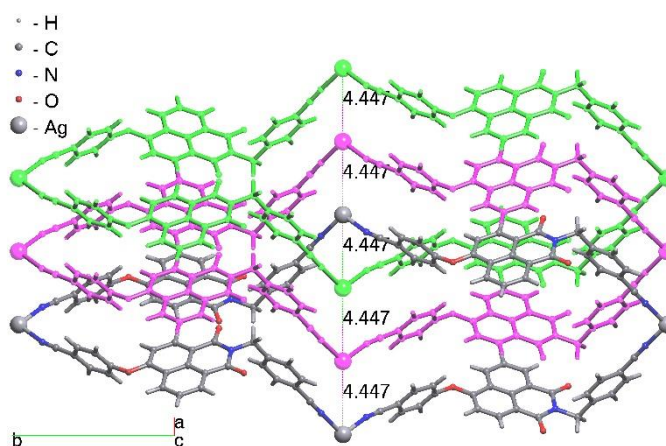


Fig. S11 Shortest distances (4.45 Å) found in the 3-fold interpenetrating structure of catena-[bis(μ -N-(4-cyanophenylmethylene)-4-(4-cyanophenoxy)-1,8-naphthalimide)-silver(I) tetrafluoroborate tetrahydrofuran solvate hydrate] (**DAMZOJ**), in which the nitrile groups of a narrow ligand coordinate to silver cations.

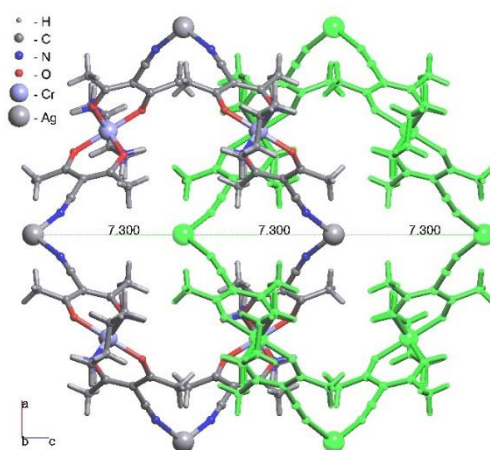


Fig. S12 Structure of the 2-fold interpenetrating compound with nitrile groups coordinated to silver(I) ([TUMBIO](#)) having a diagonal length (d) of 14.60 Å.

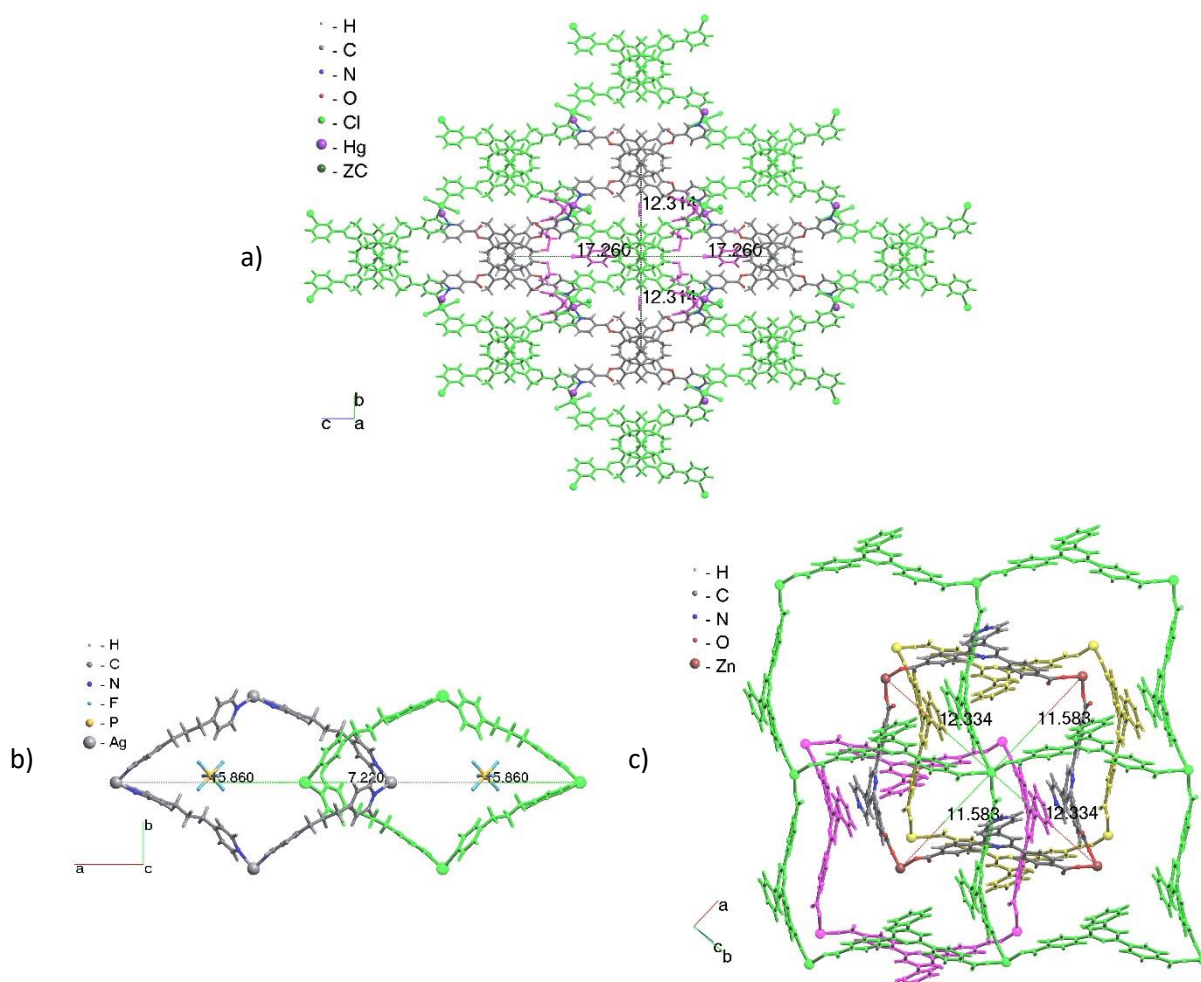


Fig. S13 Structures of compounds a) catena-[(μ_4 -dodecamethyltetrakis(3-pyridylcarboxylato)-pentacyclo(19.3.1.1^{3,7}.1^{9,13}.1^{15,19})octacos-1(25),3(28),4,6,9(27),11,12,15(26),16,18,21,23-dodecaene)-tetrachloro-di-mercury(II) chlorobenzene ethanol solvate hydrate] ([DEPHIQ](#); chlorobenzene, ethanol and water molecules are in magenta), b) catena-[bis(μ -1,3-bis(4-pyridyl)propane)-silver(I) hexafluorophosphate] ([FAGCEW](#)), and c) catena-[(μ -4,4'-(4-(pyridinium-4-yl)pyridine-2,6-diyl)dibenzoato- O,O')-(4-(pyridinium-4-yl)pyridine-2,6-diyl)dibenzoato- O,O,O')-zinc(II)] ([NIDFAJ](#)). The void within each interpenetrated array is filled, respectively, by solvate molecules (a), counterions (b) and ligands from neighboring interpenetrated array by interdigitation (c).

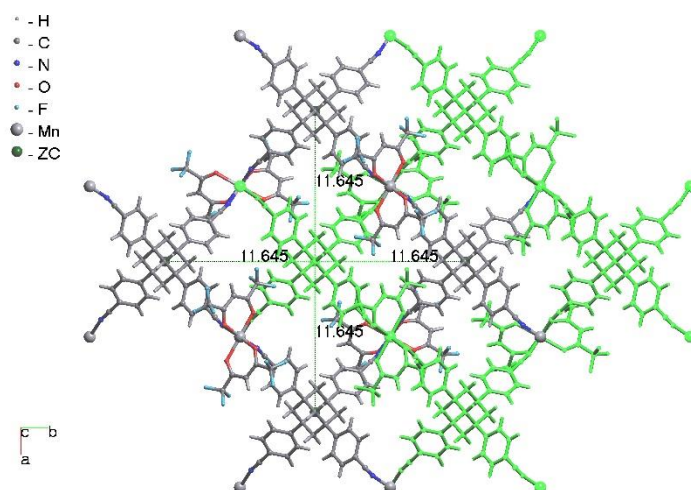


Fig. S14 Large distancing of nodes in the structure of catena-[(μ -4,4',4'',4'''-(tricyclo[3.3.1.1^{3,7}]decane-1,3,5,7-tetrayl)tetrabenzonitrile)-tetrakis(1,1,1,5,5,5-hexafluoroacetylacetonato)-di-manganese(II)] ([HAJMOX](#)) with voluminous linker and SBU.

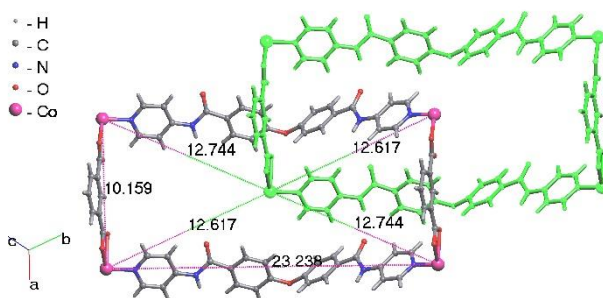


Fig. S15 The isophthalate linker in the structure catena-[(μ -isophthalato)-(μ -4,4'-oxybis(*N*-(pyridin-4-yl)benzamide))-cobalt(II) dihydrate] ([ARUCEX](#)) provides the edge of only 10.16 Å in the parallelogram ring, which is shorter more than twice of the second edge of 23.24 Å and of a diagonal of 25.23 Å.

Table S1 Crystal data, data collection and refinement details for **HL**, **1** and **2**

	HL	1	2
<i>Crystal data</i>			
Chemical formula	C ₂₉ H ₁₈ N ₂ O ₂	[C ₅₈ H ₃₆ AgN ₄ O ₄] ⁺ [CF ₃ O ₃ S] [−] = C ₅₉ H ₃₆ AgF ₃ N ₄ O ₇ S	[C ₅₈ H ₃₆ AgN ₄ O ₄] ⁺ [NO ₃] [−] ·3H ₂ O = C ₅₈ H ₄₂ AgN ₅ O ₁₀
<i>M_r</i> [g mol ^{−1}]	426.45	1109.85	1076.83
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	<i>Cc</i> (No. 9)	<i>Fdd2</i> (No. 43)	<i>Pban</i> (No. 50)
Temperature [K]	295(2)	295(2)	295(2)
<i>a</i> [Å]	11.9515(4)	50.830(4)	17.1383(10)
<i>b</i> [Å]	14.8622(5)	5.9067(4)	27.1434(15)
<i>c</i> [Å]	13.3026(5)	32.660(2)	5.0213(3)
β [°]	112.2440(10)	90	90
<i>V</i> [Å ³]	2187.04(13)	9805.9(12)	2335.9(2)
<i>Z</i>	4	8	2
μ(Mo Kα) [mm ^{−1}]	0.082	0.526	0.503
Crystal size [mm]	0.120 × 0.070 × 0.050	0.200 × 0.140 × 0.080	0.160 × 0.080 × 0.060
<i>Data collection</i>			
<i>T</i> _{min} , <i>T</i> _{max}	0.962, 0.996	0.872, 0.959	0.912, 0.970
No. of measured reflections	25004	29100	44310
No. of independent reflections	6604	4222	2919
No. of observed reflections	5055	3291	2137
[<i>I</i> > 2σ(<i>I</i>)]			
<i>R</i> _{int}	0.0201	0.0651	0.0618
<i>R</i> _σ	0.0227	0.0543	0.0246
(sin θ/λ) _{max} [Å ^{−1}]	0.714	0.595	0.667
<i>Refinement</i>			
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0477	0.0767	0.0369
<i>wR</i> (<i>F</i> ²)	0.1304	0.1482	0.0844
<i>S</i>	1.008	1.220	1.059
No. of reflections	6604	4222	2919
No. of parameters	298	340	153
No. of restraints	2	20	0
Δρ _{max} , Δρ _{min} (e Å ^{−3})	0.194, −0.198	0.679, −0.810	0.354, −0.359
Flack parameter	0.5(3)	0.35(7)	—

Table S2 Selected bond distances [Å] and angles [°] for coordination networks **1** and **2**

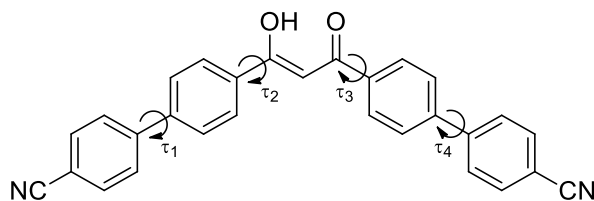
1		2	
Ag1–N1	2.304(14)	Ag1–N1	2.2800(18)
Ag1–N2 ⁱⁱ	2.271(12)	N1–Ag1–N1 ⁱ	104.61(9)
N1–Ag1–N1 ⁱ	102.0(8)	N1–Ag1–N1 ⁱⁱ	113.44(10)
N2 ⁱⁱ –Ag1–N2 ⁱⁱⁱ	129.5(6)	N1–Ag1–N1 ⁱⁱⁱ	110.49(10)
N1–Ag1–N2 ⁱⁱ	98.9(5)		
N1–Ag1–N2 ⁱⁱⁱ	112.5(4)		

For **1**, superscripts i–iii indicate atoms generated by the following symmetry operations: (i) $-x, -y, z$; (ii) $-x, -y - 3\frac{1}{2}, z - \frac{1}{2}$ and (iii) $x, y + 3\frac{1}{2}, z - \frac{1}{2}$.

For **2**, superscripts i–iii indicate atoms generated by the following symmetry operations: (i) $-x + \frac{1}{2}, -y + 1\frac{1}{2}, z$; (ii) $-x, -y + 1\frac{1}{2}, -z + 1$ and (iii) $-x + \frac{1}{2}, y, -z + 1$.

Table S3 Geometrical e topological descriptors for a set of 170 **sql** interpenetrating networks extracted from the Cambridge Structural Database
This Table has been provided as a separate Excel file.

Table S4 Selected geometric parameters [\AA and $^\circ$] for the dicyanodiketone moiety in the free ligand **HL** and in the coordination networks **1** and **2**



Compound	N...N	N...C...N	τ_1	τ_2	τ_3	τ_4	Δ^a
HL	22.649(4)	141.53(3)	$-27.5(4)$	$-2.0(4)$	$-23.2(4)$	$-39.6(4)$	0.290
1	22.540(16)	141.47(15)	$+32.8(18)$	$+22.2(19)$	$-3.0(17)$	$+30.8(15)$	0.319
2	22.659(3)	141.13(3)	$-19.0(3)$	$-5.1(3)$	$-5.1(3)$	$-19.0(3)$	0.182

^a Δ is the mean deviation from the least-squares plane defined by the chromophore.

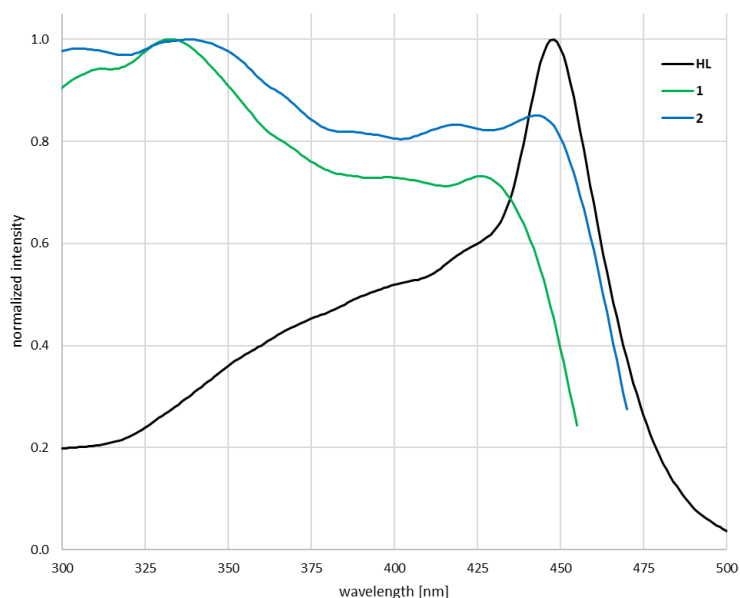


Fig. S16 Excitation spectra for the free ligand **HL** and the two coordination polymers **1** and **2**, measured in the solid state at room temperature. The emission wavelength is 530, 482 and 365 nm for **HL**, **1** and **2**, respectively.