Electronic Supplementary Information for:

The Effect of Viologen Counterions on the Topologies of La(III)– Tetraoxolene Metal-Organic Frameworks

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Additional Details of Crystal Structure Refinements

[La2(Fan)3(H2O)6]·18H2O (1)

Crystallographic data for **1** were measured at 100 K using a Rigaku XtaLAB Synergy-S diffractometer (Table S1). For the coordinated and solvent void H₂O molecules, the H atom positions were determined by examining the electron density difference (F_C – F_O) map, with interatomic distance restraints of 0.84 Å (O–H 1,2 distance) and 1.34 Å (H···H 1,3 distance) applied using the DFIX instruction.

(DiQ)[La₂(Clan)₅]·6H₂O (2-MeCN)

Crystallographic data for **2-MeCN** were measured at 100 K using a Rigaku XtaLAB Synergy-S diffractometer (Table S2). Inspection of the F_C – F_O map revealed the presence of significant positive electron density within the voids of the structure. Part of this residual electron density was readily modelled as two well-ordered H₂O molecules per asymmetric unit. For these H₂O molecules, the H atom positions were determined by examining the F_C – F_O map, with interatomic distance restraints of 0.84 Å (O–H 1,2 distance) and 1.34 Å (H…H 1,3 distance) applied using the DFIX instruction. The remaining residual electron density was ascribed to one disordered H₂O molecule per asymmetric unit, which could not be modelled satisfactorily. The scattering contribution of this disordered solvent was accounted for using the SQUEEZE¹ routine in PLATON.² The reported empirical formula and F_{000} values include the contribution from this disordered H₂O molecule in the asymmetric unit.

(DiQ)[La2(Clan)5]·6H2O (2-Acetone)

Crystallographic data for **2-Acetone** were measured at 100 K using a Rigaku XtaLAB Synergy-S diffractometer (Table S3). Inspection of the F_C - F_O map revealed the presence of significant positive electron density within the voids of the structure, which were satisfactorily modelled as three well-ordered H₂O molecules per asymmetric unit. The H atom positions for the H₂O molecules were determined by examining the electron density difference (F_C - F_O) map, with interatomic distance restraints of 0.84 Å (O-H 1,2 distance) and 1.34 Å (H···H 1,3 distance) applied using the DFIX instruction.

(DiQ)[La2(Bran)5]·3.5H2O (3-MeCN)

Crystallographic data for **3-MeCN** were measured at 100 K using the MX1 beamline of the Australian Synchrotron at $\lambda = 0.710917$ Å (Table S4).³ Examination of the F_C – F_O map revealed the presence of significant positive electron density within the voids of the structure, which could not be modelled satisfactorily. The scattering contribution of this disordered solvent was accounted for using the SQUEEZE¹ routine in PLATON,² with the solvation estimated as 1.75 H₂O per asymmetric unit based upon the electron count estimated by SQUEEZE. The absence of guest MeCN in the framework was justified on the basis of FT-IR spectroscopy (Figure S13), which did not show a significant absorption at ca. 2200 cm⁻¹ due to the C≡N vibration in MeCN. The reported

empirical formula and F_{000} values include the contribution from 1.75 disordered H₂O molecules per asymmetric unit.

(DiQ)[La₂(Bran)₅]·6H₂O (3-Acetone)

Crystallographic data for **3-Acetone** were measured at 100 K using a Rigaku XtaLAB Synergy-S diffractometer (Table S5). Inspection of the F_C – F_O map revealed the presence of significant positive electron density within the voids of the structure, which was satisfactorily modelled as three well-ordered O atoms of H₂O molecules per asymmetric unit. Refinement of the H atom positions for these solvent H₂O molecules was attempted by inspection of the F_C – F_O map, however the H atoms positions could not be refined satisfactorily in chemical reasonable positions, so these H atoms have been omitted from the refinement. The reported empirical formula and F_{000} values include the contribution from these 6 H atoms from 3 solvent H₂O molecules per asymmetric unit.

(PhenQ)[La₂(Clan)₄(H₂O)₂]·4MeCN·11H₂O (4-MeCN)

Crystallographic data for **4-MeCN** were measured at 100 K using a Rigaku XtaLAB Synergy-S diffractometer (Table S6). Rigid bond restraints were applied to all non-hydrogen atoms (N51–C66) in the PhenQ²⁺ cations. For the coordinated H₂O molecules, the H atom positions were modelled by examining the F_C — F_O map, with interatomic distance restraints of 0.84 Å (O–H 1,2 distance) and 1.34 Å (H···H 1,3 distance) applied using the DFIX instruction. The F_C — F_O map also revealed the presence of significant positive electron density within the voids of the structure, which was satisfactorily modelled as four well-ordered MeCN and 10 well-ordered H2O molecules per asymmetric unit. For the lattice H₂O molecules, the H atom positions for were modelled by examining the electron density difference (F_C — F_O) map, with interatomic distance restraints of 0.84 Å (O–H 1,2 distance) and 1.34 Å (H···H 1,3 distance) applied using the DFIX instruction. Additional distance restraints between H79B···O80 (1.92 Å) and H83B···O38 (2.02 Å) were applied using the DFIX instruction, to restrain the H atom positions in acceptable positions given the most likely H bond acceptors.

(PhenQ)[La₂(Clan)₄(H₂O)₂]·4(acetone)·2H₂O (4-Acetone)

Crystallographic data for **4-Acetone** were measured at 100 K using a Rigaku XtaLAB Synergy-S diffractometer (Table S7). As the PhenQ²⁺ cation in **4-Acetone** resides on a site of -1 symmetry, it is disordered over two symmetry equivalent positions each with 50% occupancy. Rigid bond and similarity restraints were applied to all non-hydrogen atoms in the PhenQ²⁺ cation using the RIGU and SIMU instructions respectively. The atom pairs C28 and N34, N30 and C37, C32 and C36, C33 and C35 were refined using EADP restraints, as the first atom of each pair occupies a similar position to the second atom of the pair in the symmetry generated PhenQ²⁺ molecule. Bond distances in the PhenQ²⁺ cation were restrained using DFIX instructions with the appropriate bond lengths values derived from the crystal structure of (PhenQ)Br₂ in which the cation is unambiguously in the PhenQ²⁺ valence state.⁴ For the coordinated H₂O molecule, the H atom positions were modelled by examining the F_C - F_O map, with interatomic distance restraints of 0.84 Å (O–H 1,2 distance) and 1.34 Å (H···H 1,3 distance) applied using the DFIX instruction. The

 F_C — F_O map also revealed the presence of significant positive electron density within the voids of the structure, which was satisfactorily modelled as 2 acetone molecules and 1 H₂O molecule per asymmetric unit. For the acetone, rigid bond restraints were applied to all non-hydrogen atoms using the RIGU instruction. For the H₂O molecule, the H atom positions for were modelled by examining the electron density difference (F_C — F_O) map, with interatomic distance restraints of 0.84 Å (O–H 1,2 distance) and 1.34 Å (H···H 1,3 distance) applied using the DFIX instruction.

(PhenQ)[La₂(Bran)₄(H₂O)₂]·20H₂O (5-MeCN)

Crystallographic data for 5-MeCN were measured at 100 K using a Rigaku XtaLAB Synergy-S diffractometer (Table S8). As the PhenQ²⁺ cation in **5-MeCN** resides on a site of -1 symmetry, it is disordered over two symmetry equivalent positions each with 50% occupancy. Rigid bond and similarity restraints were applied to all non-hydrogen atoms in the PhenQ²⁺ cation using the RIGU and SIMU instructions respectively. The atom pairs C28 and N34, N30 and C37, C32 and C36, C33 and C35 were refined using EADP restraints, as the first atom of each pair occupies a similar position to the second atom of the pair in the symmetry generated PhenQ²⁺ molecule. Bond distances in the PhenQ²⁺ cation were restrained using DFIX instructions with the appropriate bond lengths values derived from the crystal structure of (PhenQ)Br₂ in which the cation is unambiguously in the PhenQ²⁺ valence state.⁴ Additional same distance restraints for 1,2 and 1,3 distances were also applied to chemically equivalent bonds in the PhenQ²⁺ cation using SADI instructions. For the coordinated H₂O molecule, the H atom positions were tentatively modelled by examining the electron density difference $(F_C - F_Q)$ map, with interatomic distance restraints of 0.84 Å (O–H 1,2 distance) and 1.34 Å (H···H 1,3 distance) applied using the DFIX instruction. The F_C - F_O map also revealed the presence of significant positive electron density within the voids of the structure, which was as 10 well-ordered H₂O per asymmetric unit. The H atom positions for 8 of these H₂O molecules were modelled by examining the electron density difference ($F_C - F_O$) map, with interatomic distance restraints of 0.84 Å (O-H 1,2 distance) and 1.34 Å (H···H 1,3 distance) applied using the DFIX instruction. Additional distance restraints between H43A...O44 (2.12 Å) and H44A...O5 (2.06 Å) were applied using the DFIX instruction, to restrain the H atom positions in acceptable positions given the most likely H bond acceptors. Anti-bumping restraints between H25A and H45B, and H38B and H45A were also applied using the DFIX instruction (-2.2 Å) to prevent unphysical close O-H···H-O contacts. For the remaining two lattice H₂O per asymmetric unit (O40 and O47), the H atom positions could not be refined satisfactorily, despite repeated attempts. These H atoms have been omitted from the refinement, however the reported empirical formula and F_{000} values include the contribution from these H atoms.

(PhenQ)[La₂(Bran)₄(acetone)₂]·4(acetone) (5-Acetone)

Crystallographic data for **5-Acetone** were collected at 100 K using a Rigaku XtaLAB Synergy-S diffractometer (Table S9). Analysis of the reflection data using CrysAlisPRO revealed the presence of a two-component overlapping twin in the crystal. Data reduction and multi-scan absorption corrections upon both twin components were performed using CrysAlis PRO to produce a HKLF5 dataset with contributions from both twin components. The structure was solved

using the separated data of only one twin component using SHELXT, with subsequent structure refinements performed using the twin HKLF5 dataset and the BASF instruction. Rigid bond restraints were applied to all non-hydrogen and non-metal atoms in the structure using the RIGU instruction. As the PhenO²⁺ cation in **5-Acetone** resides on a site of -1 symmetry, it is disordered over two symmetry equivalent positions each with 50% occupancy. Additional restraints were required to achieve a satisfactory refinement. Similarity restraints were applied to all non-hydrogen atoms in the Phen Q^{2+} cation using the SIMU instruction. The atom pairs C31 and N37, N33 and C40, C35 and C39, C36 and C38 were refined using EADP restraints, as the first atom of each pair occupies a similar position to the second atom of the pair in the symmetry generated PhenQ²⁺ molecule. Bond distances in the PhenQ²⁺ cation were restrained using DFIX instructions with the appropriate bond lengths values derived from the crystal structure of (PhenO)Br₂ in which the cation is unambiguously in the PhenQ²⁺ valence state.⁴ Additional same distance restraints for 1,2 and 1,3 distances were also applied to chemically equivalent bonds in the PhenQ²⁺ cation using SADI instructions. Inspection of the F_C - F_O map revealed the presence of significant positive electron density within the voids of the structure, which was satisfactorily modelled as one ordered acetone and one disordered acetone molecule per asymmetric unit. Rigid bond restraints were applied to all non-hydrogen atoms in these acetone molecules using RIGU instructions, with all atoms in each acetone molecule restrained to lie in the same plate using the FLAT instruction. The disordered acetone molecule was modelled in two positions, with additional same distance restraints for 1,2 and 1,3 distances applied to chemically equivalent bonds in this acetone molecule using SADI instructions.

[La2(Fan)3(H2O)6]·18H2O		
Empirical formula	$C_9H_{24}F_3LaO_{18}$	
Formula weight	616.19	
T / K	99.99(10)	
Crystal system	trigonal	
Space group	<i>R</i> –3	
<i>a</i> / Å	14.5860(3)	
<i>b</i> / Å	14.5860(3)	
<i>c</i> / Å	17.4069(3)	
α / °	90	
eta / °	90	
γ / °	120	
$V/ \text{\AA}^3$	3207.19(14)	
Ζ	6	
$ ho_{ m calc}$ / g cm ⁻³	1.914	
μ / mm ⁻¹	16.480	
<i>F</i> (000)	1836.0	
Crystal size / mm ³	$0.083 \times 0.082 \times 0.035$	
Radiation	Cu <i>K</i> α (λ = 1.54184 Å)	
2θ range for data collection / °8.65 to 152.808		
Index ranges	$-17 \le h \le 17, -12 \le k \le 18, -20 \le l \le 21$	
Reflections collected	3641	
Independent reflections	1419 [$R_{int} = 0.0348$, $R_{sigma} = 0.0386$]	
Data/restraints/parameters	1419/12/119	
Goodness-of-fit on F^2	1.083	
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0314, wR_2 = 0.0800$	
Final R indexes [all data]	$R_1 = 0.0321, wR_2 = 0.0805$	
Largest diff. peak/hole / e $Å^{-3}$	1.13/-0.91	

 Table S1. Crystallographic data for [La₂(Fan)₃(H₂O)₆]·18H₂O (1).

	(DiQ)2[La2(Clan)5]·6H2O	
Empirical formula	C ₂₇ Cl ₅ H ₁₈ LaN ₂ O ₁₃	
Formula weight	894.59	
T / K	100.00(10)	
Crystal system	monoclinic	
Space group	$P 2_1/c$	
<i>a</i> / Å	11.8532(2)	
b / Å	26.2857(4)	
<i>c</i> / Å	10.5597(2)	
α / °	90	
eta / °	107.882(2)	
γ / °	90	
$V/ \text{\AA}^3$	3131.14(10)	
Ζ	4	
$ ho_{ m calc}$ / g cm ⁻³	1.898	
μ / mm^{-1}	15.105	
<i>F</i> (000)	1760.0	
Crystal size / mm ³	$0.15 \times 0.097 \times 0.086$	
Radiation	Cu $K\alpha$ ($\lambda = 1.54184$ Å)	
2θ range for data collection / °6.726 to 143.6		
Index ranges	$-13 \le h \le 14, -10 \le k \le 32, -12 \le l \le 12$	
Reflections collected	19634	
Independent reflections	5950 [$R_{\text{int}} = 0.0457, R_{\text{sigma}} = 0.0419$]	
Data/restraints/parameters	5950/6/436	
Goodness-of-fit on F^2	1.045	
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0375, wR_2 = 0.0896$	
Final R indexes [all data]	$R_1 = 0.0409, wR_2 = 0.0910$	
Largest diff. peak/hole / e ${\rm \AA}^{-3}$	2.08/-1.79	

 Table S2. Crystallographic data for (DiQ)₂[La₂(Clan)₅]·6H₂O (2-MeCN).

	(DiQ)2[La2(Clan)5]·6H2O	
Empirical formula	C ₂₇ H ₁₈ N ₂ O ₁₃ Cl ₅ La	
Formula weight	894.59	
T / K	100.00(10)	
Crystal system	monoclinic	
Space group	$P 2_1/c$	
<i>a</i> / Å	11.7957(3)	
b / Å	26.3110(5)	
<i>c</i> / Å	10.5813(3)	
α / °	90	
eta / °	108.089(3)	
γ / °	90	
$V/ \text{\AA}^3$	3121.67(14)	
Ζ	4	
$ ho_{ m calc}$ / g cm $^{-3}$	1.903	
μ / mm^{-1}	15.151	
<i>F</i> (000)	1760.0	
Crystal size / mm ³	$0.124 \times 0.065 \times 0.058$	
Radiation	Cu $K\alpha$ ($\lambda = 1.54184$ Å)	
2θ range for data collection / ° 6.718 to 159.742		
Index ranges	$-13 \le h \le 14, -33 \le k \le 33, -13 \le l \le 12$	
Reflections collected	45204	
Independent reflections	6725 [$R_{\text{int}} = 0.1074, R_{\text{sigma}} = 0.0610$]	
Data/restraints/parameters	6725/9/451	
Goodness-of-fit on F^2	1.142	
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0494, wR_2 = 0.1311$	
Final R indexes [all data]	$R_1 = 0.0582, wR_2 = 0.1380$	
Largest diff. peak/hole / e ${\rm \AA}^{-3}$	1.12/-2.50	

 Table S3. Crystallographic data for (DiQ)₂[La₂(Clan)₅]·6H₂O (2-Acetone).

(DiQ)2[La2(Bran)5]·3.5H2O		
Empirical formula	C ₂₇ H _{15.5} Br ₅ LaN ₂ O _{11.75}	
Formula weight	1094.37	
T / K	100.15	
Crystal system	monoclinic	
Space group	$P 2_1/c$	
<i>a</i> / Å	12.011(2)	
b / Å	26.422(5)	
<i>c</i> / Å	10.489(2)	
α / °	90	
eta / °	108.86(3)	
γ/°	90	
$V/\text{\AA}^3$	3150.0(12)	
Ζ	4	
$ ho_{ m calc}$ / g cm $^{-3}$	2.308	
μ / mm ⁻¹	7.764	
<i>F</i> (000)	2070.0	
Crystal size / mm ³	0.1 imes 0.05 imes 0.02	
Radiation	Synchrotron ($\lambda = 0.710917$ Å)	
2θ range for data collection / ° 3.082 to 57.312		
Index ranges	$-15 \le h \le 15, -35 \le k \le 35, -13 \le l \le 13$	
Reflections collected	20124	
Independent reflections	6303 [$R_{\text{int}} = 0.0577, R_{\text{sigma}} = 0.0540$]	
Data/restraints/parameters	6303/0/406	
Goodness-of-fit on F^2	1.038	
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0605, wR_2 = 0.1583$	
Final R indexes [all data]	$R_1 = 0.0746, wR_2 = 0.1710$	
Largest diff. peak/hole / e $Å^{-3}$	7.13/-3.62	

 Table S4. Crystallographic data for (DiQ)₂[La₂(Bran)₅]·3.5H₂O (3-MeCN).

*The empirical formula includes the contribution of disordered H_2O molecules in the channels of **3-MeCN**, which could not be modelled due to its diffuse electron density.

	(DiQ)2[La2(Bran)5]·6H2O	
Empirical formula	$C_{27}H_{18}Br_5LaN_2O_{13}$	
Formula weight	1116.873	
T/K	99.99(10)	
Crystal system	monoclinic	
Space group	$P 2_1/c$	
<i>a</i> / Å	12.1099(1)	
b / Å	26.3460(2)	
<i>c</i> / Å	10.5165(1)	
α / °	90	
eta / °	108.823(1)	
γ/°	90	
$V/\text{\AA}^3$	3175.82(5)	
Ζ	4	
$ ho_{ m calc}$ / g cm $^{-3}$	2.336	
μ / mm ⁻¹	18.392	
<i>F</i> (000)	2120.0	
Crystal size / mm ³	$0.169 \times 0.072 \times 0.042$	
Radiation	Cu <i>K</i> α (λ = 1.54184 Å)	
2θ range for data collection / ° 6.72 to 153.44		
Index ranges	$-12 \le h \le 15, -33 \le k \le 32, -13 \le l \le 12$	
Reflections collected	44705	
Independent reflections	6481 [$R_{int} = 0.0362, R_{sigma} = 0.0196$]	
Data/restraints/parameters	6481/0/433	
Goodness-of-fit on F^2	1.059	
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0259, wR_2 = 0.0637$	
Final R indexes [all data]	$R_1 = 0.0263, wR_2 = 0.0640$	
Largest diff. peak/hole / e \AA^{-3}	1.74/-1.78	

 Table S5. Crystallographic data for (DiQ)₂[La₂(Bran)₅]·6H₂O (3-Acetone).

	(PhenQ)[La2(Clan)4(H2O)2]·4MeCN·11H2O
Empirical formula	C46H50N6O29Cl8La2
Formula weight	1712.34
T / K	99.98(10)
Crystal system	triclinic
Space group	<i>P</i> –1
<i>a</i> / Å	13.0706(2)
<i>b</i> / Å	13.8311(2)
<i>c</i> / Å	18.0949(2)
α / °	92.5410(10)
eta / °	90.2890(10)
γ / °	101.0080(10)
$V/\text{\AA}^3$	3207.56(8)
Ζ	2
$ ho_{ m calc}$ / g cm ⁻³	1.773
μ / mm ⁻¹	14.001
<i>F</i> (000)	1700.0
Crystal size / mm ³	$0.279 \times 0.102 \times 0.056$
Radiation	Cu $K\alpha$ ($\lambda = 1.54184$ Å)
2θ range for data collection / θ	² 4.888 to 159.53
Index ranges	$-16 \le h \le 16, -17 \le k \le 15, -23 \le l \le 23$
Reflections collected	53712
Independent reflections	13646 [$R_{\text{int}} = 0.0559, R_{\text{sigma}} = 0.0415$]
Data/restraints/parameters	13646/182/902
Goodness-of-fit on F^2	1.049
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0463, wR_2 = 0.1276$
Final R indexes [all data]	$R_1 = 0.0481, wR_2 = 0.1294$
Largest diff. peak/hole / e ${\rm \AA^{-3}}$	2.18/-1.71

Table S6. Crystallographic data for (PhenQ)[La₂(Clan)₄(H₂O)₂]·4MeCN·11H₂O (4-MeCN).

	$(PhenQ)[La_2(Clan)_4(H_2O)_2]\cdot 4(acetone)\cdot 2H_2O$
Empirical formula	C ₂₅ H ₂₂ O ₁₂ Cl ₄ LaN
Formula weight	809.168
<i>T /</i> K	100.00(10)
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	10.7781(4)
<i>b</i> / Å	11.4423(4)
<i>c</i> / Å	12.9249(4)
lpha / °	103.513(3)
eta / °	94.393(3)
γ / °	106.749(3)
V / Å ³	1466.26(10)
Ζ	2
$ ho_{ m calc}$ / g cm ⁻³	1.833
μ / mm^{-1}	15.186
<i>F</i> (000)	800.0
Crystal size / mm ³	$0.105\times0.059\times0.043$
Radiation	Cu $K\alpha$ ($\lambda = 1.54184$ Å)
2θ range for data collection /	° 7.12 to 153.84
Index ranges	$-13 \le h \le 13, -13 \le k \le 14, -13 \le l \le 16$
Reflections collected	17670
Independent reflections	5739 [$R_{\text{int}} = 0.0480, R_{\text{sigma}} = 0.0450$]
Data/restraints/parameters	5739/131/422
Goodness-of-fit on F^2	1.033
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0381, wR_2 = 0.1016$
Final R indexes [all data]	$R_1 = 0.0404, wR_2 = 0.1038$
Largest diff. peak/hole / e Å	⁻³ 1.74/-1.72

 $\label{eq:classical} \textbf{Table S7.} Crystallographic data for (PhenQ) [La_2(Clan)_4(H_2O)_2] \cdot 4 (acetone) \cdot 2H_2O ~(\textbf{4-Acetone}).$

	(PhenQ)[La ₂ (Bran) ₄ (H ₂ O) ₂]·20H ₂ O	
Empirical formula	C19H28NO19Br4La	
Formula weight	1032.97	
<i>T</i> / K	101(2)	
Crystal system	triclinic	
Space group	<i>P</i> -1	
<i>a</i> / Å	10.7111(3)	
<i>b</i> / Å	11.8605(4)	
<i>c</i> / Å	13.2161(4)	
lpha / °	97.055(2)	
eta / °	94.584(2)	
γ / °	107.293(3)	
$V / \text{\AA}^3$	1578.87(9)	
Ζ	2	
$ ho_{ m calc}$ / g cm ⁻³	2.173	
μ / mm ⁻¹	17.123	
<i>F</i> (000)	996.0	
Crystal size / mm ³	$0.097 \times 0.039 \times 0.03$	
Radiation	Cu $K\alpha$ ($\lambda = 1.54184$ Å)	
2θ range for data collection /	° 6.79 to 159.706	
Index ranges	$-13 \le h \le 13, -15 \le k \le 14, -16 \le l \le 14$	
Reflections collected	26037	
Independent reflections	6679 [$R_{\text{int}} = 0.0515, R_{\text{sigma}} = 0.0372$]	
Data/restraints/parameters	6679/212/469	
Goodness-of-fit on F^2	1.118	
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0382, wR_2 = 0.1057$	
Final R indexes [all data]	$R_1 = 0.0399, wR_2 = 0.1070$	
Largest diff. peak/hole / e $Å^-$	³ 0.86/-2.26	

Table S8. Crystallographic data for (PhenQ)[La2(Bran)4(H2O)2]·20H2O (5-MeCN).

*The calculated empirical formula and F(000) includes the contribution of 4 H unrefined atoms from lattice H₂O molecules in the channels of **5-MeCN**.

	(PhenQ)[La ₂ (Bran) ₄ (acetone) ₂]·4(acetone)
Empirical formula	C ₂₈ H ₂₄ NO ₁₁ Br ₄ La
Formula weight	1009.03
T / K	100.0(3)
Crystal system	triclinic
Space group	<i>P</i> –1
<i>a</i> / Å	10.8019(4)
b / Å	12.6028(5)
<i>c</i> / Å	13.3338(3)
lpha / °	109.799(3)
eta / °	90.154(3)
γ / °	108.366(3)
V / Å ³	1608.68(11)
Ζ	2
$ ho_{ m calc}$ / g cm ⁻³	2.083
μ / mm ⁻¹	16.604
<i>F</i> (000)	968.0
Crystal size / mm ³	$0.192 \times 0.048 \times 0.039$
Radiation	Cu $K\alpha$ ($\lambda = 1.54184$ Å)
2θ range for data collection /	° 7.1 to 160.114
Index ranges	$-13 \le h \le 13, -16 \le k \le 15, -17 \le l \le 17$
Reflections collected	12428
Independent reflections	12428 [$R_{sigma} = 0.0240$]
Data/restraints/parameters	12428/353/470
Goodness-of-fit on F^2	1.370
Final <i>R</i> indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.1017, wR_2 = 0.2876$
Final R indexes [all data]	$R_1 = 0.1037, wR_2 = 0.2919$
Largest diff. peak/hole / e Å $$	-3 2.73/-2.75

 Table S9. Crystallographic data for (PhenQ)[La2(Bran)4(acetone)2]·4(acetone) (5-Acetone).

Geometry	Symmetry	La (1)
EP-9	D_{9h}	33.289
OPY-9	C_{8v}	24.178
HBPY-9	D_{7h}	20.579
JTC-9	C_{3v}	14.351
JCCU-9	C_{4v}	11.271
CCU-9	C_{4v}	10.181
JCSAPR-9	C_{4v}	2.368
CSAPR-9	C_{4v}	1.391
JTCTPR-9	D_{3h}	1.524
TCTPR-9	D_{3h}	1.087
JTDIC-9	C_{3v}	14.022
HH-9	C_{2v}	12.393
MFF-9	C_s	1.875

Table S10. Analysis of possible coordination geometries in $[La_2(Fan)_3(H_2O)_6]$ ·18H₂O (1) using Continuous Shape Measure (CShM) parameters.^{5, 6}

EP-9 = Enneagon; OPY-9 = Octagonal pyramid; HBPY-9 = Heptagonal bipyramid; JTC-9 = Johnson triangular cupola J3; JCCU-9 = Capped cube J8; CCU-9 = Spherical-relaxed capped cube; JCSAPR-9 = Capped square antiprism J10; CSAPR-9 = Spherical capped square antiprism; JTCTPR-9 = Tricapped trigonal prism J51; TCTPR-9 = Spherical tricapped trigonal prism; JTDIC-9 = Tridiminished icosahedron J63; HH-9 = Hula-hoop; MFF-9 = Muffin. The minimum values are indicated in bold.

Geometry	Symmetry	La (2-MeCN)	La (2-Acetone)	La (3-MeCN)	La (3-Acetone)
DP-10	D_{10h}	36.065	35.997	35.357	35.617
EPY-10	C_{9v}	23.540	23.301	23.215	23.164
OBPY-10	D_{8h}	16.677	16.669	16.319	16.409
PPR-10	D_{5h}	8.880	8.926	9.436	9.238
PAPR-10	D_{5d}	12.384	12.376	11.674	11.930
JBCCU-10	D_{4h}	12.016	11.933	11.334	11.540
JBCSAPR-10	D_{4d}	4.125	4.000	3.813	3.875
JMBIC-10	C_{2v}	8.408	8.337	8.102	8.145
JATDI-10	C_{3v}	18.025	18.086	17.826	17.870
JSPC-10	C_{2v}	2.554	2.623	2.254	2.354
SDD-10	D_2	6.251	6.266	5.775	5.954
TD-10	C_{2v}	5.535	5.446	5.486	5.538
HD-10	D_{4h}	9.872	9.842	9.371	9.576

Table S11. Analysis of possible coordination geometries in $(DiQ)_2[La_2(Clan)_5] \cdot 6H_2O(2)$ and $(DiQ)_2[La_2(Bran)_5] \cdot xH_2O(3)$ using CShM parameters.^{5,7}

DP-10 = Decagon; EPY-10 = Enneagonal pyramid; OBPY-10 = Octagonal bipyramid; PPR-10 = Pentagonal prism; PAPR-10 = Pentagonal antiprism; JBCCU-10 = Bicapped cube J15; JBCSAPR-10 = Bicapped square antiprism J17; JMBIC-10 = Metabidiminished icosahedron J62; JATDI-10 = Augmented tridiminished icosahedron J64; JSPC-10 = Sphenocorona J87; SDD-10 = Staggered Dodecahedron (2:6:2); TD-10 = Tetradecahedron (2:6:2); HD-10 = Hexadecahedron (2:6:2) or (1:4:4:1). The minimum values are indicated in bold.

Geometry	Symmetry	La1	La2	La	La	La
		(4-MeCN)	(4-MeCN)	(4-Acetone)	(5-MeCN)	(5-Acetone)
EP-9	D_{9h}	36.393	35.787	36.147	35.410	36.119
OPY-9	C_{8v}	21.179	20.004	22.278	21.298	22.724
HBPY-9	D_{7h}	19.206	19.439	19.286	18.991	17.050
JTC-9	C_{3v}	12.872	14.319	15.021	12.609	15.215
JCCU-9	C_{4v}	10.423	10.956	10.271	11.057	11.020
CCU-9	C_{4v}	9.034	9.658	8.932	9.664	9.883
JCSAPR-9	C_{4v}	2.341	2.274	2.926	2.594	2.384
CSAPR-9	C_{4v}	1.168	0.996	1.789	1.447	1.548
JTCTPR-9	D_{3h}	2.752	2.639	3.890	2.566	3.649
TCTPR-9	D_{3h}	1.060	1.053	2.020	1.195	2.579
JTDIC-9	C_{3v}	10.474	12.114	10.362	11.262	12.804
HH-9	C_{2v}	12.357	12.151	10.874	11.765	10.381
MFF-9	C_s	1.801	1.616	1.975	1.977	1.579

Table S12. Analysis of possible coordination geometries in $(PhenQ)[La_2(Clan)_4(H_2O)_2]$ ·*x*solvate (4) and $(PhenQ)[La_2(Bran)_4(solvate)_2]$ ·*x*solvate (5) using CShM parameters.^{5, 6}

EP-9 = Enneagon; OPY-9 = Octagonal pyramid; HBPY-9 = Heptagonal bipyramid; JTC-9 = Johnson triangular cupola J3; JCCU-9 = Capped cube J8; CCU-9 = Spherical-relaxed capped cube; JCSAPR-9 = Capped square antiprism J10; CSAPR-9 = Spherical capped square antiprism; JTCTPR-9 = Tricapped trigonal prism J51; TCTPR-9 = Spherical tricapped trigonal prism; JTDIC-9 = Tridiminished icosahedron J63; HH-9 = Hula-hoop; MFF-9 = Muffin. The minimum values are indicated in bold.



Figure S1. P-XRD ($\lambda = 1.54184$ Å) pattern of **1** calculated from SC-XRD structure (black), and experimental patterns for **1** synthesized using H₂Fan/Acetone (red), H₂Fan/MeCN (blue) or H₄Fan/MeCN (green).



Figure S2. P-XRD ($\lambda = 1.54184$ Å) pattern of **2-MeCN** calculated from SC-XRD structure (black), and experimental patterns for **2-MeCN** synthesized using H₂Clan/MeCN (red) or H₄Clan/MeCN (blue).



Figure S3. P-XRD ($\lambda = 1.54184$ Å) pattern of **2-Acetone** calculated from SC-XRD structure (black), and experimental patterns for **2-Acetone** synthesized using H₂Clan/Acetone (red) or H₄Clan/Acetone (blue).



Figure S4. P-XRD ($\lambda = 1.54184$ Å) pattern of **3-MeCN** calculated from SC-XRD structure (black), and experimental patterns for **3-MeCN** synthesized using H₂Bran/MeCN (red) or H₄Bran/MeCN (blue).



Figure S5. P-XRD ($\lambda = 1.54184$ Å) pattern of **3-Acetone** calculated from SC-XRD structure (black), and experimental patterns for **3-Acetone** synthesized using H₂Bran/Acetone (red) or H₄Bran/Acetone (blue).



Figure S6. P-XRD ($\lambda = 1.54184$ Å) pattern of **4-MeCN** calculated from SC-XRD structure (black), and experimental patterns for **4-MeCN** synthesized using H₄Clan/MeCN (red) or H₂Clan/MeCN (blue).



Figure S7. P-XRD ($\lambda = 1.54184$ Å) pattern of **4-Acetone** calculated from SC-XRD structure (black), and experimental patterns for **4-Acetone** synthesized using H₄Clan/Acetone (red) or H₂Clan/Acetone (blue).



Figure S8. P-XRD ($\lambda = 1.54184$ Å) pattern of **5-MeCN** calculated from SC-XRD structure (black), and experimental patterns for **5-MeCN** synthesized using H₄Bran/MeCN (red) or H₂Bran/ MeCN (blue).



Figure S9. P-XRD ($\lambda = 1.54184$ Å) pattern of **5-Acetone** calculated from SC-XRD structure (black), and experimental patterns for **5-Acetone** synthesized using H₄Bran/Acetone (red) or H₂Bran/Acetone (blue).

Compound	C=O Stretch	C–C Stretch
	(cm ⁻)	(cm ⁻¹)
$[La_2(Fan)_3(H_2O)_6] \cdot 18H_2O(1)$	1630	1480
$(DiQ)_2[La_2(Clan)_5]$ ·6H ₂ O (2-MeCN)	1610	1470
(DiQ) ₂ [La ₂ (Clan) ₅]•6H ₂ O (2-Acetone)	1611	1472
(DiQ) ₂ [La ₂ (Bran) ₅]·3.5H ₂ O (3-MeCN)	1608	1470
(DiQ) ₂ [La ₂ (Bran) ₅]·6H ₂ O (3-Acetone)	1609	1470
$(PhenQ)[La_{2}(Clan)_{4}(H_{2}O)_{2}] \cdot 4MeCN \cdot 11H_{2}O (4-MeCN)$	1616	1470
$(PhenQ)[La_{2}(Clan)_{4}(H_{2}O)_{2}]\cdot4(acetone)\cdot2H_{2}O (\textbf{4-Acetone})$	1616	1470
$(PhenQ)[La_2(Bran)_4(H_2O)_2] \cdot 20H_2O (\textbf{5-MeCN})$	1616	1470
(PhenQ)[La ₂ (Bran) ₄ (acetone) ₂]·4(acetone) (5-Acetone)	1615	1460

Table S13. Summary table displaying C=O and C–C (cm^{-1}) stretches for all compounds.



Figure S10. ATR-FTIR spectrum for $[La_2(Fan)_3(H_2O)_6]$ ·18H₂O (1).



Figure S11. ATR-FTIR spectrum for (DiQ)₂[La₂(Clan)₅]·6H₂O (2-MeCN).



Figure S12. ATR-FTIR spectrum for (DiQ)₂[La₂(Clan)₅]·6H₂O (2-Acetone).



Figure S13. ATR-FTIR spectrum for $(DiQ)_2[La_2(Bran)_5]$ ·3.5H₂O (3-MeCN).



Figure S14. ATR-FTIR spectrum for $(DiQ)_2[La_2(Bran)_5]$ ·6H₂O (3-Acetone).



 $\label{eq:Figure S15.} ATR-FTIR \ spectrum \ for \ (PhenQ)[La_2(Clan)_4(H_2O)_2] \cdot 4MeCN \cdot 11H_2O \ (\textbf{4-MeCN}).$



 $\label{eq:Figure S16.} \mbox{ATR-FTIR spectrum for (PhenQ)[La_2(Clan)_4(H_2O)_2]-4(acetone)-2H_2O~(\mbox{4-Acetone}).$



Figure S17. ATR-FTIR spectrum for (PhenQ)[La₂(Bran)₄(H₂O)₂]·20H₂O (5-MeCN).



 $Figure \ S18. \ ATR-FTIR \ spectrum \ for \ (PhenQ)[La_2(Bran)_4(acetone)_2] \cdot 4(acetone) \ (\textbf{5-Acetone}).$



Figure S19. Thermogravimetric analysis of [La₂(Fan)₃(H₂O)₆]·18H₂O (1).



Figure S20. Thermogravimetric analysis of (DiQ)₂[La₂(Clan)₅]·6H₂O (2-MeCN).



Figure S21. Thermogravimetric analysis of (DiQ)₂[La₂(Clan)₅]·6H₂O (2-Acetone).



Figure S22. Thermogravimetric analysis of (DiQ)₂[La₂(Bran)₅]·3.5H₂O (3-MeCN).



Figure S23. Thermogravimetric analysis of (DiQ)₂[La₂(Bran)₅]·6H₂O (3-Acetone).



Figure S24. Thermogravimetric analysis of (PhenQ)[La₂(Clan)₄(H₂O)₂]·4MeCN·11H₂O (**4**-**MeCN**).



Figure S25. Thermogravimetric analysis of (PhenQ)[La₂(Clan)₄(H₂O)₂]·4(acetone)·2H₂O (**4**-**Acetone**).



Figure S26. Thermogravimetric analysis of (PhenQ)[La₂(Bran)₄(H₂O)₂]·20H₂O (5-MeCN).



Figure S27. Thermogravimetric analysis of (PhenQ)[La₂(Bran)₄(acetone)₂]·4(acetone) (**5**-Acetone).

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