Elemental Supplementary Information for

CrystEngComm

Structural diversification and single-crystal-to-single-crystal transformation of alkaline earth metal-based MOFs regulated by solvent effect

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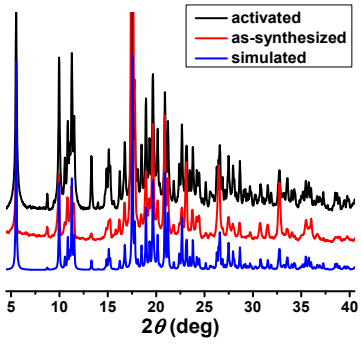
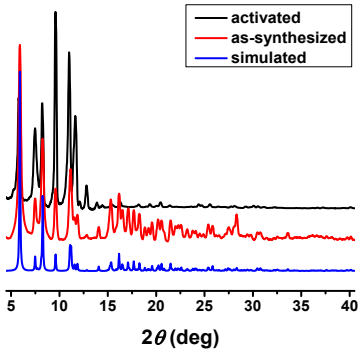
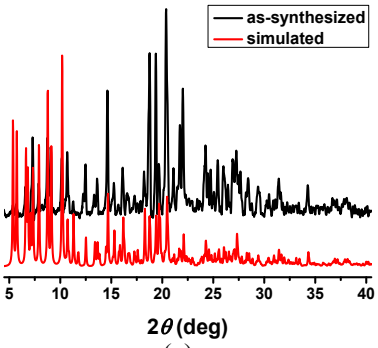


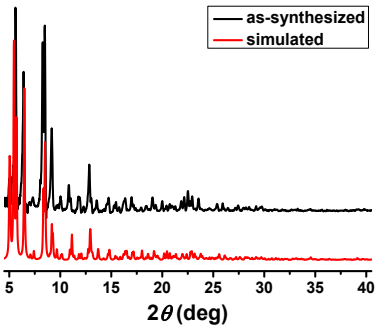
(**a**)



(**b**)

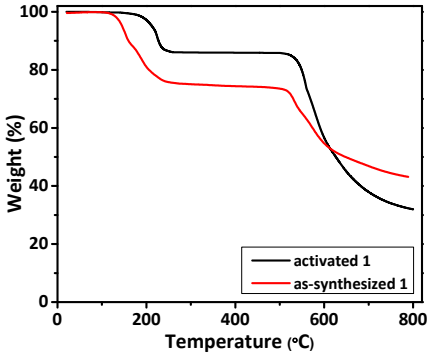


(**c**)

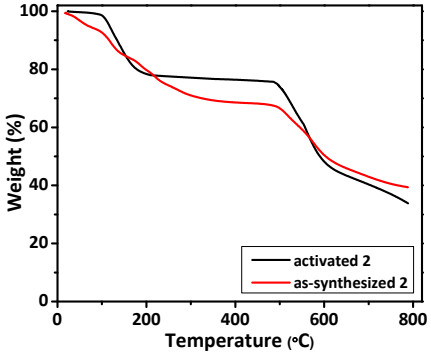


(**d**)

Fig. S1 The simulated (red) and as-synthesized (black) powder X-ray diffraction patterns for **1**–**4** (**a**–**d**).



(**a**)



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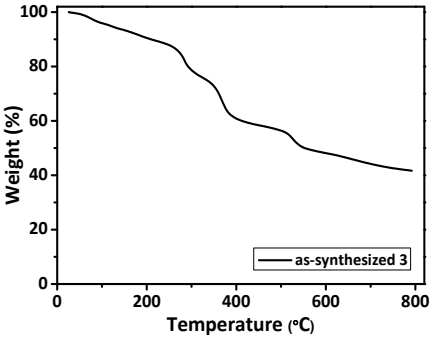

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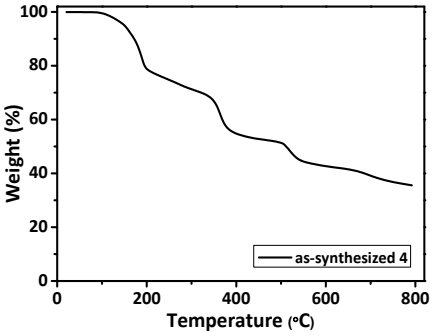


(**d**)

Fig. S2 TGA curves for **1**–**4** (**a**–**d**).

Table S1 Crystallography data and structural refinement summary for **1**–**4**

Compound reference	**1**	**2**	**3**	**4**
Chemical formula	$C_{33}H_{31}Mg_{1\cdot50}N_2O_{12}$	$C_{35}H_{33}Mg_{1\cdot50}N_2O_{11}$	$C_{72}H_{70}Ca_{2\cdot50}N_2O_{21}$	$C_{78}H_{85}Ca_3N_3O_{23}$
Formula Mass	684.06	694.10	1399.50	1552.73
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
a/Å	10.2312(10)	11.6875(12)	14.6854(4)	16.1122(8)
b/Å	11.0797(12)	12.7337(10)	17.3507(7)	19.1301(6)
c/Å	16.1049(10)	16.6287(7)	17.5650(8)	19.9491(6)
α/°	95.135(7)	107.084(6)	71.291(4)	113.359(3)
β/°	92.045(6)	106.160(7)	75.262(3)	103.862(4)
γ/°	113.333(10)	98.287(8)	66.322(3)	91.934(3)
Unit cell volume/Å^3	1664.5(3)	2202.3(3)	3841.3(3)	5423.0(4)
Temperature/K	294(2)	293(2)	293(2)	294(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
No. of formula units per unit cell, *Z*	2	2	2	2
Absorption coefficient, μ/mm^{-1}	0.129	0.097	0.251	0.207
No. of reflections measured	11996	14127	33177	51265
No. of independent reflections	6792	7721	15697	22122
R_{int}	0.0380	0.0362	0.0305	0.0579
Final R_1 values ($I > 2\sigma(I)$)	0.0514	0.0671	0.0555	0.0889
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1158	0.1896	0.1526	0.2663
Final R_1 values (all data)	0.0744	0.0965	0.0835	0.1331
Final $wR(F^2)$ values (all data)	0.1292	0.2108	0.1678	0.3045
Goodness of fit on F^2	1.016	1.013	1.028	1.004
CCDC deposition Nos	1433798	1433799	1433800	1433801

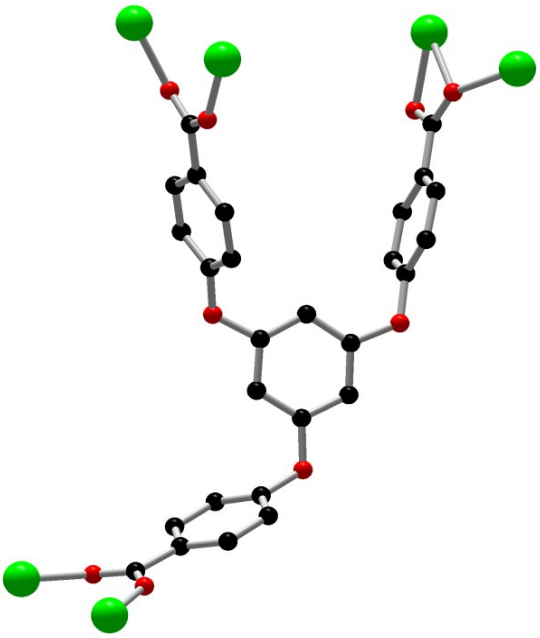


Fig. S3 Conformation and coordination mode of BTTB in **1.**

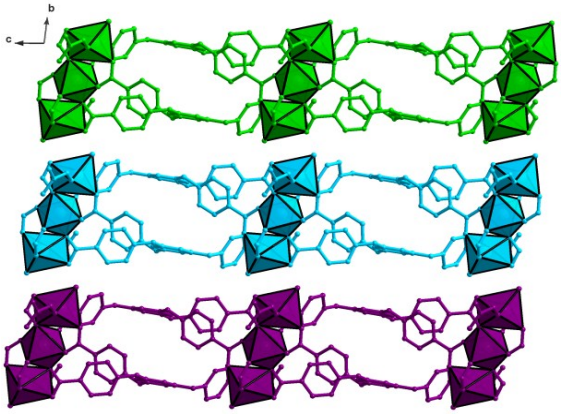


Fig. S4 The parallel arrangement of 2D bilayers in **1**. The adjacent bilayers are represented in different colors**.**

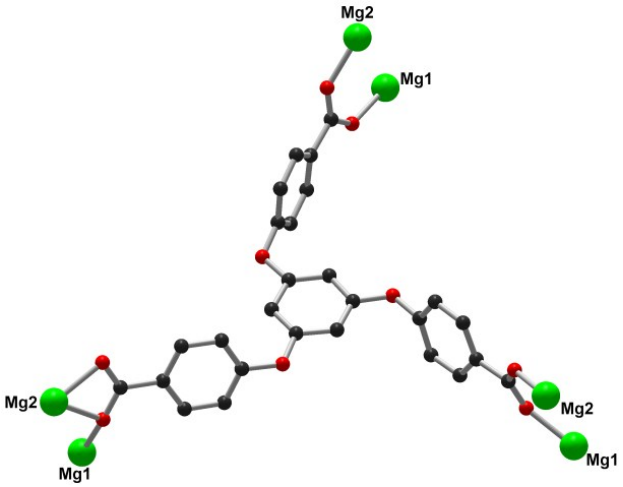


Fig. S5 Conformation and coordination mode of BTTB in **2.**

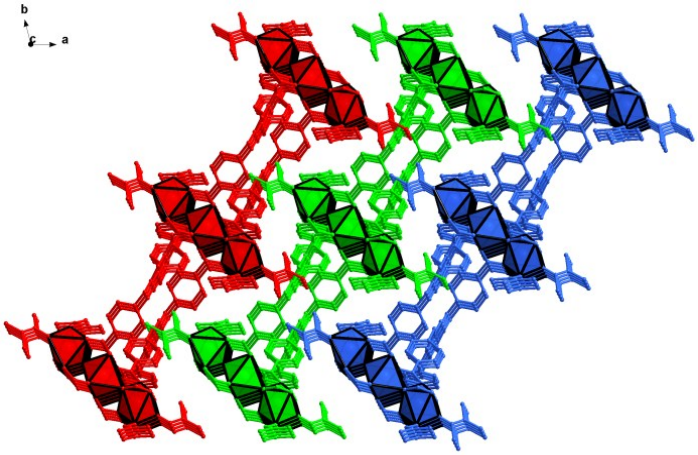
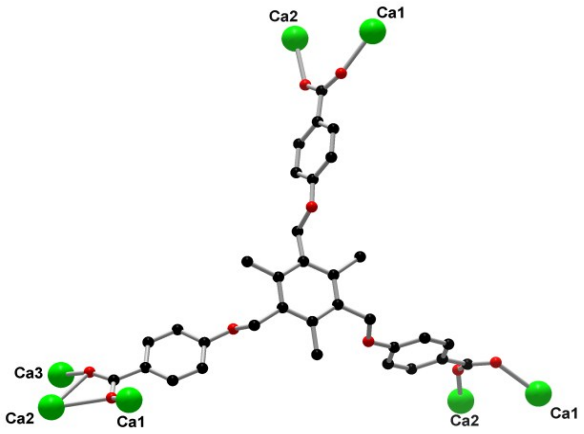
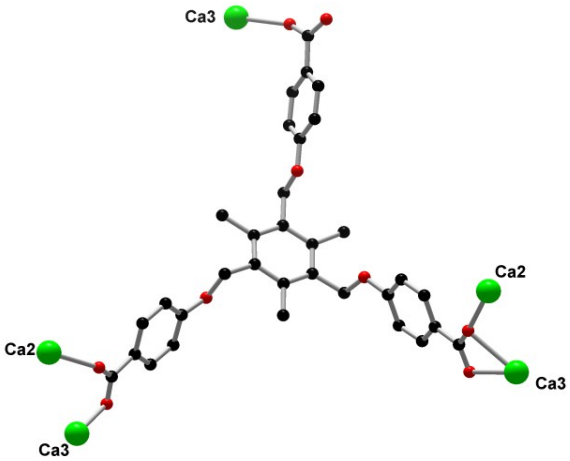


Fig. S6 The parallel arrangement of 2D bilayers in **2**. The adjacent bilayers are represented in different colors**.**



(a)



(b)

Fig. S7 Conformations and coordination modes of TCM in **3**.

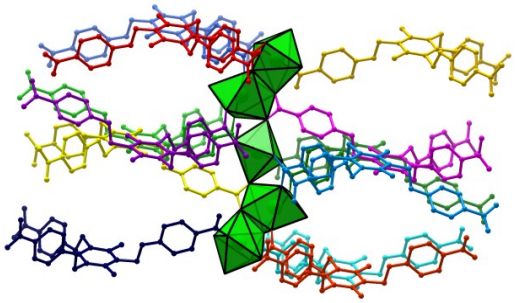


Fig. S8 View of the 12-connected Ca_5 subunit. The TCM ligands were shown in different colors.

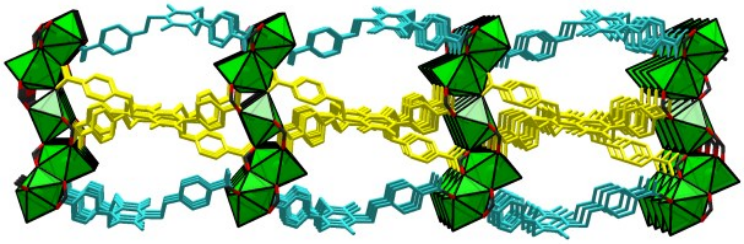


Fig. S9 View of the three ligand sub-layers shown in different colors within a single 2D network**.**

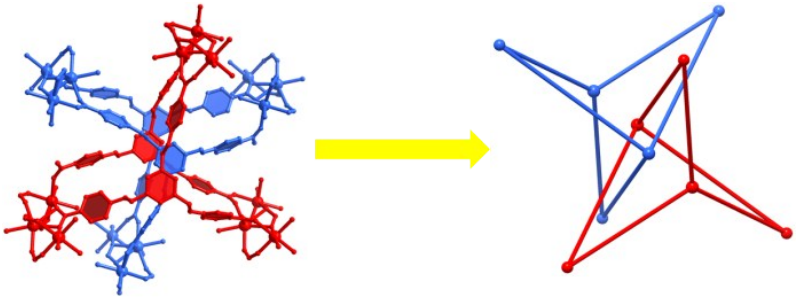
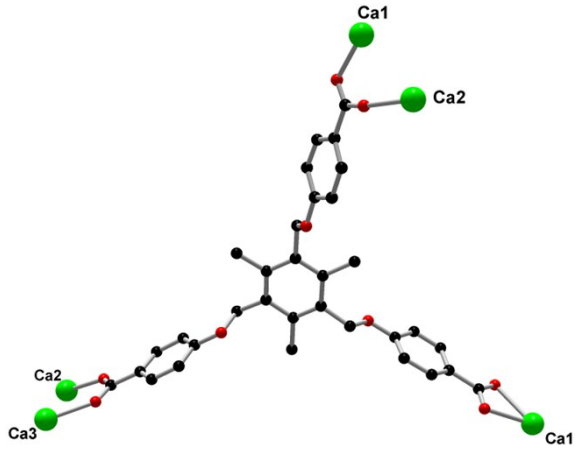
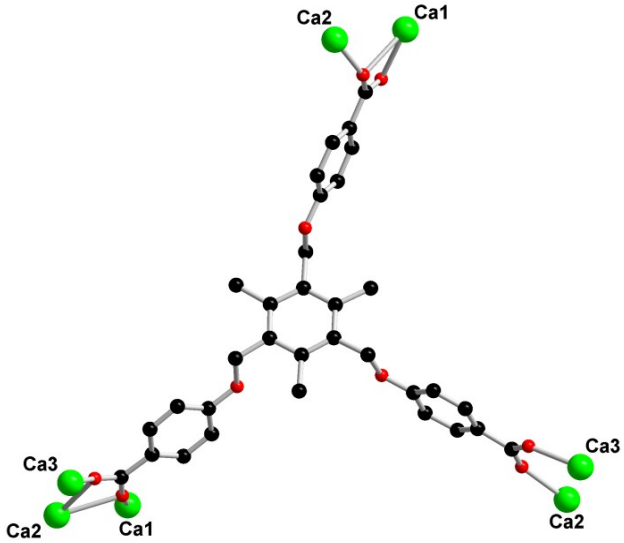


Fig. S10 The mechanical interlocking of adjacent layers (represented in different colors).



(a)



(b)

Fig. S11 Conformations and coordination modes of TCM in **4**.

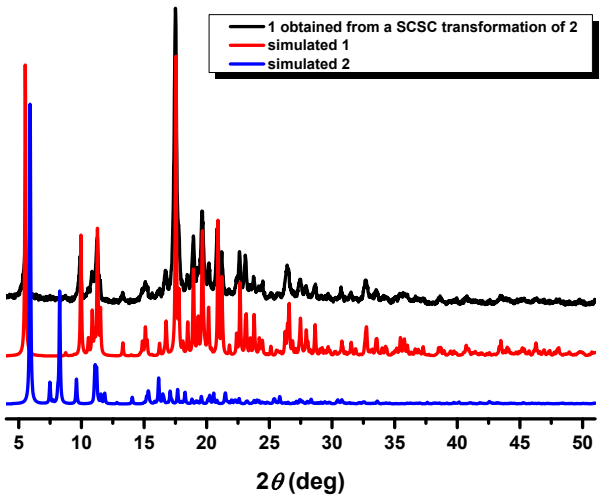


Fig. S12 PXRD patterns for simulated **1** (red line), simulated **2** (blue line), and **1** (black line) obtained from a SCSC transformation of **2**.