Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Molecular tectonics: tetracarboxythiacalix[4]arene derivatives as tectons for the formation of hydrogen-bonded networks

A. S. Ovsyannikov,[b,c] M. N. Lang,[a] S. Ferlay,*[a] S. E. Solovieva, *[b,c] I. S. Antipin, *[b,c] A. I. Konovalov,[b,c] N. Kyritsakas,[a] M. W. Hosseini*[a]

Table S1. Yields of esters **4'-8'** and corresponding acids **4-8** based on TCA and TMTCA.

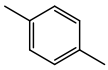
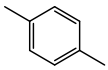
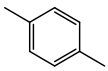
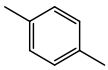
Compound	X	R	R'	Spacer	Yield, %
4'	S	*tert*-Bu	Et	-	46
5'	S	*tert*-Bu	Et	$-(CH_2)_2-$	60
6'	O	*tert*-Bu	Et	$-(CH_2)_2-$	46
7'	S	*tert*-Bu	Me		57
8'	O	H	Me		63
4	S	*tert*-Bu	Et	-	92
5	S	*tert*-Bu	Et	$-(CH_2)_2-$	95
6	O	*tert*-Bu	Et	$-(CH_2)_2-$	95
7	S	*tert*-Bu	Me		92
8	O	H	Me		94

Table S2: Distances and angles for compounds **4**-**7** obtained by X-ray diffraction on single crystals.

	4	**5**	**6**	**7**
S-C(Ar) bridge	1.783(2) 1.785(2)	1.777(3) 1.779(3) 1.781(3) 1.784(3)	1.762(6) 1.763(5) 1.767(5) 1.770(5) 1.771(5) 1.776(5) 1.778(6) 1.780(5)	1.768(2) 1.774(2) 1.777(2) 1.779(2) 1.783(2) 1.785(2)
O(S)-Ar	1.774(2)	1.773(3) 1.773(2) 1.765(3) 1.773(3)	1.371(6) 1.377(6) 1.379(5) 1.388(6)	1.764(2) 1.765(2) 1.769(2) 1.7711(19)
C-O (carboxylate)	1.234(5) and 1.256(5)	1.215(4) and 1.315(4) 1.212(5) and 1.275(5) 1.227(4) and 1.288(4) 1.224(4) and 1.299(4)	1.209(8) and 1.316(7) 1.202(8) and 1.320(7) 1.221(7) and 1.316(7) 1.203(7) and 1.303(8)	1.248(3) and 1.265(3) 1.241(4) and 1.255(4) 1.250(3) and 1.262(3) 1.255(4) and 1.265(4)
O---O (H bond)	-	2.613(4) 2.691(5) 2.682(5) 2.686(5)	2.676(7) 2.631(7) 2.740(7) 2.673(7)	2.579(4) 2.597(5) 2.617(4) 2.675(4)

Table S3: Distances and angles for compounds [$\mathbf{7}^{4-}$-($\mathbf{A}^{2+}$)$_2$], [$\mathbf{8}^{4-}$-($\mathbf{A}^{2+}$)$_2$], [$\mathbf{5}^{2-}$-$\mathbf{A}^{2+}$] and [($\mathbf{4}^{3-}$)$_2$-($\mathbf{A}^{2+}$)$_3$].

	[$\mathbf{7}^{4-}$-($\mathbf{A}^{2+}$)$_2$]	[$\mathbf{8}^{4-}$-($\mathbf{A}^{2+}$)$_2$]	[($\mathbf{4}^{3-}$)$_2$-($\mathbf{A}^{2+}$)$_3$]	[$\mathbf{5}^{2-}$-$\mathbf{A}^{2+}$]
S-C(Ar) bridge	1.765(5)	1.745(11) 1.759(12) 1.765(9) 1.774(10) 1.775(9) 1.776(11) 1.781(11) 1.782(9) 1.788(10) 1.789(9) 1.789(10) 1.789(11) 1.797(11) 1.798(10)	1.770(5) 1.772(5) 1.776(6) 1.777(5) 1.778(5) 1.782(6) 1.783(5) 1.784(5)	1.770(5) 1.771(5) 1.764(5) 1.776(5) 1.777(5) 1.780(5) 1.789(5)
O(S)-Ar	1.772(5) 1.778(5)	1.339(11) 1.359(10) 1.359(11) 1.387(12) 1.390(11) 1.362(11) 1.401(11) 1.439(11)	1.773(4) 1.773(5) 1.760(5) 1.761(5)	1.770(5) 1.771(5) 1.773(5) 1.766(5)
C-O (carboxylate)	1.258(11) and 1.301(12) 1.218(7) and 1.263(7)	1.245(13) and 1.256(12) 1.201(14) and 1.219(12) 1.229(12) and 1.266(12) 1.223(13) and 1.284(13) 1.251(13) and 1.255(13) 1.243(15) and 1.277(15) 1.252(13) and 1.259(13) 1.247(12) and 1.258(13)	1.201(9) and 1.237(9) 1.227(6) and 1.277(6) 1.188(8) and 1.242(9) 1.187(9) and 1.291(8)	1.211(9) and 1.266(8) 1.210(11) and 1.295(11) 1.219(8) and 1.291(8) 1.204(9) and 1.316(8)
O---O (H bond)	-	-	-	2.481(9) 2.508(7) 2.685(10) (MeOH)
O---N (H bond)	2.761(16) 2.769(8) 2.792(10) 2.779(13)	2.625(15) 2.705(11) 2.709(12) 2.724(15) 2.725(12) 2.734(15) 2.748(11) 2.764(8) 2.790(11) 2.781(11) 2.823(12) 2.850(14) 2.856(11) 2.878(11) 2.816(13)	2.669(10) 2.675(6) 2.713(8) 2.731(6) 2.799(8) 2.818(10)	2.725(8) 2.791(7) 2.815(10) 2.780(11) (MeOH)

Table S4 : Crystallographic Parameters for **4, 5, 6** and **7** recorded at 173 K.

Formula	**4** $C_{48}H_{56}O_8S_8$, $4(C_3H_7NO)$	**5** $C_{56}H_{72}O_8S_8$	**6** $C_{56}H_{72}O_{12}S_4$, $CHCl_3$	**7** $(C_{72}H_{72}O_8S_8)_2$ CH_2Cl_2, $2(H_2O)$
Molecular weight	1309.79	1129.62	1184.74	1305.78
Crystal system	Tetragonal	Triclinic	Monoclinic	Triclinic
Space group	$P4_2/n$	P -1	P $2_1/c$	P -1
a(Å)	16.6796(2)	12.7393(3)	15.1566(9)	12.2472(3)
b(Å)	16.6796(2)	15.3611(3)	13.6474(7)	15.6106(4)
c(Å)	11.9659(2)	17.4026(4)	28.4065(19)	20.6330(6)
α(deg)	90	64.3010(10)	90	92.390(2)
β(deg)	90	82.0540(10)	92.503(2)	96.8950(10)
γ(deg)	90	80.5920(10)	90	96.8010(10)
V(Å^3)	3329.02(8)	3018.68(12)	5870.2(6)	3882.40(18)
Z	1	2	4	1
Colour	colourless	colourless	colourless	colourless
Crystal dim (mm3)	0.09 x 0.07 x 0.05	0.06 x 0.06 x 0.06	0.18 x 0.16 x 0.15	0.060 x 0.060 x 0.070
Dcalc (gcm^{-3})	1.307	1.243	1.341	1.182
F(000)	1392	1200	2504	1454
μ (mm^{-1})	0.328	0.345	0.358	0.315
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Number of data meas.	53158	59926	44397	21001
Number of data with I> 2σ(I)	4848 [R(int) = 0.0445]	16333 [R(int) = 0.0788]	13150 [R(int) = 0.0602]	15259 [R(int) = 0.0273]
R	R1 = 0.0523, wR2 = 0.1536	R1 = 0.0573, wR2 = 0.1300	R1 = 0.0943, wR2 = 0.2132	R1 = 0.0616, wR2 = 0.1956
Rw	R1 = 0.0743, wR2 = 0.1763	R1 = 0.1074, wR2 = 0.1552	R1 = 0.1787, wR2 = 0.2653	R1 = 0.0854, wR2 = 0.2153
GOF	1.052	1.030	1.043	1. 105
Largest peak in final difference (eÅ^{-3})	0.787 and -0.551	0.832 and -0.542	0.501 and -0.436	1.296 and -0.693

Table S5 : Crystallographic Parameters for [**7**$^{4-}$-(**A**$^{2+}$)$_2$], [**8**$^{4-}$-(**A**$^{2+}$)$_2$], [**5**$^{2-}$-**A**$^{2+}$] and [(**4**$^{3-}$)$_2$-(**A**$^{2+}$)$_3$]. recorded at 173 K.

Formula	[**7**$^{4-}$-(**A**$^{2+}$)$_2$] $C_{72}H_{68}O_8S_8$ $(C_{10}H_{20}N_4)_2$ $2(H_2O)$	[**8**$^{4-}$-(**A**$^{2+}$)$_2$] $C_{56}H_{36}O_{12}S_4(C_{10}H_{20}N_4)_2$	[(**4**$^{3-}$)$_2$-(**A**$^{2+}$)$_3$]. $(C_{48}H_{53}O_8S_8)_2(C_{10}H_{20}N_4)_3$, $4(C_3H_7NO)$, H_2O	[**5**$^{2-}$-**A**$^{2+}$] $(C_{56}H_{72}O_8S_8)_2$ $(C_{10}H_{20}N_4)_2$,CH_3OH H_2O
Molecular weight	1746.37	1421.68	2928.06	2699.86
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	P $2_1/n$	P 2_1 2_1 2_1	C $2_1/c$	C 2
a(Å)	11.0804(5)	40.449(10)	41.2998(17)	33.2961(10)
b(Å)	22.8508(10)	10.2346(17)	16.5977(7)	11.7323(3)
c(Å)	19.1244(6)	33.844(8)	29.4977(11)	20.7114(5)
α(deg)	90	90	90	90
β(deg)	105.7270(10)	90	125.5250(10)	114.1140(10)
γ(deg)	90	90	90	90
V(Å^3)	4660.9(3)	14011(5)	16456.4(12)	7384.7(3)
Z	2	8	4	2
Colour	colourless	colourless	colourless	colourless
Crystal dim (mm3)	0.040 x 0.040 x 0.050	0.050 x 0.050 x 0.070	0.060 x 0.060 x 0.070	0.050 x 0.050 x 0.060
Dcalc (gcm^{-3})	1.244	1.348	1.182	1.214
F(000)	1856	5984	6240	2884
μ (mm^{-1})	0.252	0.205	0.273	0.295
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Number of data meas.	12703	54087	67396	79125
Number of data with I> 2σ(I)	5992 [R(int) = 0.0882]	31211 [R(int) = 0.1215]	23231 [R(int) = 0.0797]	20081 [R(int) = 0.0451]
R	R1 = 0.1264, wR2 = 0.2812	R1 = 0.0887, wR2 = 0.1599	R1 = 0.1084, wR2 = 0.2986	R1 = 0.0660, wR2 = 0.1821
Rw	R1 = 0.2288, wR2 = 0.3383	R1 = 0.2248, wR2 = 0.1925	R1 = 0.2029, wR2 = 0.3609	R1 = 0.0951, wR2 = 0.2051
GOF	1.019	1.026	1.045	1.021
Largest peak in final difference (eÅ^{-3})	1.426 and -0.844	1.173 and -0.705	1.678 and -0.636	1.617 and -0.477