Experimental section

Materials and General Methods: All commercially available reagents were purchased and used without further purification. 1,13-dimercapto-4,7,10-trithiatridecane were prepared according to the literature[1] and the tectons **1**-**2** have been prepared according to published procedures.[2] ^{1}H and ^{13}C NMR spectra were recorded on Bruker spectrometers at 300 MHz and 75.48MHz respectively. Microanalyses were performed by the Service de Microanalyses de la Federation de Recherche Chimie, Universite de Strasbourg.

Synthesis

Tecton **3** has been prepared using a similar procedure as the one used for the synthesis of tecton **1** and **2**[2]. Under argon, 4-mercaptopyridine (2.44 g, 22 mmol) and K_2CO_3 in excess (4.64 g, 33.4 mmol) were dissolved in dry THF (50 mL). To the stirred mixture, 1,4-dibromobutane (1 mL, 8.4 mmol) was added. The mixture was refluxed for two days. After evaporation to dryness, 30 mL of water was added to the residue and the organic mixture was extracted with CH_2Cl_2 (3 x 30 ml). The organic solvent was removed and the residue purified by column chromatography [SiO_2, $CHCl_3$] affording the pure **3** as a yellow oil in 73% yield (1.68g). ^{1}H-NMR (300 MHz, 298K, $CDCl_3$): δ [ppm] = 1.86-1.92 (m, 4H), 2.97-3.04 (m, 4H), 7.08 (dd, 4H, J = 6, 1.5), 8.80 (dd, 4H, J = 6.6, 1.8); ^{13}C-NMR (100 MHz, 298K, $CDCl_3$): δ [ppm] = 27.5, 30.1, 120.7, 148.7, 149.4.

General method for the synthesis of tectons 4-6: Under argon and at room temperature, to a degassed solution of oligoethylene thioglycolethane-1,2-dithiol or 2,2'-thiodiethanethiol or 1,13-dimercapto-4,7,10-trithiatridecane[1] (10 mmol) in dry THF (20 ml), the hydrochloride salt of *iso*nicotinoyl chloride (25 mmol) was added and the mixture was stirred at room temperature for 15 min before Et_3N (5 ml) was added and stirring was further continued for two days. After evaporation to dryness, a saturated aqueous solution of Na_2CO_3 (40 ml) was added to the residue and the mixture extracted with CH_2Cl_2 (3 x 30 ml). The organic solvent was removed and the residue purified by column chromatography [SiO_2, $CHCl_3$] affording pure compounds **4**-**6** as which powders.

Tecton **4** (2.16 g, 67%): Mp = 147 °C; ^{1}H-NMR (300 MHz, 298K, $CDCl_3$): δ [ppm] = 3.4 (s, 4H), 7.75 (dd, 4H, J = 4.5, 1.5), 8.80 (dd, 4H, J = 4.5, 1.5); ^{13}C-NMR (75 MHz, 298K, $CDCl_3$): δ [ppm] = 29.8, 120.3, 142.7, 150.9, 190.6; Calculated for $C_{14}H_{12}N_2O_2S_2$: C 55.24, H 3.97, N 9.20, O 10.51, S 21.07; found C 55.3, H 4.01, N 9.3, O 10.5, S 21.1%.

Tecton **5** (1.53 g, 43%): Mp = 72 °C; ^{1}H-NMR (300 MHz, 298K, $CDCl_3$): δ [ppm] = 2.89 (m, 4H), 3.35 (m, 4H), 7.71 (dd, 4H, J = 4.5, 1.5), 8.77 (dd, 4H, J = 4.5, 1.5); ^{13}C-NMR (75 MHz, 298K, $CDCl_3$): δ [ppm] = 29.23, 31.53, 120.27, 142.84, 150.9, 190.8; Calculated for $C_{16}H_{16}N_2O_2S_3$: C 52.72, H 4.42, N 7.69, O 8.78, S 26.39; found C 52.8, H 4.4, N 7.4, O 8.7, S 26.4%.

Tecton **6** (1.37 g, 34%): Mp = 42 °C; ^{1}H-NMR (300 MHz, 298K, $CDCl_3$): δ [ppm] = 2.85 (m, 12H), 3.30 (m, 4H), 7.72 (m, 4H), 8.77 (m, 4H); ^{13}C-NMR (75 MHz, 298K, $CDCl_3$): δ [ppm] = 29.33, 31.59, 32.2, 120.27, 139.00, 142.8, 150.88, 190.82; Calculated for $C_{20}H_{24}N_2O_2S_5$: C 49.56, H 4.99, N 5.78, O 6.60, S 33.07; found C 49.0, H 5.0, N 5.7, O 6.5, S 33.0%.

Crystallisation conditions for the title networks: In a crystallization tube (height = 15 cm, diameter = 0.4 cm), slow diffusion of an ethanol solution (*ca*. 1 mL, 5 mg) of $ZnSiF_6 \cdot xH_2O$ into the chloroform solution (1 mL) of the tecton **1**-**6** (3 mg) afforded colorless crystals after few days.

Single-Crystal Studies.

Data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-K〈 (λ = 0.71073) radiation. For all structures, diffraction data were corrected for absorption. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).

Powder diffraction studies (PXRD)

Diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-Kα radiation with a scanning range between 3.8 and 30° using a scan step size of 2°/mn.

Thermogravimetric (TGA) Studies.

TGA measurements have been performed on Pyris 6 TGA Lab System (Perkin-Elmer), using a N_2 flow of 20 ml/mn and a heat rate of 10°C/ mn.

Table TS1. Crystallographic Parameters for **1**·$ZnSiF_6$, **3**·$ZnSiF_6$, **4**·$ZnSiF_6$ and **5**·$ZnSiF_6$ recorded at 173 K.

In the case of case of **3** and **5**, the solvent molecules (EtOH and CHCl3) were found to be disordered and the Squeeze command was used.[4]

Formula	**1**·$ZnSiF_6$	**3**·$ZnSiF_6$	**4**·$ZnSiF_6$	**5**·$ZnSiF_6$
Chemical formula	$2(C_{24}H_{24}F_6N_4S_4SiZn), C_2H_2Cl_6$	$C_{28}H_{32}F_6N_4S_4SiZn$	$2(C_{28}H_{24}F_6N_4O_4S_4SiZn), 1.58(C_4H_{12}O_2), 0.25(C_4H_4Cl_{12})$	$C_{64}H_{64}F_{12}N_8O_8S_{12}Si_2Zn_2$
Molecular weight	1647.08	760.28	1897.49	1872.87
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	C2/c	C2/c	P-1
a(Å)	21.6873(6)	21.6498(14)	22.512(2)	13.1804(4)
b(Å)	7.6211(2)	7.7080(5)	14.5274(17)	15.8350(5)
c(Å)	24.1630(7)	28.670(2)	15.2352(16)	28.8368(8)
α(deg)	90	90	90	99.985(2)
β(deg)	114.128(3)	111.5450(10)	112.227(3)	94.883(2)
γ(deg)	90	90	90	106.023(2)
V(Å3)	3644.78(19)	4450.1(5)	4612.2(8)	5640.6(3)
Z	2	4	2	2
Color	Colorless	Colorless	Colorless	Colorless
Crystal dim (mm)	0.10 x 0.07 x 0.05	0.07 x 0.06 x 0.04	0.15 x 0.12 x 0.10	0.14 x 0.12 x 0.09
Dcalc (gcm^{-3})	1.501	1.135	1.366	1.103
F(000)	1664	1560	1936.3	1912
μ (mm^{-1})	1.210	0.811	0.891	0.728
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Number of data meas.	31145	12211	15152	63726
Number of data with $I > 2\sigma(I)$	4174	4889	5237	25498
R	0.0678	0.0585	0.1092	0.0819
Rw	0.1987	0.1894	0.2586	0.1862
GOF	1.027	1.075	1.045	1.004

Reference

1. (a) W. Rosen, D. H. Busch, *J. Am. Chem. Soc.*, 1969, **91**, 4694; (b) D. Pocic, PhD thesis, Universite de Strasbourg, 2005.
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3. G. M. Sheldrick, *Programs for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1996.**
4. P. van der Sluis, A. L. Speck, *Acta Cryst*, 1990, **A46**, 194.