Electronic supplementary information

Construction of a series of zero-dimensional / one-dimensional crystalline Zn-S clusters – effect of the character of bridging organic ligands on structural diversity

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Materials and General Procedures

All starting materials and solvents were purchased from commercial sources and used without further purification. The IR spectra in the range 4000-400 cm\(^{-1}\) were recorded on a PerkinElmer Spectrum One FT-IR Spectrometer. UV-vis spectra were recorded on UV-1650 PC spectrophotometer (double cell mode, baseline correction was performed a wavelength scan from 800 nm to 200 nm). \(^1\text{H}\) NMR spectra were recorded on an INOVA 400 spectrometer (400 MHz, (CD\(_3\))\(_2\)SO, 25\(^\circ\)C). Fluorescence measurements were performed on Varian Cary Eclipse fluorescence spectrophotometer. XPRD data were collected on a X’Pert PRO Powder diffractometer (40 KV, 40 mA) with Cu K\(_\alpha\) (\(\lambda = 1.5418\) Å), employing a scanning rate of 0.05\(^\circ\) s\(^{-1}\) in the 20 range from 2\(^\circ\) to 50\(^\circ\).
Synthesis of compounds 1 ~ 8

Zn₈S(SC₆H₅)₁₄[3-H₃CC₉H₆N]₂ (1):
In a Teflon-lined stainless steel autoclave (23 mL), Zn(CH₃COO)₂·2H₂O (0.8759 g, 3.99 mmol), thiourea (0.0391 g, 0.51 mmol) and 3-Methylquinoline (0.1432 g, 1.0 mmol) were dissolved in 12 mL distilled water, resulting in a clear solution and the mixture was stirred for 30 minutes. Thiophenol (0.776 g, 7.0 mmol) was added and a white sticky suspension was present. The sealed vessel was heated at 165 °C for 5 days. After cooling to room temperature, grey block crystals suitable for X-ray analysis were obtained (weight, 0.758 g; yield, 64% based on the Zn source). Anal. Calcd for C₁₀₄H₈₈N₂S₁₅Zn₈ (2370.00): C, 52.71; H, 3.74; N, 1.18%. Found: C, 52.68; H, 3.70; N, 1.12%.

ε₂₆₆: 1.15 × 10⁵ M⁻¹ cm⁻¹. FTIR data (cm⁻¹): 1577(vs, δ(C=C)), 1477(vs, δ(C=C)), 1437(vs, δ(C=C)), 1085(vs, ν(C-S)), 1024(vs, ν(C-S)), 732(vs, δ(=CH)), 685(vs, δ(=CH)).

¹H NMR (400 MHz, (CD₃)₂SO, 25 °C):
δ1.88 (s, 2CH₃, 6H), 6.86 (t, J = 6.8 Hz, 14CH, 14H), 7.05 (m, 14C(CH)₂, 28H), 7.38 (m, 14C(CH)₂, 28H), 7.46 (t, J = 9.6 Hz, 2CH, 2H), 7.55 (d, J = 4.0 Hz, 2CH, 2H), 7.78 (t, J = 4.0 Hz, 2CH, 2H), 7.95 (d, J = 4.0 Hz, 2CH, 2H), 8.02 (d, J = 4.0 Hz, 2CH, 2H), 8.12 (s, 2CH, 2H);

Zn₈S(SC₆H₅)₁₄[5-H₂NC₉H₆N]₂ (2):
The procedure was similar to above using 5-Aminoquinoline with orange-red block crystals being obtained. Yield: 65 %. Anal. Calcd for C₁₀₂H₆₆N₄S₁₅Zn₈ (2371.98): C, 51.65; H, 3.65; N, 2.36%. Found: C, 51.35; H, 3.58; N, 2.35%. ε₂₆₅: 1.42 × 10⁵ M⁻¹ cm⁻¹. FTIR data (cm⁻¹): 1621(s, ν(NH₂)), 1576(vs, δ(C=C)), 1476(vs, δ(C=C)), 1437(vs, δ(C=C)), 1083(vs, ν(C-S)), 1023(vs, ν(C-S)), 734(vs, δ(=CH)), 688(vs, δ(=CH)).

¹H NMR (400 MHz, (CD₃)₂SO, 25 °C): δ5.98 (s, 2NH₂, 4H), 6.69 (d, J = 4.0 Hz, 2CH, 2H), 6.89 (t, J = 7.2 Hz, 14CH, 14H), 7.05 (m, 14C(CH)₂, 28H), 7.19 (d, J = 6.8 Hz, 2CH, 2H), 7.34 (m, 14C(CH)₂, 28H), 7.45 (t, J = 6.8 Hz, 2CH, 2H), 7.58 (d, J = 6.8 Hz, 2H), 8.55 (d, J = 4.0 Hz, 2CH, 2H), 8.80 (d, J = 4.8 Hz, 2CH, 2H);

Zn₈S(SC₆H₅)₁₄[C₄H₃SC₅H₄N]₂ (3):
The procedure was similar to above using 3-(2-Thienyl)pyridine with grey block crystals being obtained. Yield: 71 %. Anal. Calcd for C_{102}H_{84}N_{2}S_{17}Zn_{8} (2406.08): C, 50.92; H, 3.52; N, 1.16%. Found: C, 50.67; H, 3.48; N, 1.12%. ε_{266}: 1.15 × 10^5 M^{-1} cm^{-1}. FTIR data (cm^{-1}): 1576(vs, δ(C=C)), 1476(vs, δ(C=C)), 1436(vs, δ(C=C)), 1081(vs, μ(C-S)), 1022(vs, μ(C-S)), 736(vs, δ(=CH)), 686(vs, δ(=CH)).

1H NMR (400 MHz, (CD_{3})_{2}SO, 25 °C): δ 6.86 (t, J = 7.2 Hz, 14CH, 14H), 7.02 (m, 14C(CH)_{2}, 28H), 7.25 (d, J = 4.0 Hz, 2CH, 2H), 7.36 (m, 14C(CH)_{2}, 28H), 7.40 (t, J = 4.8 Hz, 2CH, 2H), 7.58 (d, J = 4.8 Hz, 2CH, 2H), 7.66 (d, J = 5.2 Hz, 2CH, 2H), 8.02 (t, J = 5.6 Hz, 2CH, 2H), 8.55 (d, J = 4.8 Hz, 2CH, 2H), 8.95 (s, 2CH, 2H); Zn_{8}S(SC_{6}H_{5})_{14}[NC_{12}H_{8}N]_{2} (4):

The procedure was similar to above using 4,7-Phenanthroline with pale-yellow block crystals being obtained. Yield: 62 %. Anal. Calcd for C_{108}H_{86}N_{4}S_{15}Zn_{8} (2444.05): C, 53.08; H, 3.55; N, 2.29%. Found: C, 52.98; H, 3.50; N, 2.12%. ε_{266}: 9.63 × 10^4 M^{-1} cm^{-1}. FTIR data (cm^{-1}): 1577(vs, δ(C=C)), 1477(vs, δ(C=C)), 1437(vs, δ(C=C)), 1084(vs, μ(C-S)), 1023(vs, μ(C-S)), 732(vs, δ(=CH)), 684(vs, δ(=CH)).

1H NMR (400 MHz, (CD_{3})_{2}SO, 25 °C): δ 6.89 (t, J = 7.2 Hz, 14CH, 14H), 7.05 (m, 14C(CH)_{2}, 28H), 7.32 (m, 14C(CH)_{2}, 28H), 7.45 (t, J = 4.8 Hz, 2CH, 2H), 7.59 (d, J = 4.8 Hz, 2H), 7.85 (m, 2(2CH), 4H), 8.26 (s, 2(2CH), 4H), 9.08 (d, J = 6.8 Hz, 2CH, 2H), 9.36 (d, J = 6.8 Hz, 2H); [Zn_{8}S(SC_{6}H_{5})_{13}L_{1}(H_{2}O)]2H_{2}O (L = 3-carboxypryidyl) (5):

The procedure was similar to above using 3-Pyridinecarbonitrile with colorless block crystals being obtained. Yield: 67 %. Anal. Calcd for C_{84}H_{71}NO_{3}S_{14}Zn_{8} (2114.57, not include crystalline water): C, 47.71; H, 3.38; N, 0.66%. Found: C, 47.15; H, 3.32; N, 0.62%. ε_{266}: 8.48 × 10^4 M^{-1} cm^{-1}. FTIR data (cm^{-1}): 1639(s, δ(C=O)), 1575(vs, δ(C=C)), 1477(vs, δ(C=C)), 1438(vs, δ(C=C)), 1086(vs, μ(C-S)), 1024(vs, μ(C-S)), 917(m, μ(-OH), 732(vs, δ(=CH)), 684(vs, δ(=CH)).

1H NMR (400 MHz, (CD_{3})_{2}SO, 25 °C): δ 6.90 (t, J = 7.2 Hz, 13CH, 13H), 7.02 (m, 13C(CH)_{2}, 26H), 7.35 (m, 13C(CH)_{2}, 26H), 7.46 (t, 1CH, 1H), 7.55 (d, 1CH, 1H), 8.24 (d, 1CH, 1H), 8.66 (s, 1CH, 1H); Zn_{8}S(SC_{6}H_{5})_{14}L_{1} (L = 2,5-Bis(4-pyridyl)-1,3,4-thiadiazole) (6):

The procedure was similar to above using 2,5-Bis(4-pyridyl)-1,3,4-thiadiazole
(0.1212 g, 0.5 mmol) with orange-red block crystals being obtained. Yield: 63 %. Anal. Calcd for C$_{96}$H$_{78}$N$_{16}$S$_{16}$Zn$_{8}$ (2323.91): C, 49.62; H, 3.38; N, 2.41%. Found: C, 49.92; H, 3.31; N, 2.40%. $\epsilon_{269}$: 1.13 $\times$ 10$^5$ M$^{-1}$ cm$^{-1}$. FTIR data (cm$^{-1}$): 1577(vs, $\delta$(C=C)), 1477(vs, $\delta$(C=C)), 1436(vs, $\delta$(C=C)), 1082(vs, $\nu$(C-S)), 1022(vs, $\nu$(C-S)), 735(vs, $\delta$(=CH)), 687(vs, $\delta$(=CH)).

$\text{[Zn}_4\text{(SC}_6\text{H}_5\text{O})_8\text{L}_1\text{]}_2$ (L = $trans$-1,2-Bis(4-pyridyl)ethylene) (7):

In the absence of thiourea, the procedure was similar to above using $trans$-1,2-Bis(4-pyridyl)ethylene (0.0913 g, 0.5 mmol) with pale-green block crystals being obtained. Yield: 55 %. Anal. Calcd for C$_{60}$H$_{50}$N$_{2}$S$_{8}$Zn$_{4}$ (1316.98): C, 54.71; H, 3.83; N, 2.13%. Found: C, 54.95; H, 3.81; N, 2.10%. $\epsilon_{269}$: 1.03 $\times$ 10$^5$ M$^{-1}$ cm$^{-1}$. FTIR data (cm$^{-1}$): 3047(s, $\delta$(=C–H)), 1576(vs, $\delta$(C=C)), 1477(vs, $\delta$(C=C)), 1436(vs, $\delta$(C=C)), 1085(s, $\nu$(C-S)), 1021(vs, $\nu$(C-S)), 745(vs, $\delta$(=CH)), 683(vs, $\delta$(=CH)).

$\text{[Zn}_4\text{(SC}_6\text{H}_5\text{O})_8\text{L}_1\text{]}_2$ (L = 4,4$'$-Bipyridyl) (8):

The procedure was similar to 8 using raw materials as following: Zn(CH$_3$COO)$_2$.2H$_2$O (0.8775 g, 4.0 mmol), 4,4$'$-Bipyridine (0.0786 g, 0.5 mmol) and Thiophenol (0.773 g, 7.0 mmol) with pale-green needle crystals being obtained. Yield: 59 %. Anal. Calcd for C$_{116}$H$_{96}$N$_{8}$S$_{16}$Zn$_{8}$ (2581.89): C, 53.96; H, 3.75; N, 2.17%. Found: C, 53.55; H, 3.69; N, 2.11%. $\epsilon_{268}$: 1.39 $\times$ 10$^5$ M$^{-1}$ cm$^{-1}$. FTIR data (cm$^{-1}$): 3048(s, $\delta$(C–H)), 1577(vs, $\delta$(C=C)), 1477(vs, $\delta$(C=C)), 1436(vs, $\delta$(C=C)), 1082(s, $\nu$(C-S)), 1023(vs, $\nu$(C-S)), 735(vs, $\delta$(=CH)), 687(vs, $\delta$(=CH)). $^1$H NMR (400 MHz, (CD$_3$)$_2$SO, 25 oC): $\delta$ 2.99 (s, 2CH, 2H), 6.88 (t, $J$ = 6.8 Hz, 2(8CH), 16H), 7.02 (m, 8C(CH)$_2$, 16H), 7.35 (m, 8C(CH)$_2$, 16H), 7.60 (d, $J$ = 6.8 Hz, 2CH, 2H), 7.68 (d, $J$ = 6.8 Hz, 2H), 8.48 (d, $J$ = 4.8 Hz, 2CH, 2H), 8.62 (d, $J$ = 4.8 Hz, 2H).
**Fig. S1** Excitation and emission spectra: (a) compound 2 in DMSO (c = $2.5 \times 10^{-6}$ M): excited at 370 nm; (b) compound 3 in DMSO (c = $2.5 \times 10^{-6}$ M): excited at 296 nm.
Crystallography

Crystal structure of 1 ~ 8 were solved using direct methods (SHELXTL V5.1\(^1\)) from single-crystal data collected at 150 K on a Bruker SMART/CCD area detector diffractometer fitted with Mo K\(\alpha\) radiation (\(\lambda = 0.71073 \) Å) and a graphite monochromator or an Oxford Diffraction Gemini Ultra with an ATLAS charge-coupled device (CCD) detector [\(\lambda(\text{MoK}_\alpha) = 0.71073 \) Å]. Structure refinements were performed using the SHELX97/SHELXL-2013 program\(^2\) which uses a full-matrix least-squares refinement based on \(F^2\). Absorption corrections were performed using the SADABS program\(^3\).

Note: Unsurprisingly, similar to previous reports\(^4\) some unsatisfactory aspects in relation to the refinement have arisen as a consequence of a low reflection to parameter ratio for those structures. The reason for the low ratio is the relatively weak nature of the diffraction. The surface –SC\(_6\)H\(_5\) ligands have severe disorder and this is responsible for the elevated agreement values (\(R\) values) found for those structures, in particular for complexes 2, 3 and 6. Despite these difficulties, the atomic positions are well resolved in the crystal structure analysis.

CCDC reference numbers: 1012102(1), 1012103(2), 1012104(3), 1012105(4), 795210 (5), 1012106(6), 1012107(7), 1012108(8).

References:


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