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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

Xianghua Zeng,[a] Xiaojing Yao,[b] Junyong Zhang,*[,a] Qi Zhang,[a] Wenqian Wu,[a] Aihua Cai,[c] Jinlan Wang,*[,b] Qing-dao Zeng*[,d] and Jingli Xie*[,a]

[a] *College of Biological, Chemical Science and Engineering, Jiaxing University, Jiaxing 314001, P. R. China, E-mail: jlxie@mail.zjxu.edu.cn; zhangjy@mail.zjxu.edu.cn;*

[b] *Department of Physics & School of Chemistry and Chemical Engineering Southeast University, Nanjing, 211189, P. R. China, E-mail: jlwang@seu.edu.cn;*

[c] *College of Mathematics Physics and Information Engineering, Jiaxing University, Jiaxing 314001, P. R. China*

[d] *CAS Key Laboratory of Standardization and Measurement for Nanotechnology, National Center for Nanoscience and Technology (NCNST), 11 Zhongguancun Beiyitiao, Beijing 100190, P. R. China E-mail: zengqd@nanoctr.cn.*

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). ^1H NMR spectra were recorded on an INOVA 400 spectrometer (400 MHz, $(CD_3)_2SO$, 25°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_α (λ = 1.5418 Å), employing a scanning rate of 0.05^o s^{-1} in the 2θ range from 2° to 50°.

Synthesis of compounds 1 ~ 8

$Zn_8S(SC_6H_5)_{14}[3\text{-}H_3CC_9H_6N]_2$ (1):

In a Teflon-lined stainless steel autoclave (23 mL), $Zn(CH_3COO)_2{\cdot}2H_2O$ (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 ^oC 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 $C_{104}H_{88}N_2S_{15}Zn_8$ (2370.00): C, 52.71; H, 3.74; N, 1.18%. Found: C, 52.68; H, 3.70; N, 1.12%. ε_{266}: 1.15×10^5 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, $(CD_3)_2SO$, 25 ^oC):

δ 1.88 (s, $2CH_3$, 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);

$Zn_8S(SC_6H_5)_{14}[5\text{-}H_2NC_9H_6N]_2$ (2):

The procedure was similar to above using 5-Aminoquinoline with orange-red block crystals being obtained. Yield: 65 %. Anal. Calcd for $C_{102}H_{86}N_4S_{15}Zn_8$ (2371.98): C, 51.65; H, 3.65; N, 2.36%. Found: C, 51.35; H, 3.58; N, 2.35%. ε_{265}: 1.42×10^5 M^{-1} cm^{-1}. FTIR data (cm^{-1}): 1621(s, $\nu(NH_2)$), 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, $(CD_3)_2SO$, 25 ^oC): δ 5.98 (s, $2NH_2$, 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);

$Zn_8S(SC_6H_5)_{14}[C_4H_3SC_5H_4N]_2$ (3):

The procedure was similar to above using 3-(2-Thienyl)pyridine with grey block crystals being obtained. Yield: 71 %. Anal.Calcd for $C_{102}H_{84}N_2S_{17}Zn_8$ (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, ν(C-S)), 1022(vs, ν(C-S)), 736(vs, δ(=CH)), 686(vs, δ(=CH)). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 25 ^oC): 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);

$Zn_8S(SC_6H_5)_{14}[NC_{12}H_8N]_2$ (4):

The procedure was similar to above using 4,7-Phenanthroline with pale-yellow block crystals being obtained. Yield: 62 %. Anal. Calcd for $C_{108}H_{86}N_4S_{15}Zn_8$ (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, ν(C-S)), 1023(vs, ν(C-S)), 732(vs, δ(=CH)), 684(vs, δ(=CH)). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 25 ^oC): 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);

$[Zn_8S(SC_6H_5)_{13}L_1(H_2O)]\cdot 2H_2O$ (L = 3-carboxypryidyl) (5):

The procedure was similar to above using 3-Pyridinecarbonitrile with colorless block crystals being obtained. Yield: 67 %. Anal. Calcd for $C_{84}H_{71}NO_3S_{14}Zn_8$ (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, ν(C-S)), 1024(vs, ν(C-S)), 917(m, ν(-OH), 732(vs, δ(=CH)), 684(vs, δ(=CH)). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 25 ^oC): 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);

$Zn_8S(SC_6H_5)_{14}L_1$ (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

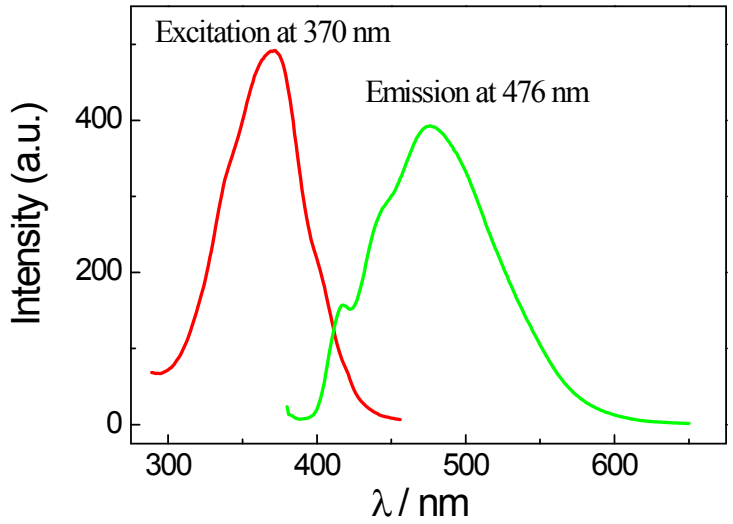
(0.1212 g, 0.5 mmol) with orange-red block crystals being obtained. Yield: 63 %. Anal. Calcd for $C_{96}H_{78}N_4S_{16}Zn_8$ (2323.91): C, 49.62; H, 3.38; N, 2.41%. Found: C, 49.92; H, 3.31; N, 2.40%. ε_{269}: 1.13×10^5 M^{-1} cm^{-1}. FTIR data (cm^{-1}): 1577(vs, δ(C=C)), 1477(vs, δ(C=C)), 1436(vs, δ(C=C)), 1082(vs, ν(C-S)), 1022(vs, ν(C-S)), 735(vs, δ(=CH)), 687(vs, δ(=CH)). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 25 ^oC): δ 6.86 (t, J = 7.2 Hz, 14CH, 14H), 7.02 (m, 14C$(CH)_2$, 28H), 7.35 (m, 14C$(CH)_2$, 28H), 7.44 (t, J = 4.8 Hz, 2CH, 2H), 7.56 (d, J = 4.8 Hz, 2CH, 2H), 8.07 (d, J = 4.8 Hz, 2CH, 2H), 8.86 (d, J = 4.8 Hz, 2CH, 2H);

$Zn_4(SC_6H_5)_8L_1$ (L = *trans*-1,2-Bis(4-pyridyl)ethylene) (**7**):

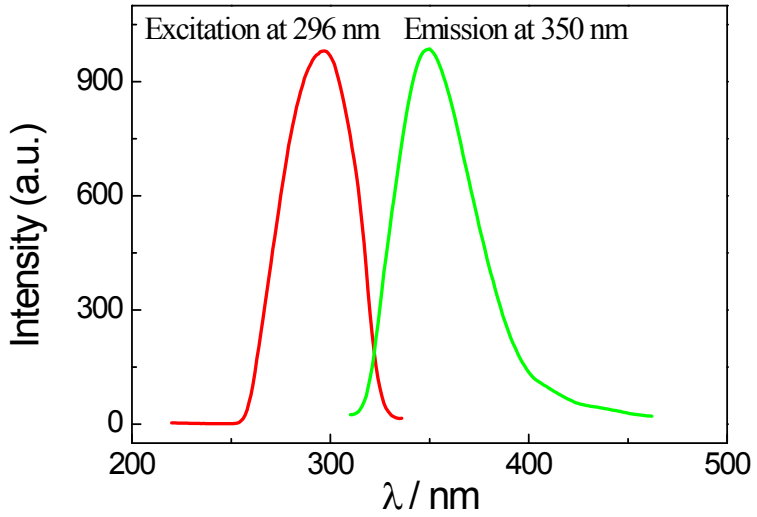
In the absence of thiourea, the procedure was similar to above using *trans*-1,2-Bis(4-pyridyl)ethylene (0.0913 g, 0.5 mmol) with pale-green block crystals being obtained . Yield: 55 %. Anal. Calcd for $C_{60}H_{50}N_2S_8Zn_4$ (1316.98): C, 54.71; H, 3.83; N, 2.13%. Found: C, 54.95; H, 3.81; N, 2.10%. ε_{269}: 1.03×10^5 M^{-1} cm^{-1}. FTIR data (cm^{-1}): 3047(s, δ(=C–H)), 1576(vs, δ(C=C)), 1477(vs, δ(C=C)), 1436(vs, δ(C=C)), 1085(s, ν(C-S)), 1021(vs, ν(C-S)), 745(vs, δ(=CH)), 683(vs, δ(=CH)). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 25 ^oC): δ 2.99 (s, 2CH, 2H), 6.90 (t, J = 6.8 Hz, 8CH, 8H), 7.06 (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);

$[Zn_4(SC_6H_5)_8L_1]_2$ (L = 4,4'-Bipyridyl) (**8**):

The procedure was similar to **8** using raw materials as following: $Zn(CH_3COO)_2{\cdot}2H_2O$ (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 $C_{116}H_{96}N_4S_{16}Zn_8$ (2581.89): C, 53.96; H, 3.75; N, 2.17%. Found: C, 53.55; H, 3.69; N, 2.11%. ε_{268}: 1.39×10^5 M^{-1} cm^{-1}. FTIR data (cm^{-1}): 3048(s, δ(=C–H)), 1577(vs, δ(C=C)), 1477(vs, δ(C=C)), 1436(vs, δ(C=C)), 1082(s, ν(C-S)), 1023(vs, ν(C-S)), 735(vs, δ(=CH)), 687(vs, δ(=CH)). ^{1}H NMR (400 MHz, $(CD_3)_2SO$, 25 ^oC): δ 6.88 (t, J = 6.8 Hz, 2(8CH), 16H), 7.02 (m, 2[8C$(CH)_2$], 32H), 7.36 (m, 2[8C$(CH)_2$], 32H), 7.42 (t, J = 6.8 Hz, 2(2CH), 4H), 7.58 (d, J = 6.8 Hz, 2(2CH), 4H), 7.86 (t, J = 4.8 Hz, 2(2CH), 4H), 8.76 (d, J = 4.8 Hz, 2(2CH), 4H).



(a)



(b)

Fig. S1 Excitation and emission spectra: (a) compound **2** in DMSO (c = 2.5 × 10^{-6} M): excited at 370 nm; (b) compound **3** in DMSO (c = 2.5 × 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_α radiation (λ = 0.71073 Å) and a graphite monochromator or an Oxford Diffraction Gemini Ultra with an ATLAS charge-coupled device (CCD) detector [$\lambda(MoK_\alpha)$ = 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 $–SC_6H_5$ 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**).

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