Electronic Supplementary Information

Structure-dependent electronic transition in a new type of π -

electron delocalized multi-sulfur bis(dithiolene) nickel complexes

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Section 1. Experimental Section

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Synthesis of 1b: The compound **1b** was prepared by the literature method.¹ Under an argon atmosphere, $(n-\text{Bu}_4\text{N})_2[\text{Zn}(\text{dmit})_2]$ (1.594 g, 1.69 mmol), 1,2-diiodobenzene (**1a**) (3.5 mmol), Cu₂O (48.7 mg, 0.34 mmol), ethyl acetoacetate (86 μ L, 0.68 mmol), and DMF (3 mL) were heated to 80 °C. After stirred at 80 °C for 10 h, the reaction mixture was cooled down to room temperature and poured into 30 mL dichloromethane. The resulting mixture was washed with distilled water (3×10 mL) and brine (10 mL) successively, and then dried over anhydrous Na₂SO₄. The crude product was purified by chromatography on silica gel with dichloromethane/petroleum ether to obtain **1b** as a yellow solid. Yield: 68%. EI-MS, m/z (I %): 271.9 (M⁺, 100). Anal. Calcd for C₉H₄S₅: C, 39.68; H, 1.48. Found: C, 39.55; H, 1.51%. ¹H NMR (500 MHz, CDCl₃): δ 7.51–7.49 (m, 2H), 7.38–7.36 (m, 2H);

Synthesis of 2b: **2b** was obtained according to the procedure reported above for **1b** by using **2a** instead of **1a**; yield: 55%. EI-MS, m/z (I %): 299.9 (M⁺, 100); Calc for $C_{11}H_8S_5$: C, 43.97; H, 2.68. Found: C, 43.74; H, 2.88%. ¹H NMR (500 MHz, DMSO): 7.46 (s, 2H), 2.24(s, 6H).

Synthesis of 3b: **3b** was obtained according to the procedure reported above for **1b** by using **3a** instead of **1a**; yield: 72%. EI-MS, m/z (I %): 331.9 (M⁺, 100); Calc for $C_{11}H_8O_2S_5$: C, 39.73; H, 2.43. Found: C, 39.54; H, 2.31%. ¹H NMR (500 MHz, CDCl₃): 6.95 (s, 2H), 3.89(s, 6H).

Synthesis of 4b: **4b** was obtained according to the procedure reported above for **1b** by using **4a** instead of **1a**; Yield: 62%; EI-MS, m/z (I %): 343.8 (M⁺, 100); Calcd for C₉F₄S₅: C, 31.39; Found: C, 31.53. IR (KBr, cm⁻¹): 3441m, 2921w, 2849w, 1614w, 1498s, 1478s, 1454s, 1083m, 1058m, 1037m, 880m, 820m, 782m, 505w.

Synthesis of 1c: To the thione **1b** (810 mg, 3.0 mmol) in chloroform (210 mL) was added mercury(II) acetate (2.8 g) in glacial acetic acid (70 mL). The mixture was stirred at room temperature for 6 h. After filtration, the filtrate was washed with water, brine and then with saturated NaHCO₃. The organic phase was dried with sodium sulfate and concentrated by rotary evaporation. Pale yellow crystals of **1c** were obtained by recrystallization from ethanol-chloroform (3:1). Yield: 70%. EI-MS, m/z

(I %): 255.9 (M⁺, 99). Anal. Calcd for C₉H₄OS₄: C, 42.16; H, 1.57; O, 6.24. Found: C, 42.28; H, 1.51; O, 6.29%. ¹H NMR (500 MHz, CDCl₃): δ 7.52–7.50 (m, 2H), 7.39–7.36 (m, 2H).

Synthesis of 2c: A similar procedure as that used for the preparation of 1c was adopted using 2b instead of 1b. A pale yellow solid was obtained. Yield: 75%. EI-MS, m/z (I %): 283.9 (M⁺, 100). Calc for $C_{11}H_8OS_4$: C, 46.45; H, 2.83. Found: C, 46.16; H, 2.71%. ¹H NMR (500 MHz, DMSO): 7.47 (s, 2H), 2.45(s, 6H).

Synthesis of 3c: A similar procedure as that used for the preparation of 1c was adopted using 3b instead of 1b. A pale yellow solid was obtained. Yield: 82%. EI-MS, m/z (I %): 315.9 (M⁺, 100). Calc for $C_{11}H_8O_3S_4$: C, 41.75; H, 2.55. Found: C, 41.86; H, 2.62%. ¹H NMR (500 MHz, CDCl₃): 6.98 (s, 2H), 3.90 (s, 6H).

Synthesis of 4c: A similar procedure as that used for the preparation of 1c wasadopted using 4b instead of 1b. A pale yellow solid was obtained. Yield: 72%. EI-MS,m/z (I %): 327.9 (M⁺, 99); Calc for C₉F₄OS₄: C, 32.92; Found: C, 32.79. IR (KBr, cm^{-1}): 3441w, 2923w, 2849w, 1744w, 1678s, 1629s, 1491s, 1457s, 1114s, 1046s,911m,887s,822s,770s,545w.

Section 2. Supplementary Characterization

2.1 Crystal structure determination

 Table S1. X-ray crystallographic data collection and refinement parameters for the complexes 1–4.

	1	2	3	4
empirical formula	C ₃₂ H ₄₄ NNiS ₈	C ₃₆ H ₅₂ NNiS ₈	C ₃₇ H ₅₃ Cl ₃ NNiO ₄ S ₈	$C_{64}H_{72}F_{16}N_2Ni_2S_{16}$
$M_{ m r}$	757.91	813.98	997.34	1803.58
cryst syst	monoclinic	triclinic	triclinic	monoclinic
Space group	C2/c	Pī	Pī	$P2_l/c$
<i>a</i> (Å)	23.2472(17)	9.685(2)	9.3127(11)	22.520(2)
<i>b</i> (Å)	11.0567(8)	15.561(3)	11.4047(13)	18.0442(18)
<i>c</i> (Å)	17.3281(13)	15.636(3)	23.822(3)	19.7173(19)
α (°)	90.00	67.636(4)	78.383(2	90.00
eta(°)	121.0040(10)	87.435(4)	89.598(2)	103.374(2)
γ(°)	90.00	74.465(4)	69.845(2)	90.00
$V(Å^3)$	3817.6(5)	2095.3(7)	2321.1(5)	7794.9(13)
Ζ	4	2	2	4
$ ho_{\rm c}({ m gcm^{-3}})$	1.360	1.290	1.427	1.537
F(000)	1644	862	1042	3704
T / K	293(2)	293(2)	296(2)	296(2)
μ (Mo-K α)/ mm ⁻¹	0.971	0.887	0.988	0.990
GOF (F^2)	1.030	0.977	1.049	1.025
$R_1^{a}, wR_2^{b} (I > 2\sigma(I))$	0.0444, 0.1254	0.0524, 0.1066	0.0512, 0.1447	0.0351,0.0828

^{*a*} $R_1 = \Sigma ||C| - |F_c|| / \Sigma F_o|$. ^{*b*} $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$

Atoms	Experimental distances (Å)	Calculated distances (Å)	Atoms	Experimental angles (°)	Calculated angles (°)
Nil—S1	2.144 (1)	2.232	S1—Ni1—S2	92.02 (4)	91.48
Ni1—S2	2.147 (1)	2.232			

Table S2 Experimental and theoretically calculated of selected bond distances [Å] and angles [°] for complex 1

Table S3 Experimental and theoretically calculated of selected bond distances [Å]

and angles [°] for complex 2								
Atoms	Experimental	Calculated	Atoms	Experimental	Calculated			
Atoms	distances (Å)	distances (Å)	Atoms	angles (°)	angles (°)			
Ni1—S1	2.153 (1)	2.232	S2—Ni1—S1	92.12 (5)	91.44			
Ni1—S2	2.138 (1)	2.232						

Table S4 Experimental and theoretically calculated of selected bond distances [Å]

and angles [°] for complex 3

Atoms	Experimental distances (Å)	Calculated distances (Å)	Atoms	Experimental angles (°)	Calculated angles (°)
Ni1—S6	2.151 (1)	2.232	S6—Ni1—S1	176.64 (3)	180.00
Ni1—S2	2.154 (1)	2.232	S2—Ni1—S1	92.19 (3)	91.46
Ni1—S1	2.161 (1)	2.232	S6—Ni1—S5	92.22 (5)	91.46
Ni1—S5	2.166 (1)	2.232	S2—Ni1—S5	177.46 (4)	179.98
			S6—Ni1—S2	85.98(4)	88.54
			S1—Ni1—S5	89.53(4)	88.54

Table S5	Experimental	and theo	oretically	calculated	of	selected	bond	distances	[Å]
and angles	s [°] for comple	ex 4							

Atoms	Experimental distances (Å)	Calculated distances (Å)	Atoms	Experimental angles (°)	Calculated angles (°)
Ni1—S1	2.149 (1)	2.232	S1—Ni1—S6	177.45 (3)	180.00
Ni1—S2	2.158 (1)	2.232	S5—Ni1—S6	92.46 (3)	91.66
Ni1—S6	2.156 (1)	2.232	S1—Ni1—S2	92.50 (3)	91.66
Ni1—S5	2.151 (1)	2.232	S5—Ni1—S2	178.76 (3)	180.00
			S1—Ni1—S5	86.33 (3)	88.34
			S6—Ni1—S2	88.73 (3)	88.34

2.2 Cyclic voltammetry



Fig. S1 Cyclic voltammogram of complex 2 measured in CH_2Cl_2 solution containing n-Bu₄NClO₄ (0.1 M). The scan rate was 100 mV/s. *indicates the start of the scan.



Fig. S2 Cyclic voltammogram of complex 3 measured in CH_2Cl_2 solution containing n-Bu₄NClO₄ (0.1 M). The scan rate was 100 mV/s. *indicates the start of the scan.



Fig. S3 Cyclic voltammogram of complex 4 measured in CH₂Cl₂ solution containing n-Bu₄NClO₄ (0.1 M). The scan rate was 100 mV/s. *indicates the start of the scan.
2.3 ESR spectra



Fig. S4 Solid ESR spectrum of complex 2 measured at 298 K.



Fig. S5 Solid ESR spectrum of complex 3 measured at 298 K.



Fig. S6 Solid ESR spectrum of complex 4 measured at 298 K.





Fig. S7 ESI-MS spectrum of complex 1 (anionic part), the calculated value (m/z): $513.77 (M^{-})$.



Fig. S8 ESI-MS spectrum of complex 2 (anionic part), the calculated value (m/z): 569.84 (M⁻).



Fig. S9 ESI-MS spectrum of complex **3** (anionic part), the calculated value (m/z): 633.82 (M⁻).



Fig. S10 ESI-MS spectrum of complex 4 (anionic part), the calculated value (m/z): $657.70 \text{ (M}^{-}\text{)}$.



Fig. S11 ¹H NMR spectrum of complex 1 in CD₃CN.



Fig. S12 ¹H NMR spectrum of complex 2 in CD₃CN.



Fig. S13 ¹H NMR spectrum of complex 3 in CD₃CN.



Fig. S14 ¹H NMR spectrum of complex 4 in CD₃CN.

Reference

1 J. Sun, X. Lu, J. Shao, Z. Cui, Y. Shao, G. Jiang, W. Yu, X. Shao, RSC Adv., 2013, 3, 10193.