ESI materials for

Metal centered oxidation or ligand centered oxidation of metal dithiolene? Spectral, electrochemical and structural studies on a nickel-4-pyridine-1,2-dithiolate system

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ESI-Fig.1. The optimized minimum energy structures afforded by the calculations of $[Ni(4\text{-pedt})_2]^-$ (top), $[Ni(4\text{-Hpedt})(4\text{-pedt})]^0$ (middle), and $[Ni(4\text{-Hpedt})_2]^+$ (bottom) (Ni, black; N, dark blue; S, yellow; C, gray; H, gray white). Front (left) and side (right) views are presented.

ESI-Fig.2. Changes of the UV-vis-NIR absorption of the oxidized compound **1** in DMF / CH_3CN (4:1 by volume), upon increasing concentration of Na_2SO_3.

ESI-Fig.3. Changes of the UV-vis-NIR absorption of protonated compound **1** in DMF / CH_3CN (4:1 by volume), upon increasing concentration of Et_3N.

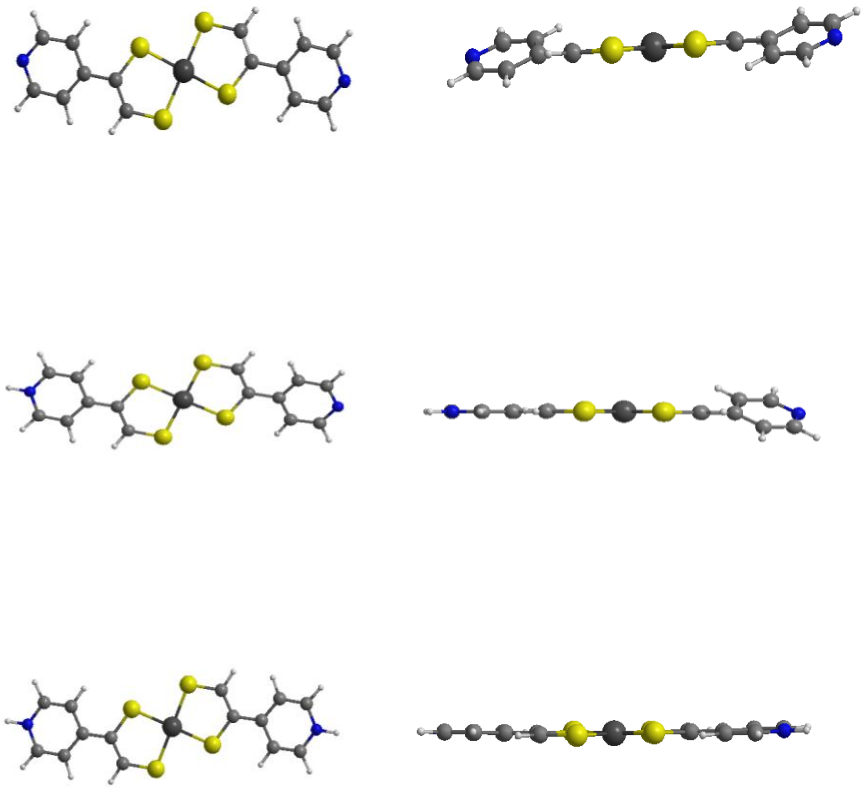
ESI-Fig.4. The mole absorption of compound **1** at various concentrations (from 1.0×10^{-5} to 2.0×10^{-4} mol·L^{-1}).

ESI-Fig.5. Cyclic voltammogram of **1** (1.0×10^{-3} mol·L^{-1}) (0.1 mol·L^{-1} Bu_4NClO_4, 100 mV s^{-1}) in the presence of high concentration of $HClO_4$ in DMF / CH_3CN (4:1 by volume) from 1.2 –1.6 equiv, showing the incresed proton reduction process (-0.66 V) under electrocatalysis.

ESI-Table 1. DFT-calculated bond lengths [Å] and angles [°] for $[Ni(4\text{-pedt})_2]^-$, $[Ni(4\text{-pedt})_2]^-\cdot H^+$, and $[Ni(4\text{-Hpedt})_2]^+$ and experimental data available (in italics) except those of pyridine ring.

ESI-Table 2. The energies of the frontier orbitals of four species: $[Ni(4\text{-pedt})_2]^0$, $[Ni(4\text{-pedt})_2]^-$, $[Ni(4\text{-pedt})_2]^-\cdot H^+$, $[Ni(4\text{-Hpedt})_2]^+$.

ESI-Table 3. Selected Bond Lengths (Å) and Angles (deg) of 1–3a



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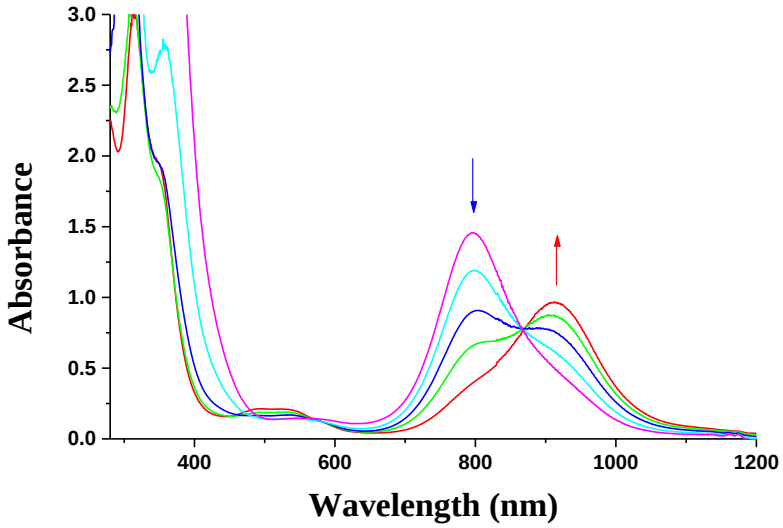

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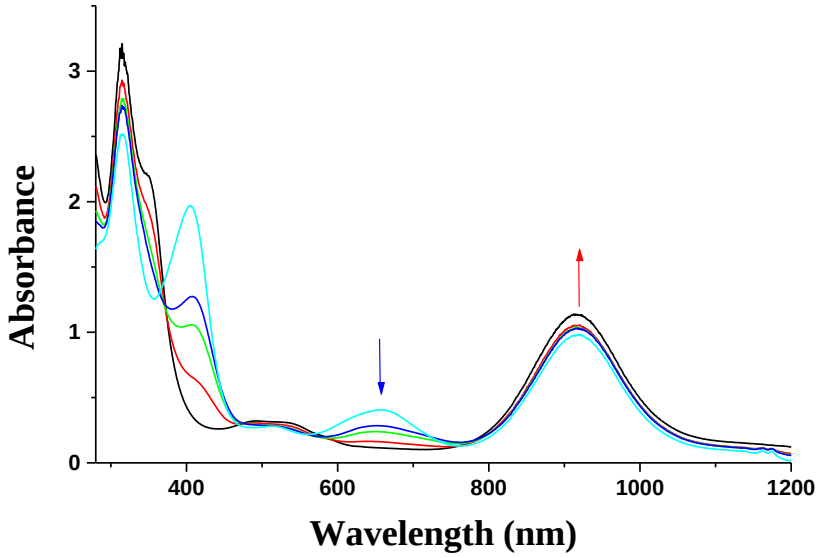

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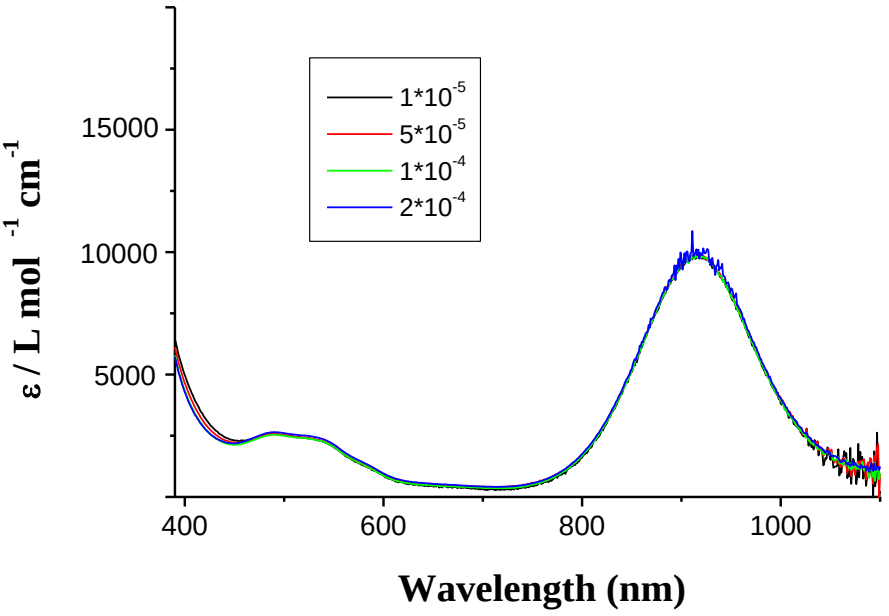

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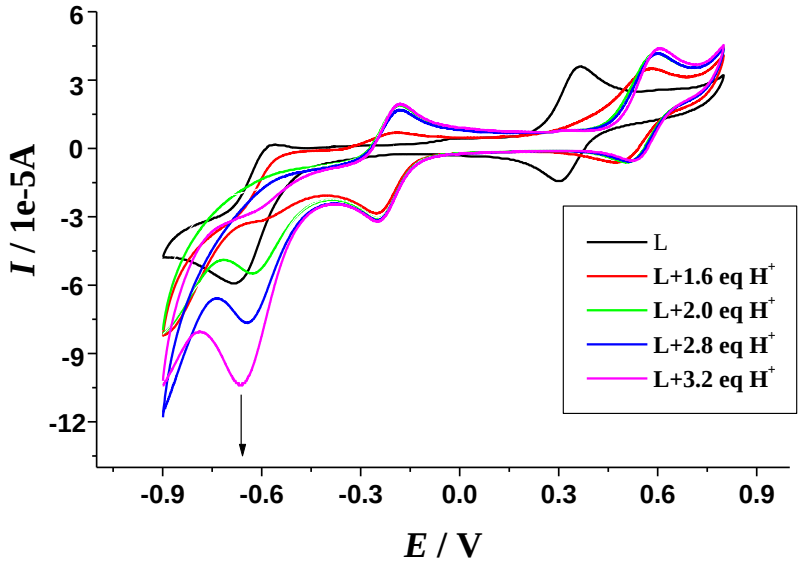

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complex	$[Ni(4\text{-}pedt)_2]^-$		$[Ni(4\text{-}pedt)_2]^-\cdot H^+$	$[Ni(4\text{-}Hpedt)_2]^+$	
Ni1–S1	2.227	*2.146*	2.222	2.205	*2.134*
Ni1–S2	2.233	*2.144*	2.238	2.235	*2.141*
Ni1–S3			2.236	2.205	*2.142*
Ni1–S4			2.235	2.235	*2.149*
S1–C1	1.756	*1.733*	1.770	1.758	*1.722*
S2–C2	1.721	*1.708*	1.689	1.689	*1.706*
S3–C8			1.731	1.758	*1.754*
S4–C9			1.703	1.689	*1.704*
C1–C2	1.368	*1.353*	1.390	1.387	*1.376*
C8–C9			1.381	1.387	*1.347*
S1–Ni1–S2	90.75	*91.22*	90.91	90.83	*91.52*
S3–Ni1–S4			90.50	90.83	*90.98*

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	$[Ni(4\text{-}pedt)_2]^0$	$[Ni(4\text{-}pedt)_2]^-$		$[Ni(4\text{-}pedt)_2]^-\cdot H^+$		$[Ni(4\text{-}Hpedt)_2]^+$	
		α	β	α	β	α	β
LUMO	–4.62	0.52	–0.66	–2.94	–3.46	–5.35	–6.29
SOMO	–6.20	–2.06	–2.40	–4.91	–5.33	–7.66	–7.99
SOMO–1	–7.35	–2.87	–3.30	–5.70	–6.12	–8.42	–8.83
SOMO–2	–7.41	–3.61	–3.66	–6.42	–6.46	–9.21	–9.25

ESI-Table 3. Selected Bond Lengths (Å) and Angles (deg) of **1**–**3**[a]

		1	
Ni1–S1	2.1457(14)	Ni1–S2	2.1444(14)
S1–C1	1.733(4)	S2–C2	1.708(4)
C1–C2	1.353(6)		
S2–Ni1–S2#1	180.0	S2–Ni1–S1#1	91.22(4)
S2–Ni1–S1#1	88.78(4)	S2–Ni1–S1#1	88.78(4)
S2–Ni1–S1	91.22(4)	S1–Ni1–S1#1	180.0
		2	
Ni1–S1	2.1380(17)	Ni1–S2	2.1480(18)
Ni1–S3	2.1475(17)	Ni1–S4	2.1517(19)
S1–C1	1.730(6)	S2–C2	1.687(6)
S3–C8	1.740(6)	S4–C9	1.693(5)
C1–C2	1.369(7)	C8–C9	1.352(7)
S1–Ni1–S3	179.16(8)	S1–Ni1–S4	88.43(6)
S1–Ni1–S2	90.86(6)	S3–Ni1–S4	91.31(6)
S3–Ni1–S2	89.37(6)	S2–Ni1–S4	177.88(7)
		3	
Ni1–S1	2.134(3)	Ni1–S2	2.141(3)
Ni1–S3	2.142(3)	Ni1–S4	2.149(3)
S1–C1	1.722(8)	S2–C2	1.706(8)
S3–C8	1.754(8)	S4–C9	1.704(8)
C1–C2	1.376(10)	C8–C9	1.347(10)
S1–Ni1–S2	91.53(10)	S1–Ni1–S4	88.78(10)
S1–Ni1–S3	179.32(13)	S2–Ni1–S4	179.17(13)
S2–Ni1–S3	88.73(10)	S3–Ni1–S4	90.97(10)

a: Symmetry transformation used to generate equivalent atoms: #1: 1– *x*, 1 – *y*, 1– *z*.