

Electronic Supplementary Information

A Simple Nickel Bis(Dithiolene) Complex as an Excellent n-Type Molecular Semiconductor for Field-Effect Transistors

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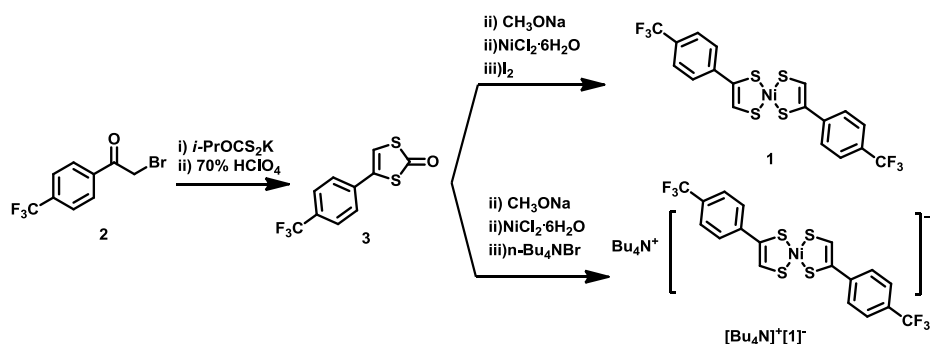
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1. Instruments

^1H NMR spectroscopies were conducted with a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta=0$ ppm) as an internal standard. EI-MS was carried out by Finnigan Trance mass spectrometer. Elemental analysis was performed by Vario EL III (German). Thermal analysis was performed on a Netzsch STA449C thermal analyzer at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in nitrogen at a flow rate of $50\text{ cm}^3\text{ min}^{-1}$ for thermogravimetric analysis (TGA). UV-visible spectra were obtained using a Shimadzu UV- 2550 spectrometer. Cyclic voltammetry (CV) was carried out on a CHI voltammetric analyzer in a three-electrode cell with a Pt counter electrode, a Ag/AgCl reference electrode, and a glassy carbon working electrode at a scan rate of 10 mV/s . The film morphology was analyzed in air using a Nanoscope III atomic force microscope (Digital Instruments) operated in tapping mode. XRD of thin films was performed in the reflection mode at 40 kV and 200 mA with Cu K α radiation using a 2 kW Rigaku D/max-2500 X-ray diffractometer. Measurements of electric properties were carried out at room temperature using a Keithley 4200 SCS semiconductor parameter analyzer.

2. Synthesis and characterization data of 1

The synthetic route of complex **1** is shown in **Scheme S1**. Potassium O-isopropylxanthate and compound **2** were synthesized according to the literature methods.



Scheme S1. Synthesis of **1** and $[\text{Bu}_4\text{N}]^+[\mathbf{1}]^-$

Synthesis of 4-(4-(trifluoromethyl)phenyl)-1,3-dithiol-2-one (3): Compound **2** (5.61 g, 20 mmol) and potassium O-isopropylxanthate (3.51 g, 20 mmol) were dissolved in 50

ml acetone, reflux for 1 h. The mixture was cooled to room temperature, filtered and washed with chloroform. The filtrates were combined and removed in vacuum, producing the crude intermediate. Then it was re-dissolved in 30 ml chloroform and 70% perchloric acid (4 ml) was added dropwise. The mixture was then refluxed for 6 h. The resulting dark product was poured into ice–water followed by extraction with chloroform. The combined extract was dried with anhyd. Na_2SO_4 , then chromatographed on a silica gel (eluent: petroleum: chloroform = 4: 1), affording a pale yellow solid (3.4 g, overall yield 61.6%). ^1H NMR (300Hz, CDCl_3) δ 6.99(1H, s), 7.55(2H, d), 7.68(2H, d).

Synthesis of 1: At room temperature, compound **3** (1.05 g, 4.0 mmol) and sodium methoxide (1.08 g, 20 mmol) were suspended in 20 ml degassed methanol and stirred under argon for 1 h, affording an orange solution. A 6 ml methanol solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.47 g, 2.0 mmol) was added, and the resulting reaction mixture was stirred for 0.5 h. Then a 6 ml acetonitrile solution of I_2 (1.03 g, 4.0 mmol) was added in air, and the reaction mixture was continuous stirred for 0.5 h resulting in the formation of a dark green precipitate. The target product was obtained by filtration and recrystallization from chloroform (0.56 g, yield 53.3%). ^1H NMR (300Hz, CDCl_3) δ 7.12(4H, d), 8.10(4H, d), 9.77(2H, s). MS (EI) m/z : 525.9 (M^+). Anal. Calcd. for $\text{C}_{18}\text{H}_{10}\text{F}_6\text{NiS}_4$: C, 41.01; H, 1.91. Found: C, 41.28; H, 1.64 (%). (Note: ^{13}C NMR signal cannot be obtained due to the low solubility of complex **1**.)

Synthesis of $[\text{Bu}_4\text{N}]^+[\text{I}]^-$: At room temperature, compound **3** (0.79 g, 3.0 mmol) and sodium methoxide (0.81 g, 15 mmol) were suspended in 20 ml degassed methanol and stirred under argon for 1 h, affording an orange solution. A 6 ml methanol solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.35 g, 1.5 mmol) was added, and the resulting reaction mixture was stirred for 0.5 h. Then a 6 ml methanol solution of $n\text{-Bu}_4\text{NBr}$ (0.96 g, 3.0 mmol) was added in air, and the reaction mixture was continuous stirred for 0.5 h. Then it was concentrated to about 5 ml, affording the dark red precipitate. The target product was obtained by filtration and washed with water and methanol (0.30 g, yield 26.1%). Anal. Calcd. for $\text{C}_{34}\text{H}_{46}\text{F}_6\text{NNiS}_4$: C, 53.06; H, 6.02; N, 1.82. Found: C, 53.38; H, 6.52; N, 1.45 (%).

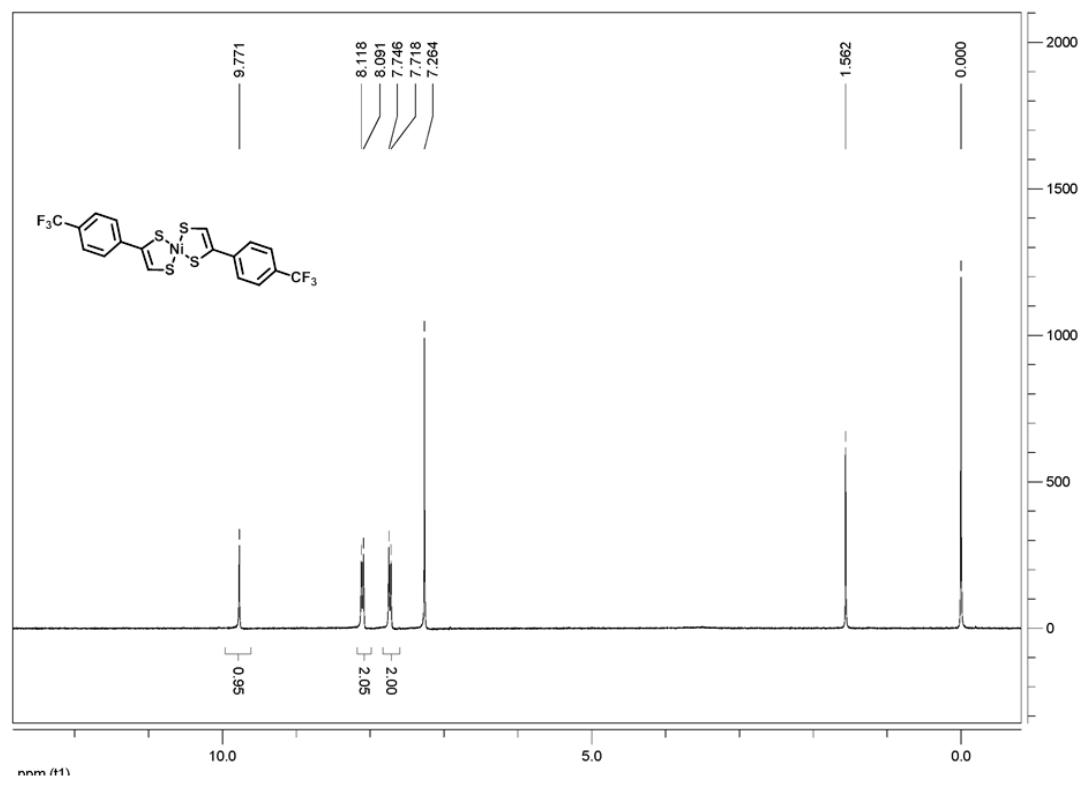


Figure S1. ¹H NMR spectra of complex **1**

3. Basic physical properties of **1**

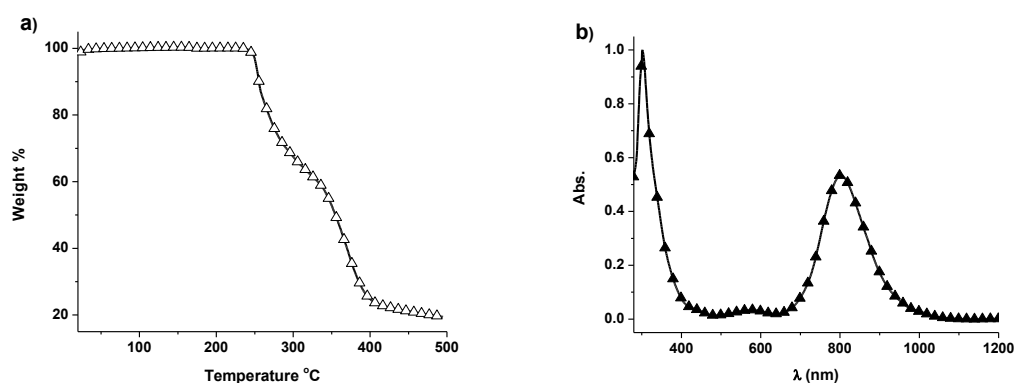


Figure S2. a) Thermogravimetric analysis. b) Normalized UV-Vis-NIR absorption spectra in chloroform

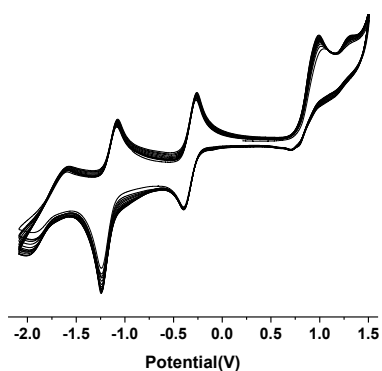


Figure S3. Cyclic voltammograms of **1** in dichloromethane solution containing 0.1 M Bu_4NPF_6 with repeated scan for 10 cycles, the potential values obtained were converted to the values versus the ferrocenium/ferrocene (Fc^+/Fc) standard.

Table S1 Relevant data of basic physical properties of **1**

	T_{dep}^a (°C)	λ_{max}^b (nm)	HOMO ^c (eV)	LUMO ^c (eV)	$\Delta E_{\text{g}}^{\text{el } c}$ (eV)
1	252	302, 804	-5.59	-4.51	1.08

^a Calculated from TGA of 5% weight loss. ^b Measured in 10^{-5} M chloroform. ^c Calculated from CV results, the unit of potential is versus the ferrocenium/ferrocene (Fc^+/Fc) standard.

4. DFT calculations of **1**

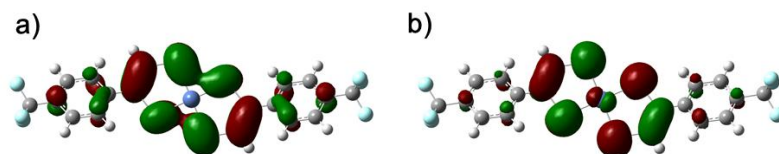


Figure S4. Electron-density-distribution of a) HOMO and b) LUMO of **1**

Table S2 Calculation data for reorganization energy of **1**

	$E^0(g^0)$	$E^0(g^a)$	$E^0(g^c)$	$E^a(g^0)$	$E^a(g^a)$	$E^c(g^0)$	$E^c(g^c)$	λ_e	λ_h
1	-3053.625	-3053.747	-3053.350	-3053.622	-3053.751	-3053.620	-3053.355	0.20	0.27

5. Selected crystal structure data

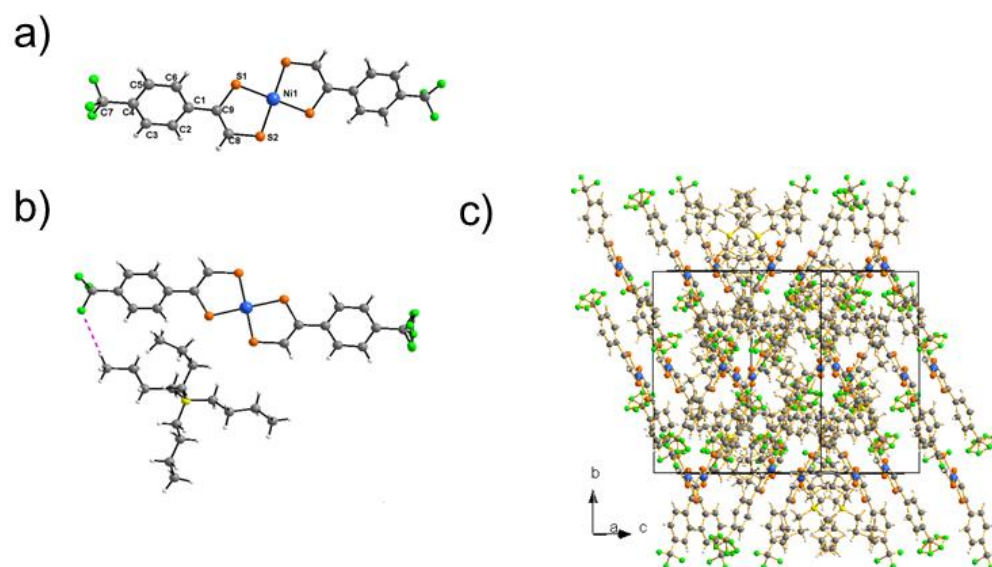


Figure S5. a) Crystal structure of **1** with labelled atoms. b, c) Crystal structure of $[\text{Bu}_4\text{N}]^+[\mathbf{1}]^-$

Table S3. Summary of Crystal Structures data of **1** and [Bu₄N]⁺[**1**]⁻

	1	[Bu ₄ N] ⁺ [1] ⁻
CCDC No.	836362	836363
Chemical Formula	C ₁₈ H ₁₀ F ₆ NiS ₄	C ₃₄ H ₄₆ F ₆ NNiS ₄
Formular Weight	527.21	769.67
Temperature	293	293
Space Group	P2(1)/c	C2/c
Unit Cell Lengths(Å)	a = 11.924	a = 27.357
	b = 9.3396	b = 17.901
	c = 8.7683	c = 16.611
	α = 90	α = 90
Unit Cell Angles(°)	β = 91.294	β = 103.722
	γ = 90	γ = 90
	976.2	7545
Cell Volume (Å ³)	976.2	7545
Z, Calculated Density(g cm ⁻³)	2, 1.794	8, 1.355
F ₀₀₀	528.0	3224.0
Reflections collected / unique	5278/1918	16866/5624
	[R(int) = 0.0232]	[R(int) = 0.0669]
R(reflections)	0.0604	0.0509
wR2(reflections)	0.1760	0.1261
Goodness-Of-Fit on F ²	1.063	1.020

Table S4. Selected bond lengths and angles as well as dihedral angles of **1** and [Bu₄N]⁺[**1**]^{-a}

	In 1	In [Bu ₄ N] ⁺ [1] ^{-b}
Bond Length(Å)		
Ni(1)-S(1)	2.1339(11)	2.1372(14), 2.1468(14)
Ni(1)-S(2)	2.1144(12)	2.1366(14), 2.1298(14)
C(9)-S(1)	1.7059(46)	1.7291(50), 1.7305(49)
C(8)-S(2)	1.6867(48)	1.7004(50), 1.6993(50)
C(8)-C(9)	1.3670(69)	1.3525(73), 1.3538(73)
C(1)-C(9)	1.4793(65)	1.4692(70), 1.4647(68)
C(1)-C(2)	1.3858(71)	1.3750(72), 1.3564(74)
C(1)-C(6)	1.3896(67)	1.3880(72), 1.3909(73)
C(2)-C(3)	1.3777(80)	1.3814(82), 1.3737(73)
C(3)-C(4)	1.3711(81)	1.3595(83), 1.3828(76)
C(4)-C(5)	1.3893(74)	1.3621(74), 1.3578(78)
C(5)-C(6)	1.3710(69)	1.3754(73), 1.3733(71)
C(4)-C(7)	1.4944(79)	1.4803(89), 1.5020(88)
Bond Angles(°)		
S(2)-Ni(1)-S(1)	91.721(44)	91.265(54), 91.383(54)
S(1)-Ni(1)-S(2) #1 ^c	88.279(44)	88.346(55), 89.085(55)
C(9)-S(1)-Ni(1)	104.739(162)	104.982(176), 104.694(175)
C(8)-S(2)-Ni(1)	104.076(166)	104.142(176), 103.959(176)
C(8)-C(9)-S(1)	117.723(359)	117.755(370), 117.277(369)
C(1)-C(9)-S(1)	119.897(328)	118.523(357), 119.590(353)
C(9)-C(8)-S(2)	121.740(374)	121.804(403), 122.401(402)
C(6)-C(1)-C(9)	121.336(417)	121.087(463), 122.275(461)
C(2)-C(1)-C(9)	119.950(424)	122.276(472), 121.821(466)

C(3)-C(4)-C(7)	120.292(507)	119.340(528), 119.540(491)
Dihedral Angles(^o)		
Between two dithiolene rings	0.00(12)	3.988(42)
Dithiolene ring and trifluoromethylphenyl ring	34.504(123)	34.616(130), 17.225(128)
^a For the atom label, please refer to Figure S5a.		
^b Two values are reported since the [1] ⁻ anion does not lie about an inversion centre.		
^c #1 label in S(2)#1 indicates that this atom is at equivalent position (1-x, 1-y, -z).		

6. FET fabrication and characterization of **1**

FET devices were fabricated with a top-contact configuration. A heavily doped n-type Si wafer with a 300 nm-thick layer of thermally grown SiO₂ and a capacitance of 10 nF cm⁻² was used as the gate. OTS and PS were used as a self-assembled surface modifier for SiO₂, respectively. Thin films of **1** (50 nm) were formed on substrates by high-vacuum evaporation (3×10⁻⁴ Pa). After that, the Au source and drain contacts (50 nm) were deposited onto the organic layer through a shadow mask under high vacuum. The channel length (L) and width (W) were 80 μm and 8800 μm, respectively.

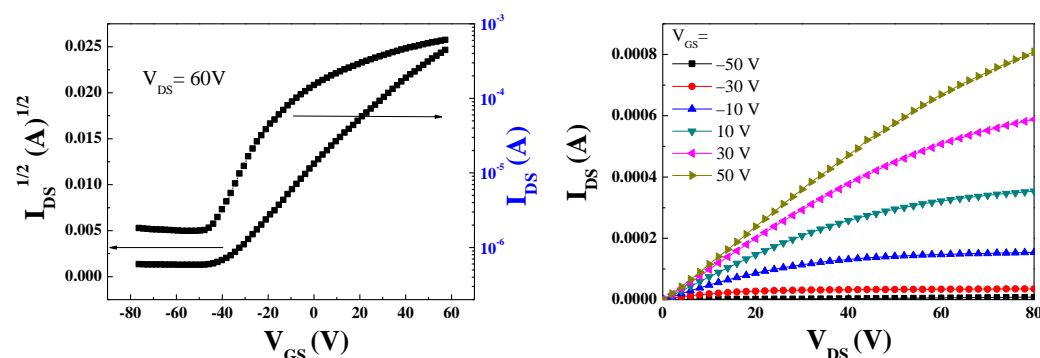


Figure S6. I–V characteristics of **1** FET prepared on OTS-SiO₂/Si substrate deposited at $T_{\text{sub}} = 70\text{C}^{\circ}$, under nitrogen atmosphere: a) Plot of I_{DS} vs. V_{GS} for $V_{\text{DS}} = 60\text{ V}$. b) Plot of I_{DS} vs. V_{DS} .

7. Stability testing of **1**

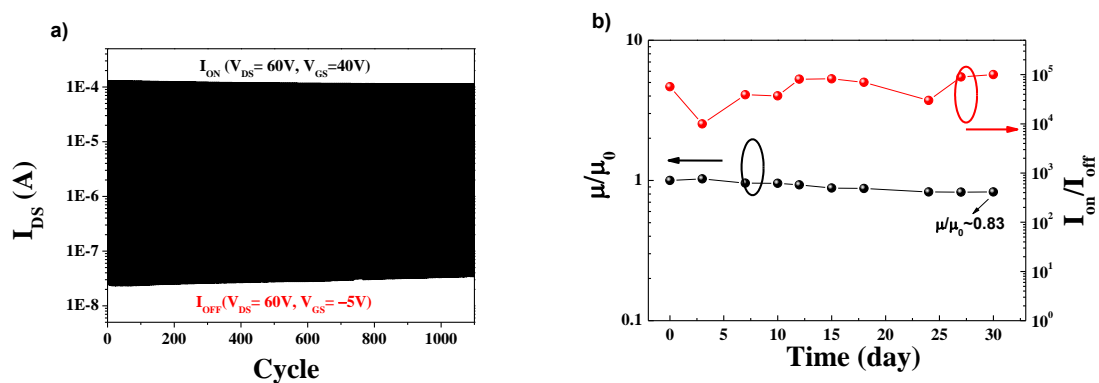


Figure S7. a) Stability test of on/off current over 1000 cycles (on PS-SiO₂/Si substrate). b) Ambient stability test for 30 days (on PS-SiO₂/Si substrate).

8. AFM image and XRD pattern of thin film of 1

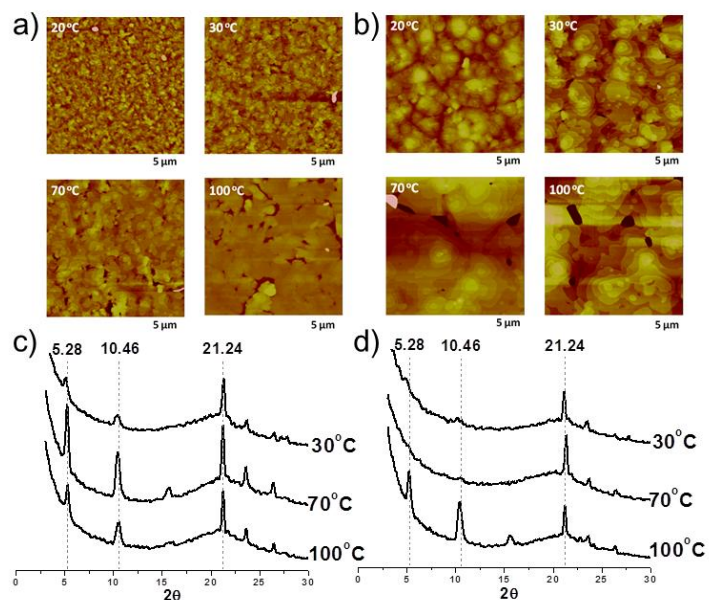


Figure S8. AFM images of the thin films of the complex **1**: a) on PS-SiO₂/Si substrate, b) on OTS-SiO₂/Si substrate. XRD patterns of the thin films of the complex **1**: c) on PS-SiO₂/Si substrate, d) on OTS-SiO₂/Si substrate.