# High electron mobility in nickel bis(dithiolene) complexes

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The charge-carrier mobilities for three Ni bis(dithiolene) complexes have been determined using the steady-state space-charge limited current technique. A high mobility of 2.8 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> was observed for one compound, which exhibits a  $\pi$ -stacked columnar structure, in an annealed unsymmetrical melt-processed device. Energy-level considerations and field-effect transistor measurements suggest that this value represents an electron mobility. However, saturation mobilities measured for this compound in spin-coated field-effect transistors were found to be over two orders of magnitude lower than the space-charge limited current values. X-Ray diffraction shows a difference in morphology between thick melt-processed and thin spin-coated films and, therefore, a significant change in intermolecular packing between the device types may explain the discrepancy in mobilities obtained using the two techniques.

# Introduction

Solution- or vapor-processible molecular or polymeric materials with high charge-carrier mobilities are critical to the development of efficient organic light-emitting diodes (OLEDs), photovoltaic cells, and field-effect transistors (FETs).<sup>1–3</sup> The hopping-type conduction mechanism in semiconductors (*i.e.* for most organic electronic materials) can be regarded as a series of electron-transfer (ET) reactions between the neutral species and its radical cation (in the case of hole-transport materials) or radical anion (electron-transport). According to Marcus theory, the barrier to such "self-exchange" ET reactions,  $\Delta G^{\ddagger}$ , depends principally on the reorganization energy,  $\lambda$ , while the pre-exponential factor influencing the ET rate increases with the intermolecular electronic coupling,  $H_{AB}$ .

The vast majority of molecular and polymeric species used as transport materials to date have been based upon the lighter p-block elements. However, transition-metal (TM) compounds have several attractive features for charge transport applications; often frontier orbitals are more-or-less non-bonding (suggesting low reorganization energies), yet with some delocalization onto the ligands (favoring intermolecular overlap). Moreover, redox processes are commonly fully reversible (indicating that the charge-bearing species are reasonably kinetically stable), with potentials that can be tuned over a wide range through variation of metal and/or ligand. Importantly, there exists empirical evidence for high self-exchange rates in solution for many metal-organic redox systems, suggesting high ET rates might also be obtainable in films.4-7 Nevertheless, TM complexes have been rather underexplored. Several studies have focused on the effect of incorporating metals into the main chains of conjugated polymers,<sup>8-10</sup> while Thompson and co-workers have used organocobalt species as hole-transport materials in OLEDs;<sup>11</sup> however, studies of carrier mobilities of neutral molecular d-metal complexes remain scarce. Mobilities have been measured in d- and f-block phthalocyanine complexes, although in most cases the redox processes involved in charge transport are likely to involve orbitals substantially localized on the ligands rather than the metal centers.<sup>12</sup> Re(I) and Ru(II) 2,2'-bipyridyl complexes and a Re(I) diimine complex have been shown to exhibit bipolar charge transport character with both electron and hole mobilities in the order of  $10^{-4}$  to  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> measured using the time-of-flight method (TOF).<sup>13,14</sup>

Very recently, FET hole mobilities as high as  $3.8 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> have been reported for Ni bis(*o*-diiminobenzo-semiquinonate) complexes such as I<sup>15</sup> (Fig. 1) and a methyl-substituted analogue.<sup>16</sup> Ni bis(dithiolene) complexes have also recently been used to fabricate FETs with electron mobilities ranging from  $3.0 \times 10^{-6}$  to  $2.0 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for II<sup>16</sup> and from *ca*.  $10^{-4}$  to *ca*.  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for III<sup>17</sup> (Fig. 1). Compound III was also found to exhibit comparable FET hole mobility and the transistors have been used to fabricate complementary circuits.<sup>17</sup>



Fig. 1 Square-planar Ni complexes previously studied as transport materials.

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Attractive features of Ni bis(dithiolene) complexes for applications as molecular transport materials<sup>18-22</sup> include: extensive delocalization of their frontier molecular orbitals over the entire complex (suggesting the possibility of significant intermolecular overlap in films, and low reorganization energies upon reduction and/or oxidation); thermal and photochemical stability; widely tunable and reversible redox chemistry (often forming chemically isolable anions); small structural changes observed on reduction (suggesting low reorganization energies for this process); and an approximately planar shape (offering the possibility of self-assembly into columnar mesophases). In addition to the recent work mentioned above, which shows that neutral Ni bis(dithiolene) complexes can act as ET materials in FETs, the potential for substantial intermolecular overlap and, consequently, for interesting electronic behavior has been shown by previous work on salts of reduced metal bis(dithiolene) anions; for example, many species of  $[X]_x[M(dmit)_2]$  (X = organic cation, dmit = 1,3-dithiol-2-thione-4,5-dithiolato) contain stacked bis(dithiolene) units and are metallic, [Me<sub>4</sub>N]<sub>0.5</sub>[Ni(dmit)<sub>2</sub>] is a superconductor under pressure,<sup>23</sup> and an electron mobility of ca. 0.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> has been measured in an FET incorporating [N-octadecylpyridinium][Ni(dmit)<sub>2</sub>].<sup>24</sup> Here we report on investigations of charge transport in neutral Ni bis(dithiolene) complexes 1, 2, and 3 (Fig. 2).

## **Results and discussion**

Complex 1 was synthesized as described by Ohta and coworkers, who reported that it exhibits a hexagonal columnar discotic liquid crystalline (LC) mesophase between 72– 108 °C.<sup>25–27</sup> Complexes 2 and 3 are new compounds and were synthesized from the corresponding diketones as described in the Experimental. Polarized optical microscopy (POM) and differential scanning calorimetry (DSC) measurements are consistent with 2 forming an LC mesophase between 140–220 °C;



Fig. 2 Syntheses and structures of the Ni bis(dithiolene) complexes studied in this work.

X-ray diffraction data at 150 °C (Fig. 3a) reveal a solitary, intense peak at low angle, indicating this mesophase to be lamellar, with 43.9 Å interlayer spacing. In contrast, **3** displays no LC behavior, melting at 219 °C. All three species exhibit reversible one-electron molecular oxidations and reductions in dichloromethane; the potentials are summarized in Table 1, along with condensed-phase HOMO and LUMO energies estimated by comparison of the potentials and electron affinities have been measured directly.<sup>28–30</sup> These values may be compared to 5.2 and 4.3 eV previously estimated for the HOMO and LUMO energies of **III** from electrochemical data.<sup>17</sup>



Fig. 3 (a) X-Ray diffraction data for mesophase of 2 measured at 150 °C, and POM photograph of SCLC device fabricated with 2 (inset); (b) X-ray diffraction data for films of 1 in SCLC (top, solid line) and FET (bottom, dotted line) devices (offset for clarity), with corresponding POM photograph of SCLC device (inset). Image sizes:  $250 \ \mu\text{m} \times 160 \ \mu\text{m}$ .

**Table 1** Electrochemical potentials (V, *vs.*  $FeCp_2^{+/0}$ , in  $CH_2Cl_2$ -0.1 M [<sup>*n*</sup>Bu<sub>4</sub>N][PF<sub>6</sub>]) and estimated solid-state orbital energies<sup>*a*</sup> (eV) for nickel bis(dithiolene) complexes

Compound	$E_{1/2}^{+/0}$	$E_{1/2}^{0/-}$	$E_{1/2}^{-/2-}$	$E_{\rm HOMO}$	E <sub>LUMO</sub>
1 2 3	+0.46 +0.61 +0.61	$-0.55 \\ -0.51 \\ -0.48$	-1.34 -1.30 -1.28	5.6 5.8 5.8	4.1 4.1 4.1
<sup>a</sup> Calculated	as described	d in referen	ce 28.		

The charge-carrier mobilities of 1, 2 and 3 were studied by the steady-state space-charge limited current (SCLC) technique.<sup>31-34</sup> For these measurements, 5 µm-thick samples were fabricated by melting each compound between two glass slides coated with conductive electrode materials. Melting was achieved on a hot plate in air at temperatures of 120, 230 and 220 °C for 1, 2 and 3 respectively. Devices with injecting contacts exhibit nonlinear current-voltage characteristics that are composed of a linear ohmic region at low current densities (J) and a nearly quadratic region (see inset of Fig. 4), due to space-charge effects, at higher J. Effective mobility values can be extracted from fitting the nearly quadratic régime to a modified Mott-Gurney equation.<sup>32,34</sup> When using indium tin oxide (ITO) as the injecting contact, the effective carrier mobilities of 1 and 2 were determined to be 0.85 and 2.5  $\times$  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, while the effective carrier mobility determined for complex 3 using the same method was determined to be much smaller, ca. 4.5  $\times$  10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Although the SCLC technique does not allow us to distinguish whether these values represent electron or hole mobilities. energetic considerations based on the estimated orbital energies in Table 1, and additional experiments described below, suggest they are more likely to be electron mobilities. The higher mobilities determined for 1 and 2 are potentially due to the greater degree of intermolecular order present in these two materials; POM images of the corresponding devices (see Fig. 3 insets) show that room-temperature films of 1 and 2 exhibit optical textures similar to those seen in their LC phases, while, under the same conditions, films of 3 show no texture, consistent with these samples being amorphous.



Fig. 4 J-V characteristics of an ITO-1 (5 µm)-Ag device; positive bias corresponds to the Ag contact as the cathode. The inset shows a log-log plot of the data for positive bias; the solid line represents Ohm's law and the dashed line represents the SCLC model.

The material showing the highest mobility, 1, was further tested in an unsymmetrical device configuration (ITO–1 (5  $\mu$ m)–Ag). The Ag electrode has a lower workfunction than ITO, and so more efficient electron injection might be anticipated from an Ag contact. As shown in Fig. 4, the *J*–*V* characteristics of this device are strongly asymmetric, as anticipated from the differences in workfunction between the two contacts. The highest current densities are measured when Ag is the cathode, consistent with more facile injection of electrons into the LUMO level of 1. With this increased injection efficiency from the Ag electrode, the effective mobility derived from an SCLC analysis is 2.8 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.

We have also investigated the utility of 1 in an FET device with an Ag source and drain electrodes. Current-voltage and transfer characteristics of a device with a channel width of 2000 µm and length of 100 µm are shown in Fig. 5. For the current-voltage characteristics shown in Fig. 5a, the gatesource voltage  $V_{GS}$  was increased from 0 to 60 V in 20 V steps. When operated as n-channel transistors, these devices exhibit characteristic saturation behavior, whereas under negative gate bias the transistors did not operate in p-channel mode, confirming that injection of electrons from the electrodes into 1 is the main origin of the current densities measured in the SCLC measurements described above (FETs based on III function as both n and p-channel transistors, but (i) the estimated HOMO of III is higher and (ii) Au, rather than Ag, contacts were used). Using eqn (1), see Experimental, an effective mobility value of  $1.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was calculated from the transfer characteristic shown in Fig. 5b. A linear fit to the  $\sqrt{I_{\rm DS}}$  vs.  $V_{\rm GS}$  data yielded a threshold voltage of 4.6 V and semi-logarithmic plots of  $I_{DS}$  vs.  $V_{GS}$  ( $I_{DS}$  = drain-source current) yielded an on-off current ratio of >10<sup>5</sup> and a



**Fig. 5** (a) Current–voltage characteristics ( $I_{\text{DS}}$  vs.  $V_{\text{DS}}$ ) as the gate voltage ( $V_{\text{GS}}$ ) is increased from 0–60 V in 20 V steps (bottom to top); (b) transfer characteristics ( $I_{\text{DS}}$  and  $\sqrt{I_{\text{DS}}}$  vs.  $V_{\text{GS}}$ ) for a bottom-contact FET device using 100 nm of **1** with  $W = 2000 \,\mu\text{m}$ ,  $L = 100 \,\mu\text{m}$ .

sub-threshold slope of 1.5 V decade<sup>-1</sup>. Mobility values were found to decrease (in general) with shorter channel length, with typical values  $1.0 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in devices with a channel width of 2000 µm and length of 25 µm.

The mobility values measured in FET geometry for 1 are comparable to, or even slightly exceed, those measured in previously studied Ni bis(dithiolene) complexes.<sup>16,17</sup> However, they are several orders of magnitude lower than that measured for 1 using SCLC. X-Ray diffraction measurements (Fig. 3b) reveal that samples of 1 in melt-processed SCLC and spincoated FET devices differ in morphology and, consequently, in the degree of long-range intermolecular order present in the films. Samples of 1 in the SCLC devices show many Bragg peaks; a single strong reflection is seen at low angle, followed by a series of weaker peaks that, together, may be indexed to a simple rectangular 2-D unit cell (unit cell parameters  $34.9 \times$ 14.2 Å), suggesting that a columnar arrangement of discotic Ni dithiolene cores is retained in this substantially crystalline sample. The cell *a*-parameter is approximately consistent with the core-core distance determined for bulk samples of 1 in its hexagonal columnar discotic LC phase (unit cell 35.6 Å);<sup>26</sup> the b-parameter is considerably smaller, indicating that the columns adopt a tilted arrangement in the unit cell, with the normal to the molecular plane inclined at ca. 66° to the columnar stacking direction. This assignment is in agreement with POM images of the SCLC devices, which display the fanshaped texture characteristic of a columnar discotic LC phase (Fig. 3b inset). Presumably, since the sample is microcrystalline, columnar stacks are arranged in all possible directions on the substrate (although not necessarily isotropically). Accordingly some columns will be aligned with the  $\pi$ -stacking between Ni dithiolene cores oriented perpendicular to the substrate, affording favorable pathways for charge transport between the electrodes and allowing for the high mobilities observed in SCLC measurements. In contrast, X-ray diffraction shows that 1 adopts a lamellar structure in the FET devices studied, with a 31.9 Å interlayer spacing indicating that the molecular planes lie at ca. 26° to the stacking direction. Thus, while there is likely to be some intralayer  $\pi$ -overlap, the long-range columnar ordering observed for the SCLC devices is not present in the FET devices. These changes in morphology are attributed to the differences in processing used to fabricate the thick and thin films used for SCLC and FET experiments, respectively.

# Experimental

# General

All reactions were carried out under an inert atmosphere of dry N<sub>2</sub> using standard Schlenk techniques. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on Varian Mercury 300 spectrometers and referenced to the residual proton solvent signals. Elemental analyses were performed at Atlantic Microlab, Inc., Norcross, GA. High-resolution mass spectral analyses were performed by the Bioanalytical Mass Spectrometry Facility at Georgia Institute of Technology. POM images were acquired using an Olympus BX51 microscope. DSC measurements were performed using a Shimadzu DSC/TGA 50, under an N<sub>2</sub>-purged atmosphere, at a scan rate of 10 °C min<sup>-1</sup>. X-Ray

diffraction data were collected using a  $\theta$ - $\theta$  Scintag powder diffractometer (Cu K $\alpha$  radiation) in the diffraction angle (2 $\theta$ ) range between  $2^{\circ}$  and  $30^{\circ}$  in  $0.02^{\circ}$  steps. Samples of 1 were prepared on a copper plate and measured at 150 °C, while samples of 2 were prepared on ITO-coated glass substrates by melt-processing (SCLC devices) or Si wafers by spin-coating (FET devices) as described below and measured at room temperature. 2-D unit cell parameters for the SCLC sample of 1 were obtained from the first five reflections observed (after indexing), using a least-squares refinement procedure in the program Chekcell.<sup>35</sup> Electrochemical measurements were carried out under argon on dry, deoxygenated dichloromethane (distilled from CaH<sub>2</sub>) solutions, ca. 10<sup>-4</sup> M in analyte and 0.1 M in ["Bu<sub>4</sub>N][PF<sub>6</sub>], using a BAS Potentiostat, a glassy carbon working electrode, a Pt auxiliary electrode, and, as a pseudo-reference electrode, an Ag wire anodized in 1 M KCl (aq).

#### Synthesis and characterization

Nickel bis[1,2-di(3',4'-didodecyloxyphenyl)ethane-1,2-dithiolenel (1). A mixture of 3,3',4,4'-tetra-*n*-dodecyloxybenzil<sup>27</sup> (S1) (3.7 g, 3.9 mmol), phosphorus pentasulfide (3.85 g, 17 mmol) in 1,4-dioxane (100 mL) was refluxed at 110 °C for 5 h under an N<sub>2</sub> atmosphere. The reaction mixture was allowed to cool down to ca. 60 °C. The hot reaction mixture was filtered under nitrogen through a sintered glass frit, to remove unreacted yellow solid. NiCl<sub>2</sub>·6H<sub>2</sub>O (0.52 g, 2.19 mmol) in H<sub>2</sub>O (1.5 mL) was added to the filtrate and the resulting mixture was refluxed for an additional 2 h. The reaction mixture was allowed to cool down to room temperature overnight. A gravish-blue solid precipitated out of the reaction mixture and was collected by filtration. The crude product was washed with acetone and ethanol and purified by column chromatography (silica gel, dichloromethane : hexanes = 3 : 1) to give a gravish-blue solid. The solid was again washed with acetone and ethanol and dried under vacuum to give a grayish-blue solid (0.89 g, 29.8%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 (dd, J = 8.2 Hz, 1.9 Hz, 4H), 6.84 (d, J = 1.9 Hz, 4H), 6.75 (d, J = 8.5 Hz, 4H), 3.96 (t, J = 6.6 Hz, 8H), 3.75 (t, J = 6.6 Hz, 8H), 1.14-1.90 (m, J = 6.6 Hz, 8Hz), 1.14-1.90 (m, J = 6.6 Hz, 8Hz), 1.14-1.90 (m, J = 6.6 Hz, 8Hz), 1.14-1.90 (m, J = 6.6 Hz), 1.14-1.90 (m, J = 6.6 Hz), 1.14-1.90 (m,160H), 0.86 (t, J = 7.1 Hz, 12H), 0.85 (t, J = 7.1 Hz, 12H).  $^{13}C{^{1}H}$  NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  180.38, 149.81, 148.39, 134.33, 121.85, 114.19, 112.69, 69.09, 32.01, 29.84, 29.78, 29.75, 29.54, 29.48, 29.28, 29.13, 26.11, 22.78, 14.22. IR (cm<sup>-1</sup>): 2923, 2853, 1594, 1514, 1356, 1260, 1139. UV (CHCl<sub>3</sub>)  $\lambda_{max}/nm$  ( $\epsilon/M^{-1}$  cm<sup>-1</sup>): 310 (57450), 348 (sh, 31395), 572 (3680), 638 (sh, 3360), 962 (35210). HRMS-MALDI (m/z):  $[M]^+$  calcd for  $C_{124}H_{212}NiS_4O_8$ , 2017.4438; found, 2017.4368. Anal. calcd for C124H212NiS4O8: C, 73.80; H, 10.59; S, 6.36; found: C, 73.88; H, 10.74; S, 6.29%.

**4,4'-{4-[5-(3,4,5-Trisdecyloxyphenyl)-[1,3,4]oxadiazol-2-yl]benzyloxy}benzil (S2).** A mixture of 4,4'-dihydroxybenzil<sup>36</sup> (0.48 g, 2 mmol), 2-(4-bromomethylphenyl)-5-(3,4,5-trisdecyl-oxyphenyl)-[1,3,4]oxadiazole<sup>37</sup> (3.14 g, 4 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.55 g, 4 mmol) in DMF (60 mL) was heated at 100 °C for 3 days. The reaction mixture was allowed to cool down to room temperature and poured into H<sub>2</sub>O. The mixture was extracted with  $CH_2Cl_2$ , and the organic layer was washed with

H<sub>2</sub>O and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure. The crude product was washed with hot hexanes to give a white solid (1.61 g, 48.8%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.14 (d, *J* = 8.5 Hz, 4H), 7.95 (d, *J* = 8.8 Hz, 4H), 7.57 (d, *J* = 8.2 Hz, 4H), 7.29 (s, 4H), 7.04 (d, *J* = 8.8 Hz, 4H), 5.21 (s, 4H), 4.06 (t, *J* = 6.6 Hz, 8H), 4.02 (t, *J* = 6.6 Hz, 4H), 1.70–1.88 (m, 12H), 1.20–1.54 (m, 84H), 0.86 (t, *J* = 6.6 Hz, 18H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  192.94, 164.66, 163.79, 163.40, 153.44, 141.28, 139.43, 132.34, 127.65, 127.17, 126.57, 123.78, 118.26, 115.01, 105.35, 73.62, 69.55, 69.37, 32.00, 31.96, 30.40, 29.79, 29.73, 29.70, 29.64, 29.46, 29.41, 29.38, 26.15, 22.77, 14.22. HRMS-MALDI (*m*/z): [M+H]<sup>+</sup> calcd for C<sub>104</sub>H<sub>151</sub>N<sub>4</sub>O<sub>12</sub>. 1648.1323; found, 1648.1373. Anal. calcd for C<sub>104</sub>H<sub>150</sub>N<sub>4</sub>O<sub>12</sub>: C, 75.78; H, 9.17; N, 3.40; found: C, 75.48; H, 9.13; N, 3.37%.

Nickel bis[1,2-di(4-{4-[5-(3,4,5-trisdecyloxyphenyl)-[1,3,4]oxadiazol-2-vl]-benzvloxy}-phenvl)ethane-1,2-dithiolene] (2). A mixture of S2 (0.99 g, 0.6 mmol), phosphorus pentasulfide (0.4 g, 0.9 mmol), in 1,4-dioxane (20 mL) was refluxed at 110  $\,^\circ\!C$  for 4 h under an  $N_2$  atmosphere. The reaction mixture was allowed to cool down to ca. 60 °C and filtered through a sintered glass frit under nitrogen. NiCl<sub>2</sub>·6H<sub>2</sub>O (72 mg, 0.3 mmol) dissolved in H<sub>2</sub>O (1 mL) was added to the filtrate. The resulting mixture was refluxed at 110 °C for an additional 2 h. The reaction mixture was allowed to cool down to room temperature. The reaction mixture was poured into ethanol. A dark green solid was collected by filtration and washed with ethanol. The crude product was purified by column chromatography (silica gel, hexanes : ethyl acetate = 1 : 1) to give a dark green solid (0.19 g, 18.5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.13 (d, J = 8.2 Hz, 8H), 7.57 (d, J = 8.2 Hz, 8H), 7.33 (d, J = 8.8 Hz, 8H), 7.29 (s, 8H), 6.88 (d, J = 9.1 Hz, 8H), 5.12 (s, 8H), 4.05 (t, J = 6.3 Hz, 16H), 4.02 (t, J = 6.6 Hz, 8H), 1.70–1.88 (m, 24H), 1.16–1.54 (m, 168H), 0.863 (t, J = 6.6 Hz, 12H), 0.859 (t, J = 6.6 Hz, 24H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 180.14, 164.60, 163.87, 158.95, 153.41, 141.22, 140.13, 134.62, 130.35, 127.68, 127.03, 123.54, 118.29, 114.63, 105.31, 73.60, 69.35, 31.96, 30.40, 29.79, 29.73, 29.70, 29.64, 29.48, 29.41, 29.38, 26.15, 22.75, 14.21. UV (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}$  cm<sup>-1</sup>): 306 (172 650), 632 (1980), 920 (40 530). Anal. calcd for C<sub>208</sub>H<sub>300</sub>N<sub>8</sub>NiO<sub>20</sub>S<sub>4</sub>: C, 73.06; H, 8.84; N, 3.28; S, 3.75; found: C, 72.86; H, 8.71; N, 3.32; S, 3.78%.

**4,4'-Bis-(2,3,4,5,6-pentafluorobenzyloxy)benzil (S3).** A mixture of 1,2-bis-(4-hydroxyphenyl)-ethane-1,2-dione (1.0 g, 4.1 mmol), 2,3,4,5,6-pentafluorobenzyl bromide (2.16 g, 8.3 mmol), and K<sub>2</sub>CO<sub>3</sub> (5.7 g, 41.3 mmol) in acetone (40 mL) was refluxed at 65 °C overnight. The reaction mixture was allowed to cool down to room temperature. Celite was added to the reaction mixture, and the mixture was filtered and washed with acetone. The filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane : hexanes = 2 : 1) to give a yellow solid (1.54 g, 61.8%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d, J = 8.8 Hz, 4H), 7.03 (d, J = 8.8 Hz, 4H), 5.18 (s, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  192.82, 162.82, 145.57 (d, <sup>1</sup> $J_{CF} = 254.2$  Hz), 141.88 (d, <sup>1</sup> $J_{CF} = 255.4$  Hz),

137.47 (d,  ${}^{1}J_{CF}$  = 254.2 Hz), 132.33, 126.97, 114.80, 109.14 (tt,  ${}^{2}J_{CF}$  = 18.3 Hz,  ${}^{3}J_{CF}$  = 3.4 Hz), 57.53. HRMS-FAB (*m*/*z*): [M+H]<sup>+</sup> calcd for C<sub>28</sub>H<sub>13</sub>F<sub>10</sub>O<sub>4</sub>, 603.06542; found, 603.06447. Anal. calcd for C<sub>28</sub>H<sub>12</sub>F<sub>10</sub>O<sub>4</sub>: C, 55.83; H, 2.01; F, 31.54; found: C, 55.71; H, 1.97; F, 31.77%.

Nickel bis{1,2-di-[4-(2,3,4,5,6-pentafluorobenzyloxy)-phenyl] ethane-1,2-dithiolene} (3). A mixture of S3 (0.90 g, 1.5 mmol), phosphorus pentasulfide (1.0 g, 2.3 mmol) in 1,4-dioxane (20 mL) was refluxed at 110 °C for 4 h under an N<sub>2</sub> atmosphere. The reaction mixture was allowed to cool down to ca. 60 °C and filtered under nitrogen. NiCl<sub>2</sub>·6H<sub>2</sub>O (0.178 g, 0.75 mmol) dissolved in H<sub>2</sub>O (1 mL) was added to the filtrate. The resulting mixture was refluxed at 110 °C for an additional 2 h. The reaction mixture was allowed to cool down to room temperature and then poured into ethanol. A gravish-green solid was collected by filtration and washed with ethanol. The crude product was purified by column chromatography (silica gel, hexanes : dichloromethane = 1 : 1) to give a grayish-green solid. The product was further purified by recrystallization from an ethyl acetate-isopropanol solvent mixture to give a gravish-green solid (0.31 g, 31.2%). <sup>1</sup>H NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.35 (d, J = 8.8 Hz, 8H), 6.87 (d, J = 8.8 Hz, 8H), 5.11 (s, 8H).  ${}^{13}C{}^{1}H$  NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  180.10, 158.47, 145.65 (d,  ${}^{1}J_{CF}$  = 250.8 Hz), 141.75 (d,  ${}^{1}J_{CF}$  = 255.4 Hz), 137.46 (d,  ${}^{1}J_{CF}$  = 254.2 Hz), 135.12, 130.41, 114.67, 109.70 (tt,  ${}^{2}J_{CF}$  = 17.2 Hz,  ${}^{3}J_{CF}$  = 3.5 Hz), 57.48. HRMS-MALDI (m/z):  $[M]^+$  calcd for C<sub>56</sub>H<sub>24</sub>F<sub>20</sub>NiO<sub>4</sub>S<sub>4</sub>, 1325.9592; found, 1325.9529. UV (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ /nm ( $\epsilon$ /M<sup>-1</sup> cm<sup>-1</sup>): 301 (40 190), 319 (sh, 33 600), 460 (sh, 3130), 612 (1540), 909 (28 610). Anal. calcd for  $C_{56}H_{24}F_{20}NiO_4S_4$ : C, 50.66; H, 1.82; S, 9.66; found: C, 50.53; H, 1.72; S, 9.46%.

### Device fabrication and testing

SCLC samples were prepared by sandwiching melt-processed films of 1, 2 or 3 between electrodes with different work functions (Ag or ITO). The active area of each device was 0.05 cm<sup>2</sup>. For SCLC experiments, the measurements of J-Vcharacteristics of all devices were performed in air and in the dark using a Keithley 2400 source meter. Capacitance was measured using Agilent 16048A test leads connected to an Agilent 4284A Precision LCR meter, yielding values of 4 pF. Transistors were fabricated in an N<sub>2</sub>-filled glovebox by spincoating (1000 rpm, 60 s) a solution of 1 in chloroform  $(20 \text{ mg mL}^{-1})$  onto heavily n-doped Si substrates with 200 nm of thermally-grown SiO<sub>2</sub> as the gate dielectric. Top contact geometry Ag (100 nm) source and drain electrodes were evaporated through a shadow mask defining channels with widths ranging from 200 µm to 2000 µm and lengths ranging from 25 µm to 200 µm. Depositions were performed at room temperature using physical vapor deposition at a pressure of  $5 \times 10^{-8}$  Torr. The typical layer thickness of 1 was 100 nm. During testing electrical connections were made with a microprobe station contained within a second N<sub>2</sub>-filled glovebox and an Agilent E5272A medium power source-monitor unit, connected to the probe station, was used to perform the electrical measurements. At no point after deposition of the organic layer were the transistor devices exposed to air. For

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each individual device current–voltage ( $I_{\rm DS}$  vs.  $V_{\rm DS}$  at multiple, discrete  $V_{\rm GS}$  values) and transfer ( $I_{\rm DS}$  vs.  $V_{\rm GS}$  at fixed  $V_{\rm DS}$ ) characteristics were measured. Field-effect mobilities were calculated in the saturation régime by fitting  $\sqrt{I_{\rm DS}}$  vs.  $V_{\rm GS}$  data to the square law:

$$I_{\rm DS} = \mu \frac{CW}{2L} (V_{\rm GS} - V_{\rm T})^2$$
(1)

where  $\mu$  is the field-effect mobility, *C* is the capacitance density of the gate dielectric (F cm<sup>-2</sup>),  $V_{\rm T}$  is the threshold voltage, and *W* (width) and *L* (length) are the dimensions of the semiconductor channel defined by the source and drain electrodes.

# Conclusion

In summary, we have found that an electron mobility as high as 2.8 cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup> can be achieved for the square-planar Ni bis(dithiolene) complex 1 in an annealed unsymmetrical meltprocessed device, as measured by SCLC experiments in a direction perpendicular to the substrate. It is also worth noting that the three Ni bis(dithiolene) complexes we have studied have very different observed SCLC mobilities despite having similar molecular electronic properties (as indicated by electrochemical and optical data); these large differences in mobility may be correlated with the differing degrees of order in films of these materials. Field-effect transistors based on spin-coated 1 show n-channel behavior with saturation electron mobilities up to  $1.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . One factor that may contribute to the discrepancy between SCLC and FET mobilities is the different molecular packing present in the films used for the two types of devices. These results further indicate the promise of Ni bis(dithiolene) complexes for organic electronics applications, while underscoring the importance of controlling solid-state packing in molecular electronic materials.

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