

Photoconducting Devices with Response in the Visible-NIR Region Based on Neutral Ni Complexes of Aryl-1,2-Dithiolene Ligands

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Dedicated to Prof. Francesco A. Devillanova in occasion of his 81st birthday

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ABSTRACT Metal Bis(1,2-dithiolene) complexes belonging to the class $[\text{Ni}(\text{Ar-edt})_2]^{x-}$ [Ar-edt^{2-} = aryethylene-1,2-dithiolate; Ar = phenyl, ($\mathbf{1}^{x-}$), 2-naphthyl ($\mathbf{2}^{x-}$); x = 0, 1] were fully characterized by NMR, UV-Vis-NIR, diffuse reflectance, and FT-IR spectroscopy, as well as cyclic voltammetry, and single crystal X-ray diffraction analysis. These complexes have emerged as new photoconducting materials that allowed for the development of a prototype of photodetectors with response in the Vis–NIR region. The photodetecting devices showed in some cases quantum efficiencies with orders of magnitude higher than those of previously reported 1,2-dithiolene systems.

INTRODUCTION

Because of the unique combination of optical, conductive, magnetic and catalytic properties, transition-metal 1,2-dithiolene complexes have attracted ever-increasing attention from the scientific community since the earliest reports in the 1960s.¹⁻⁵ While molybdenum and tungsten 1,2-dithiolene complexes have shown enzymatic activity,^{6,7} bis(1,2-dithiolene) compounds featuring d^8 metal ions have been employed as materials in disparate fields, ranging from optics^{4c,8} to laser Q-switching and mode-locking,⁹⁻¹¹ superconductors,^{12,13} water photosplitting,¹⁴ and olefin purification.¹⁵ All of the aforementioned applications depend on the electronic structure of this class of compounds,^{5b} which gives rise to crucial properties such as a high degree of π -delocalization, molecular planarity,^{3f} a widely tunable and reversible redox behaviour,^{3e,16,17,18,19} intense electrochromic visible-near infrared (Vis–NIR) absorption,^{3g,20} and high thermal and

photochemical stabilities.²¹ In particular, the “non-innocent” character of 1,2-dithiolene ligands has been shown to play a pivotal role in the chemistry of their transition metal complexes.²² In recent years, bis(1,2-dithiolene) compounds featuring d⁸ metal ions have also been investigated as new potential materials in a wide-span range of optoelectronic devices,²³ such as n-channel and ambipolar channel field effect transistors (FETs),^{24–29} heterojunction photovoltaic devices,³⁰ second- or third- order nonlinear optical (NLO) devices,^{11,31–34} and NIR liquid crystal devices.³⁵ The photoconducting properties of metal bis(1,2-dithiolene) complexes have also been investigated by a number of research groups.³⁶ For instance, Naito and co-workers reported on the giant photoconductivity shown by the NMQ[Ni(dmit)₂] molecular salt in the UV region (NMQ = *N*-methylquinolinium, dmit²⁻ = 1,3-dithiol-2-thione-4,5-dithiolate),³⁷ while the photodetection properties of bis-(4-dimethylaminodithiobenzil)nickel(II) were investigated using a Schottky-type device.³⁸

In this context, some of the authors reported on the photoconductive properties of several group 10 metal bis(1,2-dithiolene) complexes for the development of devices of importance in telecommunications, such as photodetectors and photoswitches, operative in all three optical fibre windows.^{39–43} In particular, several neutral complexes belonging to the classes [M(R,R'-timdt)₂] and [Ni(Et-dmet)₂] (R,R'-timdt²⁻ = *N,N'*-disubstituted 2-thioxoimidazoline-4,5-dithiolate, R = Et, R' = Et, pentyl, M = Ni, Pd, Pt;^{39,40} Et-dmet²⁻ = *N*-ethyl-2-thioxothiazoline-4,5-dithiolate)⁴¹ were reported to display tunable, wavelength-selective photoconductivity centered on their NIR absorption ($\lambda_{\text{max}} \sim 1000$ nm), in a wavelength region between the second (850–1000 nm) and third (1500–1800 nm) windows of optical fibres.⁴¹ Monoreduced radical anions [Pt(R,R'-timdt)₂]⁻ (R = Et; R' = Et, pentyl),^{42,43} whose NIR absorption falls at longer wavelengths ($\lambda_{\text{max}} \sim 1400$ nm for M = Ni and Pt; 1700 nm for M = Pd) exhibited solid-state photoconducting properties in the third optical fibre window.

The synthesis and characterization of variously functionalized aryl-1,2-dithiolene ligands (Ar-edt²⁻) and the neutral and monoanionic relevant nickel complexes [Ar = phenyl (Ph),⁴⁴ *p*-trifluoromethyl,²⁴ *p*-nitro, *p*-fluoro, *p*-chloro, and *p*-bromo-phenyl]⁴⁵ were reported during the past decades. The reactivity of some members of this class of metal complexes was also explored.^{44,46} Naphthalene- and coumarin-substituted dithiolene ligands were exploited as selective markers of the Ni²⁺ ion.⁴⁷

Following our previous studies on d⁸ metal complexes bearing Ar-edt²⁻ ligands showing potential-controlled spectroscopic and second-order NLO properties,^{48,49} and pursuing our interest in photoconducting bis(1,2-dithiolene) complexes, we describe here the synthesis, characterization, and the development of a novel photodetector with response in the Visible-NIR region based on the class [Ni(Ar-edt)₂]^{x-} of complexes [Ar = Ph, (**1**^{x-}), 2-naphthyl (**2**^{x-}); x = 0, 1, 2; Scheme 1].

EXPERIMENTAL SECTION

Materials and Methods. Solvents (reagent grade) were purchased from Honeywell, VWR, and Merck. Reaction solvents were dried by using standard techniques when required. CDCl₃ was stored on activated 4 Å molecular sieves before use. Reagents were purchased from Honeywell, Alfa Aesar, and Sigma-Aldrich and used without further purification. When required, manipulations were performed using standard Schlenk techniques under dry nitrogen atmosphere. Melting points were recorded on a FALC melting point apparatus mod. C (up to 300 °C) and are uncorrected. Elemental analyses were performed with a CHNS/O PE 2400 series II CHNS/O elemental analyzer (T = 925 °C). FT-IR spectra were recorded with a Thermo-Nicolet 5700 spectrometer at room temperature: KBr pellets with a KBr beam-splitter and KBr windows (4000–400 cm⁻¹, resolution 4 cm⁻¹) were used. ¹H-NMR measurements were carried out in CDCl₃

at 25 °C, using a Bruker Advance 300 MHz (7.05 T) spectrometer at the operating frequency of 300.13 MHz. Chemical shifts are reported in ppm (δ) and are calibrated to the solvent residue. Cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) measurements were recorded at 25 °C in anhydrous CH₂Cl₂ at scan rate 0.1 V s⁻¹, using a Metrohm Autolab PGSTAT 10 potentiostat at 20 °C in a Metrohm voltammetric cell, with a combined working and counter Pt electrode and a standard Ag/AgCl (in KCl 3.5 M) reference electrode. All potentials are referred to the Fc⁺/Fc couple, used as an internal standard. Tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte ($C = 1 \cdot 10^{-2}$ M). Absorption spectra were recorded at 25 °C in CH₂Cl₂ in a quartz cell of 10.00 mm optical path with a Thermo Evolution 300 (190–1100 nm) spectrophotometer. Spectrophotometric titrations of (TBA⁺)(1⁻) and (TBA⁺)(2⁻) ($C = 3.0 \cdot 10^{-5}$ M; $V = 3.00$ mL) with molecular diiodine ($C = 3.0 \cdot 10^{-3}$ M) were carried out in CH₂Cl₂ up to the molar range diiodine/dithiolene 2.5:1 (TBA = tetrabutylammonium). Diiodine solutions were previously titrated by suspending the solution (1 mL) in distilled water (50 mL), adding excess KI, and titrating with a standard solution of sodium thiosulfate (0.01 M) with a Metrohm 776 Dosimat automatic burette. Diffuse reflectance measurements were carried out on an Agilent Cary 5000 UV-Vis-NIR dual-beam spectrophotometer equipped with a diffuse reflectance accessory in the range 300–5000 nm. Spectra were corrected for the change in the detector (PMT and InGaAs) at 800 nm.

X-ray diffraction measurements. X-ray single-crystal diffraction data for 4-phenyl-[1,3]dithiol-2-one (Table S1) were collected upon Bruker-Nonius MoK α FR591 diffractometer, equipped with Bruker-Nonius Roper CCD camera, kappa-goniostat goniometer and a low-temperature device [operating at T=120(2) K]. The data were indexed and processed using DENZO⁵⁰ and COLLECT.⁵¹ The structure was solved by SHELXS-97⁵² and refined using SHELXL-

97⁵³ with Least Squares minimization. X-ray single-crystal diffraction data for **1** and **2** (Table S1) were collected upon Rigaku FRE+ MoK α diffractometer, equipped with HF Varimax confocal mirrors, an AFC12 goniometer, a HG Saturn 724+ detector and an Oxford Cryosystems low-temperature device (operating at T = 100(2) K). The data were indexed and processed using Crystal Clear-SM Expert 3.1 b22.⁵⁴ The structure was solved by Superflip and refined with SHELXL-97,⁵³ using Least Squares minimization within the WinGX suite of software.⁵⁵ X-ray single-crystal diffraction data for (TBA⁺)(1⁻) (Table S1) were collected upon a Rigaku FRE+ diffractometer, equipped with HF Varimax confocal mirrors, an AFC12 goniometer, a HG Saturn 724+ detector and an Oxford Cryosystems low-temperature device (operating at T = 100(2) K). The data indexed and processed using CrysAlisPro.⁵⁶ The structure was solved with the ShelXT structure solution program⁵⁷ with the Intrinsic Phasing solution method and by using Olex2⁵⁸ as the graphical interface. The model was refined with version 2018/3 of ShelXL⁵⁹ using Least Squares minimization. X-ray single-crystal diffraction data for (TBA⁺)(2⁻) (Table S1) were collected at 120(2) K upon Daresbury SRS station 9.8, upon a Bruker SMART diffractometer, equipped with silicon 111 monochromator, and an APEX CCD detector, and a low-temperature device (operating at T = 120(2) K). The data were indexed and processed using Bruker SAINT⁶⁰ and SADABS.⁶¹ The structure solved by SHELXS-97⁵² and refined on using SHELXL-97⁵³ with Least Squares minimization. CCDC-1953278 (4-phenyl-[1,3]dithiol-2-one), CCDC-1953277 [(TBA⁺)(1⁻)], CCDC-1009772 [(TBA⁺)(2⁻)], CCDC-1953275 (**1**), and CCDC-1953276 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Photoconductivity measurements were performed by using prototype lateral devices prepared by casting a CHCl₃ solution (C \approx 1 mg mL⁻¹) of each active complex on a quartz substrate with previously lithographed gold/chromium electrodes with inter-electrode spacings $L = 6 \mu\text{m}$. The devices were kept in vacuum (P < 10⁻³ mbar) and irradiated with

a set of light emitting diodes (LEDs) emitting a power density of a few mW cm^{-2} (calibration was obtained by means of a silicon photodetector). Photodetecting properties were investigated by applying an external bias voltage $V_{\text{BIAS}} = 60 \text{ V}$ and measuring the DC photocurrent by means of a semiconductor parameter analyzer (Agilent B1500A). In order to calculate the external quantum efficiency (EQE) we computed the ratio between the photocurrent divided by the unit charge q and the number of photons impinging on the device area per second.

Synthesis. Phenyl- and 2-naphthyl-[1,3]dithiol-2-one were synthesized according to previously published procedures.⁴⁸

Synthesis of $(\text{TBA}^+)(\mathbf{1}^-)$. An ethanol solution of KOH (45 mL; 0.25 g; 4.03 mmol) was added dropwise to 4-phenyl-[1,3]dithiol-2-one (30 mL EtOH; 0.21 g; 1.09 mmol) under a dinitrogen inert atmosphere. After addition of solutions of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (15 mL; 0.13 g; 0.55 mmol) and $(\text{TBA}^+)(\text{I}^-)$ (15 mL; 0.21 g; 0.57 mmol) in ethanol, the volume of the reaction mixture was reduced under reduced pressure and the precipitate collected by filtration. Crystals suitable for X-ray diffraction were obtained by slow infusion of diethyl ether into a dichloromethane solution of the complex. Yield 0.24 g (70.6 %); m.p. 146–147 °C; FT-IR: $\tilde{\nu} = 3025 \text{ (w)}, 2958 \text{ (s)}, 2941 \text{ (m)}, 2871 \text{ (m)}, 1589 \text{ (s)}, 1571 \text{ (w)}, 1493 \text{ (m)}, 1479 \text{ (m)}, 1454 \text{ (s)}, 1430 \text{ (s)}, 1375 \text{ (m)}, 1360 \text{ (w)}, 1220 \text{ (w)}, 1208 \text{ (s)}, 1180 \text{ (w)}, 1152 \text{ (w)}, 1104 \text{ (w)}, 1071 \text{ (w)}, 1029 \text{ (w)}, 932 \text{ (m)}, 904 \text{ (w)}, 879 \text{ (w)}, 836 \text{ (m)}, 751 \text{ (vs)}, 691 \text{ (s)}, 679 \text{ (w)}, 615 \text{ cm}^{-1} \text{ (w)}$; UV-Vis-NIR (CH_2Cl_2): $\lambda (\epsilon) = 261 \text{ (40500)}, 320 \text{ (35800)}, 531 \text{ (220)}, 942 \text{ nm (11600 M}^{-1} \text{ cm}^{-1})$; elemental analysis calcd. (%) for $\text{C}_{34}\text{H}_{48}\text{NNiS}_4$: C 60.65, H 7.46, N 2.15; found: C 59.01, H 7.46, N 2.15.

Synthesis of $(\text{TBA}^+)(\mathbf{2}^-)$. $(\text{TBA}^+)(\mathbf{2}^-)$ was synthesized as described for $(\text{TBA}^+)(\mathbf{1}^-)$ starting from 4-(2-naphthyl)-[1,3]dithiol-2-one. Crystals suitable for X-ray diffraction were obtained by slowly cooling down to room temperature a previously heated (130 °C) solution of the product in diethyl

ether/dichloromethane (30/2 mL) in a high-pressure Aldrich tube. Yield 0.170 g (51.2 %); m.p. 185–186 °C; FT-IR: $\tilde{\nu}$ = 3053 (w), 3013 (w), 2959 (s), 2938 (m), 2931 (m), 2870 (m), 1621 (m), 1592 (m), 1571 (vw), 1482 (s), 1445 (vs), 1425 (w), 1381 (s), 1341 (m), 1271 (vw), 1254 (w), 1229 (s), 1205 (w), 1172 (m), 1145 (w), 1124 (vw), 1107 (vw), 1069 (vw), 1019 (vw), 967 (m), 924 (vw), 893 (m), 881 (s), 864 (m), 816 (s), 795 (vs), 781 (s), 767 (m), 781 (s), 751 (s), 736 (vw), 645 (m), 625 (w), 647 (vw), 474 (s), 415 cm^{-1} (vw); UV-Vis-NIR (CH_2Cl_2): λ (ϵ) = 260 (47400), 320 (41900), 532 (2600), 946 nm (13500 $\text{M}^{-1} \text{cm}^{-1}$); elemental analysis calcd. (%) for $\text{C}_{40}\text{H}_{52}\text{NNiS}_4$: C 65.47, H 7.14, N 1.85; found: C 65.32, H 6.34, N 1.85.

Synthesis of 1. An anhydrous acetonitrile solution of I_2 (20 mL; 0.090 g; 3.4 mmol) was added dropwise to a solution of $(\text{TBA}^+)(\mathbf{1}^-)$ in the same solvent (75 mL CH_3CN ; 0.22 g; 3.2 mmol) under a dinitrogen inert atmosphere. The resulting precipitate was collected by filtration. Crystals suitable for X-ray diffraction were obtained by slow infusion of diethyl ether into a dichloromethane solution of the complex. Yield 0.12 g (97.5 %); m.p. 171–172 °C; FT-IR: $\tilde{\nu}$ = 3017 (vw), 1446 (w), 1381 (s), 1367 (vs), 1331 (w), 1227 (w), 1192 (s), 1132 (vw), 1031 (vw), 958 (w), 859 (s), 840 (m), 807 (w), 754 (s), 690 (s), 613 (vw), 475 cm^{-1} (vw); UV-Vis-NIR (CH_2Cl_2): λ (ϵ) = 253 (22500), 270 (23000), 303 (42000), 577 (1500), 816 nm (22900 $\text{M}^{-1} \text{cm}^{-1}$); elemental analysis calcd. (%) for $\text{C}_{16}\text{H}_{12}\text{NiS}_4$: C 49.12, H 3.09; found: C 48.76, H 3.02. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ = 9.72 (s, 2H), 8.00 (d, 4H), 7.52–7.44 (m, 6H) ppm.

Synthesis of 2. **2** was synthesized as described for **1** starting from $(\text{TBA}^+)(\mathbf{2}^-)$. Crystals suitable for X-ray diffraction were obtained by slow infusion of diethyl ether into a chloroform solution of the complex. Yield 0.070 g (90%); m.p. 232–233 °C; FT-IR: $\tilde{\nu}$ = 3051 (vw), 3021 (vw), 1467 (w), 1390 (vs), 1383 (vs), 1345 (vs), 1280 (w), 1252 (vs), 1200 (m), 1173 (vs), 1158 (s), 935 (m), 899 (s), 882 (m), 849 (m), 809 (vw), 786 (s), 770 (w), 737 (m), 676 (vw), 461 cm^{-1} (m); UV-Vis-NIR (CH_2Cl_2): λ (ϵ) = 250 (45100), 308 (51100), 576 (1840), 861 nm (27500 $\text{M}^{-1} \text{cm}^{-1}$); elemental analysis calcd. (%) for

C₂₄H₁₆NiS₄: C 58.67, H 3.28; found: C 58.21, H 2.82. ¹H-NMR (300 MHz, CDCl₃): δ = 9.90 (s, 2H), 8.10 (d, 4H), 8.01–7.96 (m, 4H), 7.60–7.55 (m, 6H) ppm.

Theoretical calculations. Theoretical calculations were performed on **1**^{x-} and **2**^{x-} (x = 0, 1) at the density functional theory (DFT)⁶² level with the Gaussian 16 (Rev. B.01)⁶³ suite of programs on a IBM x3755 server with four 12-core processors and 64 Gb of RAM (OS: SUSE Linux Enterprise Server 11 SP3). The mPW1PW functional⁶⁴ was adopted, in combination with the full-electron split valence basis sets (BSs) including polarization functions (def2-SVP)^{65,66} for light atomic species (C, H, S) and the LanLo8(d) BS⁶⁷ with effective core potentials⁶⁸ for nickel. Basis sets were obtained from Basis Set Exchange and Basis Set EMSL Library.⁶⁹ A series of preliminary calculations were performed by using **1** in its *cis* conformation as a model compound. The complex was thus optimized both in the closed-shell restricted electron configuration and in the broken-symmetry configuration of the diradical form [Ni^{II}(L^{•-})₂]. The diradical character n_{rad} was calculated from the total spin operator S^2 according to Equation 1,⁷⁰ and was found to be as large as 20.41%.

$$n_{rad} = 200 \sin^2 \vartheta = 100(1 - \sqrt{1 - S^2}) \quad (1)$$

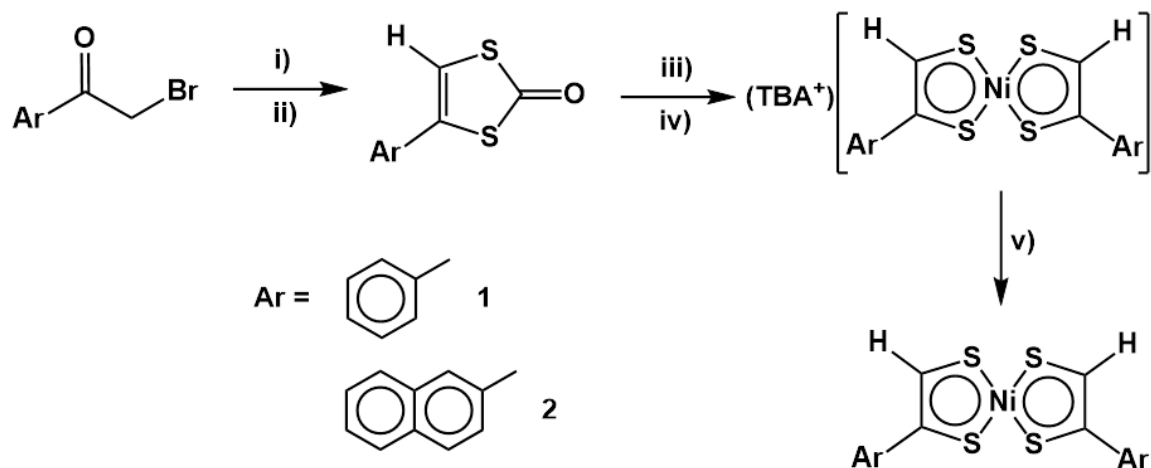
The geometries of the neutral complexes **1** and **2** were optimized in the predominant closed-shell restricted configuration. Geometry optimizations were performed on the *cis* and *trans* isomers starting from structural data, when available, and were regularized by letting the model complexes belong to an ideal C₂ point group (Tables S₃–S₁₀). Calculations were carried out also in CH₂Cl₂, implicitly taken into account by means of the Polarizable Continuum Model in its Integral Equation Formalism variant (IEF-PCM) describing the cavity of the complexes within the reaction field (SCRF) through a set of overlapping spheres (Table S₁₁–S₁₂).⁷¹ Tight SCF convergence criteria (*SCF=tight* keyword) and fine numerical integration grids (*Integral=ultrafine* keyword) were used, and the nature of the minima of each optimized structure was verified by harmonic

frequency calculations (*freq=raman* keyword). PES scans were performed on 1^{x-} and 2^{x-} ($x = 0, 1$; *cis* and *trans* isomers) by imposing the rotation of the aromatic rings (between 0 and 180 °, steps of 10 °) and optimizing the resulting geometry at each rotational step (*opt=modredundant* keyword). A natural population analysis was carried out at the optimized geometries using the natural bonding orbital (NBO) partitioning scheme (Table S13).⁷² Electronic transition energies and oscillator strength values were calculated at TD-DFT level (100 states; Table S14). The programs GaussView 6.0.16,⁷³ Molden 5.9,⁷⁴ and Chemissian 4.53⁷⁵ were used to investigate the optimized structures and the shapes of Kohn–Sham molecular orbitals. The software GaussSum 2.1⁷⁶ was used to calculate the contributions of singly excited configurations to each electronic transition.

RESULTS AND DISCUSSION

Synthesis. The synthesis of metal bis(1,2-dithiolene) complexes is commonly hampered by the tendency of 1,2-dithiolates to polymerize or decompose.^{2b,77} Accordingly, ethylene-1,2-dithiolates must be protected before being reacted with the desired metal salts. One of the most frequently encountered synthetic procedures consists of reacting α -halo-ketones with alkylxanthate anions to give the corresponding α -ketoxanthate esters, which give the relevant vinylene dithiocarbonates in strongly acidic media (Scheme 1).^{45,78} Following this route, the 4-phenyl- and 4-(2-naphthyl)-[1,3]dithiol-2-ones were synthesized as previously described^{48,49} (see details on the X-ray diffraction analysis of 4-phenyl-[1,3]dithiol-2-one in Table S1 and Figure S1). Complexes (TBA⁺)(1⁻) and (TBA⁺)(2⁻) were synthesized by treating the corresponding aryl-[1,3]dithiol-2-ones with nickel chloride hexahydrate in the presence of tetrabutylammonium (TBA) iodide. The

neutral complexes **1** and **2** were obtained by quantitative oxidation of (TBA⁺)(**1**⁻) and (TBA⁺)(**2**⁻) with molecular diiodine in MeCN solution (Scheme 1).^{46,79}



Scheme 1. Synthesis of compounds (TBA⁺)(**1**⁻-**2**⁻) and the neutral complexes **1**-**2**; the aryl substituents are depicted in the *cis* conformation; i) *i*PrOCS₂K in acetone; ii) HClO₄ concd.; iii) EtOK in EtOH; iv) NiCl₂·2H₂O, (TBA⁺)(I⁻); v) I₂ in CH₃CN.

X-ray diffractions studies. The crystal structures of (TBA⁺)(**1**⁻) and (TBA⁺)(**2**⁻) (Table S1 and Figure S2 and Figure 1, respectively), the latter being isostructural to the corresponding gold(III) complex,⁴⁸ show the central metal ion coordinated in a square-planar fashion, with the ligands assuming *trans* and *cis* conformations, respectively, and the aryl substituents twisted with respect to the dithiolene core by 18.6(2)/18.1(2) and 26.7(6)/26.9(7) °, respectively. Interestingly, the occurrence of the *cis* conformation found for (TBA⁺)(**2**⁻) (Figure 1) and tetrabutyl ammonium bis(naphthyl-1,2-ethylenedithiolato)gold(III) is uncommon.⁴⁸ (PPh₄⁺)(**2**⁻)⁴⁷ and the other nickel complexes deriving from differently asymmetrically substituted 1,2-dithiolene ligands reported in the literature, namely (TBA⁺)[Ni(CF₃Ph-edt)₂]⁻,²⁴ (TBA⁺)[Ni(FPh-edt)₂]⁻, (TBA⁺)[Ni(ClPh-edt)₂]⁻,⁴⁵ and show a *trans* conformation (CF₃Ph = *p*-trifluoromethylphenyl, FPh = *p*-fluorophenyl, ClPh

= *p*-chlorophenyl). The conformation does not affect the structural features and average Ni-S, C-S and C-C bond distances found are very similar for (TBA⁺)(1⁻) and (TBA⁺)(2⁻) (2.144, 1.729, and 1.358- and 2.147, 1.725, and 1.355 Å, respectively). These are very similar to those determined for (PPh₄⁺)(2⁻) (2.139, 1.721, and 1.358 Å) and (TBA⁺)[Ni(CF₃Ph-edt)₂]⁻, (TBA⁺)[Ni(FPh-edt)₂]⁻, and (TBA⁺)[Ni(ClPh-edt)₂]⁻ (average values 2.141, 1.727, and 1.346 Å)

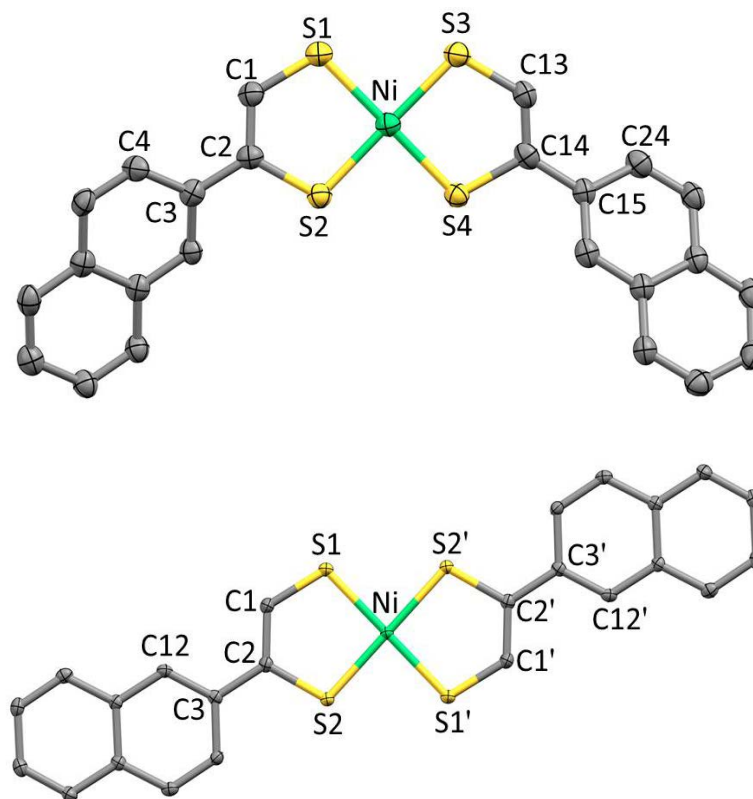


Figure 1. Drawing and atom labelling scheme for the complex anion in (TBA⁺)(2⁻) (top) and for **2** (bottom). Thermal ellipsoids are shown at the 60% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths, angles, and dihedral angles, 2⁻: Ni-S1 2.147(1), Ni-S2 2.150(1), Ni-S3 2.144(1), Ni-S4 2.148(1), S1-C1 1.717(4), S2-C2 1.732(5), S3-C13 1.706(5), S4-C14 1.747(5), C1-C2 1.361(6), C13-C14 1.349(6) Å; S1-Ni-S2 91.60(5), S3-Ni-S4 91.36(5), S1-Ni-S3 89.11(5), S2-Ni-S4 88.15(4), Ni-S1-C1 103.7(1), Ni-S2-C2 104.8(1), Ni-S3-C13 103.8(1), Ni-S4-C14 105.0(2), S1-C1-C2 121.8(3), S2-C2-C1 118.0(3), S3-C13-C14 123.0(3), S4-C14-C13 116.9(3) °; C1-C2-C3-C4 26.7(6), C13-C14-C15-C24 26.9(7), C1-S1-Ni-S3 178.4(2), C14-S4-Ni-S2 177.4(2) °. **2**: Ni-S1 2.1229(6), Ni-S2 2.1441(5), S1-C1 1.681(2), S2-C2 1.719(2),

C1–C2 1.381(3) Å; S1–Ni–S2 91.5(2), S1–Ni–S2' 88.45(2), Ni–S1–C1 104.50(8), Ni–S2–C2 104.81(8), S1–C1–C2 121.9(2), S2–C2–C1 117.2(2) °; C1–C2–C3–C12 2.0(4), C1–S1–Ni–S2' 179.17 (9) °. ' = 1-x, -y, -z.

In the crystal packing, the complex anions interact to each other and with the TBA⁺ counterions by weak S...H contacts [S1...H11A = 2.95, S2...H13Bⁱ 2.94, S2...H7ⁱⁱ 3.06 for (TBA⁺)(**1**); S4...H7ⁱⁱⁱ 2.97, S2...H21^{iv} 2.99, S3...H28^v 3.04, S2...H27a^{vi} 3.04 Å for (TBA⁺)(**2**⁻); symmetry codes: ⁱ = x, 1+y, z; ⁱⁱ = -x, y, 1/2-z; ⁱⁱⁱ = 1-x, 1/2+y, 3/2-z; ^{iv} = 1/2+x, 1/2-y, 1-z; ^v = 1/2-x, -y, 1/2+z; ^{vi} = 1-x, -1/2+y, 1/2-z]. No stacking interactions between complex ions can be observed with Ni...Ni distances no shorter than 10.288 and 8.698 Å for (TBA⁺)(**1**⁻) and (TBA⁺)(**2**⁻), respectively [Figure S3 for (TBA⁺)(**2**⁻)]. Single crystal X-ray diffraction analysis of **1** confirmed the crystallographic data reported previously by Sugimori and coworkers.⁴⁴ As expected,^{80,81} on passing from the neutral to the corresponding monoanionic species the C–C and C–S bond lengths result elongated and shortened respectively [average C–C distances: 1.377 Å for **1**/2; 1.356 Å for **1**⁻/2⁻; average C–S distances 1.701 Å for **1**/2; 1.714 Å for **1**⁻/2⁻]. Both **1** (Figure S4) and **2** (Figure 1, Table S1) show the complexes in a *trans* conformation, in analogy to the related systems [Ni(CF₃Ph-edt)₂]²⁴ and [Ni(ClPh-edt)₂].⁴⁵ Based on variable-temperature ¹H-NMR data, it was hypothesized⁴⁴ that **1** displays a rapid *cis/trans* isomerization in solution, possibly occurring through rotation of the ligand around the metal ion. Accordingly, the room temperature ¹H-NMR spectra recorded for **1** and **2** in CDCl₃ solution show a single signal for the vinyl proton (H₁ in Figure S5) at 9.72 and 9.90 ppm respectively.

In **1** the phenyl rings are tilted with respect to the dithiolene ring by 24.42–33.58(10) °; on the contrary, complex molecules in **2** are almost planar, with torsions angles of 2.0(4) ° for the naphthyl substituents. Even in the absence of counterions, no π -stacking interactions are found in the case of the neutral species, with Ni...Ni distances no shorter than 5.010 and 4.639 Å for **1**

and **2**, respectively. For both complexes, the packing is mainly governed by edge-to-face interactions involving the aromatic substituents and leading to different herringbone type arrangements (Figure S6 and S7). In **1** symmetry non-equivalent complex units (Ni_i and Ni_z in Figures S4 and S6) pack in staggered sheets through a weak S...H and edge to face interactions involving alternated C₃-C₈ and C₁₁-C₁₁ phenyl rings angled of 49.5 ° [C₇-H₇...Cnt_(C₁₁-C₁₅) 2.87, C₄-H₄...Cnt_(C₁₁-C₁₅) 2.73 Å, *a* and *b* in Figure S6]. Similar edge-to-face interactions can be found in complex **2** [C₁₀-H₁₀...Cnt_(C₃,C₄,C₅,C₆,C₁₁,C₁₂) 2.68, C₅-H₅...Cnt_(C₆-C₁₁) 2.64 Å, *a* and *b* in Figure S7]. The herringbone disposition also engendered in **2** Ni...Siⁱⁱⁱ 3.29, and Siⁱ...Si^{iv} 3.43 Å interactions showed in green and blue color in Figure S7.

Electrochemistry and Vis-NIR spectroscopy. The redox behavior of (TBA⁺)(**1**⁻) and (TBA⁺)(**2**⁻) was investigated by cyclic voltammetry in CH₂Cl₂ solution (Figure 2). Two one-electron DPV-tested redox waves were observed for both complexes, falling at about -1.20 and -0.41 V vs the Fc⁺/Fc couple (Table S2), and corresponding to the reduction of the complexes to their dianionic forms (**1**²⁻ and **2**²⁻) and their oxidation to give **1** and **2**. While the oxidation processes involving the **1**⁻/**1** and **2**⁻/**2** couples and the reductions for the **1**⁻/**1**²⁻ couple were found to be reversible (*i*_{pc}/*i*_{pa} ~ 1.0), reductions for the **2**⁻/**2**²⁻ couple were found to be only quasi-reversible (*i*_{pc}/*i*_{pa} = 0.7). It should be noted that these findings differ from those previously obtained in acetonitrile for (TBA⁺)(**1**)⁴⁵ and (PPh₄⁺)(**2**⁻),⁴⁷ where an irreversible nature was found for both the reduction and oxidation process.

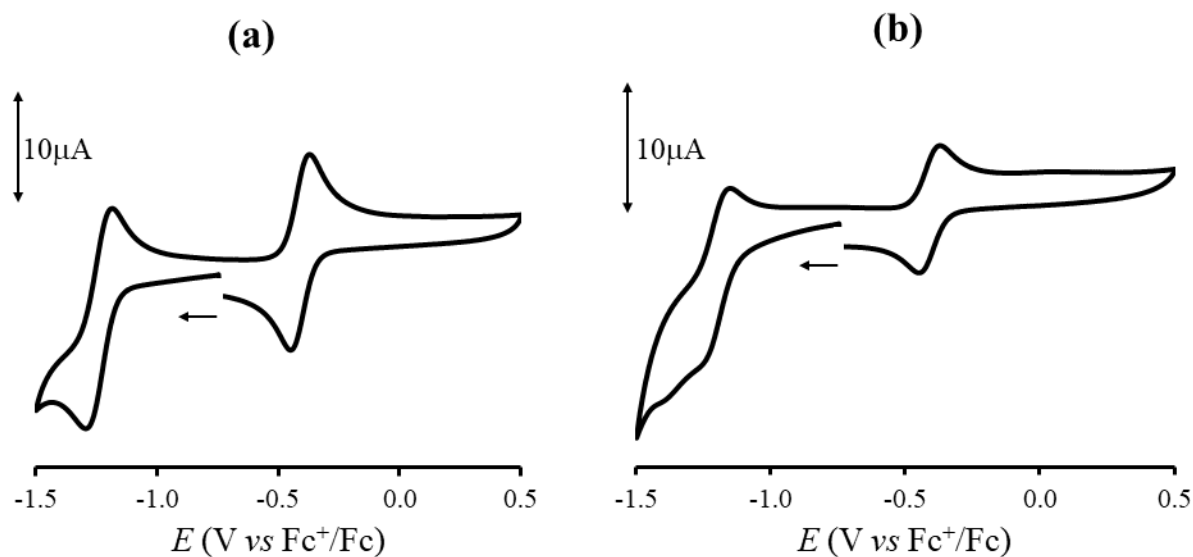


Figure 2. Cyclic voltammograms of $(\text{TBA}^+)(\mathbf{1}^-)$ (a) and $(\text{TBA}^+)(\mathbf{2}^-)$ (b) at a platinum electrode in CH_2Cl_2 [25 °C; scan rate 0.100 V s^{-1} ; supporting electrolyte $(\text{TBA}^+)(\text{PF}_6^-)$ 0.1 M].

The oxidation processes leading from $\mathbf{1}^-$ and $\mathbf{2}^-$ to $\mathbf{1}$ and $\mathbf{2}$ were investigated by spectrophotometric titration of $(\text{TBA}^+)(\mathbf{1}^-)$ and $(\text{TBA}^+)(\mathbf{2}^-)$ with diiodine in CH_2Cl_2 solution (Figure 3). Notably the *cis/trans* isomerism in solution (see above) does not prevent a spectrophotometric investigation under the hypothesis, confirmed by TD-DFT calculations (see below), that the *cis* and *trans* isomers of each metal complex feature very close UV-Vis-NIR absorption spectroscopic features. Accordingly, very well-defined isosbestic points were found during the spectrophotometric I_2 titrations. The UV-Vis-NIR electronic absorption spectra of $\mathbf{1}^-$ and $\mathbf{2}^-$ show the characteristic intense NIR absorption bands [$\lambda_{\text{max}} = 942$ and 946 nm; $\epsilon = 11600$ and 13500 $\text{M}^{-1} \text{cm}^{-1}$ for $(\text{TBA}^+)(\mathbf{1}^-)$ and $(\text{TBA}^+)(\mathbf{2}^-)$, respectively], which undergo an hypsochromic shift upon oxidation ($\lambda_{\text{max}} = 816$ and 838 nm; $\epsilon = 26600$ and 27500 $\text{M}^{-1} \text{cm}^{-1}$ for $\mathbf{1}$ and $\mathbf{2}$, respectively), as also confirmed by the absorption spectra of $\mathbf{1}$ and $\mathbf{2}$ in the same solvent (Figure S8). Solid-state diffuse reflectance spectra recorded for both neutral and

monoanionic complexes show an envelope of broad bands resulting in an uninterrupted absorption extending from the UV to the NIR region (Figure S9 for **1** and **2**).

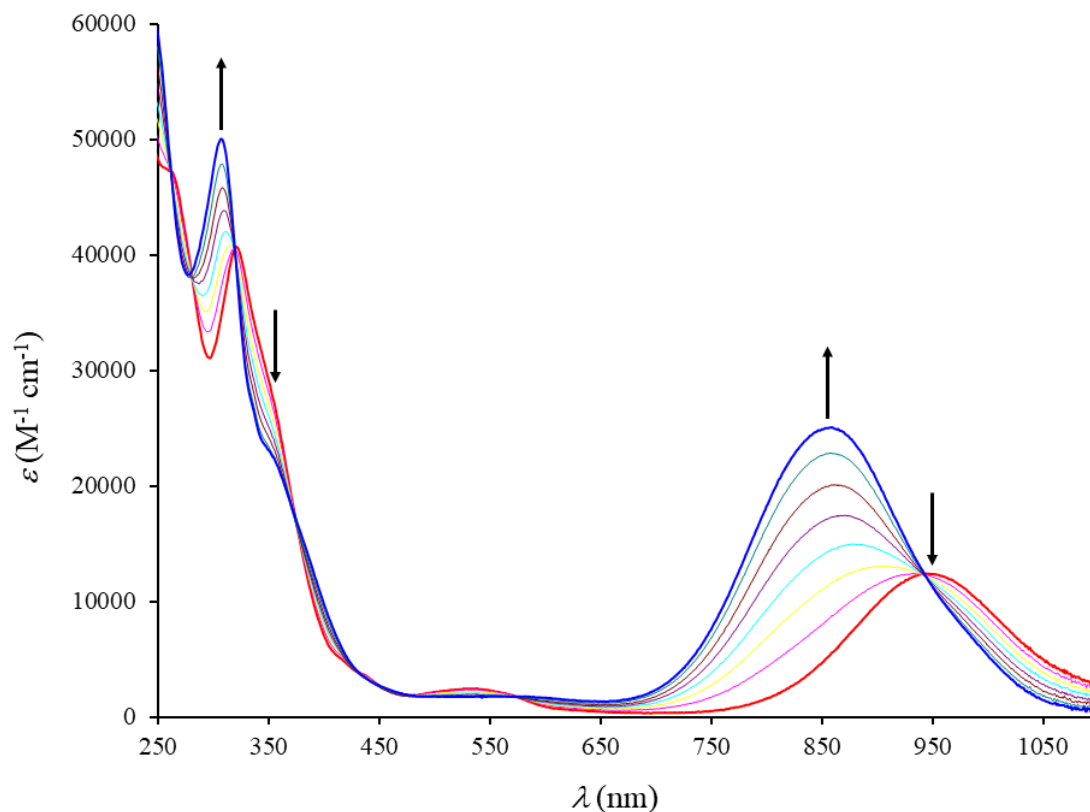
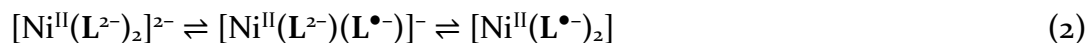


Figure 3. Dilution-corrected UV-Vis-NIR spectra recorded during the spectrophotometric titration of a solution of $(\text{TBA}^+)(2^-)$ with I_2 in CH_2Cl_2 .

Theoretical calculations. QM calculations at the density functional theory (DFT)⁶² level represent an invaluable tool in understanding the electronic structure of a plethora of compounds, including metal complexes, as they have been extensively exploited to investigate structure/property relationships in a large variety of compounds at an acceptable computational cost. Aimed at elucidating both the redox and optical properties of $1^{\text{x-}}-2^{\text{x-}}$, as well as their electronic structure and *cis/trans* isomerism, DFT calculations were carried out on the title bis(1,2-dithiolene) Ni neutral and monoanionic complexes. In agreement with previously established

approaches on related systems,^{48,49,82-86} the mPW₁PW hybrid functional⁶⁴ was used in combination with full-electron split-valence basis sets, including polarization functions from Schäfer, Horn, and Ahlrichs⁶⁵ in the Weigend formulation (def2-SVP)⁶⁶ for light atomic species (C, H, S) and the LanLo8(d) BS⁶⁷ with effective core potentials⁶⁸ for nickel.

The redox non-innocence^{22,87,88} of 1,2-dithiolene ligands generated a large debate regarding their electronic structure. While paramagnetic monoanionic metal bis(1,2-dithiolene) complexes have been reported as $[M^{III}(L^{2-})_2]^-$ species⁴⁵ or as featuring a dianionic ligand L^{2-} and monoanionic radical one $L^{\bullet-}$, i.e. $[M^{II}(L^{\bullet-})(L^{2-})]^-$, neutral species have been depicted as closed-shell species (featuring the metal in oxidation states ranging between 0 and IV) or as diradicals formed by a metal dication M^{II} and two radical monoanionic antiferromagnetically coupled ligands $L^{\bullet-}$.^{80,81} According to the latter view, the redox steps typically exhibited by bis(1,2-dithiolene) complexes of d^8 metal ions (Scheme S1), would be ligand centered and would not modify the electron population on the central Ni^{II} ion:



A series of preliminary calculations were performed on the *cis* isomer of **1** (C_2 point group) in order to ascertain the relative weight of the closed-shell and the diradical descriptions of the singlet Ground State (GS). These calculations indicated a composition of the GS made up by about 80% of the closed-shell system, with a contribution from the diradical form of 20%. The neutral complexes **1** and **2** were thus optimized in the predominant closed-shell restricted singlet configuration (1A GS in the C_2 point group). Given the possibility of the complexes to exhibit *cis/trans* isomerism, both conformations were optimized for all of the complexes (Tables S3–S10). Solvation calculations in CH_2Cl_2 were also carried out at the same level of theory, by using the

integral equation formalism of the polarizable continuous model (IEF-PCM) within the self-consistent reaction field (SCRF) approach,⁷¹ and a comparison between the structures optimized in the gas phase and in CH₂Cl₂ showed negligible differences (Tables S11 and S12 for **1**^{x-} and **2**^{x-}, respectively).

A good agreement was found between the optimized structures (Figure S10 for **1** and **2**) and the corresponding structural data of **1**, **2**, **1**⁻, and **2**⁻ discussed above, only the Ni-S bond distances being slightly overestimated (by less than 0.04 Å). In agreement with structural data, the replacement of the phenyl ring in **1**^{x-} with the 2-naphtyl substituent in **2**^{x-} does not induce significant modifications in the optimized bond lengths and angles (varying by less than 0.01 Å and 1°, respectively). The *cis/trans* isomers were found to differ by less than 0.1 kcal mol⁻¹ in their total electronic energies for all of the complexes and very small variations can be observed when their optimized geometries are compared (bond distances and angles differing by less than 0.01 Å and 1°, respectively). In all the optimized structures the aryl substituents are twisted with respect to the central metallacycles by 24.45–29.90° (25.79–30.37° in CH₂Cl₂). A scan of the potential energy surface (PES) was performed by optimizing the geometry of each complex at different frozen values of the corresponding dihedral angle τ (0° ≤ τ ≤ 180°; C₁-C₂-C₃-C₄ in Figure S10), showing that the corresponding rotational barrier is in any case small (3.0–4.4 kcal mol⁻¹; Figure S11 for **1**^{x-}). It can thus be hypothesized that a free rotation of the aryl substituents occurs in solution and that the differences observed in the crystal structure are probably steered by the solid-state packing. In agreement with the experimental structural data discussed above, neutral complexes **1** and **2** feature C-C and C-S optimized distances that are systematically longer and shorter, respectively, than those of the corresponding monoanions. Moreover, an analysis of the natural charges⁷² (Table S13) shows that the nickel charge does not undergo a significant variation on passing from **1** and **2** to **1**⁻ and **2**⁻, respectively (0.060 and 0.006 |e| on average in the gas phase

and CH₂Cl₂, respectively), thereby further confirming that the corresponding electron-transfer process is mostly ligand-based. An examination of the GS bonding scheme of **1** and **2** shows that the two complexes feature very similar Kohn–Sham molecular orbital (KS-MO) compositions, regardless of the isomerism. In particular, both the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO, respectively; KS-MOs 95/96 and 121/122 in Figure 4 and Figure S12 for the *cis* conformation of **1** and **2**, respectively, in CH₂Cl₂) are π -MOs mostly localized on the 1,2-dithiolene core, with a minor contribution (7% for **1**; 6% for **2**) from the central nickel ion in the case of the LUMO. In **1**⁻ and **2**⁻ the LUMO is an antibonding σ -MO built up by the combination of the in-plane sulfur *2p* atomic orbitals (AOs) with the nickel *3d* AO (KS-MOs 97 and 123 in Figure 4 and Figure S12). The localization of the frontier MOs on the 1,2-dithiolene core accounts for the negligible dependence of the experimental redox potentials on the substitution and isomerism of the ligands.

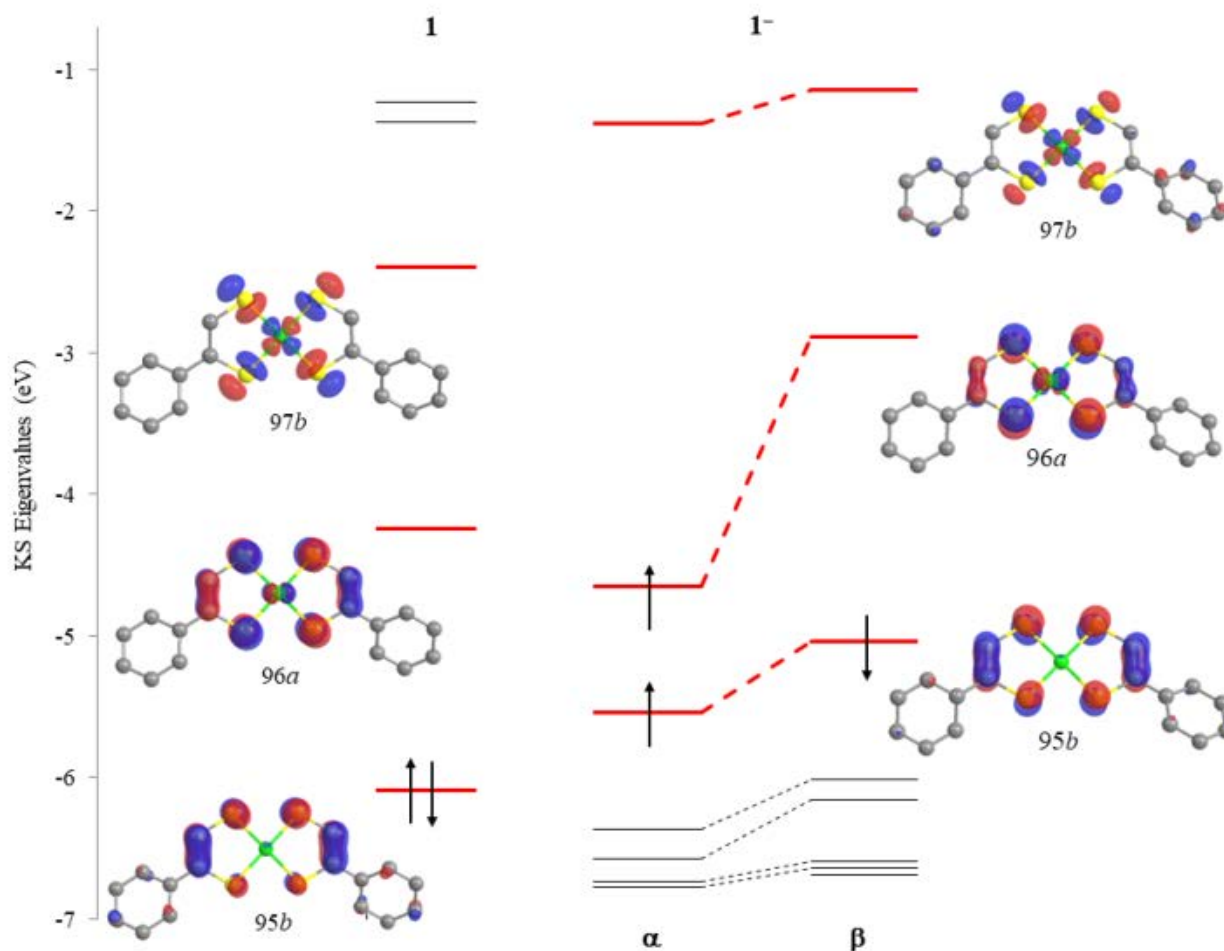


Figure 4. Correlation diagram between the eigenvalues of selected KS-MOs (-7.0/-0.7 eV) calculated for the *cis* isomer of **1** (left) and **1⁻** (right) in CH₂Cl₂ (IEF-PCM SCRF model), and drawings of the frontier KS-MOs, highlighted in red (C₂ point group; contour value = 0.05 |e|).

Time-dependent DFT calculations were carried out in CH₂Cl₂ at the optimized geometries in the GS for the *cis* and *trans* isomers of **1**, **1⁻**, **2**, and **2⁻**. Notably, the *cis* and *trans* isomers of the complexes show Vis-NIR electronic transitions energies differing by less than 0.03 eV (Table S14 in SI). TD-DFT calculations show that for the neutral complexes **1** and **2**, the intense NIR absorption (calculated at 780 and 845 nm, respectively; Table S14) should be attributed to the So ~~electronic~~ vertical transition, corresponding to an almost pure (94 and 97%, respectively) one-electron excitation between the HOMO and LUMO (KS-MOs 95 and 96 for **1**; 121 and 122 for **2**). On the other hand, for **1⁻** and **2⁻** the NIR absorption (988 and 1002 nm, respectively)

corresponds to the Do

$\mathbf{1}^-$ and $\mathbf{2}^-$, respectively) to the SOMO-1 (~~95~~ $\rightarrow 121\beta$ for $\mathbf{1}^-$; $121\beta \rightarrow 12\beta$ for $\mathbf{2}^-$, Table S14 and Figure S12 in SI) one-electron excitation. The lower oscillator strengths f and energies of the NIR transition calculated for $\mathbf{1}^-$ and $\mathbf{2}^-$ (average $f = 0.23$) compared to $\mathbf{1}$ and $\mathbf{2}$ (average $f = 0.57$) are consistent with the smaller ε and larger λ_{\max} values observed experimentally.

Photoconductivity measurements. The photoconductive properties of the title complexes were investigated through prototype lateral devices prepared by spraying CHCl_3 solutions ($C \approx 1 \text{ mg mL}^{-1}$) of each complex on a quartz substrate with previously lithographed gold/chromium electrodes with an interelectrode spacing of $6 \mu\text{m}$ (Figure 5). The devices were kept in vacuum (pressure below 10^{-3} mbar) and irradiated with a set of light emitting diodes (LEDs) emitting a power density of a few mW cm^{-2} . Photodetecting properties were investigated by applying an external bias voltage $V_{\text{BIAS}} = 60 \text{ V}$ and measuring the DC photocurrent by means of a semiconductor parameter analyzer. The applied voltage, besides allowing collection of the photo-generated charge carriers, is crucial in the photocarrier generation process: in fact, in amorphous molecular solids, optical excitations do not directly lead to the generation of free charge carriers since the primary excitations are in the form of strongly-bound molecular excitons.⁸⁹

While the compounds $(\text{TBA}^+)(\mathbf{1}^-)$ and $(\text{TBA}^+)(\mathbf{2}^-)$ did not show any photo-detecting behavior, the neutral complexes $\mathbf{1}$ and $\mathbf{2}$ proved to be photoconductive. In agreement with diffuse reflectance spectrophotometric measurements (see above), the devices based on complexes $\mathbf{1}$ and $\mathbf{2}$ show a wide spectral responsivity, which extends from the Vis to the NIR region of the spectrum, complex $\mathbf{2}$ showing a larger NIR-selectivity of the photo-response (Figure 5). Interestingly, the observed external quantum efficiency (EQE) values ($7 \cdot 10^{-1} \%$ and $8 \cdot 10^{-3}$ at 770 nm for $\mathbf{1}$ and $\mathbf{2}$, respectively, Table S15) were found to be about one to two orders of magnitude larger than those of analogous devices based on pristine dithiolenes investigated previously.⁴¹⁻⁴³

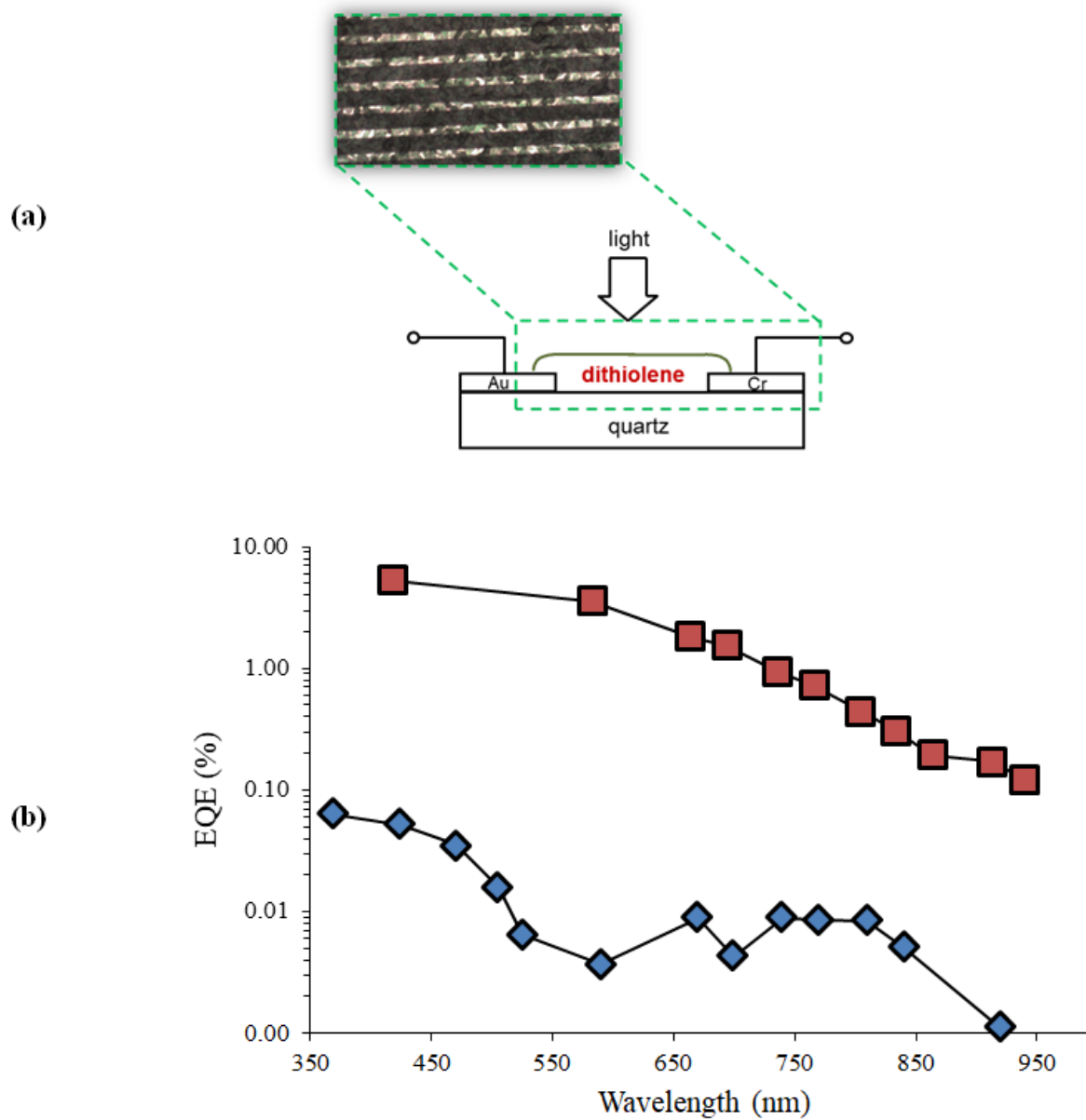


Figure 5. (a) Sketch of the planar photodetector prototype and darkfield optical microscope image (1000X magnification) of the device based on **1**, showing the complex cast on the lithographed quartz substrate (b) External quantum efficiency spectrum recorded for the photoconductive devices based on **1** and **2** (red and blue squares, respectively).

The differences observed in the photoconductive properties of $(\text{TBA}^+)(\mathbf{1}^- \text{-} \mathbf{2}^-)$ and **1-2** might be possibly attributed to differences in their solid-state packing.⁹⁰⁻⁹³ In this context, the lack of photoconductivity of the monoanionic complexes could be ascribed to the presence of the bulky

TBA⁺ counter-cations, which in the solid state interpose between the complex molecules as described above. In contrast, in the case of complexes **1** and **2** the possibility of neighboring molecules to interact through S...S and Ni...S contacts, evidenced in the crystal structures, may allow for an electron hopping process responsible for the photo-induced conductivity. This notwithstanding, the deposition process results in an amorphous deposition on the device, so that the effective solid-state intermolecular interactions, as well as the balance between the *cis* and *trans* isomers, are unknown and fine differences might be responsible for the larger efficiency observed for complex **1** with respect to complex **2**.

CONCLUSIONS

In conclusion, metal bis(1,2-dithiolene) complexes belonging to the class [Ni(Ar-edt)₂]^{x-} (Ar = phenyl, 2-naphthyl; x = 0, 1) represent promising active materials for optoelectronic applications, and air-stable prototype photodetectors sensitive to the NIR region of the spectrum have been developed based on these systems. Several factors render these devices appealing for telecommunication. First, metal 1,2-dithiolene complexes feature a high thermal and photochemical stability,¹⁻³ uncommon among photoactive organic materials showing low HOMO-LUMO energy gaps.^{43,94} In addition, the possibility to deposit the active complexes on substrates of any extension and shape allows for applications precluded to inorganic semiconductors. Finally, the possibility of casting the complexes from organic solvents enables the fabrication of devices directly on the surface of optical elements, such as beam splitters and fibre-optical cleaved surfaces, solving alignment problems at the root.

Importantly, EQE values orders of magnitude higher than those of analogous devices based on pristine dithiolene materials were recorded, representing a great step forward in solving the previously encountered limitations represented by low quantum efficiency. Significant variations

in the photo-response were observed upon modifying both the oxidation state of the complexes and the substituents at the ligands.

Since photoconductivity is dependent on the number of the photogenerated electron-hole pairs and the mobility of the carriers,⁹⁵ the larger efficiency of [Ni(Ar-edt)₂] metal bis(1,2-dithiolene) complexes with respect to those reported in the past,³⁹⁻⁴³ as well as the differences between **1** and **2**, can be tentatively attributed to their different solid-state structures, given the extreme sensitivity of the solid-state electronic properties of molecular materials to minute changes of the molecular shapes and intermolecular interactions. Future studies will be directed at addressing these aspects.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information, including is available free of charge on the ACS Publications Web site at DOI: XXXX. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8bo26o4.

Crystallographic data and packing details for 4-phenyl-[1,3]dithiol-2-one, **1**, **2**, (TBA⁺)(**1**⁻), and (TBA⁺)(**2**⁻), ¹H-NMR spectrum of **1**, CV data for (TBA⁺)(**1**⁻) and (TBA⁺)(**2**⁻), absorption UV-Vis-NIR spectra of (TBA⁺)(**1**⁻), (TBA⁺)(**2**⁻), **1**, and **2**, diffuse reflectance spectra, DFT-optimized geometries and relative metric parameters, NBO charges, and TD-DFT data for **1**^{x-} and **2**^{x-}, PES surfaces for **1**^{x-}, KS-MOs drawings and correlation diagram for **2**^{x-}, photoconductivity data for **1** and **2** (x = 0, 1).

Accession Codes

CCDC 1953272, 1953275-1953278 contain the supplementary crystallo- graphic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cam- bridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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SYNOPSIS

Prototype photodetectors sensitive to the NIR region of the spectrum have been developed based on neutral nickel bis(1,2-dithiolene) complexes featuring aryl-substituted ligands, which emerge therefore as promising active materials for optoelectronic applications.

