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Heteroleptic Bis(*cis*-1,2-disubstituted ethylene-1,2-dithiolato)nickel Complexes Obtained by Ligand-Exchange Reaction: Synthesis and Properties

Thi Minh Ha Vuong,[†,§] Thanh-Tuan Bui,[‡] Alix Sournia-Saquet,[†,§] Alain Moreau,[†,§] and Kathleen I. Moineau-Chane Ching*,[†]

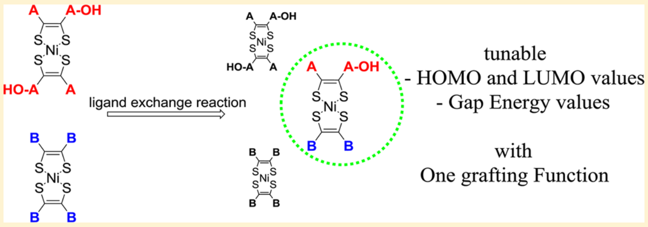
[†]Laboratoire de Chimie de Coordination (LCC), CNRS UPR8241, 205 route de Narbonne, BP 44099, F-31077 Toulouse, France

[‡]Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI), Université de Cergy-Pontoise, 5 mail Gay Lussac/Neuville-sur-Oise, 95031 Cergy-Pontoise cedex, France

[§]Université de Toulouse, UPS, INP, LCC, F-31077 Toulouse, France

Supporting Information

ABSTRACT: The ligand-exchange reaction has been investigated to synthesize nickel bis(dithiolene) complexes bearing one hydroxyl functional group aimed at being grafted thereafter onto polymer materials. This reaction leads easily to heteroleptic complexes with the ethylene-1,2-dithiolato core substituted by either alkyl or aryl moieties. Details on synthetic parameters are given. A direct link between the electronic properties of the obtained molecules and those of the parent complexes involved in the ligand-exchange reaction is highlighted and also demonstrates that this reaction is a powerful method for preparing nickel complexes with tailor-made frontier orbital energies.



INTRODUCTION

The field of organic electronics (OE) has made great scientific progress over the last 20 years, as evidenced by the numerous publications concerning organic materials such as light-emitting diodes (OLEDs), field-effect transistors (OFETs), photovoltaic cells (OPVs), or photodiodes (OPDs). These applications may be envisioned thanks to the development of semiconducting properties of conjugated organic materials, through fundamental studies in materials sciences and more precisely in chemistry and physics. During the past year, encouraging advances have been made in OPVs thanks to small molecules or polymers.[1] Molecular design is an essential key factor for the efficiency of OE devices that have been clearly correlated to the frontier orbital energies of the individual components.[2] Thus, the objectives of numerous research works focus on the fine-tuning of the HOMO−LUMO energies levels and the HOMO−LUMO gaps for molecules with the aim of realizing molecular electronic devices and the investigation of charge, energy, or electron-transfer processes. This tuning can be achieved via molecular engineering based on theoretical calculations or by modifying the molecular structure of already-known molecules. The last strategy is applied in the present work that is dedicated to nickel bis(dithiolene) complexes. These molecules have attracted much attention due to their unique optical, electronic, magnetic, and electrochemical properties, leading to various uses.[3]

During the past four decades, a large number of bis(dithiolene) complexes have been studied,[4] and our group has successfully developed a series of substituted Ni(dpedt)$_2$ compounds, where dpedt is diphenylethylenedithiolate, which aims to act as an electron acceptor for the OE.[5] However, compared to the large number of symmetrical complexes, there have been fewer studies on unsymmetrical nickel bis(dithiolene) molecules, as the synthesis of the latter is more difficult. Recently, the synthesis of heteroleptic complexes such as Ni(tmedt)(dddt), Ni(tmedt)(dmit), and Ni(dpedt)(dmio), (where tmedt is trimethylene-ethylenedithiolate, dddt is 5,6-dihydro-1,4-dithin-2,3-dithiolate, dmit is 1,3-dithiol-2-thione-4,5-dithiolate, dpedt is diphenyl-ethylenedithiolate, and dmio is 1,3-dithiol-2-one-4,5-dithiolate) have been realized by engaging the two corresponding ligands in equal molar proportions with yields up to only 10% for the neutral complexes.[6] The desired molecule is always obtained with the corresponding homoleptic derivatives and other degradation products that complicate the purification process and contribute to lower the overall yield. In this work, several heteroleptic nickel bis(dithiolene) complexes were synthesized by ligand-exchange reaction, which was first reported for monoanionic nickel bis(dithiolene) complexes.[7] To date, there have been limited reports of ligand-exchange reactions with neutral nickel bis(dithiolene) complexes.[8]

In an effort to synthesize new complexes bearing only one grafting function, the hydroxyl function (chosen for its high chemical compatibility with nickel bis(dithiolene) complexes

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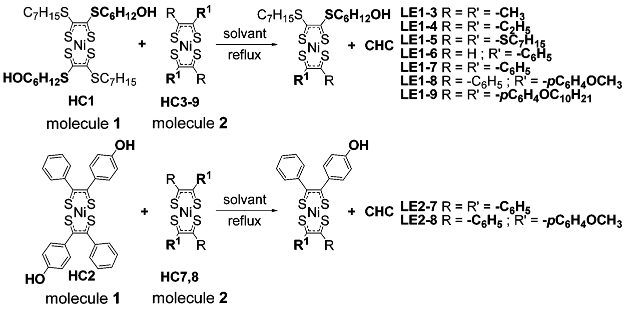
and the ease of etherification or O-alkylation reaction), we report the synthesis and characterization of new heteroleptic neutral nickel bis(dithiolene) complexes with tailor-made frontier orbital energies. Consequently, the feasibility of tuning their optical and electrochemical properties by the combination of different ligands is also highlighted.

■ RESULTS AND DISCUSSION

Nine heteroleptic nickel complexes were synthesized through ligand-exchange (LE) reaction between two homoleptic complexes (HC), a dihydroxylic nickel bis(dithiolene) complex, and another nickel bis(dithiolene) complex without any hydroxyl function. Thus, a series of molecules (**LE1−3** to **LE1−9**) was synthesized through ligand-exchange reaction between the dialcohol **HC1** and molecules **HC3** to **HC9**. Two other molecules (**LE2−7** and **LE2−8**) were obtained following a similar method, by reaction of the dihydroxylic **HC2** with **HC7** and **HC8**, respectively (see Scheme 1). Our strategy was first to select and synthesize HC as starting materials aimed at leading to heteroleptic complexes bearing only one hydroxyl function via ligand-exchange reactions. Therefore, we chose several molecules obtained by different synthetic routes, as described below.

Scheme 1. Synthesis of Heteroleptic Complexes Bearing a Hydroxyl Functional Group from Homoleptic Precursors[a]



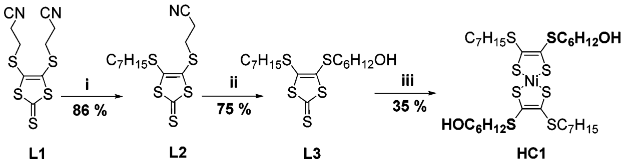
[a]CHC = corresponding homoleptic complexes.

Synthesis of the Precursors. The complex **HC1** is obtained in three steps. The reaction of 4,5-bis(2′-cyano-ethylthio)-1,3-dithiole-2-thione (**L1**) with an electrophilic alkylating agent as 1-bromoheptane in the presence of 1 equiv of cesium hydroxide hydrate allows the formation of 4-(2-cyano-ethylthio)-5-heptylthio-1,3-dithiole-2-thione (**L2**), which is then easily alkylated by 6-bromohexanol to give 4-(1-ol-hexylthio)-5-heptylthio-1,3-dithiole-2-thione (**L3**). Preparation of nickel complex **HC1** is carried out using the one-pot sequential addition of sodium methoxide to ligand **L3**, then tetrabutylammonium bromide and nickel(II) chloride. Oxidation of the product by a solution of iodine and sodium iodide in acetone generates the neutral complex **HC1** as a dark green wax. (See Scheme 2 and Supporting Information for full details.)[9]

In previous works, we have achieved the synthesis of many complexes from substituted diketones,[5] according to described procedures[10] that inspired us to prepare several symmetric complexes bearing phenyl rings or alkyl moieties. The overall synthetic route is shown in Scheme 3.

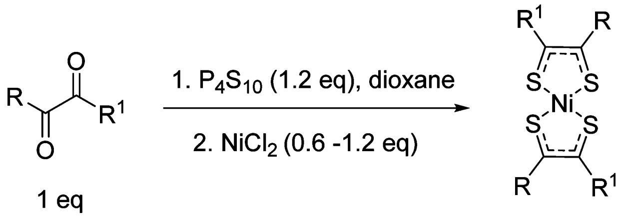
The conditions of preparations and yields in homoleptic complexes used in this work are summarized in Table 1. When 1 equiv of nickel dichloride was used, as recommended by Basu et al.,[11] we obtained similar results with acceptable yields (around 25%). Decreasing the amount of nickel salt up to 0.6 equiv[16] resulted in an increased yield. The low yield obtained in the case of complex **HC4** may have been due to its very low solubility. Complexes **HC5** and **HC6** were obtained in a different way according to published procedures.[12]

Scheme 2. Preparation Route of Complex HC1[a]



[a]Reagents and conditions: (i) CsOH·H_2O (1.05 equiv) in MeOH, $C_7H_{15}Br$ (1.2 equiv) in MeCN, 16 h at r.t.; (ii) CsOH·H_2O (1.05 equiv) in MeOH, $HOC_6H_{12}Br$ (1.2 equiv) in MeCN, 16 h at r.t.; (iii) NaOMe (2.5 equiv) in MeOH, reflux 2.5 h, NBu_4Br (2 equiv) then $NiCl_2$·$6H_2O$ (0.75 equiv) followed by NaI/I_2 (2.5/1 equiv) in acetone, for 16 h at r.t.

Scheme 3. General Route for Synthesis of Homoleptic Complexes from the "Diketone Route"



To resume, the dihydroxylic complexes were obtained after multistep syntheses and with modest overall yields: the **HC1** complex was obtained after five steps with an overall yield of 20%, and the **HC2** complex was obtained via a four-step synthesis with an overall yield of 47%. These two molecules were then engaged in the ligand-exchange reaction for heteroleptic complexes synthesis.

Synthesis of the Heteroleptic Complexes. Ligand-exchange reactions employing dithiolene complexes and other metal complexes has been widely used for generating mixed-ligand complexes.[13] The mechanism of ligand-exchange reaction was followed for the first time for monoanionic complexes of cobalt by the polarographic technique, and a mechanism was proposed.[14a] The first step is the formation of a stacking dinuclear intermediate in which the ligand exchange occurs, leading to a mixed-ligand dinuclear species. The final step is the dissociation of the mixed-ligand dinuclear species into two mixed-ligand complexes. In agreement with this mechanism, addition of a base such as phosphine or arsine, which is likely to suppress the last dissociation step, inhibits the reaction. Generally, ligand-exchange reactions between nickel bis(dithiolene) complexes are carried out from an equimolar mixture of the two reactants under reflux of poorly coordinating solvent.[8] For our part, we have tried to follow two different routes: route A involves the reaction between a formed complex (i.e., **HC7**) and a free ligand (i.e., ligand **L3**) in chloroform or toluene at reflux for 24 h. This route gave rise to no ligand-exchange. Only nonreacted starting materials were recovered in quantitative yield. Route B involves the reaction of two nickel complexes as generally described. Under such conditions and assuming that the affinities of ligands for nickel are equivalent, we logically expect to collect a mixture of which

Table 1. Syntheses Conditions and Yields of Homoleptic Complexes

complex	R, R^1	equiv of $NiCl_2$	yield^a (%)
HC2	$-pC_6H_4OH$, $-C_6H_5$	0.6	65
HC3	$-CH_3$, $-CH_3$	1.2	23
HC4	$-C_2H_5$, $-C_2H_5$	0.6	16
HC7	$-C_6H_5$, $-C_6H_5$	0.6	29
HC8	$-pC_6H_4OCH_3$, $-C_6H_5$	0.6	53
HC9	$-pC_6H_5OC_{10}H_{21}$, $-pC_6H_5OC_{10}H_{21}$	0.6	70^{b}i

[a] Isolated yield. [b] 2 equiv of P_4S_{10} were used.

Table 2. Heteroleptic Nickel Bis(dithiolene) Complexes Formation by Ligand-Exchange Reaction in Chloroform

molecule **1**	molecule **2** (R, R^1)	**1**/**2** molar ratio	reflux time (h)	product	yield (%)	(%) mol **1**^{a}	(%) mol **2**^{a}
HC1	**HC3** (CH_3, CH_3)	1/1.8	16	**LE1−3**	33		
HC1	**HC4** (C_2H_5, C_2H_5)	1/3	27	**LE1−4**	39	0	70
		1/4	16^b		50		
HC1	**HC5** (SC_7H_{15}, SC_7H_{15})	1/1.2	16	**LE1−5**	31		
HC1	**HC6** (Ph, H)	1/1.6	16	**LE1−6**	7		
HC1	**HC7** (Ph, Ph)	1/3	16	**LE1−7**	46		
HC1	**HC8** ($PhOCH_3$, Ph)	1/3	48	**LE1−8**	23	9	67
HC1	**HC9** ($PhOC_{10}H_{21}$, $PhOC_{10}H_{21}$)	1/3	32	**LE1−9**	20	0	82
HC2	**HC7** (Ph, Ph)	1/3	15	**LE2−7**	13	27	68
		1/3	15^b		10	23	69
HC2	**HC8** ($PhOCH_3$, Ph)	1/3	15	**LE2−8**	22	0	44

[a] Yield of recovered starting complexes, when possible, by means of column chromatography. [b] In this case, the used solvent is toluene.

Table 3. Ligand Effects on the $\pi-\pi^*$ Transition Energies in Nickel Bis(dithiolenes) (Solvent = Dichloromethane)^a

molecule **1**	λ_{max} (nm)	$E_{max}{}^1$ (eV)	molecule **2**	λ_{max} (nm)	$E_{max}{}^2$ (eV)	product	λ_{max} (nm)	E^{exp}_{max} (eV)	$[E_{max}{}^1 + E_{max}{}^2]/2$ (eV)
HC1	1007	1.23	**HC3**	772	1.61	**LE1−3**	890	1.39	1.42
HC1	1007	1.23	**HC4**	775	1.60	**LE1−4**	885	1.40	1.42
HC1	1007	1.23	**HC5**	1015	1.22	**LE1−5**	1007	1.23	1.23
HC1	1007	1.23	**HC6**	820	1.51	**LE1−6**	900	1.38	1.37
HC1	1007	1.23	**HC7**	867	1.43	**LE1−7**	911	1.36	1.33
HC1	1007	1.23	**HC8**	892	1.39	**LE1−8**	927	1.34	1.31
HC1	1007	1.23	**HC9**	932	1.33	**LE1−9**	951	1.30	1.28
HC2	870	1.42	**HC7**	867	1.43	**LE2−7**	871	1.42	1.43
HC2	870	1.42	**HC8**	892	1.39	**LE2−8**	890	1.39	1.41

[a] The values of energies (E_{max}) are taken at the maximum of the absorption band.

the molar composition of the equilibrium mixture $HC_x/LE_{x-y}/HC_y$ is 1:2:1.[8a] Our experience has shown that route A is not appropriate and that route B is better adapted to the ligand-exchange. However, since the ligand-exchange reaction was carried out at reflux for a long time, the operating conditions led to deterioration of the reagents and never led to this ideal composition. We therefore chose operating conditions for which the consumption of the functionalized reagents (**HC1** and **HC2**) was favored by using an excess amount of the second reagent (**HC3−9**, **HC7**, and **HC8**). Attempts to detect free ligand released during ligand-exchange by NMR spectroscopy have been unsuccessful because this reaction is in equilibrium and is very slow at room temperature (r.t).[14]

The yield of the reaction was calculated from the isolated heteroleptic product with respect to the engaged starting material (**HC1** or **HC2**) and not from any chromatography data. We did not observe significant changes in yields depending on the total concentration of reactants or used solvent. Improved yields are obtained when increasing the excess of molecule **2** as indicated for **LE1−4** synthesis. Table 2 summarizes the reaction conditions, with the solvent used being chloroform unless indicated.

Optical Properties. Studies of the optical properties of the nickel bis(dithiolene) complexes were carried out by ultraviolet−visible−near-infrared (UV−vis−NIR) absorption spectroscopy in dichloromethane. Generally, these complexes exhibit a fairly broad and intense absorption in the near-IR region (ε = 20 000 to 40 000 L mol^{-1} cm^{-1}) that has been assigned to a $\pi-\pi^*$ transition between the relatively high-lying HOMO and LUMO levels of the nickel bis(dithiolene) core.[15] To comprehend the optical characteristic of the heteroleptic complexes, the effects of ligand structure on the electronic spectra of their related symmetrical complexes "molecule **2**" are discussed below. As seen in Table 3 (see also Supporting Information, Table S1), the strong donating effect of the heptylthio chains in **HC5** induced a significant bathochromic shift in comparison to the tetrahydro complex (λ = 720 nm in hexane).[15] A more modest shift was observed for the tetramethyl or -ethyl derivatives, **HC3** and **HC4**, respectively.[15] Additionally, the delocalized π-system of arene-substituted **HC7** and **HC8** increased the electron density on the bis(dithiolene) core and also led to a shift of the absorption band to lowest energy.[15] Furthermore, a slight extension in the maximum wavelength λ_{max} can be noted when sequential substitutions by alkoxy groups take place on the phenyl ring (**HC8** and **HC9**). Similar trends can be observed for the corresponding heteroleptic complexes. It is noteworthy that when the parent molecules exhibit significantly different absorption domains, the absorption of the produced molecule lies in between (see Figure 1). As can be seen in Table 3 in the two last columns, the experimental values of the energies at the maximum absorption of the products obtained by ligand-exchange reaction (E_{max}) are very close to those of the average values for the corresponding parent molecules ($[E_{max}{}^1 + E_{max}{}^2]/2$). This illustrates how, as a powerful method for preparation of heteroleptic nickel bis(dithiolenes), the ligand-exchange reaction reveals another advantage: the possibility to predict the value of the π–π* transition energy (i.e., E_{max}, taken at the maximum of absorption) of a heteroleptic complex knowing those of its corresponding homoleptic parent molecules.

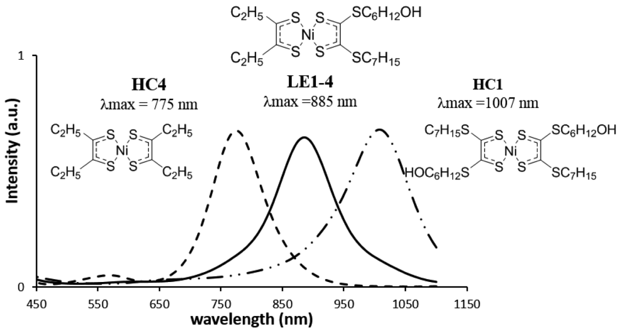


Figure 1. UV–vis–NIR spectra in CH_2Cl_2 of two parent molecules (**HC1** and **HC4**) and their product by ligand exchange reaction (**LE1–4**).

Electrochemical Properties. For each complex, excellent reversibility of first reduction and oxidation signals was observed. The cyclic voltammetry of complex **LE1–5** is shown in Figure 2 as an example. On the basis of experimental studies and theoretical calculations,[16] the noninnocent behavior of the dithiolene ligand has been described.[17] Therefore, it is well-known that the redox processes in nickel bis(dithiolene) complexes are built on their ligand-centered part: the charge is delocalized all over the complex core without any change of the formal oxidation +II of nickel.[13a,20] Generally, three redox couples are observed for these neutral nickel complexes and are attributed to two successive monoelectron reductions at around −0.77 and −0.13 V saturated calomel electrode (SCE), respectively, and one monoelectron oxidation near 0.73 V SCE (for an example, see Supporting Information, Figure S1). The first oxidation (reduction) potential corresponds to the HOMO (LUMO) level of the complex;[13a,18] the molecular orbital energies can thus be estimated directly from electrochemical results calibrated with ferrocene ($E_{1/2}$ $Fc^+/Fc = 0.44$ V SCE) with a value of −5.39 eV,[19] as listed in Table 4.

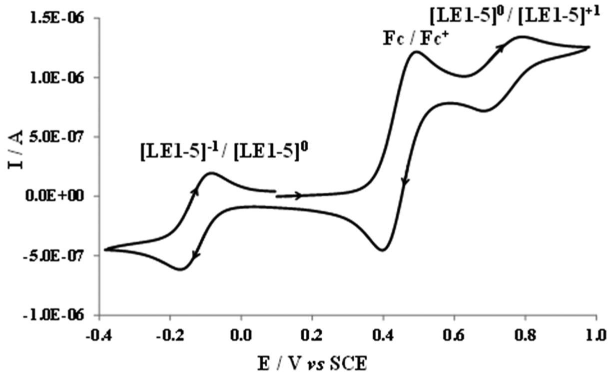


Figure 2. Cyclic voltammogram of complex **LE1–5** (4.6×10^{-3} mol L^{-1} in CH_2Cl_2) in the presence of ferrocene (1.07×10^{-2} mol L^{-1}) on platinum electrode ($r = 0.25$ mm) at 0.1 V/s with 0.1 mol L^{-1} of $(^nBu_4N)[PF_6]$ at room temperature.

As seen from this Table, a slight shift in the values of band gap E_g^{CV} due to the different ligand effect is noted. In the homoleptic complex series, the lowest values for E_g^{CV} (0.86 eV) were observed with thioalkyl ligands (**HC1** and **HC5**), while the highest values (1.29 and 1.27 eV) were observed with alkyl ligands (**HC3** and **HC4**); intermediate values (around 1 eV) were obtained with aryl ligands (**HC2**, **HC7–9**). This indicates that the electron-donating effect of the ligand results in a low value of the molecular gap. It was not possible to accurately measure the electrochemical characteristics of molecule **HC6** because of its weak stability due to the above-mentioned reactivity of hydrogen atom of the nickel dithiolene ring, in particular in diluted dichloromethane solution, which is a solvent that is particularly subject to radical formation. By closer inspection of the HOMO and LUMO energies, we also noticed that the nature of ligand affects clearly their values. The thioalkyl, alkyl, and aryl ligands led to complexes with LUMO levels located around 4.8, 4.7, and 4.9 eV, respectively, and with HOMO levels located around 5.7, 6.0, and 5.9 eV, respectively.

In the heteroleptic complex series, the same trends were observed. More interestingly, and as for optical transition energies (vide supra), we observed that the energetic values measured for the formed molecules were, in general, in between those of the parent molecules. This confirms the possibility offered by the ligand-exchange reaction to anticipate and tune the desirable values of HOMO and LUMO energies as well as E_g^{CV} of bis(dithiolene) complexes.

■ CONCLUSION

We have demonstrated for the first time a suitable route for incorporating only one hydroxyl function on nickel bis(dithiolene) complexes by the ligand-exchange reaction. This method is very convenient for (i) obtaining functionalized nickel bis(dithiolene) complexes in good yield, and (ii) generating molecules with predetermined energy levels. These nine molecules are stable dark-green solids with low band gap, a strong absorption in the near-IR region, good solubility in organic solvents, and high electron affinity. Furthermore, they can be readily and reversibly reduced, pointing to their potential as n-type conjugated materials for organic field-effect transistors and organic solar cells.

They all have only one hydroxyl function, offering the ability to graft them onto suitable polymers (in circumventing problem due to reticulation) by trans-etherification or O-alkylation, leading to materials with interesting electronic properties that are easy to set up. A study of their charge-transport properties and evaluation of their potential as acceptors in organic solar cells is under way and will be published separately.

■ EXPERIMENTAL SECTION

General Remarks. All chemicals and solvents were purchased from chemical suppliers and were used as received, unless otherwise mentioned. Purification of products was performed by flash

Table 4. Electrochemical Data and Related LUMO and HOMO Energies of Investigated Complexes

molecule	$E_{1/2}^{red}$ (V) (Fc^+/Fc)	$E_{1/2}^{ox}$ (V) (Fc^+/Fc)	E_{LUMO}[a] (eV)	E_{HOMO}[a] (eV)	E_g^{CV} (eV)
HC1	−0.58	+0.28	−4.81	−5.67	0.86
HC2	−0.45	+0.53	−4.94	−5.92	0.98
HC3	−0.65	+0.64	−4.74	−6.03	1.29
HC4	−0.66	+0.61	−4.73	−6.00	1.27
HC5	−0.57	+0.29	−4.82	−5.68	0.86
HC6	*b*	*b*			
HC7	−0.44	+0.73	−4.95	−6.12	1.17
HC8	−0.48	+0.59	−4.91	−5.98	1.07
HC9	−0.53	+0.47	−4.86	−5.86	1.0
LE1−3	−0.57	+0.41	−4.82	−5.80	0.98
LE1−4	−0.61	+0.40	−4.78	−5.79	1.01
LE1−5	−0.57	+0.29	−4.82	−5.68	0.86
LE1−6	−0.50	+0.44	−4.89	−5.83	0.93
LE1−7	−0.55	+0.41	−4.84	−5.80	0.96
LE1−8	−0.56	+0.39	−4.83	−5.78	0.94
LE1−9	−0.55	+0.36	−4.84	−5.75	0.92
LE2−7	−0.48	+0.65	−4.91	−6.04	1.13
LE2−8	−0.48	+0.59	−4.91	−5.98	1.07

[a] $E_{LUMO} = -[E_{1/2}^{red} + 5.39]$ eV; $E_{HOMO} = -[E_{1/2}^{ox} + 5.39]$ eV.[19] [b] No accurate value (see text).

chromatography on Geduran Si 60 silica gel (40−63 μm) from Merck with analytically pure solvents. For analytical thin layer chromatography (TLC), silica gel-coated substrates "60 F254" from Merck were used, and compounds were detected by illumination with UV lamp (λ = 254 or 365 nm). NMR spectra were recorded with a Bruker ARX 250 spectrometer at 250 MHz (^1H) and at 62.5 MHz (^{13}C), a Bruker DPX 300 spectrometer at 300 MHz (^1H) and at 75 MHz (^{13}C), and with a Bruker Avance 400 spectrometer at 400 MHz (^1H) and at 100 MHz (^{13}C). Chemical shifts are reported in parts per million (ppm) and were calibrated to the residual signals of the deuterated solvents; coupling constants (J) are indicated in Hz. Mass analyses were carried out by the Service de Spectrométrie de Masse de la Structure Fédérative Toulousaine en Chimie Moléculaire. Elemental analyses were carried out at the Service de microanalyse, CNRS, Gif sur Yvette. Electrochemical experiments were performed at r.t. in a homemade airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of an SCE separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface. The working electrode was a Pt microdisk (radius = 0.25 mm). The supporting electrolyte ($(^nBu_4N)[PF_6]$) (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. The dichloromethane, CH_2Cl_2, was freshly purified prior to use. The solutions used during the electrochemical studies were typically 5×10^{-3} mol L^{-1} in complex compound and 10^{-1} mol L^{-1} in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling argon through them, and the working electrode was polished with a polishing machine (Presi P230). UV−vis−NIR absorption spectra were recorded on two spectrometers, a Perkin-Elmer Lambda 35 and a Perkin-Elmer GX 2000, using the dichloromethane as solvent. The solutions used during the electronic absorption studies were typically about 10^{-5} mol L^{-1} in the complex.

Syntheses. General procedure for the synthesis of mono functionalized heteroleptic nickel bis(dithiolene) complexes. A mixture of molecule **1** and molecule **2** (see Table 2 for molar ratio) in $CHCl_3$ or toluene was heated to reflux. After the required time, the mixture was concentrated in vacuum to give a black residue that was purified by flash chromatography (silica gel; eluent = CH_2Cl_2/petroleum ether (1/1)) to give the desired product as a dark green powder.

Complex LE1−3. This was prepared from a mixture of **HC1** (0.17 mmol) and **HC3** (0.31 mmol) in 40 mL of $CHCl_3$, giving a dark green powder (33% yield). Anal. Calcd for $C_{19}H_{34}NiOS_6$: C, 43.10; H, 6.47; S, 36.33. Found: C, 43.23, H, 6.51, S, 36.35%. ^1H NMR (250 MHz, $CDCl_3$, δ): 3.70 (2H, t, 5 Hz m, $\underline{CH_2}OH$), 3.41 (4H, m, $\underline{CH_2}S$), 2.89 (1H, t, J = 5 Hz, $O\underline{H}$), 2.59 (6H, s, $\underline{CH_3}$), 1.93 (4H, m, $\underline{CH_2}CH_2S$), 1.76−1.31 (18H, m, $\underline{CH_2}$), 0.93 (3H, t, J = 6.36 Hz, $CH_2\underline{CH_3}$). UV−vis−NIR: λ_{max} = 890 nm (23 510). IR: 1084 (s), 1328 (s), 1375 (s), 1429 (s), 2898 (s), 3359 (br, $\nu CH_2{-}OH$) cm^{-1}.

Complex LE1−4. This was prepared from a mixture of **HC1** (0.5 mmol) and **HC4** (2.10 mmol) in 40 mL of $CHCl_3$, giving a dark green powder (39% yield). Anal. Calcd for $C_{21}H_{38}NiOS_6$: C, 45.24; H, 6.87; S, 34.50. Found: C, 45.13, H, 6.79, S, 34.52%. ^1H NMR (300 MHz, $CDCl_3$, δ): 3.70 (2H, m, $\underline{CH_2}OH$), 3.42 (4H, m, $\underline{CH_2}S$), 2.94 (4H, m, $C{=}C\underline{CH_2}$), 2.64 (1H, s, $O\underline{H}$), 1.94 (4H, m, $\underline{CH_2}CH_2S$), 1.71−1.20 (20H, m, $\underline{CH_2}$ and $C{=}CCH_2\underline{CH_3}$), 0.92 (3H, t, J = 6.66 Hz, $\underline{CH_3}$). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 177.153, 62.88, 37.05, 36.84, 32.60, 31.69, 30.96, 29.02, 28.82, 28.80, 28.00, 27.97, 25.31, 22.63, 15.61, 14.11, UV−vis−NIR: λ_{max} = 885 nm (25 110). IR: 1198 (s), 1208 (s), 1452 (s), 2852 (s), 2923 (s), 3361 (br, $\nu CH_2{-}OH$) cm^{-1}.

Complex LE1−5. This was prepared from a mixture of **HC1** (0.53 mmol) and **HC5** (0.64 mmol) in 50 mL of $CHCl_3$, giving a dark green powder (31% yield). Anal. Calcd for $C_{31}H_{58}NiOS_8$: C, 48.87; H, 7.67; S, 33.66. Found: C, 48.81, H, 6.71, S, 33.54%. ^1H NMR (300 MHz, $CDCl_3$, δ): 3.68 (2H, t, J = 6.4 Hz, $\underline{CH_2}OH$), 3.40 (8H, t, J = 7.29 Hz, $\underline{CH_2}S$), 1.87 (8H, m, $\underline{CH_2}CH_2S$), 1.73−1.20 (m, 28H, $\underline{CH_2}$), 0.92 (9H, t, J = 6.37 Hz, $\underline{CH_3}$). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 176.28, 175.81, 62.86, 36.69, 36.50, 32.60, 31.71, 29.98, 28.84, 28.75, 28.47, 25.33, 22.64, 14.13. HRMS (CI−CH_4) (m/z): [M^+] calcd for 760.1594; found, 760.1757. UV−vis−NIR: λ_{max} = 1007 nm (35 500). IR: 1161 (s, br), 1213 (s, br), 1417 (s), 1456 (s), 2851 (s), 2921 (s, br), 3272 (br, $\nu CH_2{-}OH$) cm^{-1}.

Complex LE1−6. This was prepared from a mixture of **HC1** (0.36 mmol) and **HC6** (0.61 mmol) in 50 mL of $CHCl_3$, giving a dark green powder (7% yield). Anal. Calcd for $C_{23}H_{34}NiOS_6$: C, 47.83; H, 5.93; S, 33.30. Found: C, 47.91, H, 5.87, S, 33.44%. ^1H NMR (250 MHz, $CDCl_3$, δ): 8.78 (1H, s, H of dithiolene ring) 7.92 (2H, d, J = 7.37 Hz, aromatic H), 7.46 (3H, m, aromatic H), 3.67 (2H, t, J = 5.79 Hz, $\underline{CH_2}OH$), 3.46 (4H, dt, J = 7.29 Hz, 4.64 Hz, $\underline{CH_2}S$), 1.99 (4H, m, $\underline{CH_2}CH_2S$), 1.69−1.28 (14H, m, $\underline{CH_2}$), 0.95 (3H, t, J = 6.51 Hz, $\underline{CH_3}$). ^{13}C NMR (62.5q MHz, $CDCl_3$, δ): 189.07, 172.74, 154.30, 138.51, 128.84, 128.75, 126.72, 62.61, 37.48, 37.33, 32.64, 31.66, 28.99, 28.81, 28.78, 27.62, 25.31, 22.61, 13.85. HRMS (CI−CH_4): [M +] calcd for 576.0287; found, 576.0301. UV−vis−NIR: λ_{max} = 900 nm (30 200). IR: 683 (s), 745 (s), 844 (s, $\nu R{-}C({=}S)2$), 959 (s, br), 1159 (s, br, $\nu C{=}S$), 1177 (s, br), 1228 (s), 1425 (s), 1454 (s), 2849 (s), 2916 (s), 3337 (br, $\nu CH_2{-}OH$) cm^{-1}.

Complex LE1−7. This was prepared from a mixture of **HC1** (0.64 mmol) and **HC7** (1.92 mmol) in 50 mL of $CHCl_3$, giving a dark green powder (46% yield). Anal. Calcd for $C_{29}H_{38}NiOS_6$: C, 53.29; H, 5.86;

S, 29.43. Found: C, 53.35, H, 5.87, S, 29.38%. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.36 (4H, d, *J* = 6.58 Hz, aromatic H), 7.28 (6H, m, aromatic H), 3.72 (2H, dd, *J* = 11.97 Hz, 6.19 Hz, $\underline{CH_2}OH$), 3.42 (4H, m, $\underline{CH_2}S$), 1.97 (4H, m, $\underline{CH_2}CH_2S$), 1.70−1.30 (14H, m, $\underline{CH_2}$), 1.26 (1H, t, *J* = 5.29 Hz, $O\underline{H}$), 0.93 (3H, t, *J* = 6.71 Hz, $\underline{CH_3}$). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 168.75, 140.80, 129.45, 128.21, 128.15, 62.85, 37.44, 37.21, 32.57, 31.67, 29.06, 28.84, 28.82, 27.69, 27.66, 25.33, 22.62, 14.11. HRMS (CI−CH$_4$) (*m*/*z*): [M + H$^+$] calcd for 655.0633; found, 655.0635. UV−vis−NIR: λ_{max} = 911 nm (35 157). IR: 699 (s), 747 (s), 883 (s, νR−C(=S)$_2$), 1028 (s), 1157 (s, br, νC=S), 1236 (s, br), 1417 (s), 1448 (s), 2849, 2924, 3349 (br, νCH$_2$−OH) cm^{-1}.

Complex LE1−8. This was prepared from a mixture of **HC1** (0.26 mmol) and **HC8** (0.78 mmol) in 30 mL of CHCl$_3$, giving a dark green powder (23% yield). Anal. Calcd for $C_{30}H_{40}NiO_2S_6$: C, 52.70; H, 5.90; S, 28.14. Found: C, 52.78, H, 5.86, S, 28.12%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.33 (7H, m, aromatic H), 6.80 (2H, d, *J* = 8.30 Hz, aromatic H), 3.82 (3H, s, br, $\underline{CH_3}OPh$), 3.69 (2H, t, *J* = 6.07 Hz, $\underline{CH_2}OH$), 3.41 (4H, m, $\underline{CH_2}S$), 1.96 (4H, m, $\underline{CH_2}CH_2S$), 1.71−1.25 (15H, m, $\underline{CH_2}$ and OH), 0.92 (3H, t, *J* = 5.73 Hz, $\underline{CH_3}$). HRMS (CI−CH$_4$) (*m*/*z*): [M$^+$] calcd for 682.0706; found, 682.0709. UV−vis−NIR: λ_{max} = 928 nm (34 590). IR: 689 (s), 1145 (s, br, νC=S), 1171 (s), 1235 (s, br, νC−O), 1592 (s), 2848 (s), 2918 (s), 3323 (br, νCH$_2$−OH) cm^{-1}.

Complex LE1−9. This was prepared from a mixture of **HC1** (0.26 mmol) and **HC9** (0.78 mmol) in 30 mL of CHCl$_3$, giving a dark green powder (20% yield). Anal. Calcd for $C_{49}H_{78}NiO_3S_6$: C, 60.91; H, 8.14; S, 19.91. Found: C, 60.85, H, 8.07, S, 19.85%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.30 (4H, d, *J* = 8.71 Hz, aromatic H), 6.80 (4H, d, *J* = 8.71 Hz, aromatic H), 3.96 (4H, t, *J* = 6.50 Hz, $\underline{CH_2}OPh$), 3.69 (2H, t, *J* = 6.40 Hz, $\underline{CH_2}OH$), 3.41 (4H, m, $\underline{CH_2}S$), 1.95 (4H, m, $\underline{CH_2}CH_2S$), 1.80 (5H, m, $\underline{CH_2}$ and $O\underline{H}$), 1.68−1.20 (48H, m, $\underline{CH_2}$), 0.91 (3H, t, *J* = 5.73 Hz, $\underline{CH_3}$). ^{13}C NMR (75 MHz, CDCl$_3$, δ): 186.27, 186.06, 169.91, 159.56, 133.57, 130.61, 114.08, 68.14, 62.65, 37.34, 37.19, 31.93, 31.70, 29.60, 29.58, 29.41, 29.34, 29.25, 29.03, 28.83, 27.84, 27.82, 26.03, 25.36, 22.71, 22.63, 13.90. HRMS (CI−CH$_4$) (*m*/*z*): [M$^+$] calcd for 964.3629; found, 964.3631. UV−vis−NIR: λ_{max} = 951 nm (36 800). IR: 1161 (d, br, νC=S), 1238 (s, br, νC−O), 1599 (s), 2852 (s), 2923 (s), 3345 (br, νCH$_2$−OH).

Complex LE2−7. This was prepared from a mixture of **HC2** (0.175 mmol) and **HC7** (0.525 mmol) in 40 mL of CHCl$_3$, giving a dark green powder (13% yield). Anal. Calcd for $C_{28}H_{20}NiOS_4$: C, 60.12; H, 3.60; S, 22.92. Found: C, 60.18, H, 3.55, S, 22.86%. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, δ): 7.46−7.28 (17H, m, aromatic H), 6.79 (2H, d, *J* = 8.70 Hz, aromatic H), 5.07 (1H, s, br, PhOH). ^{13}C NMR (75 MHz, CDCl$_3$, δ): 182.74, 182.15, 156.92, 141.55, 141.23, 134.93, 130.65, 128.99, 128.88, 128.80, 128.46, 128.34, 115.35. HRMS (CI−CH$_4$) (*m*/*z*): [M$^+$] calcd for 557.9750; found, 557.9766. UV−vis−NIR: λ_{max} = 871 nm (25 830).

Complex LE2−8. This was prepared from a mixture of **HC2** (0.19 mmol) and **HC8** (0.57 mmol) in 40 mL of CHCl$_3$, giving a dark green powder (22% yield). Anal. Calcd for $C_{29}H_{22}NiO_2S_4$: C, 59.09; H, 3.76; S, 21.76. Found: C, 59.13, H, 3.71, S, 21.69%. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.47−7.26 (14H, m, aromatic H), 6.79 (4H, m, aromatic H), 5.14 (1H, s, br, $PhO\underline{H}$), 3.84 (3H, s, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$, δ): 168.75, 140.80, 129.45, 128.21, 128.15, 62.85, 37.44, 37.21, 32.57, 31.67, 29.06, 28.84, 28.82, 27.69, 27.66, 25.33, 22.62, 14.11. HRMS (CI−CH$_4$) (*m*/*z*): [M$^+$] calcd for 587.9856; found, 587.9854. UV−vis−NIR: λ_{max} = 890 nm (23 480).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table showing the effect of ligands on the NIR absorption band of molecule **2**; cyclic voltammogram of complex **LE1−5**; synthetic procedures of ligands and complexes and their characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kathleen.chane@lcc-toulouse.fr. Phone: +33 5 61 33 31 52.

Notes

The authors declare no competing financial interest.

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