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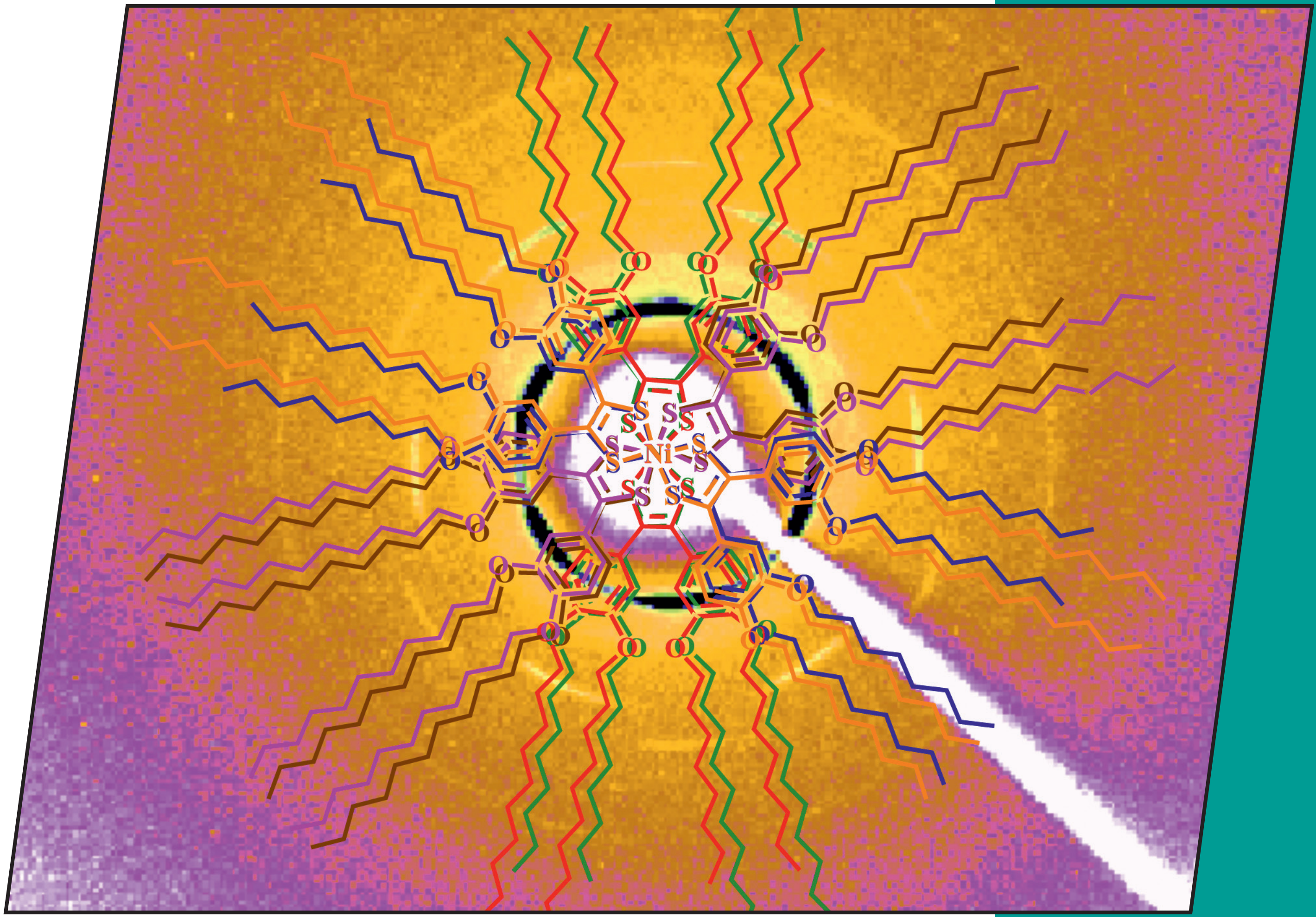

***Cover Picture***

*Bénédicte Garreau-de Bonneval, Kathleen I. Moineau-Chane Ching et al.*
*Discotic Nickel Bis(dithiolene) Complexes*

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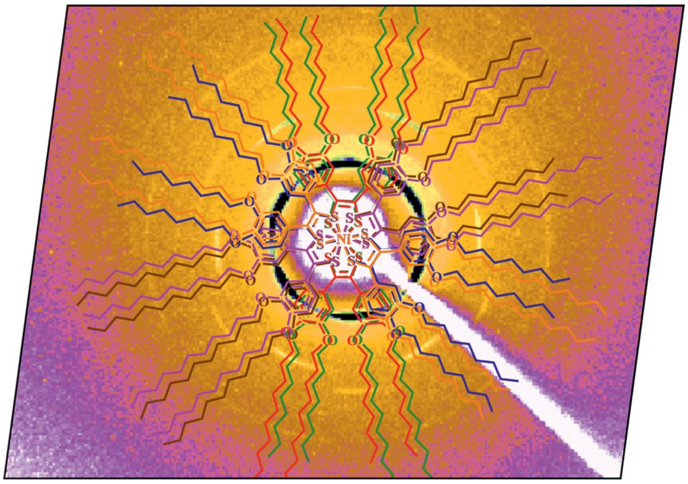
## COVER PICTURE

**The cover picture shows** nickel bis(dithiolene) compounds in which different lengths of alkyl chains are grafted on the periphery of the octasubstituted core molecule. The synthesis affords a mixture, which was analyzed by X-ray diffraction. The obtained X-ray pattern at 70 °C is presented as the background and corresponds to a hexagonal columnar liquid-crystalline phase. Such a pattern is not observed for the corresponding pure isolated compounds. Details are discussed in the article by B. Garreau-de Bonneval, K. I. Moineau-Chane Ching et al. on p. 2663 ff. The authors thank the French National Research Agency (ANR) for supporting this work.



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# Discotic Nickel Bis(dithiolene) Complexes – Synthesis, Optoelectrochemical and Mesomorphic Properties

Thanh-Tuan Bui,[a,b] Olivier Thiebaut,[c] Eric Grelet,[c] Marie-France Achard,[c]
Bénédicte Garreau-de Bonneval,*[a,b] and Kathleen I. Moineau-Chane Ching*[a,b]

**Keywords:** Nickel / S ligands / Liquid crystals / Electrochemistry / Organic electronics

Fifteen neutral long-chain-substituted discotic nickel bis(1,2-diphenyl-1,2-ethenedithiolene) complexes [Ni(dpedt)$_2$], including thirteen new compounds, have been synthesized by new short and efficient synthetic pathways. Physical investigations show that these complexes are thermally stable, possess good electron-accepting properties, and absorb light strongly in the near-infrared spectral region. Electrochemical and optical properties of [Ni(dpedt)$_2$] depend moderately on the functionalities attached to the phenyl rings of the complexes. Their LUMO and HOMO energy levels are in the range –4.7 to –5.0 and –5.7 to –6.0 eV, respectively. Two octa($n$-alkoxy)-substituted complexes exhibit a columnar liquid crystalline phase with hexagonal symmetry. These highly soluble complexes are potential candidates for use as electron-accepting and electron-transporting materials for active layers in organic electronic applications, such as field-effect transistors or photovoltaic devices.

## Introduction

In the last decade, the research in organic photovoltaics has led to many important achievements. The power conversion efficiency of devices initially reported by Tang,[1] was 1%; nowadays it has risen to values higher than 7%.[2] The most promising results have been obtained with bulk heterojunction device architectures, which are based on the association of electron-donating and electron-accepting semiconducting materials. Absorption of photons generates excitons, which diffuse to the donor/acceptor interface, where they are dissociated into free charge carriers, holes and electrons, respectively. Donor/acceptor heterojunctions in organic electronics can be created with different materials for the active layer, and a smart way to improve the charge carrier mobility is to use liquid crystalline ordering.[3] Discotic columnar liquid crystals have been shown to exhibit high exciton diffusion lengths and charge carrier mobilities along the columns relative to conventional materials used in organic photovoltaic cells.[4,5]

In the last few years, many research activities have focused on the use of liquid crystalline materials in organic photovoltaics.[6] In this aim, the realization of an oriented bilayer heterojunction has been recently achieved by annealing-induced macroscopic self-assembly of two columnar liquid crystals based on perylene and pyrene derivatives,[7] bringing the first proof of principle of an organic heterojunction based on two *oriented* columnar liquid crystal layers. To continue, we are now expanding our investigations towards new electron-accepting columnar liquid crystalline materials that absorb in the near-infrared (NIR). Nowadays, only a few discotic materials are known to absorb in the NIR region.[8] Moreover, research on new NIR materials for organic photovoltaics is mainly focused on electron-donating materials;[9] less work has been dedicated to their electron-accepting counterparts. A recent example of NIR acceptor materials is 9,9′-bifluorenylidene, which leads to a power conversion efficiency of up to 2%.[10] In this context, neutral nickel bis(dithiolene) complexes are promising potential candidates. The optical, magnetic, conductive, and superconductive properties of these complexes have placed them among the most important families of precursors to new generations of optoelectronic devices.[11] In the present work, we are interested in the synthesis and physical features of discotic compounds based on neutral nickel bis(1,2-diphenylethene-1,2-dithiolene) complexes, abbreviated as [Ni(dpedt)$_2$].

## Results and Discussion

### Material Synthesis

The synthetic pathways are outlined in Scheme 1, and the list of nickel complexes is presented in Table 1.

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[a] CNRS: LCC (Laboratoire de Chimie de Coordination),
205 Route de Narbonne, 31077 Toulouse, France
Fax: +33-561553003
E-mail: bdb@lcc-toulouse.fr
kathleen.chane@lcc-toulouse.fr
[b] Université de Toulouse (UPS, INPT, LCC),
31077 Toulouse, France
[c] Centre de Recherche Paul-Pascal, CNRS – Université de Bordeaux,
115 Avenue Schweitzer, 33600 Pessac, France

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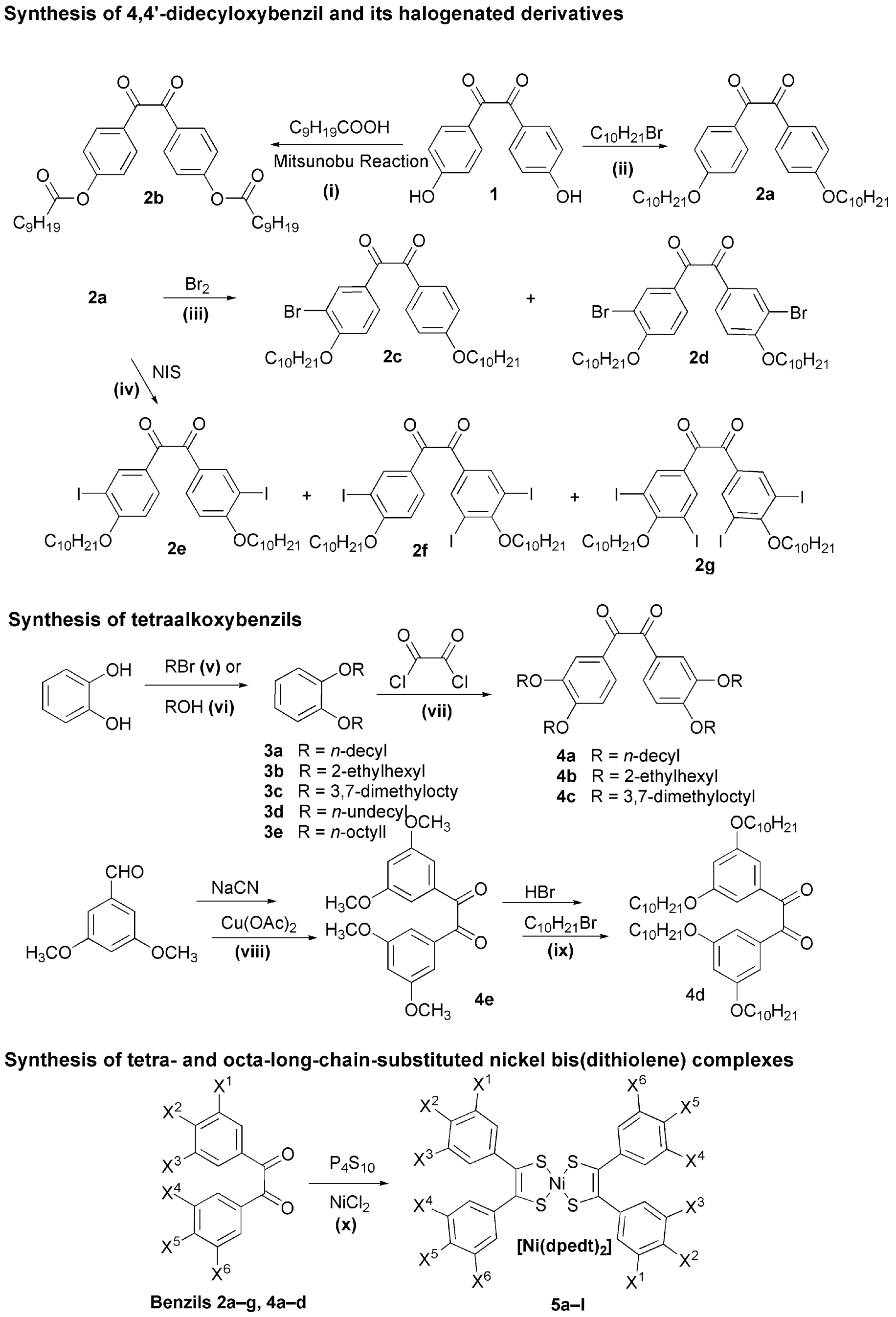


Scheme 1. Synthesis of nickel bis(dithiolene) complexes. Reagents and conditions: (i) DEAD (2.4 equiv.), $PPh_3$ (2.4 equiv.), decanoic acid (2.4 equiv.), tetrahydrofuran, 0 °C then 1 h at room temperature; (ii) and (v) RBr (2.4 equiv.), $K_2CO_3$ (3.0 equiv.), dimethylformamide, 90 °C; (iii) $Br_2$ (2 to 5.0 equiv.), $FeCl_3$ (1.0 to 2.0 equiv.), dichloromethane/acetonitrile (1:0 to 1:1 v/v), room temperature or reflux overnight; (iv) NIS, trifluoroacetic acid, reflux 3.5 h; (vi) ROH (2.4 equiv.), DEAD (2.4 equiv.), $PPh_3$ (2.4 equiv.), tetrahydrofuran, 0 °C then 1 h at room temperature; (vii) oxalyl chloride (0.6 equiv.), $AlCl_3$ (0.5 equiv.), 1,2-dichloroethane, 0 °C then overnight at room temperature; (viii) 1) NaCN (0.4 equiv.), water/ethanol (1:2 v/v), reflux 36 h 2) $Cu(OAc)_2$ (0.01 equiv.), $NH_4NO_3$ (1.25 equiv.), acetic acid/water (4:1 v/v), reflux 2 h; (ix) 1) bromohydric acid/acetic acid (1:1 v/v), reflux 5 h 2) excess $C_{10}H_{21}Br$, $K_2CO_3$, dimethylformamide, 18 h at 90 °C; (x) $P_4S_{10}$ (2.2 equiv.), dioxane, reflux 5 h then adding $NiCl_2{\cdot}6H_2O$ (0.55 equiv.), water, reflux 2 h in air.

### *Synthesis of 4,4′-Didecyloxybenzil and Its Halogenated Derivatives*

In this part, we present the synthesis of disubstituted benzil derivatives. The substituents are in all cases long alkyl chains. In order to study the influence of the connecting group on the mesomorphic and physical properties of nickel complexes, we use the ether and ester functions. The symmetric 4,4′-didecyloxybenzil (**2a**) is obtained by the Mitsunobu reaction from the 4,4′-dihydroxybenzil (**1**) in quantitative yield by heating the mixture of **1** with a large excess of decyl bromide and potassium carbonate in dimethylformamide. As demonstrated in a previous study,[12]

Table 1. List of long-chain-substituted nickel bis(dithiolene) complexes [Ni(dpedt)$_2$].

| | | $X^1$ | $X^2$ | $X^3$ | $X^4$ | $X^5$ | $X^6$ | Yield[c] (%) |
|---|---|---|---|---|---|---|---|---|
| Tetrasubstituted | **5a** | H | $OC_{10}H_{21}$ | H | H | $OC_{10}H_{21}$ | H | 70 |
| | **5b** | Br | $OC_{10}H_{21}$ | H | H | $OC_{10}H_{21}$ | H | 76 |
| | **5c** | Br | $OC_{10}H_{21}$ | H | H | $OC_{10}H_{21}$ | Br | 65 |
| | **5d** | I | $OC_{10}H_{21}$ | H | H | $OC_{10}H_{21}$ | I | 81 |
| | **5e** | I | $OC_{10}H_{21}$ | I | H | $OC_{10}H_{21}$ | I | 55 |
| | **5f** | I | $OC_{10}H_{21}$ | I | I | $OC_{10}H_{21}$ | I | 30 |
| | **5g** | H | $OC(=O)C_9H_{19}$ | H | H | $OC(=O)C_9H_{19}$ | H | 10 |
| Octasubstituted | **5i** | $OC_{10}H_{21}$ | $OC_{10}H_{21}$ | H | H | $OC_{10}H_{21}$ | $OC_{10}H_{21}$ | 30 |
| | **5j** | $OC_{10}H_{21}$ | H | $OC_{10}H_{21}$ | $OC_{10}H_{21}$ | H | $OC_{10}H_{21}$ | 28 |
| | **5k** | $OC_{10}H_{21}$[a] | $OC_{10}H_{21}$[a] | H | H | $OC_{10}H_{21}$[a] | $OC_{10}H_{21}$[a] | 28 |
| | **5l** | $OC_8H_{17}$[b] | $OC_8H_{17}$[b] | H | H | $OC_8H_{17}$[b] | $OC_8H_{17}$[b] | 41 |

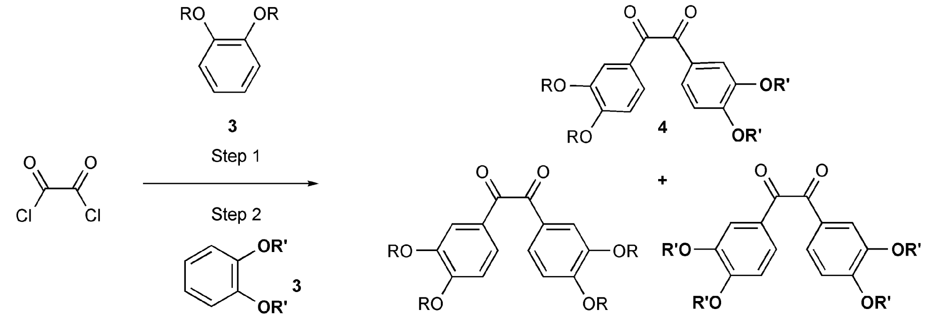
[a] Racemic-3,7-dimethyloctyloxy. [b] Racemic-2-ethylhexyloxy. [c] Yields are related to complex formation.

the Mitsunobu reaction[13] is a powerful tool for synthesis of aromatic ethers directly from phenol derivatives and alcohols. In this case, phenol derivatives play the role of the weak acid. Interestingly, in the Mitsunobu reaction, the phenol derivatives may play an ambivalent role. When the alcohol is replaced by *n*-decanoic acid, **1** reacts as an alcohol, providing the corresponding ester **2b** in good yield (93%) without any optimization. The halogenation of **2a** resulting in benzil derivatives **2c**–**2g** is performed by using modified procedures reported elsewhere.[14] The treatment of **2a** with excess bromine in dichloromethane only gives 3-bromo-4,4′-didecyloxybenzil (**2c**) in low yield (12% after 12 h at room temperature). The introduction of one stoichiometric equivalent of ferric chloride gives a mixture of **2c** and dibromo-substituted benzil **2d** with a mass ratio **2c**/**2d** of approximately 1:2 after reaction overnight at ambient temperature. Compound **2d** can be also achieved in good yield (94%) by heating **2a** at reflux overnight with an excess of $Br_2$ and two equivalents of ferric chloride in an equivolumetric mixture of dichloromethane and acetonitrile. Di/tri/tetraiodo-substituted benzils **2e**–**2g** are synthesized by heating **2a** at reflux with *N*-iodosuccinimide (NIS) in trifluoroacetic acid as solvent. Depending on the NIS/**2a** stoichiometry (2:1, 3:1, or 5:1), **2e**, **2f**, and **2g** are isolated as major products in acceptable yields 88%, 43%, and 59%, respectively. During the synthesis of **2e**, careful purification of crude product gives a small quantity of **2f**. When the quantity of NIS is raised up to five equivalents, **2g** is obtained as main product in addition to a small quantity of **2f**. The use of three equivalents of NIS gives a mixture of the three compounds: **2e**–**2g**, **2f** being the major product.

### *Synthesis of Tetraalkoxybenzils*

1,2-Dialkoxybenzenes **3** are obtained from pyrocathecol. The desired linear and branched alkyl chains are attached to the phenol functions by either the classical nucleophilic substitution (**3a**, **3b**, **3d**–**3e**) or the Mitsunobu method (**3c**), depending on the commercial availability of the alkyl chains. 3,3′,4,4′-Octaalkoxybenzil derivatives **4** are achieved by the double Friedel–Crafts reaction with oxalyl chloride as the acylating agent.[15] The benzil backbone is created in one step in moderate yields (around 30–40%). Although Mohr et al.[15] reported that two equivalents of aluminum chloride per equivalent of oxalyl chloride are needed, it is found that only one is sufficient. We then attempted to couple the intermediate complex aroyl chloride with additional 1,2-dialkoxybenzene in situ to prepare and isolate the asymmetrical 1,2-diketones by a one-pot procedure as presented in Scheme 2 (see Experimental Section for more detail).

However, in each case, after purification by column chromatography, a mixture of inseparable benzil derivatives is obtained. The three benzil derivative mixtures, **B10.10** (R = *n*-decyl, R′ = 3,7-dimethyloctyl), **B11.10** (R = *n*-undecyl, R′ = 3,7-dimethyloctyl), and **B11.8** (R = *n*-undecyl, R′ = *n*-octyl), appeared as a single spot when analyzed by thin layer chromatography. This is due to the very similar molecular structures, weights, and polarities of these products. The analysis of these mixtures by high-performance liquid chromatography shows the presence of three benzils with a mass proportion of approximately 1:2:1. None of the mixtures was further purified or characterized but transformed directly into nickel bis(dithiolene) complexes.



Scheme 2. Synthesis of mixture of asymmetrical benzils.

The synthesis of 3,3′,5,5′-tetradecyloxybenzil (**4d**) is depicted in Scheme 1. This synthesis was developed by following the modified route of Wenz[16] and Ohta.[17] The benzoin condensation of 3,5-dimethoxybenzaldehyde catalyzed by sodium cyanide gives the corresponding benzoin. This product is not purified but directly used in the next step. The cupric acetate catalytic oxidation of benzoin to benzil[18] provides 3,3′,5,5′-tetramethoxybenzil (**4e**) in moderate yields after two steps (22%). Compound **4e** is then demethylated in a boiling mixture of bromic and acetic acids, giving the 3,3′,5,5′-tetrahydroxybenzil intermediate as a yellow solid. This intermediate is then heated without any purification with a large excess of decyl bromide and potassium carbonate, providing 3,3′,5,5′-tetradecyloxybenzil (**4d**). The yellow solid **4d** is obtained in a 53% yield after two steps of demethylation and alkylation from **4e**. Globally, the desired benzil **4d** is achieved in a 12% yield from the commercially available 3,5-dimethoxybenzaldehyde.

### *Synthesis of Tetra- and Octa-Long-Chain-Substituted Nickel Bis(dithiolene) Complexes*

As depicted in Scheme 1, the final neutral nickel complexes are achieved from the benzil precursors. This step has been already discussed in a previous work.[12] Almost all nickel complexes were obtained in quite good yields (see Table 1), except for **5g**, for which a major portion of black crude product could not be purified because of its low solubility. Repeated column chromatography purification provides two green compounds in small quantities (**5g** and **5h** with a mass ratio **5g/5h** of ca. 6:1). The structure of **5h** (Figure 1) was elucidated by $^1$H and $^{13}$C NMR spectroscopy and mass spectrometry.

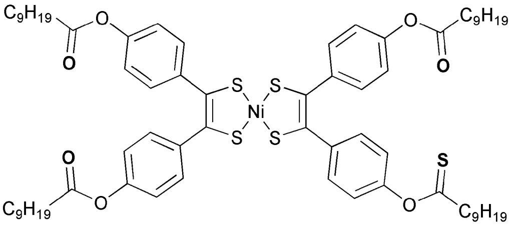
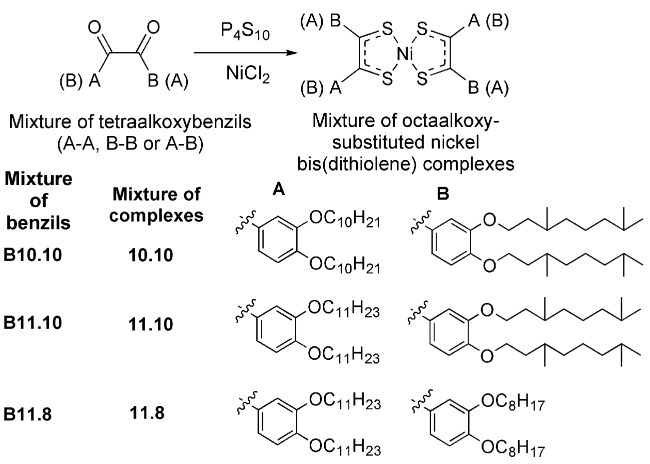


Figure 1. Structure of **5h**.

The three benzil mixtures **B10.10**, **B11.10**, and **B11.8** are transformed into three black mixtures of octaalkoxy-substituted nickel bis(dithiolene) complexes, called **10.10**, **11.10**, and **11.8**, respectively (Scheme 3).



Scheme 3. Synthesis of mixtures of octaalkoxy-substituted nickel complexes.

Theoretically, each of the three mixtures may contain up to eight nickel complexes (*cis*/*trans* configuration is ignored). Byproducts and impurities are eliminated by repeated precipitation processes from dichloromethane solution and repeated column chromatography with mixtures of hexane and dichloromethane as eluents. However, it is not possible to separate the nickel complexes from these mixtures.

By convention, all complexes in the present work are presented in their *trans* configuration, as their exact configurations were not elucidated, because no suitable crystals for single-crystal X-ray diffraction analysis were obtained. Except for mixtures of complexes, all compounds were identified by usual analytical methods such as $^1$H and $^{13}$C NMR spectroscopy, mass spectrometry, electronic absorption spectroscopy, and elemental analysis.

In order to envisage the use of our nickel bis(dithiolene) complexes as active materials in organic electronic devices, physical properties of these complexes have to be characterized. In the following text, the electrochemical, optical and phase behavior properties of these compounds will be presented.

## Electrochemical and Optical Properties

The electrochemical properties of these long-chain-substituted nickel complexes were investigated by cyclic and square wave voltammetry (see Table S1 in the Supporting Information). In some cases, we recorded irreversible redox processes on platinum electrodes, and the results were somewhat less exploitable than those obtained by using glassy carbon electrodes. However, the results globally remained in good accordance, regardless of the working electrode. To a first approximation, the reduction potential (couple 2) can be related to the electron affinity, EA, and thus to the LUMO energy level, according to the following equation: EA ($E_{\text{LUMO}}$) = $-(E_{1/2}{}^2 + 4.8)$.[19,20] A similar relationship can be used for the oxidation potential (couple 3), the ionization potential, IP, and the HOMO energies: IP ($E_{\text{HOMO}}$) = $-(E_{1/2}{}^3 + 4.8)$.

The optical properties of the nickel complexes were investigated by UV/Vis/NIR absorption spectroscopy in dichloromethane. The experimental values of the maximum of absorption ($\lambda_{\max}$), the molar extinction coefficient ($\varepsilon$), and the optical band gap ($E_g{}^{\text{opt}}$) are summarized in Table 2. The optical band gap is calculated by the equation: $E_g{}^{\text{opt}} = hc/\lambda_{\text{onset}}$ according to Tauc's law.[20] The typical cyclic voltammograms of **5a**, **5g**, and **5f** in dichloromethane solution are shown in Figure 2. Three redox waves are observed for each compound, as described before.[21]

All the electrochemical and optical data of the nickel complexes in dichloromethane solution are presented in Table 2. From cyclic voltammetry measurements, the half-wave potentials of reversible electrochemical processes are measured and used to evaluate the LUMO and HOMO energy levels.

## Tetra-Long-Chain-Substituted Nickel Complexes and Related Compounds

### *Influence of the Connecting Group*

It has been demonstrated for the tetra-long-chain-substituted [Ni(dpedt)$_2$] that the replacement of alkoxy substituents by alkyl ones causes moderate variation in their electrochemical properties.[22] This is due to the difference of the nature of the connecting group between the chains and the phenyl groups. Compound **5g** was synthesized to study the influence of the connecting group. It differs from **5a** by the nature of the connecting group [–O– in **5a** and –OC(=O)– in **5g**], whereas the chain lengths are the same (C$_{10}$). The replacement of *n*-decyloxy substituents by *n*-decanoate ones slightly increases the values of both redox potentials of **5g** in comparison with those of **5a**. This is attributed to the electron-attracting effect of the carbonyl group, which decreases the electron density on the complex core. As a consequence, the $E_{1/2}{}^2$ and $E_{1/2}{}^3$ values for **5g** are shifted to higher potential values (ca. 140 and 270 mV, respectively), while the electrochemical band gap is slightly broadened (ca. 130 mV) relative to that of **5a**. The measured values of **5h** are nearly identical to those of **5g**. The replacement of one oxygen atom in **5g** by a sulfur atom in **5h** has a negligible influence on the electrochemical properties of the complex (see the energy levels of **5g** and **5h** in Table 2). Both HOMO and LUMO levels are lowered, while the band gap of the new materials is increased. Table 2 also presents the optical data for **5g** and **5h**. They have identical absorption spectra as a result of the very small difference between the two compounds and show a blue shift relative to **5a** (Table 2). The optical band gaps of **5h** and **5g** are 1.26 eV and are consistent with values obtained from electrochemical measurements. In conclusion, the electrochemi-

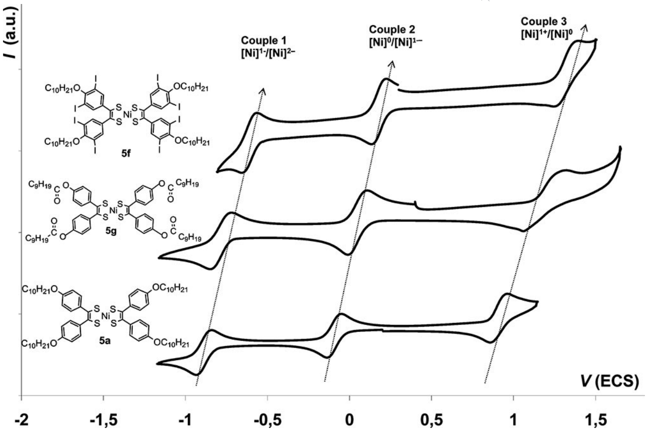


Figure 2. Cyclic voltammograms of **5a**, **5g**, and **5f** in dichloromethane ($10^{-3}$ mol L$^{-1}$) on glassy carbon at 0.1 V s$^{-1}$ with 0.1 mol L$^{-1}$ ($n$Bu$_4$N)[PF$_6$]; starting potential: 0.2 V/ECS.

Table 2. Electrochemical and optical data of tetra-long-chain-substituted nickel bis(dithiolene) complexes.

| Complex | $E_{1/2}{}^{2[a]}$ (V) | $E_{1/2}{}^{3[b]}$ (V) | $E_g{}^{\text{CV[c]}}$ (V) | $E_{\text{LUMO}}$ (eV) | $E_{\text{HOMO}}$ (eV) | $\lambda_{\max}$ (nm) | $\varepsilon$ (L cm$^{-1}$ mol$^{-1}$) | $E_g{}^{\text{opt[d]}}$ (eV) |
|---|---|---|---|---|---|---|---|---|
| **5a** | –0.09 | 0.91 | 1.00 | –4.7 | –5.7 | 932 | 39000 | 1.17 |
| **5b** | –0.04 | 0.97 | 1.01 | –4.8 | –5.8 | 927 | 39000 | 1.17 |
| **5c** | 0.01 | 1.04 | 1.03 | –4.8 | –5.8 | 920 | 33000 | 1.18 |
| **5d** | 0.01 | 1.02 | 1.01 | –4.8 | –5.8 | 927 | 31000 | 1.16 |
| **5e** | 0.09 | 1.17 | 1.08 | –4.9 | –6.0 | 900 | 50000 | 1.19 |
| **5f** | 0.18 | 1.32 | 1.14 | –5.0 | –6.1 | 877 | 43000 | 1.23 |
| **5g** | 0.05 | 1.18 | 1.13 | –4.8 | –6.0 | 865 | 34000 | 1.26 |
| **5h** | 0.04 | 1.17 | 1.13 | –4.8 | –6.0 | 865 | 36000 | 1.26 |

[a] $E_{1/2}{}^2$: half-wave potential of couple 2. [b] $E_{1/2}{}^3$: half-wave potential of couple 3. [c] $E_g{}^{\text{CV}} = E_{1/2}{}^3 - E_{1/2}{}^2$. [d] $E_g{}^{\text{opt}} = hc/\lambda_{\text{onset}}$.

cal properties of tetra-long-chain substituted [Ni(dpedt)$_2$] depend to some extent on the nature of the connecting group.

### *Influence of Halogenation*

The introduction of halogen atoms such as bromine and iodine on the phenyl rings of tetraalkoxy-substituted [Ni(dpedt)$_2$] is expected to have an important influence on their physical properties. The redox properties of these halogenated compounds (**5b**–**f**) and their HOMO and LUMO energy levels derived from cyclic voltammetry measurements are given in Table 2. The results obtained from cyclic or square wave voltammetry are in good agreement. The redox potentials and electrochemical band gaps obtained from cyclic voltammetry studies are gathered, together with **5a** as reference, in Table 2 (see also Figures S1 and S2 in the Supporting Information). The electron affinity and the electrochemical band gap of **5b** increase slightly in comparison with those of **5a**. When two more bromine atoms are introduced (**5c**), the electron affinity and ionization potentials, expressed as $E_{1/2}^2$ and $E_{1/2}^3$ values, show more significant variation (a difference of 100 mV in comparison with the value for **5a**). The introduction of four iodine atoms gives **5d**, whose properties are nearly identical to those of **5c**. When the number of iodine atoms in the complex increases, one clearly observes the linear increase in both redox properties and electrochemical band gaps as a function of the number of iodine atoms (see also Figures S1 and S2 in the Supporting Information). The introduction of halogen atoms on the phenyl rings of dpedt ligands lowers to some extent the HOMO and LUMO levels. However, as already discussed, the more abundant the halogen atoms are, the larger are the band gaps.

Table 2 also summarizes the optical data for the halogenated complexes. The spectra of **5b**–**5d** are nearly identical to that of **5a**. However, **5e** (containing six iodine atoms) and **5f** (containing eight iodine atoms) show a significant blue shift. The optical band gaps vary from 1.16 to 1.23 eV, according to the electrochemical data. Generally, we show that adding halogen atoms to the dpedt ligand is a common, effective route toward the modulation of the redox properties of tetra-long-chain-substituted [Ni(dpedt)$_2$] without a major change in their electrochemical band gaps. This interesting finding opens the way to modulate the energy levels of semiconducting materials based on [Ni(dpedt)$_2$] derivatives for organic electronic applications.

## Octa-Long-Chain-Substituted Nickel Complexes

The electrochemical data for octaalkoxy-substituted [Ni(dpedt)$_2$] are gathered in Table 3.

The results obtained from cyclic and square wave voltammetry experiments are in good consistency with data reported elsewhere.[17,23] The first one-electron oxidation process of these compounds is irreversible. Therefore, the electrochemical band gap of these compounds is undeterminable. When comparing the electrochemical data of octaalkoxy-substituted [Ni(dpedt)$_2$] **5i**, **5k**, and **5l** summed up in Table 3, it can be deduced that their electrochemical properties depend neither on the alkyl chain length nor on their configuration. Compound **5j** differentiates from its isomer **5i** by the position of *n*-decyloxy chains on the phenyl pendent rings; consequently these two compounds present significant variation in their electrochemical properties. The electron affinity and ionization potential of **5j** are higher than those of **5i**. It is well known for [Ni(dpedt)$_2$] derivatives (or their heteroaromatic analogues) that there is a steric constraint on the ligand, resulting in an out-of-plane twist of the two phenyl (or heteroaromatic) rings, as attested by crystal structures obtained by X-ray diffraction.[24] Nevertheless, the conjugation of the ether moieties is less efficient in the *meta*-substituted **5j** than that in the *para*-substituted **5i**. The electronic communication between the phenyl rings and the bis(dithiolene) complex core in **5j** is reduced in comparison to that in **5i**, **5k**, and **5l**. This interesting result is further confirmed by optical measurements.

Table 3 also presents the LUMO levels of all the octaalkoxy-substituted [Ni(dpedt)$_2$]; their values are around –4.7 eV and are nearly identical to those of tetra-long-chain-substituted complexes.

Table 3 summarizes optical properties of all octaalkoxy-substituted complexes (**5i**–**5l**) in dichloromethane solution. Complexes **5i**, **5k**, and **5l** have the same electronic absorption behavior.

The typical UV/Vis/NIR absorption spectra of tetradecyloxy-substituted complex **5a**, octadecyloxy-substituted **5i**,

Table 3. Electrochemical and optical data for octa-long-chain-substituted nickel bis(dithiolene) complexes; working electrode: Pt or glassy carbon.[a]

| Complex | $E_{1/2}^{2}$[b] (V) | $E_{1/2}^{3}$[c] (V) | $E_g^{CV}$[d] (V) | $E_{LUMO}$ (eV) | $E_{HOMO}$ (eV) | $\lambda_{max}$ (nm) | $\varepsilon$ (L cm$^{-1}$ mol$^{-1}$) | $E_g^{opt}$[e] (eV) |
|---|---|---|---|---|---|---|---|---|
| **5i** | –0.10 | * | * | –4.7 | * | 961 | 50000 | 1.12 |
| **5j** | –0.01 | * | * | –4.8 | * | 870 | 41000 | 1.25 |
| **5k** | –0.10 | * | * | –4.7 | * | 965 | 48000 | 1.12 |
| **5l** | –0.12 | * | * | –4.7 | * | 971 | 45000 | 1.12 |
| **10.10** | –0.09 | * | * | –4.7 | * | 964 | * | 1.13 |
| **11.10** | –0.09 | * | * | –4.7 | * | 961 | * | 1.13 |
| **11.8** | –0.08 | * | * | –4.7 | * | 961 | * | 1.13 |

[a] *: not workable. [b] $E_{1/2}^3$: half-wave potential of couple 3. [c] $E_{1/2}^3$: half-wave potential of couple 3. [d] $E_g^{CV} = E_{1/2}^3 - E_{1/2}^2$. [e] $E_g^{opt} = hc/\lambda_{onset}$.

and its regioisomer **5j** are shown in Figure 3. These complexes have a maximum absorption peak in the near-infrared spectral region, which can be attributed to a π–π* transition of the nickel bis(1,2-dithiolene) core.

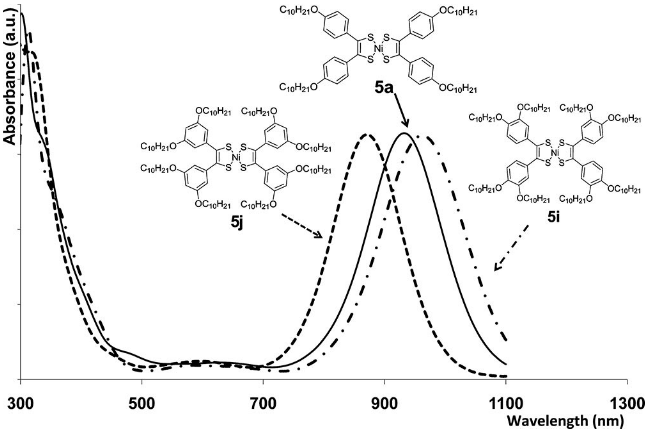


Figure 3. UV, visible, and NIR absorption spectra of **5a**, **5i**, and **5j** in dichloromethane.

By comparison of the $\lambda_{\max}$ and optical band gap values for the octasubstituted **5i**, **5k**, and **5l** with those of the tetrasubstituted **5a**, we observe that increasing the number of the side-chain substituent in [Ni(dpedt)$_2$] results in a small redshift (ca. 30 nm). In compounds **5i** and **5j**, the change of the position of the two *n*-decyloxy chains on the phenyl rings from "3,4" (in **5i**) to "3,5" (in **5j**) induces a blueshift of about 100 nm, their optical band gap moderately changing from 1.12 (**5i**) to 1.25 eV (**5j**). The electrochemical and optical properties of three mixtures, **10.10**, **11.10**, and **11.8**, have also been studied (See Table 3). Their properties are similar to those of their parent complexes **5i**, **5k**, and **5l**. Interestingly, electrochemical and optical measurements show that the size, as well as the configuration or number of alkoxy chains attached to dpedt ligands, do not influence significantly the electronic properties of these alkoxy-substituted [Ni(dpedt)$_2$] compounds. Therefore, we can tune the nature of the side chains to obtain mesomorphic properties without a major change in the electronic properties. Meanwhile, the halogenations of the dithiolene ligand, the connecting groups, and the relative positions of the alkoxy chains have moderate influence on the properties of target compounds. Generally, all the synthesized [Ni(dpedt)$_2$] derivatives present LUMO and HOMO energy levels around 4.7–5.0 and 5.7–6.1 eV, respectively, depending on the functional groups on the dithiolene ligands. Additionally, the high molar absorption coefficient (*ε*) values range from 30000 to 55000 L cm$^{-1}$ mol$^{-1}$, demonstrating that these [Ni(dpedt)$_2$] derivatives are efficient NIR absorbent materials. For all complexes, the optical and electrochemical data are in good accordance.

## Phase Behavior with Temperature

Good thermal stability of targeted compounds is required to envisage their use as active layers in optoelectronic devices. Thermal analysis studies show that neutral nickel bis(1,2-dithiolene) complexes are stable up to 300 °C as observed in Figure 4 for octadecyloxy-substituted complex **5i**. At higher temperature, decomposition of the product is observed, in accordance with data reported in the literature.[12,25]

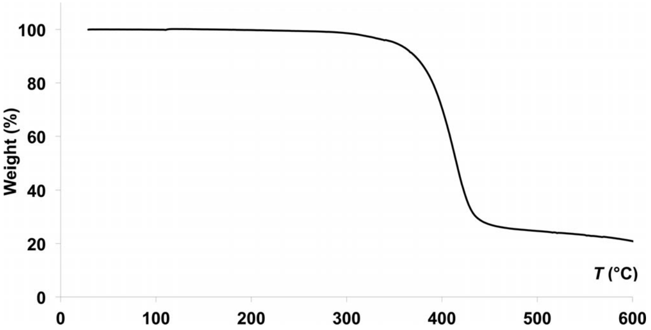


Figure 4. Weight loss with temperature in **5i**. Scan rate: 10 °C min$^{-1}$.

The phase behaviors of **5a**–**5l** and of the three mixtures **10.10**, **11.10**, and **11.8** were studied by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and powder X-ray diffraction. For calorimetry experiments, all pristine samples were heated from ambient temperature until they melted into their isotropic liquid (IL) phase and subsequently cooled down. The heating–cooling cycles were generally repeated twice with a scan rate of 10 °C min$^{-1}$.

## Tetraalkoxy-Substituted Complexes and Related Compounds

The multiphase transition behavior of **5a**, both on heating and cooling (see Figure S3 in the Supporting Information), is in good accordance with reported data.[22] In

Table 4. Phase transition (*T*) and enthalpy changes (Δ*H*), during the second scan, of the tetraalkoxy-substituted complexes and related compounds (scan rate: 10 °C min$^{-1}$).

| | $T$ (°C) [$\Delta H$ (J g$^{-1}$)] |
|---|---|
| Complex | Phase $\longrightarrow$ Phase |
| **5a** | $\mathrm{Cryst^1} \underset{82.4\ [-15.2]}{\overset{111.0\ [18.3]}{\rightleftarrows}} \mathrm{Cryst^2} \underset{167.2\ [-29.9]}{\overset{178.0\ [33.4]}{\rightleftarrows}} \mathrm{IL}$ |
| **5b** | $\mathrm{Cryst^1} \underset{70.1\ [-13.5]}{\overset{119.8\ [18.6]}{\rightleftarrows}} \mathrm{IL}$ |
| **5c** | No dectable transition |
| **5d** | No dectable transition |
| **5e** | No dectable transition |
| **5f** | No dectable transition |
| **5g** | $\mathrm{Cryst^1} \underset{179.8\ [-65.11]}{\overset{191.9\ [68.7]}{\rightleftarrows}} \mathrm{IL}$ |

the present work, **5a** has not been further studied. The introduction of halogen atoms, either bromine or iodine, strongly influences the phase behavior towards a simpler phase sequence relative to that in **5a**, as reported in Table 4. However, complementary POM studies reveal a direct crystal-to-isotropic-liquid phase transition, showing that none of these halogenated complexes exhibits liquid crystalline properties.

## Octaalkoxy-Substituted [Ni(dpedt)$_2$]

Prior to our work, only the liquid-crystalline property of **5i** has been reported, and our structural investigations confirm the described results.[17,23,26] (see Supporting Information Figures S4, S5, and S6). None of the other octaalkoxy-substituted nickel bis(dithiolene) complexes have ever been described before this present work. A considerable change of the phase behavior of the new complexes is evidenced, which depends on the nature and configuration of the side alkoxy chain (see Table 5).

Table 5. Phase transition ($T$) and enthalpy changes ($\Delta H$), during the second scan, of the octaalkoxy-substituted complexes and related compounds (scan rate: 10 °C min$^{-1}$).

| Complex | $T$ (°C) [$\Delta H$ (J g$^{-1}$)]<br>Phase $\longrightarrow$ Phase |
|---|---|
| **5i** | Liq Cryst$^1$ $\underset{107.0\ [-5.1]}{\overset{111.6\ [6.1]}{\rightleftarrows}}$ IL |
| **5j** | No visible transition |
| **5k** | Cryst$^1$ $\underset{22.8\ [-6.8]}{\overset{40.6\ [7.3]}{\rightleftarrows}}$ IL |
| **5l** | Cryst$^1$ $\xrightarrow[70.1\ [-13.5]]{119.8\ [18.6]}$ IL |
| **11.8** | Cryst$^1$ $\underset{39.5\ [1.1]}{\overset{53.5\ [1.5]}{\rightleftarrows}}$ Liq Cryst$^1$ $\underset{80.6\ [3.8]}{\overset{87.6\ [3.4]}{\rightleftarrows}}$ IL |

The replacement of the *n*-decyl group by the branched decyl chain 3,7-dimethyloctyl results in **5k**. The behavior of **5k** differs from that of **5i** in the following way: On heating from ambient temperature, the pristine black paste-like powder of **5k** directly melts into an isotropic liquid phase at about 50 °C. On cooling down, the recrystallization peak is recorded at approximately 25 °C, and no mesophase is detected. The use of the bulky 3,7-dimethyloctyl group influences the molecular packing and decreases the melting point dramatically from approximately 110 °C (for **5i**), to approximately 50 °C (for **5k**). Even when the linear decyl chains are replaced in **5l** by 2-ethylhexyl chains, used for instance on arene tetraesters to very efficiently generate mesomorphic behavior,[27] no liquid-crystalline phase is observed. Only a melting transition is seen on heating, whereas the compound remains in a glassy isotropic state on cooling down. Within discotic octaalkoxy-substituted [Ni(dpedt)$_2$] molecules, the introduction of that kind of bulky group does not induce mesomorphic properties. This could arise from the fact that two alkoxy chains on the same phenyl ring (at position "4" or "5") of the dpedt ligand are too close, and they therefore disturb the planar shape of the discotic molecules. We have then studied the influence of two alkoxy chain positions on the same phenyl ring of the dpedt ligand in **5i** and **5j**. In **5j**, the two aliphatic chains are far enough for a free rotation of the molecules and an optimized self-organization to be expected. However, DSC and POM studies do not reveal any mesophase in **5j**. When the thermal behaviors of **5j**, **5k**, and **5l** are compared with that of the columnar liquid crystal (CLC) **5i**, one can conclude that the mesomorphic properties of octaalkoxy-substituted [Ni(dpedt)$_2$] are very sensitive to their detailed chemical structure. The replacement of linear alkyl chains by branched ones or the modification of the position of the alkoxy chain on the phenyl ring of the dpedt ligand changes the melting temperature but does not favor the establishment of a mesophase.

## *Mixtures of Octaalkoxy-Substituted [Ni(dpedt)$_2$]*

Differential scanning calorimetry analysis of the three mixtures of octaalkoxy-substituted [Ni(dpedt)$_2$] suggests that **10.10**, **11.10**, and **11.8** probably exhibit liquid-crystalline phases. Only the results for **11.8** are presented here, whereas **10.10** and **11.10** will not be further studied in the present work.

In Figure 5, after the first thermal cycle where a peak exhibiting a high enthalpy characteristic of the fusion of a crystal can be seen, two other peaks with a small enthalpy are observed, the first one of which can be attributed to a transition to liquid-crystalline phases and the second one to a partial crystallization of the compound at low temperature. Further investigations by POM are shown in Figure 6, where typical optical images of **11.8** at different temperatures are given. After cooling down from the isotropic liquid phase, densely branched dendrites grow at $T$ = 84 °C without birefringence, which is characteristic of a hexagonal CLC mesophase in homeotropic orientation. This optically isotropic dendritic texture (in coexistence with some birefringent topological defects) is present down to ambient temperature after a slow cooling process (Figure 6B). Contrary to the calorimetry study, where a phase transition occurs at $T$ = 40 °C, no phase transition to another phase is evidenced by optical microscopy: the hexagonal columnar mesophase remains in a metastable state at room temperature. However, after a few hours, a new birefringent phase appears (Figure 6C and D). The nature of this new phase is ambiguous, and it is difficult to say whether it is a liquid crystal or a pure crystal.

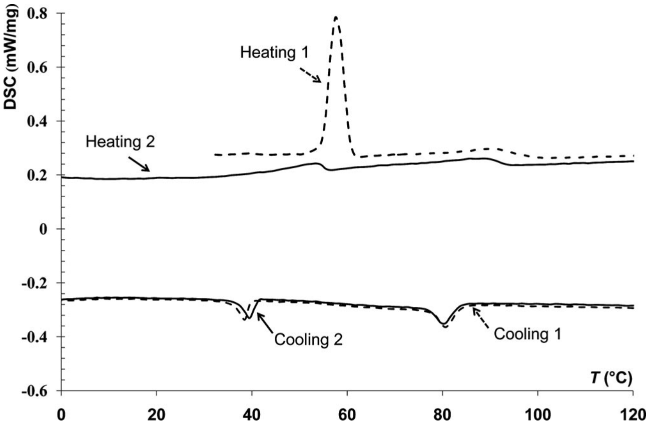


Figure 5. Differential scanning calorimetry (DSC) thermogram of **11.8**, which shows, after the first heating, typical peaks characteristic of mesophases on both heating and cooling (see data in Table 5). Scan rate: 10 °C min$^{-1}$.

Nevertheless, DSC analysis shows that, after cooling down slowly to ambient temperature in two days, the fusion peak at 57 °C, which is attributed to the melting of the crystalline phase into the liquid crystal phase, reappears (data not shown). This confirms that the liquid crystal is metastable at ambient temperature and slowly recrystallizes. X-ray diffraction experiments have been performed at 70 °C and are presented in Figure 7. The X-ray pattern at $T$ = 70 °C exhibits both a clear sixfold symmetry and many Bragg peaks (100, 110, 200, 210), whose positions in reciprocal space relative to the position of the first reflection are $1{:}\sqrt{3}{:}\sqrt{4}{:}\sqrt{7}$. This corresponds to the signature for **11.8** of the hexagonal columnar liquid-crystalline phase.[4] The signal of the disordered aliphatic chains corresponds to the broad reflection at about 14 nm$^{-1}$, characteristic of a liquid-like order.

This interesting finding opens new ways to form ambient temperature CLCs based on nickel bis(dithiolene) complexes. As the synthesis of pure nickel bis(dithiolene) discotic liquid crystals (DLC) is very delicate, the formulation of different nickel complexes seems to be a very promising direction.

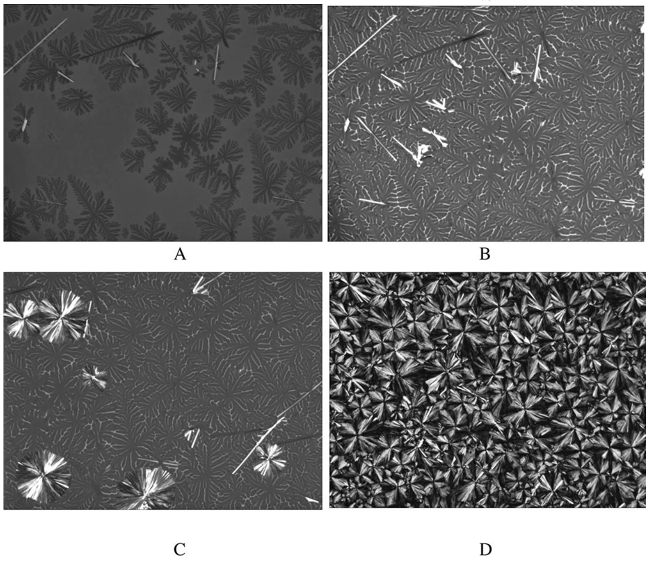


Figure 6. Optical microscopy for **11.8**, in transmission with slightly uncrossed polarizers, observed at 84 °C (A) with the dendritic growth of the hexagonal columnar mesophase in homeotropic orientation, and at 28 °C (B), just after the cooling down from the isotropic liquid phase. (C) Observation after one day at room temperature where a birefringent crystalline phase has nucleated, which finally covers all the sample area (D). Each image size is 660 µm × 490 µm.

## Conclusions

This work is devoted to new short and efficient synthetic pathways of discotic nickel bis(dithiolene) complexes. The electrochemical, optical, and thermal properties of these complexes show that all these compounds absorb efficiently in the near infrared spectral domain, according to a measured band gap of around 1 to 1.1 eV. Their electrochemical and optical properties can be only moderately tuned, depending on the nature and position of the functional groups attached to the phenyl rings. The octadecyloxy-substituted complex **5i** and the mixture **11.8** present an interesting hexagonal columnar liquid-crystalline mesophase. However, this mesophase is metastable at ambient temperature. The possibility of stabilization of such mesophases by chemical

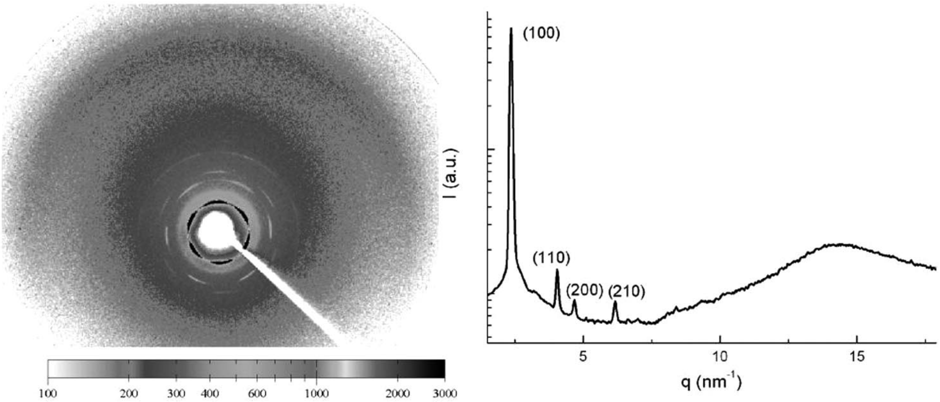


Figure 7. X-ray diffraction pattern (left) of a single domain of **11.8** probed at 70 °C, which exhibits Bragg peaks characteristic of a hexagonal columnar mesophase (right).

engineering or by mixing appropriate ligands is a crucial point for their use in organic electronics and will be further investigated.

## Experimental Section

### General Remarks

All used chemicals and solvents were purchased from chemical companies and used as received, unless otherwise mentioned. All reactions were performed in an ambient atmosphere of air unless indicated otherwise. Purification of products was performed by column chromatography on silica gel from Merck with a grain size of 0.04–0.063 mm (flash silica gel, Geduran Si 60) with analytically pure solvents. For analytical thin layer chromatography, "60 F254" substrates coated with silica gel from Merck were used.

$^1$H and $^{13}$C NMR spectroscopic experiments were recorded in the listed deuteriated solvents (internal standard) with 4 Bruker Spectrometers (ARX 250, DPX 300, Avance 300 and Avance 400). The multiplicity of the NMR signal is denoted as br (broad), m (multiplet), s (singlet), d (doublet), t (triplet), quart (quartet), quint (quintet), sext (sextet), sept (septet), dd (double doublet), and dt (double triplet).

Mass spectrometric analyses were performed at the Service de Spectrométrie de Masse de la Structure Fédérative Toulousaine en Chimie Moléculaire. Elemental analyses (C, H, S, Ni) were carried out on the nickel complexes at the Service Central d'Analyse du CNRS in Lyon.

Phase transition was determined by differential scanning calorimetry (DSC) thermograms, which were obtained with a DSC 204 NETZSCH system by using 2–5 mg samples in 30 µL sample pans and a scan rate of 10 °C min$^{-1}$. $\Delta H$ is the enthalpy associated with each phase transition, calculated in kJ mol$^{-1}$.

Voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100 controlled by GPES 4.09 software. Experiments were performed at room temperature in a homemade airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counterelectrode was a platinum wire of ca 1 cm$^2$ apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter) or a glassy carbon (1 mm diameter) electrode. The supporting electrolyte ($n$Bu$_4$N)[PF$_6$] (Fluka, 99% electrochemical grade) was used as received after being simply degassed under argon. Dichloromethane was freshly distilled from CaH$_2$ prior to use. The solutions used during the electrochemical studies were typically 10$^{-3}$ mol L$^{-1}$ in complex compound and 0.1 mol L$^{-1}$ in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar through them, and the working electrode was polished with a polishing machine (Presi P230).

UV/Vis/NIR absorption spectra were recorded with two spectrometers, Perkin–Elmer Lambda 35 and Perkin–Elmer GX 2000, by using dichloromethane as solvent. The concentration of complex in solutions used for the electronic absorption analyses was typically about 10$^{-5}$ mol L$^{-1}$.

Optical observations were performed with a polarizing microscope (Olympus, BX51), combined with both a color CCD camera (JAI, CV-M7) and a heating stage (Mettler, FP90) with a temperature accuracy of ±0.1 °C.

X-ray diffraction experiments were performed by using a Rigaku rotating anode generator having a wavelength of 1.54 Å together with a homemade heating stage with a thermal stability of ±0.1 °C. The spectra were recorded with a bidimensional detector located at 180 mm from the sample, which was in the geometry of an open supported droplet.

### Material Synthesis

**4,4′-Bis(decyloxy)benzil (2a):** A mixture of 4,4′-dihydroxybenzil (**1a**) (3 g, 12.39 mmol), decyl bromide (6.15 mL, 29.73 mmol), and powdered potassium carbonate (5.14 g, 37.17 mmol) was stirred overnight in DMF (75 mL) at 100 °C. Upon cooling to ambient temperature, the reaction was quenched by adding water, and the resulting mixture was extracted with dichloromethane. The organic phases were combined, rinsed several times with water, dried with anhydrous magnesium sulfate, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (hexane/dichloromethane, 50:50) to provide a yellowish solid (6.35 g, 98%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ = 7.94 (dt, $J$ = 2.7–9.0 Hz, 4 H, aromatic H), 7.01 (dt, $J$ = 2.7–9.0 Hz, 4 H, aromatic H), 4.08 (t, $J$ = 6.3 Hz, 4 H, -OC$H_2$-), 1.84 (quint, $J$ = 6.6 Hz, 4 H, -OCH$_2$C$H_2$-), 1.52–1.32 (m, 28 H), 0.92 (t, $J$ = 6.3 Hz, 6 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ = 193.55, 164.58, 132.17, 126.00, 114.68, 68.58, 31.90, 29.54, 29.31, 29.00, 25.89, 22.68, 13.88 ppm. MS (CI-NH$_3$): found 523.4 [M]$^+$, 540.4 [M + NH$_4$]$^+$.

**4,4′-Bis(decanoate)benzil (2b):** A THF (50 mL) solution of 4,4′-dihydroxy benzil (2 g, 8.26 mmol), PPh$_3$ (5.2 g, 19.82 mmol), and decanoic acid (3.4 g, 19.82 mmol) was cooled to 0 °C. To the solution was added diethyl azodicarboxylate in toluene solution (9 mL, 19.82 mmol, 40% w/v), the mixture was kept at that temperature for 1 h and then was warmed to room temperature and stirred for 1 h. The reaction mixture was then concentrated. After addition of hexane (500 mL), the mixture was filtered. The filtrate was concentrated, and the residue was purified by silica gel column chromatography (hexane/dichloromethane, 25:75) to give a pure yellow solid (4.25 g, 93%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ = 8.06 (dt, $J$ = 2.4–9.3 Hz, 4 H, aromatic H), 7.31 (dt, $J$ = 2.4–9.3 Hz, 4 H, aromatic H), 2.63 [t, $J$ = 7.5 Hz, 4 H, -OC(=O)C$H_2$-], 1.79 [m, 4 H, -OC(=O)CH$_2$C$H_2$-], 1.49–1.30 (m, 24 H), 0.94 (t, $J$ = 6.6 Hz, 6 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ = 192.91, 171.42, 156.09, 131.51, 130.29, 122.44, 34.27, 31.88, 29.42, 29.26, 29.25, 29.03, 24.75, 22.68, 13.89 ppm. MS (CI-NH$_3$): found 568.3 ([M + NH$_4$]$^+$).

**3-Bromo-4,4′-bis(decyloxy)benzil (2c):** A suspension of FeCl$_3$ (0.28 g, 1.72 mmol) and 4,4′-didecyloxybenzil (**2a**) (0.9 g, 1.72 mmol) in dichloromethane (30 mL) was cooled to 0 °C. To the suspension was added Br$_2$ (0.2 mL, 3.93 mmol), and the mixture was allowed to reach ambient temperature overnight. The reaction was quenched by a 10% aqueous solution of Na$_2$S$_2$O$_3$ (50 mL) and then extracted with dichloromethane. The organic phases were combined, rinsed several times with water, dried with anhydrous magnesium sulfate, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (hexane/dichloromethane, 40:60 then 60:40) to provide a yellowish solid of **2c** (0.51 g, 49%) and **2d** (0.26 g, 21%). For **2c**: $^1$H NMR (250 MHz, CD$_2$Cl$_2$): $\delta$ = 8.22 (d, $J$ = 2.1 Hz, 1 H, aromatic H), 7.94 (m, 3 H, aromatic H), 7.90 (dt, $J$ = 2.8–9.8 Hz, 3 H, aromatic H), 4.16 (t, $J$ = 6.3 Hz, 2 H, -OC$H_2$-), 4.09 (t, $J$ = 6.5 Hz, 2 H, -OC$H_2$-), 1.87 (m, 4 H, -OCH$_2$C$H_2$-), 1.55–1.44 (m, 28 H), 0.93 (6 H, -C$H_3$) ppm. $^{13}$C NMR (62.5 MHz, CD$_2$Cl$_2$): $\delta$ = 192.70, 192.39, 164.77, 160.61, 134.68, 132.27, 131.45, 126.91, 125.71, 114.75, 112.64, 112.30, 69.78, 68.64, 31.89, 29.51, 29.30, 29.22, 28.98, 28.80, 25.87, 25.83, 22.67, 13.86 ppm. MS (CI-NH$_3$):

found 601.3 [MBr$^{79}$ + H]$^+$, 603.3 [MBr$^{81}$ + H]$^+$, 618.3 [MBr$^{79}$ + NH$_4$]$^+$, 620.3 [MBr$^{81}$ + NH$_4$]$^+$.

**3,3′-Dibromo-4,4′-bis(decyloxy)benzil (2d):** To a solution of 4,4′-didecyloxybenzil (**2a**) (1.5 g, 2.87 mmol) in a mixture of dichloromethane (25 mL) and acetonitrile (25 mL) were added Br$_2$ (0.73 mL, 14.35 mmol) and FeCl$_3$ (0.93 g, 5.74 mmol). The mixture was heated at reflux overnight (ca. 16 h). The reaction was quenched by a 10% aqueous solution of Na$_2$S$_2$O$_3$ (200 mL) and then extracted with dichloromethane. The organic phases were combined, rinsed several times with water, dried with anhydrous magnesium sulfate, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography (hexane/dichloromethane, 50:50) to provide a yellowish solid (1.83 g, 94%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.22 (d, $J$ = 2.1 Hz, 2 H, aromatic H), 7.90 (dd, $J$ = 2.1–8.4 Hz, 2 H, aromatic H), 6.96 (d, $J$ = 8.4 Hz, 2 H, aromatic H), 4.13 (t, $J$ = 6.6 Hz, 4 H, -OC$H_2$-), 1.88 (m, 4 H, -OCH$_2$C$H_2$-), 1.57–1.29 (m, 28 H), 0.89 (t, $J$ = 6.6 Hz, 6 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 191.46, 160.74, 135.02, 131.55, 126.67, 113.00, 112.16, 69.69, 31.89, 29.51, 29.30, 29.23, 28.79, 25.86, 22.68, 14.11 ppm. MS (CI-NH$_3$): found 696.3 [MBr$^{79}$Br$^{79}$ + NH$_4$]$^+$, 698.3 [MBr$^{79}$Br$^{81}$ + NH$_4$]$^+$, 700.3 [MBr$^{81}$Br$^{81}$ + NH$_4$]$^+$.

**General Procedure for the Synthesis of 2e–2g:** To a round-bottomed flask were added 4,4′-didecyloxybenzil (**2a**) (1.54 g, 2.95 mmol), TFA (35 mL), and NIS (2.0, 3.0, or 5.0 molar equivalents for **2e**, **2f**, and **2g**, respectively). After stirring for 5 min at ambient temperature, the reaction mixture was heated at reflux for 3.5 h. The mixture was cooled to ambient temperature overnight and was poured into ice water (300 mL), then dichloromethane (200 mL) was added. The organic layers were separated, and the aqueous phase was extracted with dichloromethane. The combined organic phase was washed with a 10% aqueous solution of Na$_2$S$_2$O$_3$ and dried with MgSO$_4$. Removal of solvent in vacuo followed by silica gel column chromatography (hexane/dichloromethane) provided the desired products.

**3,3′-Diiodo-4,4′-bis(decyloxy)benzil (2e):** Yellowish solid (2.24 g, 88%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.41 (d, $J$ = 2.1 Hz, 2 H, aromatic H), 7.90 (dd, $J$ = 2.1–8.4 Hz, 2 H, aromatic H), 6.83 (d, $J$ = 8.7 Hz, 2 H, aromatic H), 4.10 (t, $J$ = 6.3 Hz, 4 H, -OCH$_2$-), 1.86 (m, 4 H, -OCH$_2$CH$_2$-), 1.55–1.27 (m, 28 H), 0.88 (t, $J$ = 6.6 Hz, 6 H, -CH$_3$) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 191.31, 162.74, 141.26, 132.56, 127.36, 111.08, 87.09, 69.81, 31.91, 29.52, 29.31, 29.22, 28.81, 25.96, 22.69, 14.13 ppm. MS (CI-NH$_3$): found 775.2 [M + H]$^+$, 792.2 [M + NH$_4$]$^+$.

**3,3′,4-Triiodo-4,4′-bis(decyloxy)benzil (2f):** White solid (1.14 g, 43%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.40 (d, $J$ = 2.1 Hz, 1 H, aromatic H), 8.34 (s, 2 H, aromatic H), 7.91 (dd, $J$ = 2.1–8.7 Hz, 1 H, aromatic H), 6.84 (d, $J$ = 8.7 Hz, 1 H, aromatic H), 4.11 (t, $J$ = 6.3 Hz, 2 H, -OC$H_2$-), 4.03 (t, $J$ = 6.6 Hz, 2 H, -OC$H_2$-), 1.50 (m, 4 H, -OCH$_2$C$H_2$-), 1.58–1.28 (m, 28 H), 0.88 (m, 6 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 190.10, 189.94, 163.44, 163.06, 141.54, 141.40, 132.69, 131.89, 126.86, 111.16, 91.54, 87.21, 73.99, 69.88, 31.90, 30.94, 30.04, 29.59, 29.52, 29.46, 29.34, 29.31, 29.22, 28.80, 25.95, 25.88, 22.69, 14.13 ppm. MS (CI-NH$_3$): found 901.1 [M + H]$^+$, 918.1 [M + NH$_4$]$^+$.

**3,3′,4,4′-Tetraiodo-4,4′-bis(decyloxy)benzil(2g):** Yellowish solid (2.12 g, 59%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.34 (s, 4 H, aromatic H), 4.04 (t, $J$ = 6.6 Hz, 4 H, -OC$H_2$-), 1.94 (m, 4 H, -OCH$_2$C$H_2$-), 1.60–1.28 (m, 28 H), 0.88 (t, $J$ = 6.3 Hz, 6 H, -C$H_3$) ppm. $^{13}$C NMR (62.5 MHz, CDCl$_3$): $\delta$ = 188.81, 163.81, 141.66, 131.39, 91.65, 74.08, 31.91, 30.05, 29.59, 29.47, 29.34, 25.89, 22.71, 14.14 ppm. HRMS (CI-CH$_4$): calcd. 1026.9653 for [M + H]$^+$ and 1054.9966 for [M + C$_2$H$_5$]$^+$; found 1026.9668 and 1054.9985, respectively.

**General Procedure for the Synthesis of 1,2-Dialkyloxybenzenes 3a, 3b, 3d, and 3e:** A mixture of 1,2-benzenediol (1.0 equiv.), alkyl bromide (2.4 equiv.), and powdered potassium carbonate (3.0 equiv.) was stirred in dimethylformamide at 90 °C. The reaction was monitored by TLC (hexane/ethyl acetate: 95:5 v/v). Upon being cooled to ambient temperature, the reaction was quenched by adding water, and the resulting mixture was extracted with dichloromethane. The organic phases were combined, rinsed several times with water, dried with anhydrous magnesium sulfate, and concentrated under reduced pressure. The crude products were then purified by column chromatography (hexane/ethyl acetate).

**1,2-Didecyloxybenzene (3a):** White solid (3.6 g, yield 77%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ = 6.91 (s, 4 H, aromatic H), 4.00 (t, $J$ = 6.6 Hz, 4 H, -OC$H_2$-), 1.86–1.32 (m, 32 H, -C$H_2$-), 0.92 (t, $J$ = 6.9 Hz, 6 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 149.29, 121.02, 114.15, 69.29, 31.95, 29.68, 29.63, 29.48, 29.39, 26.10, 22.72, 14.13 ppm. GC–MS: found 390 [M]$^+$.

**1,2-Bis(2-ethylhexyloxy)benzene (3b):** Colorless liquid (7.35 g, yield 81%). $^1$H NMR (250 MHz, CD$_2$Cl$_2$): $\delta$ = 6.93 (m, 4 H, aromatic H), 3.92 (d, $J$ = 5.8 Hz, 4 H, -OC$H_2$-), 1.84–1.73 (m, 2 H, -OCH$_2$C$H$-), 1.62–1.39 (m, 16 H, -C$H_2$-), 1.00 (t, $J$ = 7.5 Hz, 12 H, -C$H_3$) ppm. $^{13}$C NMR (62.5 MHz, CD$_2$Cl$_2$): $\delta$ = 149.68, 120.77, 113.89, 71.58, 39.70, 30.59, 29.14, 23.91, 23.10, 13.86, 10.95 ppm. HRMS (CI-NH$_3$): calcd. for [M + H]$^+$ 335.2950; found 335.2948.

**1,2-Diundecyloxybenzene (3d):** White solid (45.9 g, yield 97%). $^1$H NMR (250 MHz, CD$_2$Cl$_2$): $\delta$ = 6.93 (m, 4 H, aromatic H), 4.02 (t, $J$ = 6.6 Hz, 4 H, -OC$H_2$-), 1.81 (m, 4 H, -OCH$_2$C$H_2$-), 1.55–1.35 (m, 32 H, -C$H_2$-), 0.95 (t, $J$ = 6.2 Hz, 6 H, -C$H_3$) ppm. $^{13}$C NMR (62.5 MHz, CD$_2$Cl$_2$): $\delta$ = 149.35, 120.92, 114.12, 69.23, 31.96, 29.68, 29.48, 29.47, 29.40, 26.10, 22.72, 13.90 ppm. MS (CI-NH$_3$): found 436.3 [M + NH$_4$]$^+$.

**1,2-Dioctyloxybenzene (3e):** Colorless oil (13.47 g, yield 90%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ = 6.94 (m, 4 H, aromatic H), 4.03 (t, $J$ = 6.6 Hz, 4 H, -OC$H_2$-), 1.90 (m, 4 H, -OCH$_2$C$H_2$-), 1.60–1.38 (m, 20 H, -C$H_2$-), 1.00–0.95 (m, 6 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ = 149.36, 120.94, 114.11, 69.22, 31.91, 29.49, 29.47, 29.36, 26.13, 22.73, 13.92 ppm. HRMS (CI-CH$_4$): calcd. for [M + H]$^+$ 335.2950; found 335.2948.

**1,2-Bis(3,7-dimethyloctyloxy)benzene (3c):** A THF (50 mL) solution of pyrocathecol (1.5 g, 6.2 mmol), PPh$_3$ (3.9 g, 14.9 mmol), and alcohol (14.9 mmol) was cooled to 0 °C. To the solution was added diethyl azodicarboxylate in toluene solution (6.8 mL, 14.9 mmol, 40% w/v), the mixture was kept at that temperature for 1 h and then was warmed to room temperature and stirred for 1 h. The reaction mixture was then concentrated. After addition of hexane (300 mL), the mixture was filtered. The filtrate was concentrated, and the residue was purified by silica gel column chromatography (eluent: hexane/dichloromethane, 1:1 v/v) to provide a colorless oil (3.95 g, yield 74%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 6.93 (m, 4 H, aromatic H); 4.08 (m, 4 H, -OC$H_2$-); 1.95–1.14 (m, 20 H); 1.00–0.91 (m, 18 H, -C$H_3$) ppm. $^{13}$C NMR (62.5 MHz, CD$_2$Cl$_2$): $\delta$ = 149.43, 133.89, 133.58, 128.74, 128.58, 128.47, 120.98, 114.11, 67.56, 39.37, 37.47, 36.49, 30.01, 28.09, 24.82, 22.59, 22.50, 19.57 ppm. HRMS (CI-CH$_4$): calcd. for [M + H]$^+$ 391.3576; found 391.3584.

**General Procedure for the Synthesis of Tetraalkoxy-Substituted Benzils (4a–4c):** Solvents and glassware used in this synthesis were dried thoroughly prior to use. To a 100 mL side-arm round-bottomed flask under argon containing a solution of dialkyloxybenzene (7.68 mmol) in 1,2-dichloroethane (30 mL), was added oxalyl chloride (400 µL, 4.61 mmol) by a microsyringe at 0 °C. The reaction mixture was kept at 0 °C for 10 min, and then aluminum chloride (0.51 g, 3.84 mmol) was added. After 30 min at 0 °C, the mixture was warmed gently to ambient temperature overnight. The reaction mixture was then poured into an HCl solution (1 M). The organic layer was separated, and the aqueous layer was extracted twice with dichloromethane. The combined organic extracts were dried with $MgSO_4$ and concentrated. The residue was chromatographed (hexane/dichloromethane) to give **5** as a pure product.

**3,3′,4,4′-Tetra(decyloxy)benzil (4a):** White solid (0.55 g, yield 51%). $^1$H NMR (250 MHz, $CD_2Cl_2$): $\delta$ = 7.58 (d, $J$ = 1.75 Hz, 2 H, aromatic H), 7.47 (dd, $J$ = 2.0–8.5 Hz, 2 H, aromatic H), 6.94 (d, $J$ = 8.25 Hz, 2 H, aromatic H), 4.10 (m, 8 H, -OC$H_2$-), 1.86 (m, 8 H, -OCH$_2$C$H_2$-), 1.52–1.33 (m, 56 H), 0.93 (t, $J$ = 4.75 Hz, 12 H, -C$H_3$) ppm. $^{13}$C NMR (62.5 MHz, $CD_2Cl_2$) 193.81, 155.00, 149.32, 126.22, 126.13, 112.31, 111.61, 69.26, 69.14, 31.94, 29.65, 29.60, 29.41, 29.36, 29.10, 28.95, 26.01, 25.94, 22.71, 14.14. MS (CI-$NH_3$): found 835.6 [M]$^+$, 836.7 [M + H]$^+$.

**3,3′,4,4′-Tetra(2-ethylhexyloxy)benzil (4b):** Yellowish oil (1.69 g, yield 49%). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.58 (d, $J$ = 2.1 Hz, 2 H, aromatic H), 7.45 (dd, $J$ = 2.1–8.4 Hz, 2 H, aromatic H), 6.93 (d, $J$ = 8.4 Hz, 2 H, aromatic H), 3.99 (d, $J$ = 5.4 Hz, 8 H, -OC$H_2$CH-), 1.80 (m, 4 H, -OCH$_2$C$H$-), 1.58–1.35 (m, 32 H), 1.00–0.91 (m, 24 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 193.95, 155.40, 149.70, 126.02, 125.83, 111.77, 111.37, 71.46, 71.37, 39.52, 39.40, 30.57, 30.49, 29.08, 29.03, 23.93, 23.92, 23.87, 23.85, 23.05, 23.02, 13.83, 13.81, 10.96, 10.91 ppm. HRMS (CI-$CH_4$): calcd. for [M + H]$^+$ 723.5564; found 723.5578.

**3,3′,4,4′-Tetra(3,7-dimethyloctyloxy)benzil (4c):** Yellowish oil (1.58 g, yield 49%). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.59 (d, $J$ = 2.1 Hz, 2 H, aromatic H), 7.47–7.42 (m, 2 H, aromatic H), 6.94 (m, 2 H, aromatic H), 4.16 (m, 8 H, -OC$H_2$-), 1.94–0.89 (m, 76 H) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 193.83, 155.06, 152.75, 149.36, 148.67, 130.67, 126.12, 125.89, 124.44, 114.49, 112.11, 111.56, 111.46, 67.60, 39.24, 39.21, 37.33, 37.28, 36.25, 36.10, 35.90, 29.96, 28.02, 24.74, 22.48, 22.38, 19.47, 19.41 ppm. HRMS (CI-$NH_3$): calcd. for [M + H]$^+$ 835.6816; found 835.6859.

**General Procedure for the Synthesis of Benzil Mixtures B10.10, B11.10, and 11.8:** Solvents and glassware used in this synthesis were dried thoroughly prior to use. To a 100 mL side-arm round-bottomed flask under argon containing a solution of the first dialkoxybenzene (3.84 mmol) in 1,2-dichloroethane (20 mL) was added oxalyl chloride (400 µL, 4.61 mmol) by a microsyringe at 0 °C. The reaction mixture was kept at 0 °C for 10 min, and then aluminum chloride (0.51 g, 3.84 mmol) was added. After 30 min at 0 °C, the solution of the second dialkoxybenzene (3.84 mmol) in 1,2-dichloroethane (20 mL) was added dropwise over a period of 30 min. The mixture was then warmed gently to ambient temperature overnight. The reaction mixture was then poured into an HCl solution (1 M). The organic layer was separated, and the aqueous layer was extracted twice with dichloromethane. The combined organic extracts were dried with $MgSO_4$ and concentrated. The residue was chromatographed with a mixture of hexane and dichloromethane to give a mixture of benzils B10.10 (1.77 g, yellow solid), B11.10 (1.71 g, yellow solid), and B11.8 (4.65 g, yellow solid).

**3,3′,5,5′-Tetramethoxybenzil (4e):** Sodium cyanide (1.0 g, 22.4 mmol) was dissolved in water (10 mL). To this solution were added 3,5-dimethoxybenzaldehyde (9.3 g, 56.0 mmol) and ethanol (20 mL of ). The mixture was heated at reflux with stirring for 36 h, extracted with dichloromethane, and the organic layer was washed with water, and then dried with $MgSO_4$. The dichloromethane was evaporated to give a yellowish brown viscous liquid (mass: 7.8 g). This product was directly used in the next step without purification. The mixture of crude 3,3′,5,5′-tetramethoxybenzoin (7.8 g), copper(II) acetate (0.1 g, 0.24 mmol), $NH_4NO_3$ (2.5 g, 29.35 mmol) in acetic acid (20 mL) and water (5 mL) was heated at reflux. After 2 h of reflux, water was introduced, and the yellow precipitate was collected by filtration. The filtrate was then extracted several times with dichloromethane. The organic phases and the yellow precipitate were combined, washed several times with water, dried with $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by recrystallization from ethyl acetate to provide a yellow solid (2.0 g, yield 22%). $^1$H NMR (250 MHz, $CD_2Cl_2$): $\delta$ = 7.09 (d, $J$ = 2.3 Hz, 4 H, aromatic H), 6.79 (t, $J$ = 2.3 Hz, 2 H, aromatic H), 3.86 (s, 12 H, -OC$H_3$) ppm.

**3,3′,5,5′-Tetradecyloxybenzil (4d):** 3,3′,5,5′-tetramethoxybenzil (1.05 g) was heated at reflux for 5 h in a mixture of aqueous HBr (48%) and glacial acetic acid (100 mL, 50:50). The reaction mixture was cooled in a bath of ice-water and extracted several times with ethyl ether. The organic phases were combined, and the solvent was removed under reduced pressure. The residue was analyzed by TLC with a mixture of acetone and dichloromethane (50:50). Only one product was observed. The residue was not purified but directly used in the next step. To this residue were added decyl bromide (4 mL), $K_2CO_3$ (5.5 g), and dimethylformamide (40 mL), and the mixture was heated at reflux for 18 h. The reaction mixture was cooled in a bath of ice-water and extracted several times with dichloromethane. The organic phases were combined, rinsed several times with water, dried with $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel: hexane/dichloromethane, 50:50) to provide a yellow solid (1.41 g, yield 53%). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.04 (d, $J$ = 2.1 Hz, 4 H, aromatic H), 6.76 (t, $J$ = 2.1 Hz, 2 H, aromatic H), 4.00 (t, $J$ = 6.6 Hz, 8 H, -OC$H_2$-), 1.79 (quint, $J$ = 6.6 Hz, 8 H, -OCH$_2$C$H_2$-), 1.49–1.32 (m, 56 H), 0.92 (t, $J$ = 6.3 Hz, 12 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 194.48, 160.71, 134.60, 107.95, 107.68, 104.46, 68.52, 68.34, 31.90, 29.55, 29.34, 29.31, 29.23, 29.18, 29.10, 25.94, 22.68, 13.87 ppm. MS (CI-$NH_3$): found 835.7 [M + H]$^+$, 853.7 [M + $NH_4$]$^+$.

**General Procedure for the Synthesis of Nickel Bis(1,2-dithiolene) Complexes and Mixtures of Nickel Complexes:** A mixture of dialkoxybenzil (4.91 mmol) and $P_4S_{10}$ (4.8 g, 10.80 mmol) in dioxane (25 mL) was heated to reflux at 130 °C for 5 h. When the initial yellow suspension became a clear dark brown solution, the hot mixture was filtered to remove an insoluble pale yellow solid. To the filtrate was added a solution of $NiCl_2\cdot 6H_2O$ (0.64 g, 2.70 mmol) in water (5 mL), and the mixture was heated to reflux for 2 h. The mixture was then cooled to room temperature, and a small quantity of water was added. The black crystalline precipitate appeared and was collected by filtration. The crude product was purified by repeated precipitation from solution in dichloromethane by using ethanol (3 times), and the final purification was performed by column chromatography (hexane/dichloromethane).

**Nickel Bis[1,2-bis(4-decyloxyphenyl)ethene-1,2-dithiolene] Complex (5a):** Brown solid (1.6 g, yield 70%). $C_{68}H_{100}NiO_4S_4$ (1168.48): calcd. C 69.90, H 8.63, S 10.98; found C 69.22, H 8.72, S 10.62. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.37 (dt, $J$ = 3.0–9.6 Hz, 8 H, aromatic H), 6.86 (dt, $J$ = 3.0–9.6 Hz, 8 H, aromatic H), 4.00 (t, $J$ = 6.6 Hz, 8 H, -OC$H_2$-), 1.82 (quint, $J$ = 6.6 Hz, 8 H, -OCH$_2$C$H_2$-), 1.51–1.33 (m, 56 H), 0.92 (t, $J$ = 6.6 Hz, 12 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 180.73, 160.08, 134.10, 130.31, 114.28, 68.20, 31.89, 29.57, 29.55, 29.37, 29.31, 29.19, 25.97, 22.67, 13.86 ppm. HRMS (CI-$CH_4$): calcd. for $[M]^+$ 1166.5858; found 1166.5695.

**Nickel Bis[1-(4-decyloxy-3-bromophenyl)-2-(4-decyloxyphenyl)ethene-1,2-dithiolene] Complex (5b):** Black solid (0.5 g, yield 76%). $C_{68}H_{98}Br_2NiO_4S_4$ (1326.27): calcd. C 61.58, H 7.45, S 9.67, Br 12.05; found C 61.81, H 7.46, S 10.89, Br 11.94. $^{1}$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 7.72 (d, $J$ = 2.4 Hz, 2 H, aromatic H), 7.36 (dt, $J$ = 3.2–10 Hz, 4 H, aromatic H), 7.26 (dd, $J$ = 2.4–8.8 Hz, 2 H, aromatic H), 6.86 (m, 6 H, aromatic H), 4.07 (t, $J$ = 6.4 Hz, 4 H, -OC$H_2$-), 4.07 (t, $J$ = 6.8 Hz, 4 H, -OC$H_2$-), 1.85 (m, 8 H, -OCH$_2$C$H_2$-), 1.56–1.33 (m, 56 H), 0.93 (t, $J$ = 6.8 Hz, 12 H, -C$H_3$) ppm. $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 181.37, 178.57, 160.26, 156.12, 135.07, 133.64, 133.53, 130.37, 129.20, 114.43, 112.41, 111.90, 69.39, 68.27, 31.91, 29.58, 29.56, 29.39, 29.32, 29.18, 29.02, 25.99, 25.95, 22.68, 13.87 ppm. HRMS (CI-$CH_4$): calcd. for $[M]^+$ 1326.4039; found 1326.4076.

**Nickel Bis[1,2-(4-decyloxy-3-bromophenyl)ethene-1,2-dithiolene] Complex (5c):** Black solid (1.1 g, yield 65%). $C_{68}H_{96}Br_4NiO_4S_4$ (1484.07): calcd. C 55.03, H 6.52, S 8.64, Br 21.54; found C 54.80, H 6.59, S 8.41, Br 21.57. $^{1}$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.71 (d, $J$ = 2.7 Hz, 4 H, aromatic H), 7.18 (dd, $J$ = 2.4–8.7 Hz, 4 H, aromatic H), 6.76 (d, $J$ = 8.7 Hz, 4 H, aromatic H), 4.06 (t, $J$ = 6.3 Hz, 8 H, -OC$H_2$-), 1.88 (quint, $J$ = 6.6 Hz, 8 H, -OCH$_2$C$H_2$-), 1.57–1.37 (m, 56 H), 0.93 ($J$ = 6.6 Hz, 12 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 178.77, 156.17, 134.60, 133.53, 129.36, 112.39, 111.96, 69.41, 31.93, 29.58, 29.36, 29.35, 29.04, 25.97, 22.70, 13.90 ppm. MS (CI-$CH_4$): found 1483.43 $[M]^+$.

**Nickel Bis[1,2-(4-decyloxy-3-iodophenyl)ethene-1,2-dithiolene] Complex (5d):** Black solid (2.16 g, yield 81%). $C_{68}H_{96}I_4NiO_4S_4$ (1672.07): calcd. C 48.85, H 5.79, S 7.67, I 30.36; found C 48.91, H 5.67, S 8.35, I 29.73. $^{1}$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.96 (d, $J$ = 2.4 Hz, 4 H, aromatic H), 7.22 (dd, $J$ = 2.4–8.7 Hz, 4 H, aromatic H), 6.72 (d, $J$ = 8.7 Hz, 4 H, aromatic H), 4.06 (t, $J$ = 6.3 Hz, 8 H, -OC$H_2$-), 1.88 (quint, $J$ = 6.6 Hz, 8 H, -OCH$_2$C$H_2$-), 1.58–1.33 (m, 56 H), 0.93 (m, 12 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 178.81, 158.42, 139.66, 135.26, 130.28, 111.27, 86.29, 69.55, 31.93, 29.58, 29.35, 29.33, 29.03, 26.05, 22.70, 13.90 ppm. HRMS (CI-$CH_4$): calcd. for $[M + H]^+$ 1671.1802; found 1671.1726.

**Nickel Bis[1-(4-decyloxy-3,5-diiodophenyl)-2-(4-decyloxy-3-iodophenyl)ethene-1,2-dithiolene] Complex (5e):** Black solid (0.85 g, yield 55%). $C_{68}H_{94}I_6NiO_4S_4$ (1923.86): calcd. C 42.45, H 4.92, S 6.67, I 39.58; found C 42.67, H 4.90, S 6.43, I 38.00. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.88 ($J$ = 2.0 Hz, 2 H, aromatic H), 7.77 (s, 4 H, aromatic H), 7.20 (dd, $J$ = 2.4–8.8 Hz, 2 H, aromatic H), 6.68 (d, $J$ = 8.8 Hz, 2 H, aromatic H), 4.05 (t, $J$ = 6.4 Hz, 4 H, -OC$H_2$-), 4.02 (t, $J$ = 6.8 Hz, 4 H, -OC$H_2$-),1.93 (quint, $J$ = 6.8 Hz, 4 H, -OCH$_2$C$H_2$-), 1.86 (quint, $J$ = 6.8 Hz, 4 H, -OCH$_2$C$H_2$-), 1.59–1.28 (m, 56 H), 0.89 (m, 12 H, -C$H_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 180.19, 176.12, 158.75, 158.68, 140.01, 139.89, 139.82, 134.37, 130.17, 111.36, 90.77, 86.73, 69.59, 31.93, 30.08, 29.63, 29.60, 29.54, 29.51, 29.36, 29.32, 28.97, 26.04, 25.98, 22.72, 14.14 ppm. MS (CI-$CH_4$): found 1923.8342 $[M]^+$.

**Nickel Bis[1,2-(4-decyloxy-3,5-diiodomophenyl)ethene-1,2-dithiolene] Complex (5f):** Black solid (0.66 g, yield 30%). $C_{68}H_{92}I_8NiO_4S_4$ (2175.65): calcd. C 37.54, H 4.26, S 5.90, I 46.66; found C 37.94, H 4.34, S 5.00, I 45.56. $^{1}$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 7.80 (s, 8 H, aromatic H), 4.07 (t, $J$ = 6.8 Hz, 8 H, -OC$H_2$-), 1.97 (quint, $J$ = 6.4 Hz, 8 H, -OCH$_2$C$H_2$-), 1.63–1.34 (m, 56 H), 0.93 (t, $J$ = 6.8 Hz, 12 H, -C$H_3$) ppm. $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 177.70, 159.19, 140.10, 139.06, 90.70, 73.88, 31.93, 30.06, 29.62, 29.51, 29.36, 25.95, 22.71, 13.89 ppm.

**Nickel Bis[1,2-bis(4-decanoylphenyl)ethene-1,2-dithiolene] Complex (5g):** Green solid (0.4 g, yield 10%). $C_{68}H_{92}NiO_8S_4$ (1224.42): calcd. C 66.70, H 7.57, S 10.48; found C 66.28, H 7.88, S 10.74. $^{1}$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 7.45 (dt, $J$ = 2.8–9.6 Hz, 8 H, aromatic H), 7.09 (dt, $J$ = 2.8–9.6 Hz, 8 H, aromatic H), 2.60 [t, $J$ = 7.2 Hz, 8 H, -OC(=O)C$H_2$-], 1.77 [quint, $J$ = 7.60 Hz, 8 H, OC(=O)CH$_2$C$H_2$-], 1.49–1.33 (m, 48 H), 0.93 (t, $J$ = 6.8 Hz, 12 H, -C$H_3$) ppm. $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 180.78, 171.77, 151.60, 138.43, 130.00, 121.81, 34.30, 31.86, 29.41, 29.25, 29.06, 24.83, 22.67, 13.86 ppm. HRMS (CI-$CH_4$): calcd. for $[M + H]^+$ 1223.5107; found 1223.5134.

**Nickel [1,2-Bis(4-decanoylphenyl)ethene-1,2-dithiolene][1-(4-decanoylphenyl)-2-(4-thiodecanoatephenyl)ethene-1,2-dithiolene] Complex (5h) Isolated During the Synthesis of 5g:** Green solid (70 mg). $C_{68}H_{92}NiO_7S_5$ (1240.48): calcd. C 65.84, H 7.48, S 12.92; found C 65.32, H 7.73, S13.94. $^{1}$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.46 (m, 8 H, aromatic H), 7.05 (m, 8 H, aromatic H), 3.00 [t, $J$ = 7.5 Hz, 2 H, -OC(=S)C$H_2$-], 2.59 [t, $J$ = 7.5 Hz, 6 H, -OC(=O)C$H_2$-], 1.94 [quint, $J$ = 7.5 Hz, 2 H, -OC(=S)CH$_2$C$H_2$-], 1.75 [quint, $J$ = 7.8 Hz, 6 H, -OC(=O)CH$_2$C$H_2$-], 1.47–1.33 (m, 48 H), 0.94 (m, 12 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 181.03, 180.81, 180.42, 171.78, 155.12, 151.62, 139.13, 138.42, 138.31, 130.20, 130.06, 130.00, 122.34, 121.84, 46.77, 34.31, 31.88, 29.43, 29.27, 29.07, 24.84, 22.69, 13.88 ppm. HRMS (CI-$CH_4$): calcd. for $[M + H]^+$ 1239.4878; found 1239.4738.

**Nickel Bis[1,2-bis(3,4-di-*n*-decyloxyphenyl)ethene-1,2-dithiolene] Complex (5i):** Black green powder (0.1 g, yield 30%). $C_{108}H_{180}NiO_8S_4$ (1793.55): calcd. C 72.32, H 10.12; found C 72.70, H 10.16. $^{1}$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.12 (dd, $J$ = 2.1–8.4 Hz, 4 H, aromatic H), 6.87 (s, 4 H, aromatic H), 6.85 (d, $J$ = 2.1 Hz, 4 H, aromatic H), 4.04 (t, $J$ = 6.6 Hz, 8 H, -OC$H_2$-), 3.80 (t, $J$ = 6.6 Hz, 8 H, -OC$H_2$-), 1.84 (m, 8 H, -OCH$_2$C$H_2$-), 1.69 (m, 8 H, -OCH$_2$C$H_2$-), 1.56–1.32 (m, 112 H), 0.92 (m, 24 H, -C$H_3$) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 180.84, 150.24, 148.58, 134.36, 121.96, 114.40, 112.84, 69.17, 69.07, 31.94, 31.92, 29.70, 29.62, 29.60, 29.43, 29.39, 29.35, 29.26, 29.09, 26.03, 25.99, 22.69, 13.87 ppm. MS (FAB): found 1792 $[M]^+$.

**Nickel Bis[1,2-bis(3,5-di-*n*-decyloxyphenyl)ethene-1,2-dithiolene] Complex (5j):** Black powder (0.36 g, yield 28%). $C_{108}H_{180}NiO_8S_4$ (1793.55): calcd. C 72.32, H 10.12, S 7.15; found C 72.08, H 10.28, S 7.17. $^{1}$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 6.53 (d, $J$ = 2.0 Hz, 4 H, aromatic H), 6.47 (t, $J$ = 2.0 Hz, 2 H, aromatic H), 3.82 (t, $J$ = 6.8 Hz, 8 H, -OC$H_2$-), 1.68 (quint, $J$ = 6.4 Hz, 8 H, -OCH$_2$C$H_2$-), 1.41–1.29 (m, 56 H), 0.88 (t, $J$ = 6.8 Hz, 12 H, -C$H_3$) ppm. $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 181.73, 160.09, 159.50, 142.68, 107.31, 106.72, 102.63, 68.30, 67.71, 31.92, 31.33, 29.62, 29.58, 29.35, 29.06, 29.03, 28.99, 28.76, 28.47, 25.96, 25.37, 22.69, 22.10, 13.89, 13.30 ppm. HRMS (CI-$CH_4$): calcd. for $[M + H]^+$ 1792.1993; found 1792.0989.

**Nickel Bis[1,2-bis(3′,4′-bis(3,7-dimethyloctyloxy)phenyl)ethene-1,2-dithiolene] Complex (5k):** Black paste-like powder (0.44 g, yield 28%). $C_{108}H_{180}NiO_8S_4$ (1793.55): calcd. C 72.32, H 10.12; found C 72.40, H 10.18. $^{1}$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ = 7.13 (dd, $J$ = 2.0 Hz, 4 H, aromatic H), 6.87 (dd, $J$ = 2.0–8.4 Hz, 8 H, aromatic H), 4.06 (m, 8 H, -OC$H_2$-), 3.80 (m, 8 H, -OC$H_2$-), 1.95–0.90 (m, 152 H) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ = 180.83, 150.23, 148.60, 134.34, 121.92, 114.23, 112.67, 67.47, 67.39, 39.25, 37.35, 36.18, 36.05, 29.98, 29.96, 28.00, 24.75, 24.71, 22.46, 22.37, 19.45, 19.32 ppm. HRMS (CI-$CH_4$): calcd. for $[M + H]^+$ 1792.1993; found 1792.1937.

**Nickel Bis[1,2-bis(3′,4′-bis(2-ethylhexyloxy)phenyl)ethene-1,2-dithiolene] Complex (5l):** Black paste-like powder (0.56 g, yield 41%).

$C_{92}H_{148}NiO_8S_4$ (1569.12): calcd. C 70.42, H 9.51; found C 70.77, H 9.56. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta = 7.10$ (dd, $J = 2.1–8.4$ Hz, 4 H, aromatic H), 6.86 (dd, $J = 2.1–8.4$ Hz, 8 H, aromatic H), 3.90 (d, $J = 5.7$ Hz, 8 H, -OC$H_2$-), 3.64 (d, $J = 5.7$ Hz, 8 H, -OC$H_2$-), 1.81–0.88 (m, 120 H) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta = 180.89$, 150.60, 148.97, 134.28, 121.83, 114.21, 112.55, 71.53, 71.37, 39.59, 39.33, 30.58, 30.52, 29.13, 29.01, 23.92, 23.81, 23.06, 13.85, 10.98, 10.88 ppm. HRMS (CI-$CH_4$): calcd. for $[M]^+$ 1566.9563; found 1566.9460.

**Three Mixtures of Octaalkoxy-Substituted Nickel Bis(dithiolene) Complexes: 10.10**: 0.77 g (black paste-like powder), **11.10**: 0.66 g (black paste-like powder), **11.8**: 1.75 g (black paste-like powder).

**Supporting Information** (see footnote on the first page of this article): CV and SWV data of the nickel complexes, DSC of compounds **5a** and **5i**, POM images of compound **5i**.

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[1] C. W. Tang, *Appl. Phys. Lett.* **1986**, *48*, 183–185.

[2] H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu, G. Li, *Nat. Photonics* **2009**, *3*, 649–653; S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, A. J. Heeger, *Nat. Photonics* **2009**, *3*, 297–302.

[3] W. Pisula, M. Zorn, J. Y. Chang, K. Müllen, R. Zentel, *Macromol. Rapid Commun.* **2009**, *30*, 1179–1202.

[4] S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, *Angew. Chem. Int. Ed.* **2007**, *46*, 4832–4887.

[5] S. Sergeyev, W. Pisula, Y. H. Geerts, *Chem. Soc. Rev.* **2007**, *36*, 1902–1929; D. Markovitsi, S. Marguet, J. Bondkowski, S. Kumar, *J. Phys. Chem. B* **2001**, *105*, 1299–1306.

[6] M. Oukachmih, P. Destruel, I. Seguy, G. Ablart, P. Jolinat, S. Archambeau, M. Mabiala, S. Fouet, H. Bock, *Sol. Energy Mater. Sol. Cells* **2005**, *85*, 535–543; L. Schmidt-Mende, A. Fechtenkotter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119–1122; E. Charlet, E. Grelet, P. Brettes, H. Bock, H. Saadaoui, L. Cisse, P. Destruel, N. Gherardi, I. Seguy, *Appl. Phys. Lett.* **2008**, *92*, 024107; E. Grelet, H. Bock, *Europhys. Lett.* **2006**, *73*, 712–718; L. Cisse, P. Destruel, S. Archambeau, I. Seguy, P. Jolinat, H. Bock, E. Grelet, *Chem. Phys. Lett.* **2009**, *476*, 89–91; E. Grelet, S. Dardel, H. Bock, M. Goldmann, E. Lacaze, F. Nallet, *Eur. Phys. J. E* **2010**, *31*, 343–349.

[7] O. Thiebaut, H. Bock, E. Grelet, *J. Am. Chem. Soc.* **2010**, *132*, 6886–6887.

[8] J. Wu, W. Pisula, K. Mullen, *Chem. Rev.* **2007**, *107*, 718–747; Y. Avlasevich, C. Li, K. Müllen, *J. Mater. Chem.* **2010**, *20*, 3814–3826; N. G. Pschirer, C. Kohl, F. Nolde, J. Qu, K. Müllen, *Angew. Chem. Int. Ed.* **2006**, *45*, 1401–1404; M. Veber, R. Fugnitto, H. Strzelecka, *Mol. Cryst. Liq. Cryst.* **1983**, *96*, 221–227.

[9] E. Bundgaard, F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 954–985; R. Kroon, M. Lenes, J. C. Hummelen, P. W. M. Blom, B. de Boer, *Polym. Rev.* **2008**, *48*, 531–582; M. Koppe, H.-J. Egelhaaf, G. Dennler, M. C. Scharber, C. J. Brabec, P. Schilinsky, C. N. Hoth, *Adv. Funct. Mater.* **2010**, *20*, 338–346; E. H. Sargent, *Nat. Photonics* **2009**, *3*, 325–331.

[10] F. G. Brunetti, X. Gong, M. Tong, A. J. Heeger, F. Wudl, *Angew. Chem. Int. Ed.* **2010**, *49*, 532–536.

[11] B. Garreau-de Bonneval, K. Moineau-Chane Ching, F. Alary, T.-T. Bui, L. Valade, *Coord. Chem. Rev.* **2010**, *254*, 1457–1467; S. Dalgleish, N. Robertson, *Coord. Chem. Rev.* **2010**, *254*, 1549–1558; D. Belo, M. Almeida, *Coord. Chem. Rev.* **2010**, *254*, 1479–1492; M. Arca, M. C. Aragoni in *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium* (Ed.: F. A. Devillanova), RSC, Cambridge, **2007**, pp. 797–830; P. Deplano, M. L. Mercuri, A. Serpe, L. Pilia in *The Chemistry of Metal Enolates* (Ed.: J. Zabicky), John Wiley & Sons, Chichester, **2009**, pp. 879–928; A. Kobayashi, E. Fujiwara, H. Kobayashi, *Chem. Rev.* **2004**, *104*, 5243–5264; R. Kato, *Chem. Rev.* **2004**, *104*, 5319–5346; E. I. Stiefel in *Prog. Inorg. Chem. Vol. 52* (Ed.: K. D. Karlin), John Wiley and Sons, Hoboken NJ, **2004**.

[12] T.-T. Bui, B. Garreau-de Bonneval, K. Moineau-Chane Ching, *New J. Chem.* **2010**, *34*, 337–347.

[13] O. Mitsunobu, M. Yamada, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 935–939; O. Mitsunobu, M. Yamada, *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2380–2382.

[14] Y. Shirai, A. J. Osgood, Y. Zhao, Y. Yao, L. Saudan, H. Yang, C. Yu-Hung, L. B. Alemany, T. Sasaki, J.-F. Morin, J. M. Guerrero, K. F. Kelly, J. M. Tour, *J. Am. Chem. Soc.* **2006**, *128*, 4854–4864; B. N. Boden, A. Abdolmaleki, C. T.-Z. Ma, M. J. MacLachlan, *Can. J. Chem.* **2008**, *86*, 50–64.

[15] B. Mohr, V. Enkelmann, G. Wegner, *J. Org. Chem.* **1994**, *59*, 635–638.

[16] G. Wenz, *Makromol. Chem. Rapid Commun.* **1985**, *6*, 577–584.

[17] K. Ohta, H. Hasebe, H. Ema, M. Moriya, T. Fujimoto, I. Yamamoto, *Mol. Cryst. Liq. Cryst.* **1991**, *208*, 21–32; K. Ohta, Y. Inagaki-Oka, H. Hasebe, I. Yamamoto, *Polyhedron* **2000**, *19*, 267–274.

[18] M. Weiss, M. Appel, *J. Am. Chem. Soc.* **1948**, *70*, 3666–3667.

[19] J. L. Bredas, R. Silbey, D. S. Boudreaux, R. R. Chance, *J. Am. Chem. Soc.* **1983**, *105*, 6555–6559; S. Janietz, D. D. C. Bradley, M. Grell, C. Giebeler, M. Inbasekaran, E. P. Woo, *Appl. Phys. Lett.* **1998**, *73*, 2453; E. M. Stuve, A. Krasnopoler, D. E. Sauer, *Surf. Sci.* **1995**, *335*, 177–185.

[20] J. Tauc, R. Grigorovici, A. Vancu, *Phys. Status Solidi* **1966**, *15*, 627–637.

[21] A. Sournia-Saquet, B. Garreau-de Bonneval, K. I. Chane-Ching, L. Valade, *J. Electroanal. Chem.* **2008**, *624*, 84–90.

[22] K. Ohta, A. Takagi, H. Muroki, I. Yamamoto, K. Matsuzaki, T. Inabe, Y. Maruyama, *Mol. Cryst. Liq. Cryst.* **1987**, *147*, 15–24; H. Horie, A. Takagi, H. Hasebe, T. Ozawa, K. Ohta, *J. Mater. Chem.* **2001**, *11*, 1063–1071.

[23] K. Ohta, H. Hasebe, M. Moriya, T. Fujimoto, I. Yamamoto, *Mol. Cryst. Liq. Cryst.* **1991**, *208*, 33–41.

[24] D. Sartain, M. R. Truter, *Chem. Commun. (London)* **1966**, 382–383; D. Sartain, M. R. Truter, *J. Chem. Soc. A* **1967**, 1264–1272; T. Anjos, S. J. Roberts-Bleming, A. Charlton, N. Robertson, A. R. Mount, S. J. Coles, M. B. Hursthouse, M. Kalaji, P. J. Murphy, *J. Mater. Chem.* **2008**, *18*, 475–483; R. Perochon, L. Piekara-Sady, W. Jurga, R. Clerac, M. Fourmigue, *Dalton Trans.* **2009**, 3052–3061; C. L. Kean, D. O. Miller, P. G. Pickup, *J. Mater. Chem.* **2002**, *12*, 2949–2956.

[25] C.-T. Chou, Y.-F. Pai, C.-C. Lin, T. K. Misra, C.-Y. Liu, *J. Chromatogr. A* **2004**, *1043*, 255–263.

[26] K. Ohta, H. Hasebe, H. Ema, T. Fujimoto, I. Yamamoto, *J. Chem. Soc., Chem. Commun.* **1989**, 1610–1611.

[27] S. Saïdi-Besbes, É. Grelet, H. Bock, *Angew. Chem. Int. Ed.* **2006**, *45*, 1783–1786; H. Bock, M. Rajaoarivelo, S. Clavaguera, É. Grelet, *Eur. J. Org. Chem.* **2006**, 2889–2893; N. Buffet, E. Grelet, H. Bock, *Chem. Eur. J.* **2010**, *16*, 5549–5553.

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## ***SUPPORTING INFORMATION***

***DOI:*** 10.1002/ejic.201001288
***Title:*** Discotic Nickel Bis(dithiolene) Complexes – Synthesis, Optoelectrochemical and Mesomorphic Properties
***Author(s):*** Thanh-Tuan Bui, Olivier Thiebaut, Eric Grelet, Marie-France Achard, Bénédicte Garreau-de Bonneval,* Kathleen I. Moineau-Chane Ching*

Table S1. Full CV and SWV data (GC working electrode) of nickel complexes (**5a-l**) and three mixtures **10.10**, **11.10** and **11.8** (V/SCE), ΔE (V) = $E_{1/2}^3$ - $E_{1/2}^2$

| **Complexes** | **CV** | | | **SWV** | | |
|---|---|---|---|---|---|---|
| | $E_{1/2}^2$ | $E_{1/2}^3$ | $\Delta E_{CV}$ | $E_{1/2}^2$ | $E_{1/2}^3$ | $\Delta E_{SWV}$ |
| **5a** | -0.09 | 0.91 | 1.00 | -0.11 | 0.94 | 1.04 |
| **5b** | -0.04 | 0.97 | 1.01 | -0.05 | 0.98 | 1.03 |
| **5c** | 0.01 | 1.04 | 1.03 | 0.01 | 1.07 | 1.06 |
| **5d** | 0.01 | 1.02 | 1.01 | 0.00 | 1.06 | 1.06 |
| **5e** | 0.09 | 1.17 | 1.08 | 0.07 | 1.19 | 1.12 |
| **5f** | 0.18 | 1.32 | 1.14 | 0.17 | 1.36 | 1.19 |
| **5g** | 0.05 | 1.17 | 1.13 | 0.03 | 1.21 | 1.18 |
| **5h** | 0.04 | 1.18 | 1.14 | 0.03 | 1.21 | 1.18 |
| **5i** | -0.10 | * | * | -0.11 | 0.92 | 1.03 |
| **5j** | -0.01 | * | * | -0.03 | 1.28 | 1.31 |
| **5k** | -0.10 | * | * | -0.11 | 0.96 | 1.07 |
| **5l** | -0.12 | * | * | -0.13 | 0.93 | 1.06 |
| **10.10** | -0.09 | * | * | -0.10 | 0.96 | 1.07 |
| **11.10** | -0.09 | * | * | -0.09 | 0.95 | 1.05 |
| **11.8** | -0.08 | * | * | -0.08 | 0.95 | 1.03 |

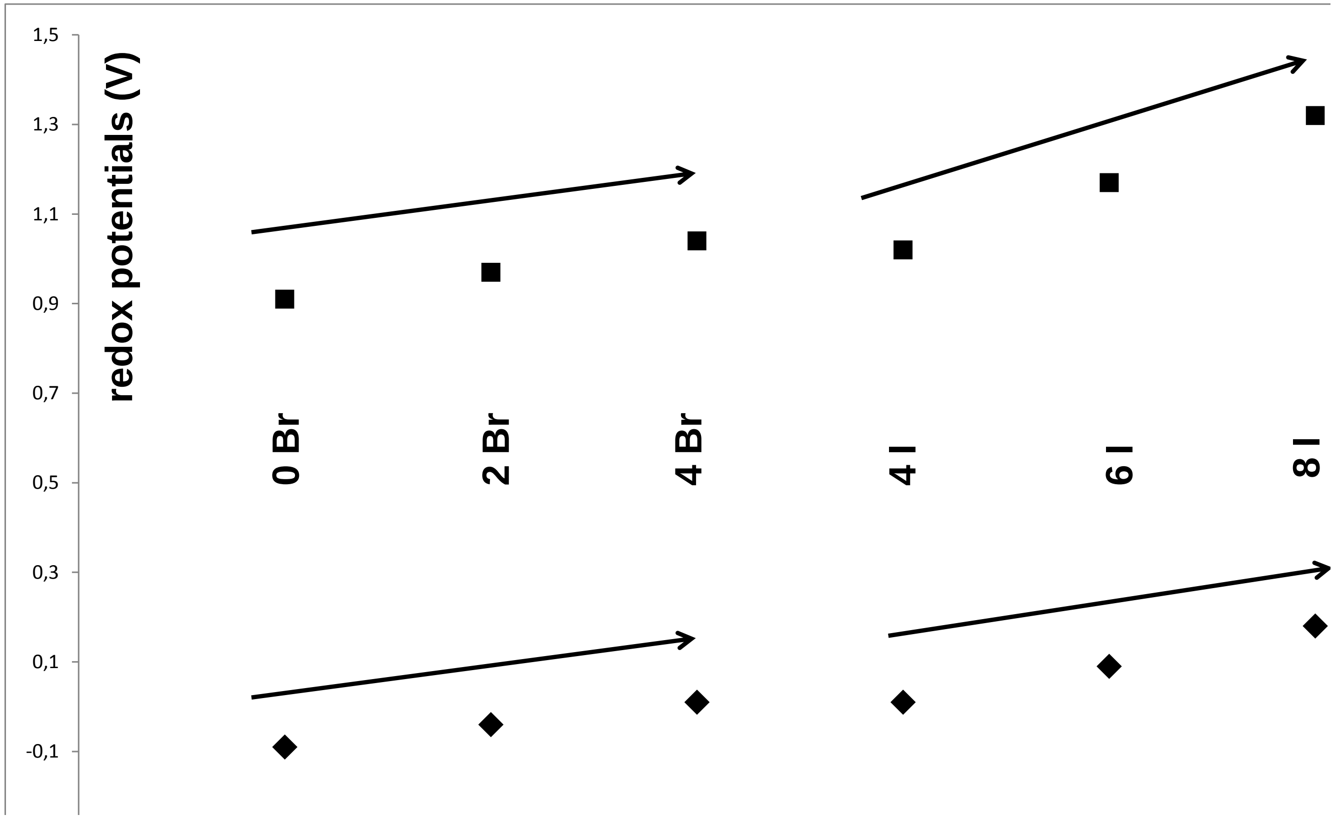


Figure S1. Schematic presentation of CV redox properties of halogenated complexes (**5b-f**) *vs* parent compound **5a**

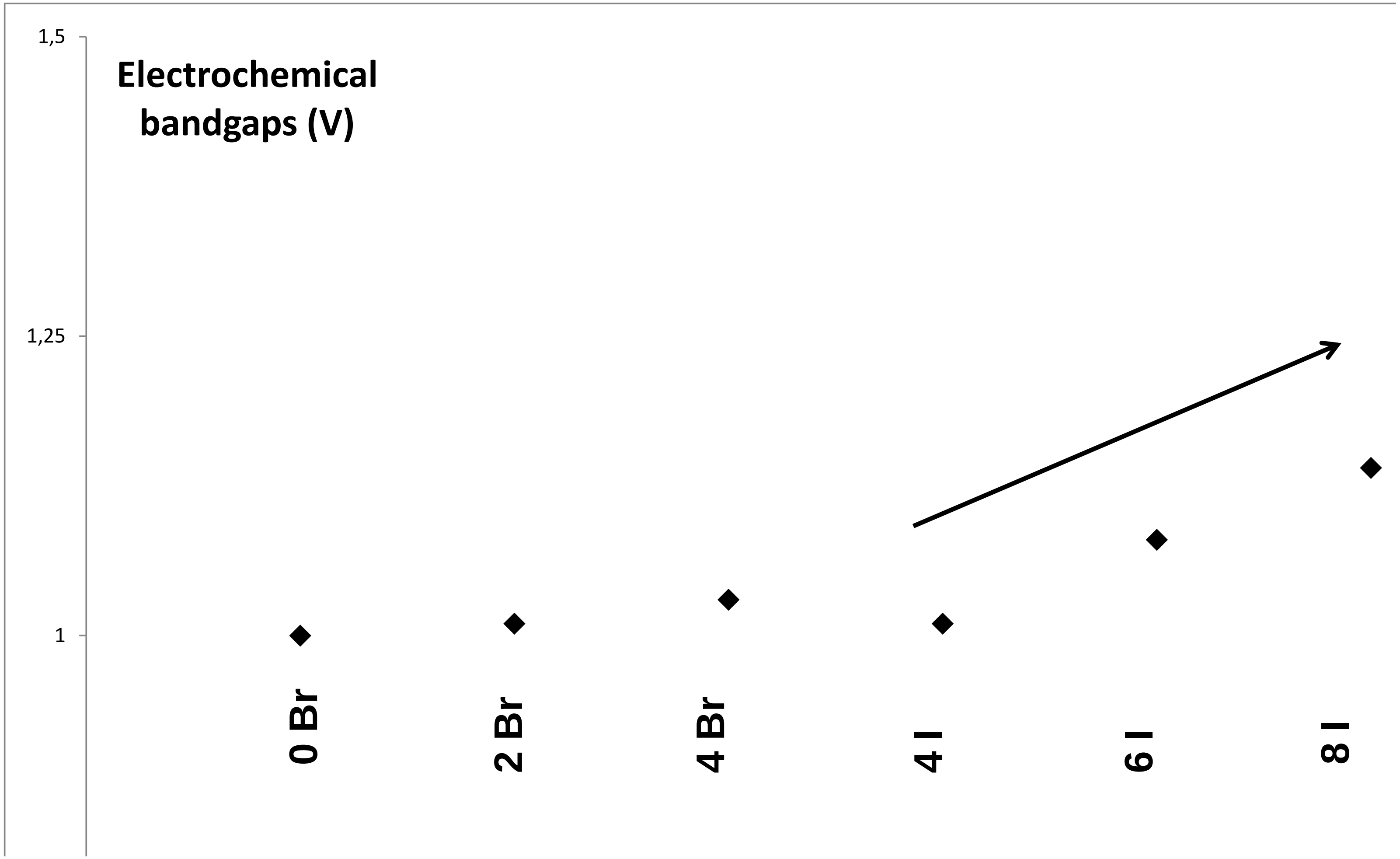


Figure S2. Schematically presentation of CV electrochemical bandgaps of halogenated complexes (**5b-f**) *vs* parent compound **5a**

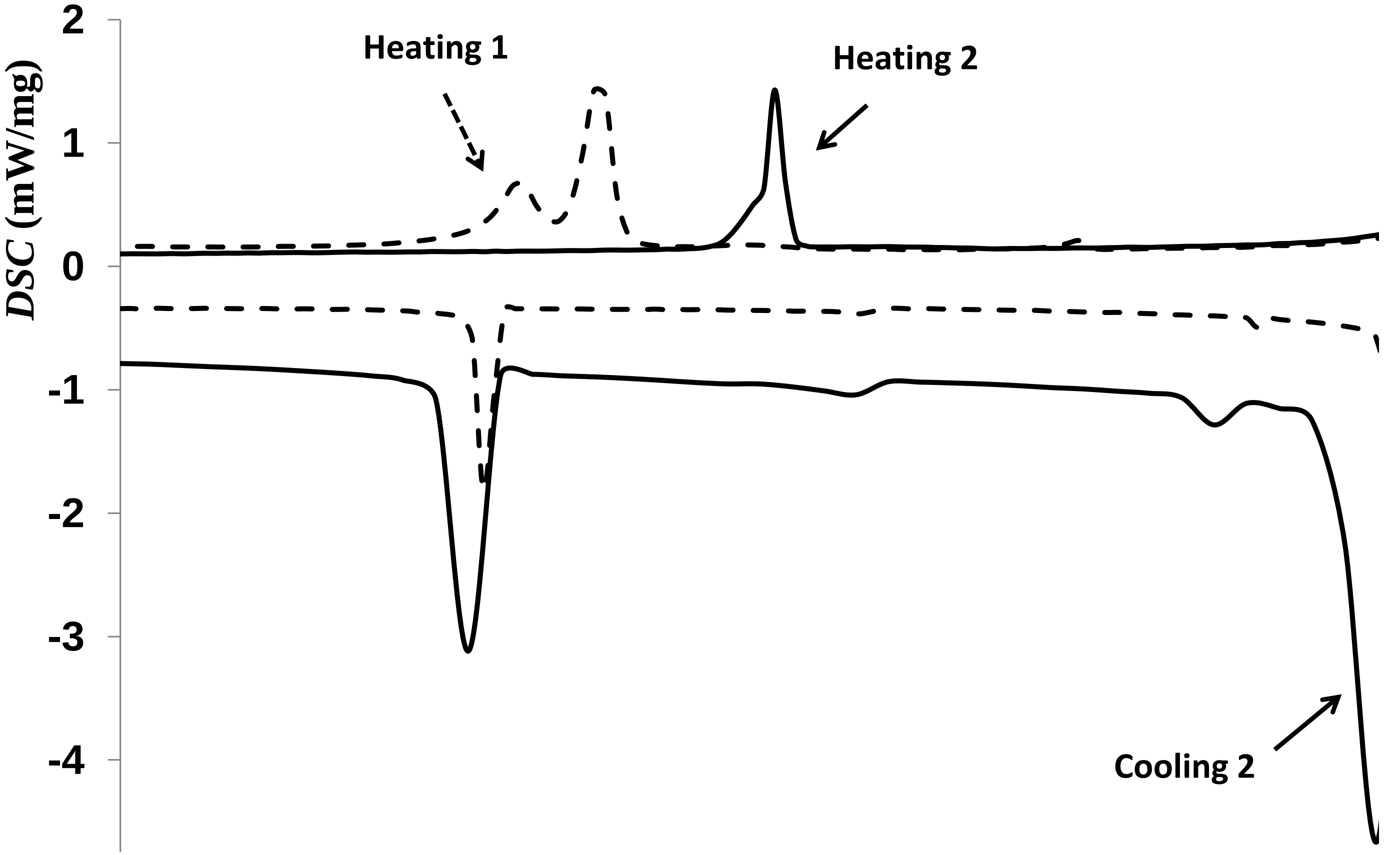


Figure S3. DSC of tetradecyloxy-substituted **5a**, scan rate 10°C/min

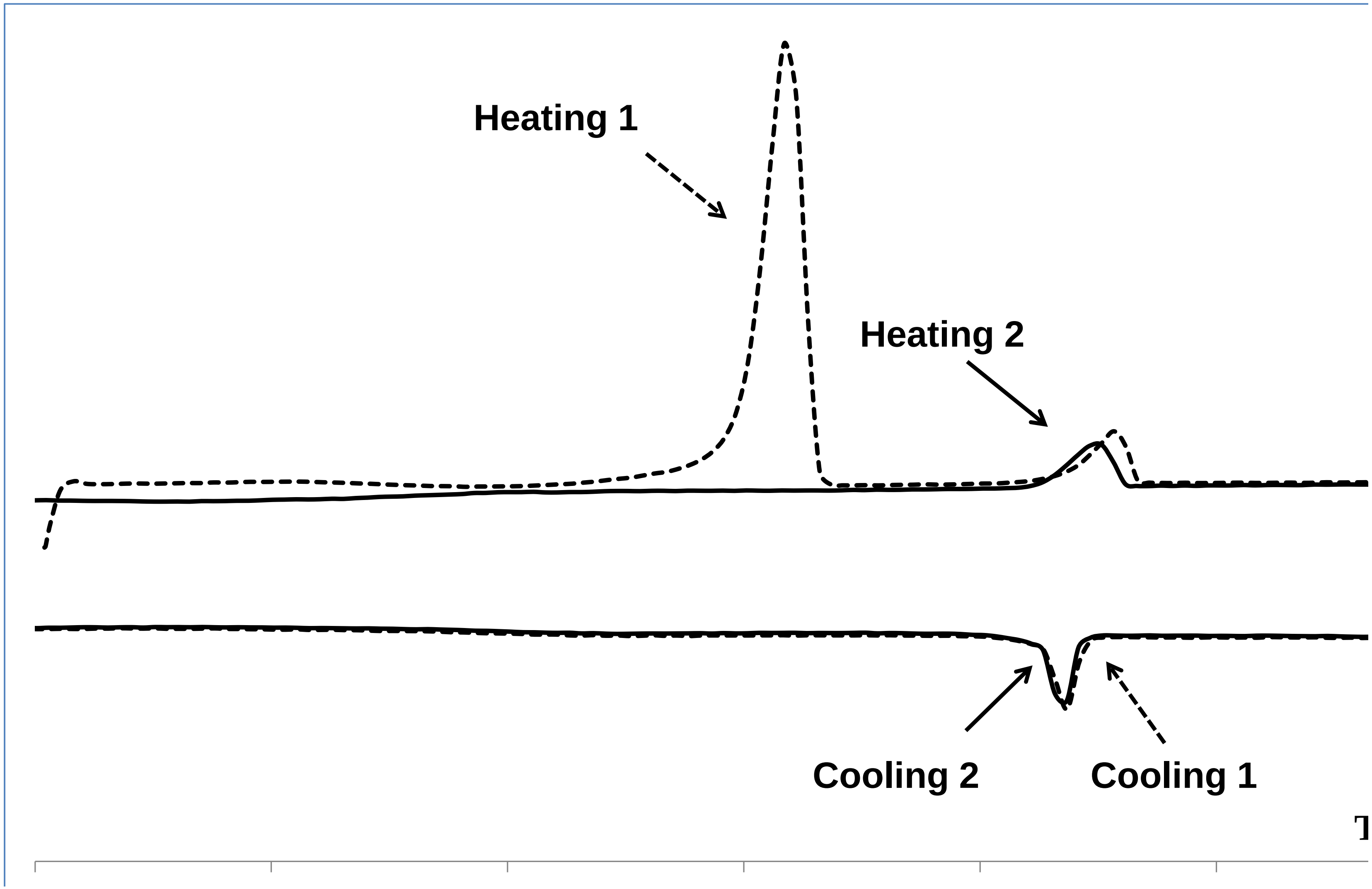
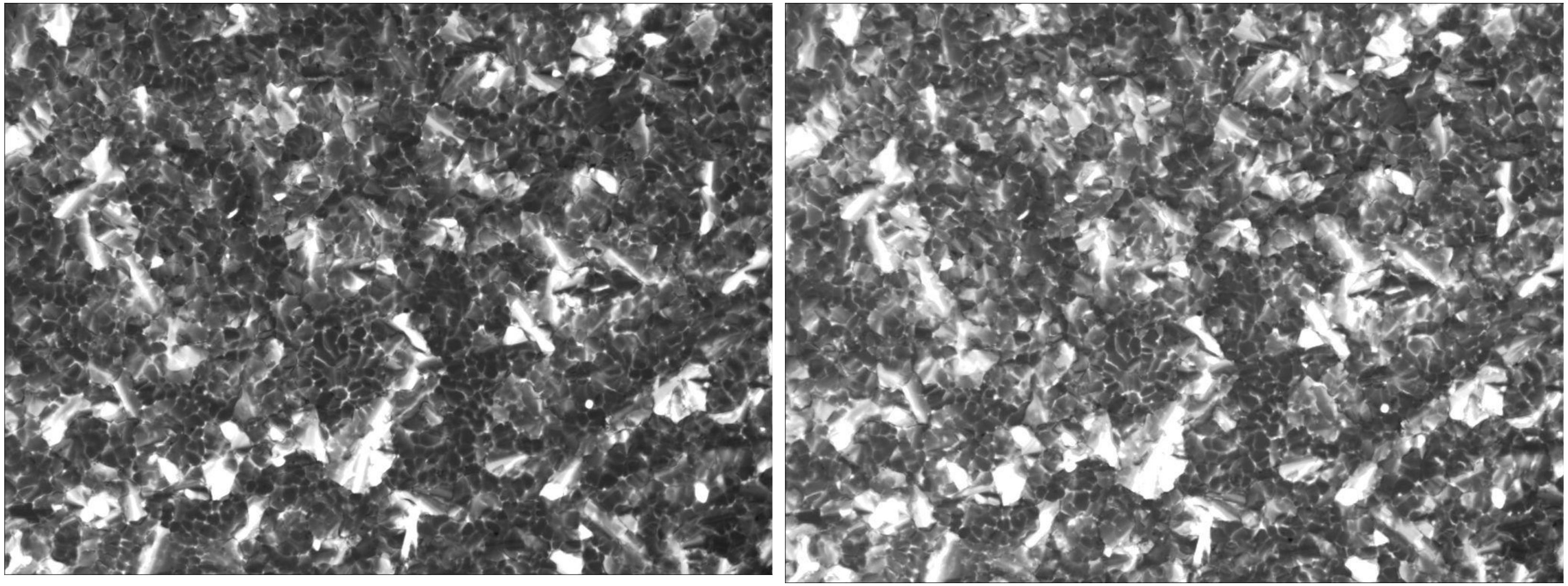


Figure S4. DSC of octadecyloxy-substituted **5i**, scan rate 10°C/min



a) b)

Figure S5. POM images of **5i** at 65°C (A) and room temperature (B) on cooling down from isotropic liquid, 1°C/min

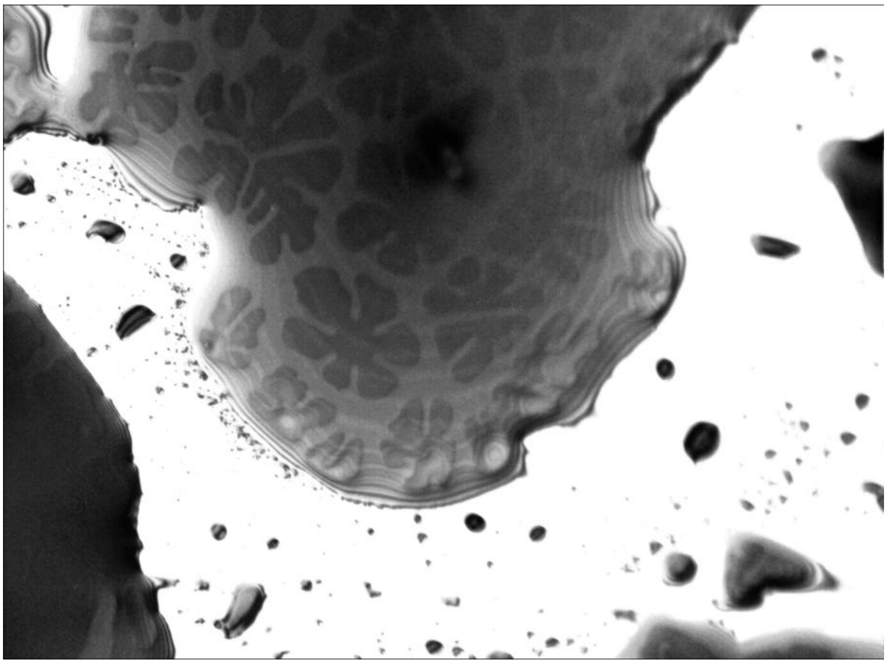


Figure S6. POM image of free (open) droplet of **5i**