

# Synthesis and preliminary physical properties of new neutral tetraalkoxy-substituted nickel bis(1,2-dithiolene) complexes†

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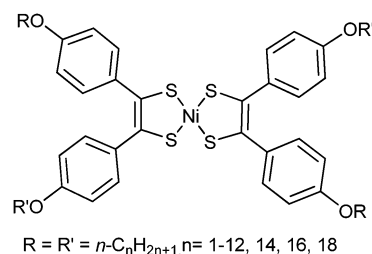
Nineteen neutral nickel bisdiphenylethenedithiolene complexes  $[\text{Ni}(\text{dpedt})_2]$ , including seventeen new compounds, were synthesized and characterized by a new short, efficient and multigram-scale synthetic method. Preliminary physical investigations show that these complexes are electron-withdrawing materials exhibiting good thermal stability and high molecular absorption coefficient in the near-infrared spectral region. Electrochemical and optical properties of  $[\text{Ni}(\text{dpedt})_2]$  depend strongly on the nickel bis(1,2-dithiolene) core and very slightly on the alkyl chain lengths or configurations. These highly soluble coordination compounds are potential candidates as acceptor solution-processable materials for active layers in organic electronic devices, such as field effect transistors or photovoltaic devices.

## Introduction

The chemistry of neutral transition-metal (1,2-dithiolene) complexes in the 1960's decade started with the first report on an authentic trisdithiolene complex by Gilbert *et al.*<sup>1</sup> In 1962, Schrauzer *et al.*<sup>2</sup> reported the preparation of an unusual nickel complex, formulated as  $[\text{NiS}_4\text{C}_4\text{Ph}_4]$ , in the somewhat esoteric reaction between  $\text{Ni}(\text{CO})_4$ , sulfur and diphenylacetylene. This new nickel complex, quite unlike any other nickel complex known at that time, was intensely colored (green), diamagnetic, and volatile. This was the first authentic neutral nickel bisdiphenylethenedithiolene  $[\text{Ni}(\text{dpedt})_2]$  reported. Later, they reported the formation of a large number of neutral metal complexes with diaryl and dialkyl “ $\alpha,\beta$ -dithioketones”  $[\text{MS}_4\text{C}_4\text{R}_4]$ .<sup>3</sup> Their methods only give low yields and are not sufficiently general. A little later, they reported a new synthetic method using benzoin.<sup>4</sup> This method is still generously used nowadays in order to prepare (a)symmetric tetra(hetero)aryl-substituted nickel bis(1,2-dithiolene) complexes.<sup>5,6</sup> However, it cannot be adopted for long-chain substituted complexes, because one cannot obtain long alkyl/alkoxy chain-substituted benzoin by the benzoin condensation, except for dimethyl-, dimethoxy- and tetramethoxy-benzoin. Ohta *et al.*<sup>7–10</sup> overcame this limitation and succeeded in obtaining several series of alkyl- and alkoxy-substituted nickel bis(1,2-bisphenylethene-1,2-dithiolene) complexes by using the corresponding benzils as the precursors. Based on the chemical reactivities and physical properties of the nickel bis(1,2-dithiolene) complexes, many applications were developed such as near

infrared (NIR) photodetectors,<sup>11</sup> optical switching devices,<sup>12</sup> organic dyes,<sup>6</sup> non linear optics,<sup>13</sup> and organic electronics.<sup>14</sup> Results of extensive research on metal bis(1,2-dithiolene) complexes chemistry have been the subject of several reviews.<sup>15</sup> These kinds of complexes are potentially molecular materials for organic electronic applications due to their high molecular absorption coefficients in the NIR spectral region. In this work, our interest is concentrated on synthesizing new neutral nickel bis[1,2-bis(4-alkoxyphenyl)-ethene-1,2-dithiolene] complexes in order to obtain room temperature discotic liquid crystals (DLC) for a new conception of multi-layer organic photovoltaic device based on NIR absorbent DLC semiconducting materials. The use of DLC semiconducting molecules would help increasing the efficiency of organic photovoltaic devices due to their high charge mobilities.<sup>16</sup> The first discotic mesogenic neutral nickel bis(1,2-dithiolene) complexes, which contains four *n*-dodecyloxy chains (Fig. 1), was reported in 1983 by Veber *et al.*<sup>17</sup>

Later, Ohta *et al.*<sup>8</sup> synthesized two new homologous discotic mesospheric complexes with *n*-nonyloxy and *n*-undecyloxy chains (Fig. 1). In 2001, they synthesized a new series of nickel bis(1,2-dithiolene) complexes containing 4-fold linear alkoxy moieties and fully re-studied this family.<sup>10</sup> They claimed that these complexes with  $n \geq 9$  exhibit discotic liquid



**Fig. 1** First discotic mesogenic neutral nickel bis(1,2-dithiolene) complexes reported by Veber *et al.*<sup>17</sup> and then Ohta *et al.*<sup>8,10</sup>

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crystalline properties. Prior to this work, the lowest transition temperatures reported were situated between 50 °C and 60 °C with linear dodecyloxy and linear tetradecyloxy chains.<sup>10</sup>

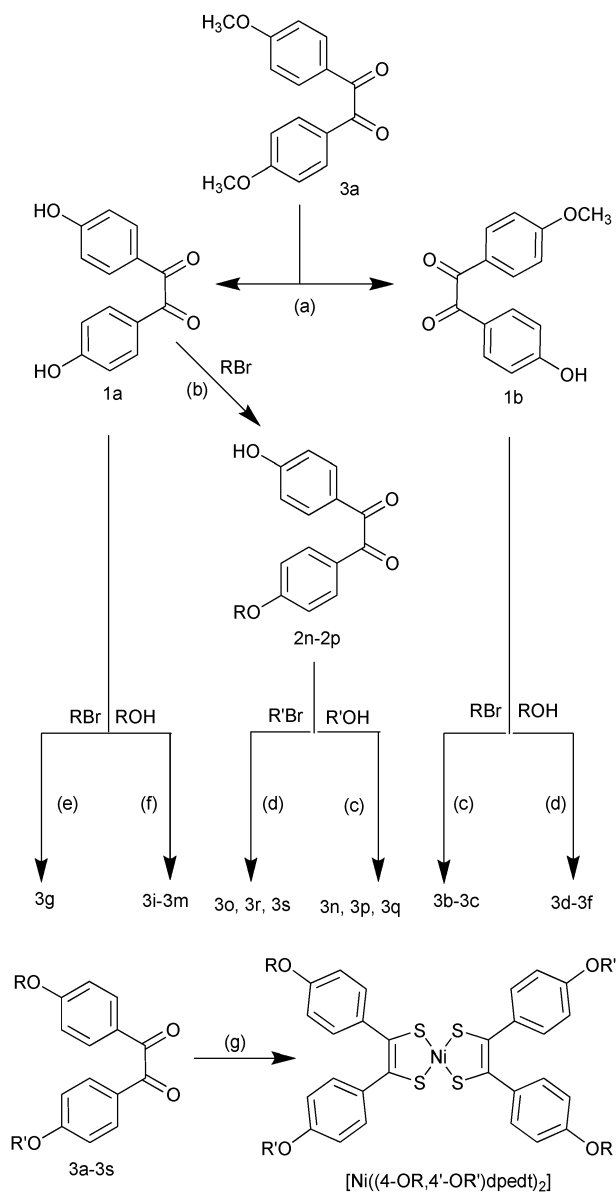
The introduction of branched alkyloxy chains and the synthesis of asymmetric complexes, *i.e.* complexes containing two kinds of alkyloxy (either linear (L) or branched (B)) chains could play an important role on the molecular packing, and thus on the transition temperature.

## Results and discussion

### Synthesis

Based on the successful benzil method of Ohta *et al.*,<sup>8,10</sup> new synthetic pathways were developed to obtain asymmetric compounds or new symmetric complexes. The starting material, *p*-anisil, is a commercially available product. It can be also easily prepared from 4-methoxybenzaldehyde by the method of Wenz.<sup>18</sup> The synthetic pathways are outlined in Scheme 1. The list of all intermediate and final complexes is given in Table 1. As depicted in Scheme 1, the final neutral complexes are achieved from the benzil precursors **3a–3s**. The transformation of **3a–3s** into nickel bis(1,2-dithiolene) complexes is well known as a “one-pot” procedure.<sup>4,19</sup> The thionating reaction of the  $\alpha$ -diketone **3** is performed by  $P_4S_{10}$  in boiling dioxane leading to thiophosphate ester intermediates.<sup>4</sup> Recently Arumugam *et al.*<sup>20</sup> demonstrated the preparation and isolation of stable thiophosphate ester consisting in the protected forms of 1,2-dithiolene ligands. According to our synthesis pathway, this thiophosphate ester is not isolated but directly hydrolyzed in the reaction medium. The hydrolysis followed by adding nickel salt in air condition gives neutral products  $[Ni(dpdt)_2]$  with quite good yields after purification by repeated processes of precipitation and column chromatography. By convention, all  $[Ni(dpdt)_2]$  derivatives in the present work are presented as *trans* configuration as the exact configuration of nickel complexes are not elucidated. In order to obtain the long alkoxy chain-substituted benzil derivatives **3b–3s**, we started from *p*-anisil **3a**. By removing one methyl-group of **3a** in hydrobromic acid we obtained the phenol derivative **1b**. We were then able to graft another linear or branched alkyl chain to get asymmetric benzils **3b–3f**. If both methoxy groups are removed, two free phenol functions are available for chemical modification. The introduction of two-fold alkyl chain yielded to symmetric benzils **3g–3m**. At this stage, it was possible to graft two different alkyl chains on **1a** by successive substitutions. The monoalkoxy-substituted intermediates **2n–2p** were systematically purified before the second alkyl chains were introduced. All branched alkyl chains were used as racemic mixtures. The 4,4'-dihydroxybenzil **1a** was prepared in big quantities from **3a**. The demethylation reaction was performed by a boiling mixture of concentrated hydrobromide acid and glacial acetic acid according to the literature.<sup>21</sup> In this reaction conditions, the conversion of 4,4'-dimethoxybenzil to  $\alpha$ -diketone **1a** strongly depends on the reaction times and the quantity of starting material (the longer the reflux time is, the higher the conversion rate is). We started from 26 g of **3a** in 550 ml of acid mixture and the desired product **1a** was obtained with nearly quantitative yield

after 50 h of reflux. The complete treatment of reaction mixture after only 17 h gave a mixture of three products: starting 1,2-diketone ( $\approx 20\%$  of starting materials), mono-demethylation intermediate product **1b**,  $\approx 30\%$  and **1a**,  $\approx 30\%$ . Example of high yield synthesis of **1b** was also reported<sup>22</sup> but in the present work the synthesis of **1b** was not optimized. Both **1a** and **1b** were engaged in the next steps for preparing long chain substituted benzils: the precursor of 1,2-dithiolene ligands.



**Scheme 1** Synthetic pathways of neutral nickel bis(1,2-dithiolene) complexes. Reagents and conditions: (a) HBr 48%, glacial  $CH_3COOH$ , reflux; (b) RBr (0.9 equiv.),  $K_2CO_3$  (0.9 equiv.), DMF, 90 °C, 1 h; (c) RBr (1.2 equiv.),  $K_2CO_3$  (1.5 equiv.), DMF, 90 °C; (d) ROH (1.2 equiv.), DEAD (1.2 equiv.),  $PPh_3$  (1.2 equiv.), THF, 0 °C then 1 h at R.T.; (e) RBr (2.4 equiv.),  $K_2CO_3$  (3.0 equiv.), DMF, 90 °C; (f) ROH (2.4 equiv.), DEAD (2.4 equiv.),  $PPh_3$  (2.4 equiv.), THF, 0 °C then 1 h at R.T.; (g)  $P_4S_{10}$  (2.2 equiv.), dioxane, reflux 5 h then  $NiCl_2 \cdot 6H_2O$  (0.55 equiv.),  $H_2O$ , reflux 2 h.

**Table 1** Intermediate and final synthesized compounds. All branched alkyl chains are racemic mixture and yields (%) are listed in bracket. **3h** was isolated from the synthesis of **2p** and **3a** is a commercial product. Melting points (°C) are determined from DSC diagrams

R	R'	1	2	3	Nickel complexes	Yield/color/M <sub>p</sub>
H	H	<b>1a</b> (96)	—	—		
Methyl	H	<b>1b</b> (28)	—	—		
2-Ethylhexyl	H	—	<b>2n</b> (41)	—	—	
<i>n</i> -Decyl	H	—	<b>2o</b> (57)	—	—	
<i>n</i> -Dodecyl	H	—	<b>2p</b> (46)	—	—	
Methyl	Methyl	—	—	<b>3a</b>	[Ni((4-OC <sub>1</sub> ,4'-OC <sub>1</sub> )dpdt) <sub>2</sub> ]	18/black/nd
<i>n</i> -Decyl	Methyl	—	—	<b>3b</b> (95)	[Ni((4-OC <sub>1</sub> ,4'-OC <sub>10L</sub> )dpdt) <sub>2</sub> ]	51/black/147.3
2-Ethylhexyl	Methyl	—	—	<b>3c</b> (97)	[Ni((4-OC <sub>1</sub> ,4'-OC <sub>8B</sub> )dpdt) <sub>2</sub> ]	45/brown/199.1
3,7-Dimethyloctyl	Methyl	—	—	<b>3d</b> (84)	[Ni((4-OC <sub>1</sub> ,4'-OC <sub>10B</sub> )dpdt) <sub>2</sub> ]	53/black/170.3
2-Butyloctyl	Methyl	—	—	<b>3e</b> (77)	[Ni((4-OC <sub>1</sub> ,4'-OC <sub>12B</sub> )dpdt) <sub>2</sub> ]	49/black/154.8
2-Hexyldecyl	Methyl	—	—	<b>3f</b> (96)	[Ni((4-OC <sub>1</sub> ,4'-OC <sub>16B</sub> )dpdt) <sub>2</sub> ]	50/black/147.4
2-Ethylhexyl	2-Ethylhexyl	—	—	<b>3g</b> (70)	[Ni((4-OC <sub>8B</sub> ,4'-OC <sub>8B</sub> )dpdt) <sub>2</sub> ]	47/brown/163.7
<i>n</i> -Dodecyl	<i>n</i> -Dodecyl	—	—	<b>3h</b>	[Ni((4-OC <sub>12L</sub> ,4'-OC <sub>12L</sub> )dpdt) <sub>2</sub> ]	48/brown/168.8
3,7-Dimethyloctyl	3,7-Dimethyloctyl	—	—	<b>3i</b> (78)	[Ni((4-OC <sub>10B</sub> ,4'-OC <sub>10B</sub> )dpdt) <sub>2</sub> ]	59/black/129.9
2-Butyloctyl	2-Butyloctyl	—	—	<b>3j</b> (90)	[Ni((4-OC <sub>12B</sub> ,4'-OC <sub>12B</sub> )dpdt) <sub>2</sub> ]	51/black/103.2
2-Hexyldecyl	2-Hexyldecyl	—	—	<b>3k</b> (69)	[Ni((4-OC <sub>16B</sub> ,4'-OC <sub>16B</sub> )dpdt) <sub>2</sub> ]	49/black/-
2-Octyldodecyl	2-Octyldodecyl	—	—	<b>3l</b> (75)	[Ni((4-OC <sub>20B</sub> ,4'-OC <sub>20B</sub> )dpdt) <sub>2</sub> ]	43/black/-
2-Decyltetradecyl	2-Decyltetradecyl	—	—	<b>3m</b> (82)	[Ni((4-OC <sub>24B</sub> ,4'-OC <sub>24B</sub> )dpdt) <sub>2</sub> ]	57/black/-
2-Ethylhexyl	<i>n</i> -Decyl	—	—	<b>3n</b> (69)	[Ni((4-OC <sub>10L</sub> ,4'-OC <sub>8B</sub> )dpdt) <sub>2</sub> ]	73/black/153.2
<i>n</i> -Decyl	3,7-Dimethyloctyl	—	—	<b>3o</b> (91)	[Ni((4-OC <sub>10L</sub> ,4'-OC <sub>10B</sub> )dpdt) <sub>2</sub> ]	59/black/158.5
<i>n</i> -Dodecyl	<i>n</i> -Tetradecyl	—	—	<b>3p</b> (99)	[Ni((4-OC <sub>12L</sub> ,4'-OC <sub>14L</sub> )dpdt) <sub>2</sub> ]	52/brown/163.7
<i>n</i> -Dodecyl	<i>n</i> -Undecyl	—	—	<b>3q</b> (80)	[Ni((4-OC <sub>12L</sub> ,4'-OC <sub>11L</sub> )dpdt) <sub>2</sub> ]	68/brown/171.9
<i>n</i> -Dodecyl	2-Butyloctyl	—	—	<b>3r</b> (100)	[Ni((4-OC <sub>12L</sub> ,4'-OC <sub>12B</sub> )dpdt) <sub>2</sub> ]	71/black/99.0
<i>n</i> -Dodecyl	3,7-Dimethyloctyl	—	—	<b>3s</b> (95)	[Ni((4-OC <sub>12L</sub> ,4'-OC <sub>10B</sub> )dpdt) <sub>2</sub> ]	55/brown/149.7

### Synthesis of symmetric 4,4'-dialkoxybenzils (3g–3m)

The symmetric 4,4'-dialkoxybenzils **3g–3m** were synthesized by grafting alkyl chains on the phenol function of **1a**. Two different methods were used, depending on the commercial availability of alkyl chains as halogenated alkanes or alcoholic compounds. In the first case, the classical nucleophilic substitution reaction gave **3g** in high yield by heating the mixture of **1a** and large excess of 2-ethylhexylbromide and a Lewis base (K<sub>2</sub>CO<sub>3</sub>) in DMF.

In the later case, the Mitsunobu's method<sup>23</sup> was applicable leading to **3i–3m**. The Mitsunobu reaction is very efficient in mild experimental conditions (ambient temperature) and an easy work-up reaction. This allows the conversion of primary and secondary alcohols to esters, phenyl ethers, thioethers and various other compounds with high yields. We are able to graft a large choice of alkyl chains in one step, particularly branched ones that are often available as primary or secondary alcohols.

### Synthesis of asymmetric 4,4'-dialkoxybenzils (3b–3f, 3n–3s)

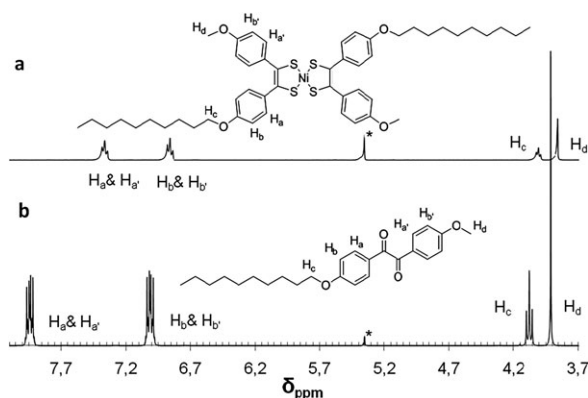
The asymmetric precursors 4,4'-dialkoxybenzil **3n–3s**, which contain two different alkyl chains (different from methyl), were synthesized from **1a**. For this, the two chains were successively introduced. The reaction of **1a** with a little less than one equivalent of alkyl bromide in short reaction time forms monoalkoxy-substituted benzils **2n–2p** with acceptable yields (41–57%). Usually the symmetric benzils **3** were also isolated as co-products (e.g. 4,4'-dodecyloxybenzil **3h** is isolated in the synthesis of **2p** in 30% yield). The quantitative conversion of **1a** to **2o–2p** could be realized by using a large excess of **1a** as described for a similar reaction.<sup>24</sup> The introduction of the second alkyl chain was performed either by nucleophilic substitution or the Mitsunobu reaction, as described above,

resulting in **3n–3s**. The dialkoxy-substituted benzils containing one methyl chain **3b–3f** were synthesized from **1b** in similar conditions.

In comparison with other methods of synthesis of asymmetrical long alkoxy-substituted benzils,<sup>25</sup> this method presents some advantages. It uses common intermediates such as **1a** and **1b** and allows synthesizing many asymmetric benzils without any difficulty. Moreover, the alkyl chains are introduced in the last steps starting from either halogenated alkanes or alcohols that allow numerous alkyl chains combinations.

All of the synthesized compounds were identified by <sup>1</sup>H and <sup>13</sup>C NMR spectra. The elemental analyses and mass spectrometry analyses gave complementary confirmations. The analytical data of all [Ni(dpdt)<sub>2</sub>] such as visual colors, melting points, elemental analysis results, mass studies are summarized in Table 1 and the experimental section. All attempts to form a suitable crystal for single crystal X-ray diffraction analysis failed. As observed from Table 1, the introduction of long chains generally decreases the melting temperature of the nickel bis(1,2-dithiolene) complexes.

<sup>1</sup>H NMR spectra of benzil derivatives and corresponding nickel complexes are similar. Two typical spectra are gathered in Fig. 2: <sup>1</sup>H NMR spectra of 4-decyloxy-4'-methoxybenzil (Fig. 2b) and the corresponding nickel dithiolene complex (Fig. 2a). As observed, the peaks corresponding to protons Hc (triplet) and Hd (singlet) are well distinguishable, both in the case of benzil and dithiolene complex. In the aromatic region, the protons in the metal complex are shifted to higher fields. The metal bis(1,2-dithiolene) core is less electro-attractive than the corresponding 1,2-diketonic group. In addition to the NMR analysis, the good cohesiveness between the theoretical and experimental values of elemental analyses and mass spectroscopy studies confirmed the purity of the



**Fig. 2** Partial <sup>1</sup>H NMR spectra of (b) 4-decyloxy-4'-methoxybenzil 3d and (a) the corresponding nickel complex [Ni((4-OC<sub>8B</sub>,4'-OC<sub>8B</sub>)dpedt)<sub>2</sub>]. The peaks of CD<sub>2</sub>Cl<sub>2</sub> solvent have a star.

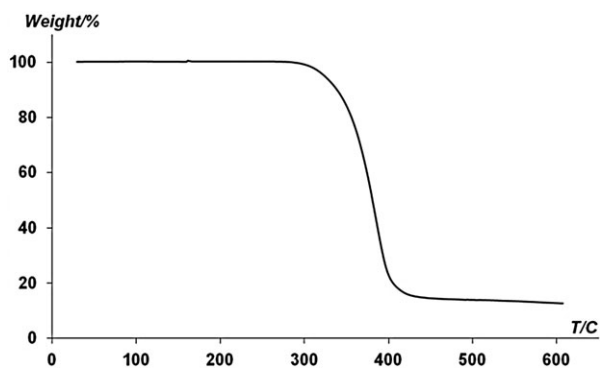
synthesized products. It is noteworthy that all nickel complexes were obtained from repeated precipitation processes and finally purified by silica-gel column chromatography. Table 1 also summarizes the visual aspects of all [Ni(dpdt)<sub>2</sub>]. The colors of some compounds appear to be different. Six of them are brown and thirteen others are black/dark-green.

### Preliminary physical investigations

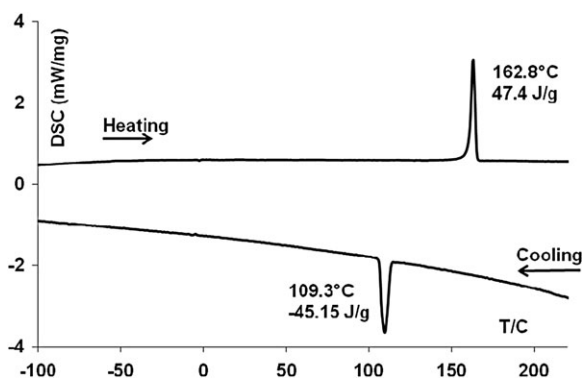
In order to envisage their use as active materials in organic electronic devices, the physical properties of these complexes have to be characterized. Currently, advanced studies are being carried out. Only the preliminary physical properties are given and discussed in this present paper. The typical results on [Ni((4-OC<sub>8B</sub>,4'-OC<sub>8B</sub>)dpedt)<sub>2</sub>] are presented.

### Thermal behaviors

The highly thermal stability of the targeted compounds is required to envisage their use as active materials in organic electronic devices (*e.g.* OPV, OFET). The thermal analysis studies show that neutral nickel bis(1,2-dithiolene) complexes are thermally stable until 300 °C, as observed in Fig. 3 for compound [Ni((4-OC<sub>8B</sub>,4'-OC<sub>8B</sub>)dpedt)<sub>2</sub>]. At higher temperature, the decomposition of the product is observed. This thermal behavior is in good accordance with data reported in the literature.<sup>26</sup>



**Fig. 3** Thermal analysis trace of [Ni((4-OC<sub>8B</sub>,4'-OC<sub>8B</sub>)dpedt)<sub>2</sub>].



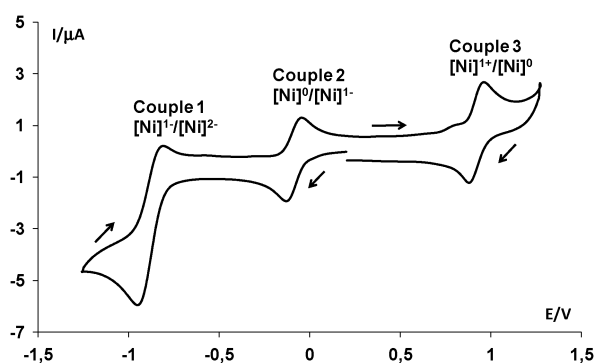
**Fig. 4** DSC trace of [Ni((4-OC<sub>8B</sub>,4'-OC<sub>8B</sub>)dpedt)<sub>2</sub>], scan rate: 10 °C min<sup>-1</sup>.

The phase transition behaviors of [Ni(dpdt)<sub>2</sub>] are studied by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and temperature-dependence powder X-rays diffraction. Fig. 4 shows the phase transition of the [Ni((4-OC<sub>8B</sub>,4'-OC<sub>8B</sub>)dpedt)<sub>2</sub>]. This complex was obtained as a brown powder. On heating, it melts into an isotropic liquid at 162.8 °C and on cooling down, the crystallization peak appears at 109.3 °C. This phase behavior of [Ni((4-OC<sub>8B</sub>,4'-OC<sub>8B</sub>)dpedt)<sub>2</sub>] is much simpler than its analogue's: the tetraoctyloxy-substituted [Ni(dpdt)<sub>2</sub>],<sup>10</sup> which contains four linear octyl chains. Its lower melting point is due to the highly steric bulky effect of the 2-ethylhexyl chain.

### Optical and electrochemical properties

The electrochemical and optical properties of the synthesized compounds were studied by cyclic voltammetry and UV-VIS-NIR absorption spectroscopy. The cyclic voltammogram of [Ni((4-OC<sub>8B</sub>,4'-OC<sub>8B</sub>)dpedt)<sub>2</sub>] in dichloromethane is shown in Fig. 5. Three pairs of redox waves are observed. In reduction, two successive near -0.1 and -0.8 V *vs.* SCE waves correspond to 1- and 2-electron reduction (respectively, couple 2 and couple 1).<sup>27</sup> In oxidation, the first 1-electron oxidation is observed near 1 V *vs.* SCE (Couple 3).<sup>27</sup> The solution absorption spectra in the UV-VIS-NIR region of [Ni((4-OC<sub>8B</sub>,4'-OC<sub>8B</sub>)dpedt)<sub>2</sub>] is presented in Table 2. The complex shows 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. All potentials are determined in CH<sub>2</sub>Cl<sub>2</sub> solution using a Pt electrode except for [Ni((4-OC<sub>12B</sub>,4'-OC<sub>12B</sub>)dpedt)<sub>2</sub>] and [Ni((4-OC<sub>24B</sub>,4'-OC<sub>24B</sub>)dpedt)<sub>2</sub>]: for these two compounds, reproducible results are obtained using a glassy carbon electrode.

From this table, it appears that the reduction potentials of these complexes change very slightly depending on the alkoxy chain length and configuration. These experimental values are in good agreement with values reported in the literature.<sup>10</sup> The values, -0.06 to -0.12 V *vs.* SCE, observed for these complexes are less positive than that of the core complex, the [Ni(dpdt)<sub>2</sub>] (*E*<sub>red</sub><sup>1/2</sup> = 0.03 V *vs.* SCE in CH<sub>2</sub>Cl<sub>2</sub>).<sup>10</sup> This difference is attributable to the mesomeric electron donating effect of the alkoxy substituents. As observed from Table 2, the values of λ<sub>max</sub> change only slightly from 924–936 nm. The nature of the alkyl chains does not influence the optical properties of



**Fig. 5** Cyclic voltammogram of  $[\text{Ni}((4\text{-OC}_{8\text{B}},4'\text{-OC}_{8\text{B}})\text{dpedt})_2]$  in  $\text{CH}_2\text{Cl}_2$  containing  $0.1 \text{ mol L}^{-1}$   $(\text{Bu}_4\text{N})\text{PF}_6$  as an electrolyte by using Pt metal working and counter electrodes and a standard SCE reference electrode at  $25^\circ\text{C}$  (scan rate  $0.1 \text{ V s}^{-1}$ ).

**Table 2** First half-wave reduction potentials and electronic absorption data for  $[\text{Ni}(\text{dpedt})_2]$

Nickel complexes	$E^{1/2}/\text{V}^a$	$\lambda_{\text{max}}/\text{nm}^b$	$\epsilon/\text{L mol}^{-1}\text{cm}^{-1}$
$[\text{Ni}((4\text{-OC}_1,4'\text{-OC}_1)\text{dpedt})_2]$	-0.09	924	47 000
$[\text{Ni}((4\text{-OC}_1,4'\text{-OC}_{10\text{L}})\text{dpedt})_2]$	-0.09	929	50 000
$[\text{Ni}((4\text{-OC}_1,4'\text{-OC}_{8\text{B}})\text{dpedt})_2]$	-0.09	931	38 000
$[\text{Ni}((4\text{-OC}_1,4'\text{-OC}_{10\text{B}})\text{dpedt})_2]$	-0.09	928	44 000
$[\text{Ni}((4\text{-OC}_1,4'\text{-OC}_{12\text{B}})\text{dpedt})_2]$	-0.10	931	54 000
$[\text{Ni}((4\text{-OC}_1,4'\text{-OC}_{16\text{B}})\text{dpedt})_2]$	-0.08	929	51 000
$[\text{Ni}((4\text{-OC}_{8\text{B}},4'\text{-OC}_{8\text{B}})\text{dpedt})_2]$	-0.10	934	47 000
$[\text{Ni}((4\text{-OC}_{12\text{L}},4'\text{-OC}_{12\text{L}})\text{dpedt})_2]$	-0.10	934	49 000
$[\text{Ni}((4\text{-OC}_{10\text{B}},4'\text{-OC}_{10\text{B}})\text{dpedt})_2]$	-0.10	933	50 000
$[\text{Ni}((4\text{-OC}_{12\text{B}},4'\text{-OC}_{12\text{B}})\text{dpedt})_2]$	-0.11	935	43 000
$[\text{Ni}((4\text{-OC}_{16\text{B}},4'\text{-OC}_{16\text{B}})\text{dpedt})_2]$	-0.12	936	54 000
$[\text{Ni}((4\text{-OC}_{20\text{B}},4'\text{-OC}_{20\text{B}})\text{dpedt})_2]$	-0.09	935	51 000
$[\text{Ni}((4\text{-OC}_{24\text{B}},4'\text{-OC}_{24\text{B}})\text{dpedt})_2]$	-0.11	935	54 000
$[\text{Ni}((4\text{-OC}_{10\text{L}},4'\text{-OC}_{8\text{B}})\text{dpedt})_2]$	-0.10	934	47 000
$[\text{Ni}((4\text{-OC}_{10\text{L}},4'\text{-OC}_{10\text{B}})\text{dpedt})_2]$	-0.06	933	51 000
$[\text{Ni}((4\text{-OC}_{12\text{L}},4'\text{-OC}_{14\text{L}})\text{dpedt})_2]$	-0.11	933	48 000
$[\text{Ni}((4\text{-OC}_{12\text{L}},4'\text{-OC}_{11\text{L}})\text{dpedt})_2]$	-0.11	933	51 000
$[\text{Ni}((4\text{-OC}_{12\text{L}},4'\text{-OC}_{12\text{B}})\text{dpedt})_2]$	-0.12	934	51 000
$[\text{Ni}((4\text{-OC}_{12\text{L}},4'\text{-OC}_{10\text{B}})\text{dpedt})_2]$	-0.12	933	52 000

<sup>a</sup> Volts vs. SCE in  $\text{CH}_2\text{Cl}_2$  using platinum metal electrode, except for  $[\text{Ni}((4\text{-OC}_{12\text{B}},4'\text{-OC}_{12\text{B}})\text{dpedt})_2]$  and  $[\text{Ni}((4\text{-OC}_{24\text{B}},4'\text{-OC}_{24\text{B}})\text{dpedt})_2]$  using Glassy carbon electrode. Cyclic voltammogram of  $[\text{Ni}((4\text{-OC}_{8\text{B}},4'\text{-OC}_{8\text{B}})\text{dpedt})_2]$  in  $\text{CH}_2\text{Cl}_2$  containing  $0.1 \text{ mol L}^{-1}$   $(\text{Bu}_4\text{N})\text{PF}_6$  as an electrolyte and a standard SCE reference electrode at  $25^\circ\text{C}$  (scan rate  $0.1 \text{ V s}^{-1}$ ). <sup>b</sup> In  $\text{CH}_2\text{Cl}_2$  solution.

$[\text{Ni}(\text{dpedt})_2]$ . In addition, the high values of molecular absorption coefficient  $\epsilon$  range from 38 000 to 54 000  $\text{M}^{-1} \text{ cm}^{-1}$  demonstrating that the  $[\text{Ni}(\text{dpedt})_2]$  are efficient NIR absorbent materials. The full results of cyclic voltammetry and electronic absorption spectroscopy will be used further to estimate the optical and electrochemical bandgaps, electron affinities ( $E_a$ ) and ionization potentials ( $I_p$ ) of all  $[\text{Ni}(\text{dpedt})_2]$ . From the first results of electrochemical and electronic absorption measurements, one can conclude that the nature of alkyl chains do not influence significantly electrochemical or optical properties in this  $[\text{Ni}(\text{dpedt})_2]$  series. This could be a very interesting result because the mesomorphic property of the complexes depends on the alkoxy chain length and configuration, whereas the reduction potential and optical absorption do not. That is to say, we can change the peripheral chain length to obtain the mesomorphic properties without changing the electrochemical

or optical properties. The same result and claim were reported for the first time by Ohta *et al.* in 1991<sup>9</sup> and then in 2001.<sup>10</sup>

## Conclusion

Nineteen  $[\text{Ni}(\text{dpedt})_2]$ , including seventeen new compounds, were synthesized by new short and efficient synthetic pathways. The synthesis of two common intermediates 4,4'-dihydroxybenzil **1a** and 4-hydroxy-4'-methoxybenzil **1b** and the introduction of alkyl chains in the later steps allows us to synthesize easily a series of  $[\text{Ni}(\text{dpedt})_2]$ . The Mitsunobu reaction has proven to be a very efficient method to prepare various alkoxy-substituted aromatic compounds from phenol derivatives. The alternative choice of either the classical nucleophilic substitution reaction or the Mitsunobu reaction gives us a large source of alkyl chains, either from alkyl halides or from primary or secondary alcohols. The complete investigation of mesomorphic properties of this  $[\text{Ni}(\text{dpedt})_2]$  series and advanced studies by electrochemical and optical methods are being carried out and will be fully discussed in a separate article.

## Experimental

### General remarks

All used chemicals and solvents were purchased from chemical companies and used as received, unless otherwise mentioned. All reactions were realized under ambient atmosphere unless special indication.  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments were recorded in the listed deuterated solvents (internal standard) on a 4 Bruker Spectrometers (ARX 250, DPX 300, Avance 300 and Avance 400). Purification of product 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 (TLC), silica gel coated substrates “60 F254” from Merck were used and compounds were detected by fluorescence quenching at 254 nm, self-fluorescence at 365 nm. Melting points were determined by DSC thermograms, which were obtained on a DSC 204 NETZSCH system using 2–5 mg samples in 30  $\mu\text{L}$  sample pans and a scan rate of  $10^\circ\text{C min}^{-1}$ .  $\Delta H$  is calculated in  $\text{J g}^{-1}$ . Mass analyses were performed at the MS Service at the Paul Sabatier University. Elemental analyses (C, H, S, Ni) were carried out at the CNRS Central Analyses Service in Lyon. UV-VIS-NIR absorption spectra were recorded on two spectrometers Perkin-Elmer Lambda 35 and Perkin-Elmer GX 2000. 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 in a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca. 1  $\text{cm}^2$  apparent surfaces. The working electrode was a Pt microdisk (0.5 mm diameter) or a glassy carbon (1 mm diameter). The supporting electrolyte  $(n\text{Bu}_4\text{N})[\text{PF}_6]$  (Fluka, 99% electrochemical grade) was used as received and simply degassed

under argon.  $\text{CH}_2\text{Cl}_2$  was freshly distilled over  $\text{CaH}_2$  prior to use. The solutions used during the electrochemical studies were typically  $10^{-3} \text{ mol L}^{-1}$  in complex compound and  $0.1 \text{ mol L}^{-1}$  in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230).

**4,4'-Dihydroxybenzil (1a).** 4,4'-Dimethoxybenzil (26 g, 96.2 mmol) was heated to reflux for 50 h in a mixture of aqueous HBr (48%) and glacial acetic acid (550 mL, 50/50). The reaction mixture was cooled by a bath of ice-water and the yellow precipitate was collected by filtration. The filtrate was then extracted several times with ethyl acetate. The organic phases and the yellow precipitate were combined, washed several times with water, dried with  $\text{MgSO}_4$  and the solvent was removed under reduced pressure. The residue was purified by column chromatography ( $\text{CH}_2\text{Cl}_2$ /acetone: 85/15) giving **1a** as pure yellowish solid (22.45 g, 96%).  $\delta_{\text{H}}$ (250 MHz,  $\text{CD}_3\text{OD}$ ) 7.82 (4 H, d,  $J = 9.0 \text{ Hz}$ , aromatic H), 6.91 (4 H, d,  $J = 9.0 \text{ Hz}$ , aromatic H), 4.92 (2 H, br s, phenol H).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_3\text{OD}$ ): 194.26, 164.09, 132.17, 124.89, 115.51. HRMS(CI): found 243.0669,  $[\text{M} + \text{H}]^+$  requires 243.0657.

**4-Hydroxy-4'-methoxybenzil (1b).** As described for the synthesis of **1a** but the reflux time was decreased to 17 h. Complete workup gave a mixture of three products: 4,4'-dimethoxybenzil (18% of starting material), **1a** (yellowish solid, 33%) and **1b** (yellow solid, 28%).  $\delta_{\text{H}}$ (250 MHz,  $(\text{CD}_3)_2\text{CO}$ ) 9.58 (1 H, s, phenol H), 7.93 (2 H, d,  $J = 9.0 \text{ Hz}$ , aromatic H), 7.87 (2 H, d,  $J = 9.0 \text{ Hz}$ , aromatic H), 7.13 (2 H, d,  $J = 9.0 \text{ Hz}$ , aromatic H), 7.03 (2 H, d,  $J = 9.0 \text{ Hz}$ , aromatic H), 3.94 (3 H, s,  $-\text{OCH}_3$ ).  $\delta_{\text{C}}$ (62.5 MHz,  $(\text{CD}_3)_2\text{CO}$ ) 193.46, 165.04, 163.51, 132.30, 131.94, 126.29, 125.45, 115.95, 114.47, 55.31. HRMS(CI): found 257.0826,  $[\text{M} + \text{H}]^+$  requires 257.0814.

#### General procedure for the synthesis of benzils **3b**, **3c**, **3n**, **3p**, **3q**

A mixture of **1b** (for **3b–3c**) or **2n–2p** (for **3n**, **3o**, **3p**, **3q**) (3.9 mmol), alkyl bromide (5.9 mmol), and powdered potassium carbonate (1.1 g, 7.8 mmol) was stirred in DMF (25 mL) at  $90^\circ\text{C}$ . The reaction was monitored by TLC (hexane/ $\text{CH}_2\text{Cl}_2$  50/50). Upon cooling to room temperature, the reaction was quenched by adding water and the resulting mixture was extracted by  $\text{CH}_2\text{Cl}_2$ . The organic phases were combined, rinsed several time by water, dried over anhydrous magnesium sulfate and concentrated under reduced pressure resulting in the crude product which was purified by silica gel column chromatography (hexane/ $\text{CH}_2\text{Cl}_2$  50/50).

**4-Decyloxy-4'-methoxybenzil (3b).** Yellowish solid (1.47 g, 95%).  $\delta_{\text{H}}$ (300 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.95 (4 H, m, aromatic H), 7.02 (4 H, m, aromatic H), 4.08 (2 H, t,  $J = 6.6 \text{ Hz}$ ,  $-\text{OCH}_2-$ ), 3.92 (3 H, s,  $-\text{OCH}_3$ ), 1.84 (2 H, m,  $-\text{OCH}_2\text{CH}_2-$ ), 1.49–1.32 (14 H, m), 0.92 (3 H, t,  $J = 6.6 \text{ Hz}$ ,  $-\text{CH}_2\text{CH}_3$ ).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.58, 193.51, 164.94, 164.61, 132.18, 126.25, 125.95, 114.69, 114.25, 68.60, 55.68, 31.89, 29.53, 29.30, 28.99, 25.88, 22.67, 13.86.

**4-Methoxy-4'-(2-ethylhexyloxy)benzil (3c).** Yellowish oil (1.4 g, 97%).  $\delta_{\text{H}}$ (300 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.96 (4 H, m, aromatic H), 7.03 (4 H, m, aromatic H), 3.98 (2 H, d,  $J = 5.7 \text{ Hz}$ ,  $-\text{OCH}_2-$ ), 3.92 (3 H, s,  $-\text{OCH}_3$ ), 1.79 (1 H, m,  $-\text{CH}_2-\text{CH}-$ ), 1.53–1.35 (8 H, m), 0.97 (6 H, t,  $J = 7.5 \text{ Hz}$ ,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.60, 193.52, 164.94, 164.84, 132.17, 132.10, 126.26, 125.92, 114.72, 114.28, 70.99, 55.68, 39.24, 30.37, 28.99, 23.75, 23.00, 13.81, 10.82.

**4-Decyloxy-4'-(2-ethylhexyloxy)benzil (3n).** Yellow oil (0.54 g, 69%).  $\delta_{\text{H}}$ (250 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.96 (4 H, dd,  $J = 1.75$ – $7.0 \text{ Hz}$ , aromatic H), 7.02 (4 H, m, aromatic H), 4.09 (2 H, t,  $J = 6.5 \text{ Hz}$ ,  $-\text{OCH}_2\text{CH}_2-$ ), 4.00 (2 H, d,  $J = 5.75 \text{ Hz}$ ,  $-\text{OCH}_2\text{CH}-$ ), 1.87–1.77 (3 H, m), 1.51–1.33 (22 H, m), 1.00–0.90 (9 H, m,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (62.5 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.60, 164.82, 164.60, 132.17, 126.01, 125.97, 114.70, 71.01, 68.61, 39.27, 31.91, 30.40, 29.55, 29.32, 29.02, 25.90, 23.77, 23.02, 22.69, 13.88, 13.82, 10.84.

**4-Dodecyloxy-4'-tetradecyloxybenzil (3p).** Yellow solid (1.17 g, 99%).  $\delta_{\text{H}}$ (250 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.96 (4 H, m, aromatic H), 7.03 (4 H, m, aromatic H), 4.11 (4 H, t,  $J = 6.5 \text{ Hz}$ ,  $-\text{OCH}_2-$ ), 1.87–1.32 (44 H, m,  $-\text{CH}_2-$ ), 0.95 (6 H, t,  $J = 6.3 \text{ Hz}$ ,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (62.5 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.57, 164.59, 161.06, 132.17, 126.00, 114.68, 68.60, 64.01, 31.92, 29.64, 29.57, 29.54, 29.50, 29.34, 29.31, 29.19, 29.00, 28.53, 25.88, 25.80, 22.68, 13.87.

**4-Dodecyloxy-4'-undecyloxybenzil (3q).** Yellowish solid (1.1 g, 80%).  $\delta_{\text{H}}$ (300 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.96 (4 H, dt,  $J = 9.6$ – $2.7 \text{ Hz}$ , aromatic H), 7.03 (4 H, dt,  $J = 9.6$ – $2.7 \text{ Hz}$ , aromatic H), 4.08 (4 H, t,  $J = 6.6 \text{ Hz}$ ,  $-\text{OCH}_2-$ ), 1.84 (4 H, m,  $-\text{OCH}_2\text{CH}_2-$ ), 1.51–1.31 (34 H, m), 0.92 (6 H, t,  $J = 6.3 \text{ Hz}$ ,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.57, 164.59, 132.17, 125.99, 114.69, 68.60, 66.75, 31.93, 29.59, 29.55, 29.33, 29.01, 25.90, 22.70, 13.89. HRMS(CI): found 565.4244,  $[\text{M} + \text{H}]^+$  requires 565.4257.

#### General procedure for the synthesis of benzils **3d**, **3e**, **3f**, **3o**, **3r**, **3s**

A THF (50 mL) solution of 4-hydroxy-4'-methoxy benzil (1.5 g, 5.85 mmol),  $\text{PPh}_3$  (1.85 g, 7.02 mmol), and alcohol (7.02 mmol) were cooled to  $0^\circ\text{C}$ . To the solution was added diethyl azodicarboxylate in toluene solution (3.2 mL, 7.02 mmol, 40% w/v), the mixture was kept at that temperature for 1 h and then was allowed to warm to room temperature and stirred for 1 h. The reaction mixture was then evaporated. After addition of 300 mL of hexane, the mixture was filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography (hexane/ $\text{CH}_2\text{Cl}_2$  50/50).

**4-(3,7-Dimethyloctyloxy)-4'-methoxybenzil (3d).** Yellow oil (1.95 g, 84%).  $\delta_{\text{H}}$ (250 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.96 (4 H, m, aromatic H), 7.03 (4 H, m, aromatic H), 4.13 (2 H, t,  $J = 6.6 \text{ Hz}$ ,  $-\text{OCH}_2-$ ), 3.93 (3 H, s,  $-\text{OCH}_3$ ), 1.93–1.20 (10 H, m), 1.00 (3 H, d,  $J = 6.4 \text{ Hz}$ ,  $-\text{CH}_3$ ), 0.93 (6 H, d,  $J = 6.6 \text{ Hz}$ ,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (62.5 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.58, 193.51, 164.95, 164.60, 132.19, 126.27, 125.98, 114.73, 114.27, 66.97, 61.01, 55.70, 39.21, 37.20, 35.90, 29.83, 27.99, 24.64, 22.44, 22.34, 19.36, 13.89.

**4-(2-Butyloctyloxy)-4'-methoxybenzil (3e).** Yellow oil (1.92 g, 77%).  $\delta_{\text{H}}$ (250 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.95 (4 H, m, aromatic H), 7.05

(2 H, d,  $J = 9.0$  Hz, aromatic H), 7.00 (2 H, d,  $J = 8.8$  Hz, aromatic H), 3.99 (2 H, d,  $J = 5.8$  Hz,  $-\text{OCH}_2-$ ), 3.93 (3 H, s,  $-\text{OCH}_3$ ), 1.88–0.92 (23 H, m).  $\delta_{\text{C}}$ (62.5 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.60, 193.53, 164.94, 164.86, 132.18, 126.28, 125.93, 114.74, 114.26, 71.43, 65.46, 55.69, 40.58, 37.81, 31.84, 31.23, 30.93, 29.64, 29.01, 26.75, 23.03, 22.66, 13.87, 13.83.

**4-(2-Hexyldecyloxy)-4'-methoxybenzil (3f).** Yellow oil (2.71 g, 96%).  $\delta_{\text{H}}$ (250 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.95 (4 H, m, aromatic H), 7.05 (2 H, d,  $J = 9.0$  Hz, aromatic H), 7.00 (2 H, d,  $J = 8.8$  Hz, aromatic H), 3.99 (2 H, d,  $J = 5.8$  Hz,  $-\text{OCH}_2-$ ), 3.93 (3 H, s,  $-\text{OCH}_3$ ), 1.88–0.90 (31 H, m).  $\delta_{\text{C}}$ (62.5 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.6, 164.86, 132.17, 126.28, 125.91, 114.74, 114.26, 71.44, 65.47, 55.70, 40.60, 37.82, 31.91, 31.22, 29.96, 29.64, 29.56, 29.31, 26.76, 22.69, 13.88.

**4-Decyloxy-4'-(3,7-dimethyloctyloxy)benzil (3o).** Yellow solid (2.45 g, 91%).  $\delta_{\text{H}}$ (300 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.96 (4 H, m, aromatic H), 7.03 (4 H, m, aromatic H), 4.15–4.06 (4 H, m,  $-\text{OCH}_2-$ ), 1.86–1.19 (26 H, m), 1.00–0.90 (12 H, m,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.56, 164.58, 164.56, 132.17, 126.00, 114.69, 68.59, 66.95, 39.19, 37.18, 35.88, 31.89, 29.80, 29.54, 29.31, 29.00, 27.97, 25.89, 24.62, 22.68, 22.43, 22.33, 19.35, 13.88.

**4-Dodecyloxy-4'-(2-butyloctyloxy)benzil (3r).** Yellow solid (1.97 g, 100%).  $\delta_{\text{H}}$ (300 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.96 (4 H, dt,  $J = 9.6$ –2.7 Hz, aromatic H), 7.03 (4 H, dt,  $J = 9.6$ –2.7 Hz, aromatic H), 4.09 (2 H, t,  $J = 6.6$  Hz,  $-\text{OCH}_2\text{CH}_2-$ ), 3.98 (2 H, d,  $J = 6.6$  Hz,  $-\text{OCH}_2\text{CH}_2-$ ), 1.86 (4 H, m), 1.51–1.31 (33 H, m), 0.94 (9 H, m,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_2\text{Cl}_2$ ): = 193.59, 164.83, 164.59, 132.17, 126.01, 125.95, 114.72, 114.69, 71.41, 68.60, 37.80, 31.93, 31.84, 31.23, 30.92, 29.64, 29.59, 29.55, 29.36, 29.33, 29.01, 26.75, 25.90, 23.03, 22.70, 22.67, 13.87, 13.83. HRMS(CI): found 579.4433,  $[\text{M} + \text{H}]^+$  requires 579.4413.

#### Synthesis of 4,4'-di(2-ethylhexyloxy)benzil (3g)

A mixture of 4,4'-dihydroxybenzil (**3**) (3.26 g, 13.5 mmol), alkyl bromide (40.5 mmol), potassium iodide (0.68 mmol) and powdered potassium carbonate (54 mmol) was stirred in DMF (80 mL) at 90 °C and the reaction was monitored by TLC. Upon cooling to room temperature, the reaction was quenched by adding water and the resulting mixture was extracted by  $\text{CH}_2\text{Cl}_2$ . The organic phases were combined, rinsed several times with water, dried over anhydrous magnesium sulfate and concentrated under reduced pressure resulting in a crude product which was purified by silica gel column chromatography (hexane/ $\text{CH}_2\text{Cl}_2$  50/50). Yellowish oil (4.32 g, 70%).  $\delta_{\text{H}}$ (250 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.94 (4 H, d,  $J = 9.0$  Hz, aromatic H), 7.02 (4 H, d,  $J = 9.0$  Hz, aromatic H), 3.99 (4 H, d,  $J = 5.8$  Hz,  $\text{OCH}_2\text{CH}$ ), 1.83–1.78 (2 H, m,  $\text{OCH}_2\text{CH}$ ), 1.52–1.24 (16 H, m,  $-\text{CH}_2-$ ), 1.01–0.93 (12 H, m,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_2\text{Cl}_2$ ): 193.61, 164.81, 132.15, 125.97, 114.71, 70.98, 39.25, 30.37, 29.00, 23.75, 23.00, 13.81, 10.82.

#### General procedure for the synthesis of benzils 3i–3m

A THF (50 mL) solution of 4,4'-dihydroxybenzil (1.5 g, 6.2 mmol),  $\text{PPh}_3$  (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 allowed to warm to room temperature and stirred for 1 h. The reaction mixture was then evaporated. After addition of 300 mL of hexane, the mixture was filtered. The filtrate was evaporated, and the residue was purified by silica gel column chromatography (hexane/ $\text{CH}_2\text{Cl}_2$  50/50).

**4,4'-Di(3,7-dimethyloctyloxy)benzil (3i).** Yellow oil (2.52 g, 78%).  $\delta_{\text{H}}$ (300 MHz,  $\text{CD}_2\text{Cl}_2$ ) 8.13 (4 H, d,  $J = 9.0$  Hz, aromatic H), 7.20 (4 H, d,  $J = 9.0$  Hz, aromatic H), 4.31 (4 H, m,  $-\text{OCH}_2-$ ), 2.09–1.37 (20 H, m), 1.17 (6 H, d,  $J = 6.6$  Hz,  $-\text{CH}_3$ ), 1.10 (12 H, d,  $J = 6.6$  Hz,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.75, 164.75, 132.36, 126.18, 114.89, 67.15, 39.39, 37.37, 36.07, 31.78, 30.00, 28.17, 24.82, 22.62, 22.52, 19.54, 14.07.

**4,4'-Di(2-butyloctyloxy)benzil (3j).** Yellow oil (4.3 g, 90%).  $\delta_{\text{H}}$ (250 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.96 (4 H, dd,  $J = 1.8$ –8.8 Hz, aromatic H), 7.03 (4 H, d,  $J = 8.8$  Hz, aromatic H), 3.99 (4 H, d,  $J = 5.8$  Hz,  $-\text{OCH}_2-$ ), 1.88–1.83 (2 H, m,  $-\text{OCH}_2\text{CH}-$ ), 1.47–1.34 (32 H, m,  $-\text{CH}_2-$ ), 0.95–0.91 (12 H, m,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (62.5 MHz,  $\text{CD}_2\text{Cl}_2$ ) = 193.62, 164.83, 132.16, 125.98, 114.73, 71.42, 37.81, 31.84, 31.24, 30.94, 29.65, 29.01, 26.76, 23.03, 22.67, 13.87, 13.84.

**4,4'-Di(2-hexyldecyloxy)benzil (3k).** Yellow oil (3.94 g, 69%).  $\delta_{\text{H}}$ (250 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.96 (4 H, d,  $J = 9.0$  Hz, aromatic H), 7.04 (4 H, d,  $J = 9.0$  Hz, aromatic H), 3.99 (4 H, d,  $J = 5.5$  Hz,  $-\text{OCH}_2-$ ), 1.88–1.81 (2 H, m,  $-\text{OCH}_2\text{CH}-$ ), 1.46–1.21 (48 H, m,  $-\text{CH}_2-$ ), 0.95–0.90 (12 H, m,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (62.5 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.61, 164.83, 132.16, 125.98, 114.73, 71.44, 37.83, 31.91, 31.85, 31.61, 31.24, 29.97, 29.65, 29.57, 29.32, 26.77, 22.69, 13.88.

**4,4'-Di(2-octyldodecyloxy)benzil (3l).** Yellow oil (5 g, 75%).  $\delta_{\text{H}}$ (250 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.96 (4 H, d,  $J = 8.8$  Hz, aromatic H), 7.03 (4 H, d,  $J = 8.8$  Hz, aromatic H), 3.99 (4 H, d,  $J = 5.6$  Hz,  $-\text{OCH}_2-$ ), 1.87–1.83 (2 H, m,  $-\text{OCH}_2\text{CH}-$ ), 1.46–1.31 (64 H, m,  $-\text{CH}_2-$ ), 0.95–0.90 (12 H, t,  $J = 5.9$  Hz,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (62.5 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.60, 164.82, 132.14, 125.96, 114.72, 71.42, 37.80, 31.91, 31.20, 29.95, 29.63, 29.58, 29.55, 29.34, 29.30, 26.75, 22.68, 13.87.

**4,4'-Di(2-decyltetradecyloxy)benzil (3m).** Yellow oil (6.21 g, 82%).  $\delta_{\text{H}}$ (250 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.96 (4 H, d,  $J = 8.8$  Hz, aromatic H), 7.04 (4 H, d,  $J = 8.8$  Hz, aromatic H), 3.99 (4 H, d,  $J = 5.6$  Hz,  $-\text{OCH}_2-$ ), 1.88–1.31 (82 H, m), 1.03–0.90 (12 H, m,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (62.5 MHz,  $\text{CD}_2\text{Cl}_2$ ) 193.60, 164.82, 132.14, 125.97, 114.72, 71.43, 37.80, 31.92, 31.20, 29.95, 29.64, 29.59, 29.35, 26.76, 22.69, 13.87.

#### General procedure for the synthesis of 4-alkoxy-4'-hydroxybenzil 2n–2p and 3h

To a mixture of 4,4'-dihydroxybenzil (**3**) (1.0 g, 4.13 mmol), powdered potassium carbonate (3.72 mmol) in DMF (40 mL) at 90 °C was added dropwise and slowly (in about 1 h) a solution of alkyl bromide (3.72 mmol) in DMF (40 mL). After 1 h, the reaction was quenched by adding water and the resulting mixture was extracted by ethyl acetate. The organic phases were combined, rinsed several times with water, dried

over anhydrous magnesium sulfate and concentrated under reduced pressure resulting in the crude product which was purified by silica gel column chromatography (hexane/CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>: 75/25).

**4-(2-Ethylhexyloxy)-4'-hydroxybenzil (2n).** Yellow oil (0.54 g, 41%).  $\delta_{\text{H}}$ (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.91 (4 H, m, aromatic H), 7.00 (4 H, m, aromatic H), 6.74 (1 H, br s, phenol H), 3.98 (2 H, d,  $J$  = 5.7 Hz, -OCH<sub>2</sub>-), 1.79 (1 H, m, -OCH<sub>2</sub>CH-), 1.50–1.28 (8 H, m, -CH<sub>2</sub>-), 0.99–0.91 (6 H, m, -CH<sub>3</sub>).  $\delta_{\text{C}}$ (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 193.79, 193.69, 164.98, 162.00, 132.56, 132.27, 126.16, 125.80, 115.89, 114.78, 71.04, 60.55, 39.25, 30.38, 29.00, 23.76, 23.01, 20.85, 13.96, 13.82, 10.83.

**4-Decyloxy-4'-hydroxybenzil (2o).** Yellow solid (4.06 g, 57%).  $\delta_{\text{H}}$ (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.96–7.88 (4 H, m, aromatic H), 7.03–6.93 (4 H, m, aromatic H), 6.01 (1 H, br s, phenol H), 4.1 (2 H, t,  $J$  = 6.3 Hz, -OCH<sub>2</sub>-), 1.88–1.79 (2 H, m, -OCH<sub>2</sub>CH<sub>2</sub>-), 1.51–1.31 (14 H, m, -CH<sub>2</sub>-), 0.94 (3 H, t,  $J$  = 6.3 Hz, -CH<sub>3</sub>).  $\delta_{\text{C}}$ (62.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 193.72, 193.64, 164.75, 161.86, 132.56, 132.28, 126.25, 125.86, 115.88, 114.76, 68.66, 31.91, 29.55, 29.32, 29.01, 25.90, 22.69, 13.98, 13.88.

**4-Dodecyloxy-4'-hydroxybenzil (2p).** Yellow solid (3.47 g, 46%).  $\delta_{\text{H}}$ (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 8.04 (1 H, br s, phenol H), 7.96 (4 H, m, aromatic H), 7.09 (4 H, m, aromatic H), 4.11 (2 H, t,  $J$  = 6.5 Hz, -OCH<sub>2</sub>-), 1.87–1.31 (20 H, m), 0.95 (3 H, t,  $J$  = 6.2 Hz, -CH<sub>3</sub>). HRMS(CI): found 411.2546, [M + H]<sup>+</sup> requires 411.2535.

**4,4'-Didodecyloxybenzil (3h).** Yellowish solid isolated from the synthesis of **2p** (3.59 g, 30%).  $\delta_{\text{H}}$ (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.96 (4 H, m, aromatic H), 7.03 (4 H, m, aromatic H), 4.11 (4 H, t,  $J$  = 6.5 Hz, -OCH<sub>2</sub>-), 1.87–1.32 (40 H, m, -CH<sub>2</sub>-), 0.95 (6 H, t,  $J$  = 6.3 Hz, -CH<sub>3</sub>).  $\delta_{\text{C}}$ (62.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 193.57, 164.59, 132.17, 126.00, 114.68, 68.60, 45.33, 31.93, 29.64, 29.59, 29.56, 29.36, 29.33, 29.02, 25.90, 22.70, 13.89. HRMS(CI): found 579.4441, [M + H]<sup>+</sup> requires 579.4413.

#### General procedure for the synthesis of nickel bis(1,2-dithiolene) complexes (4a–4s)

A mixture of dialkoxybenzil (4.91 mmol) and P<sub>4</sub>S<sub>10</sub> (4.8 g, 10.80 mmol) in 25 mL of dioxane 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<sub>2</sub>·6H<sub>2</sub>O (0.64 g, 2.70 mmol) in 5 mL of water, 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 CH<sub>2</sub>Cl<sub>2</sub> by ethanol (3 times) and the final purification was performed by column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub>).

#### Nickel bis[1,2-di(4-methoxyphenyl)ethene-1,2-dithiolene] complex ([Ni((4-OC<sub>1</sub>,4'-OC<sub>1</sub>)dpdtt)<sub>2</sub>])

Black powder (0.87 g, 18%). Elemental analysis: found C, 57.88; H, 4.19; Ni, 8.71; S, 19.58. C<sub>32</sub>H<sub>28</sub>NiO<sub>4</sub>S<sub>4</sub> requires C, 57.93; H, 4.25; Ni, 8.85; S, 19.33%.  $\delta_{\text{H}}$ (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)

7.39 (8 H, d,  $J$  = 7.5 Hz, aromatic H), 6.88 (8 H, d,  $J$  = 7.5 Hz, aromatic H), 3.86 (12 H, s, -OCH<sub>3</sub>).  $\delta_{\text{C}}$ (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 180.77, 160.48, 134.28, 130.34, 113.81, 55.37. HRMS(CI): found 663.0297, [M + H]<sup>+</sup> requires 663.0302.

#### Nickel bis[1-(4-decyloxyphenyl)-2-(4-methoxyphenyl)ethene-1,2-dithiolene] complex ([Ni((4-OC<sub>10</sub>,4'-OC<sub>10L</sub>)dpdtt)<sub>2</sub>])

Black powder (0.86 g, 51%, mp 147.3 °C). Elemental analysis: found C, 65.60; H, 7.10; Ni, 6.25; S, 14.10. C<sub>50</sub>H<sub>64</sub>NiO<sub>4</sub>S<sub>4</sub> requires C, 65.56; H, 7.04; Ni, 6.41; S, 14.00%.  $\delta_{\text{H}}$ (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.37 (8 H, m, aromatic H), 6.86 (8 H, m, aromatic H), 4.03 (4 H, t,  $J$  = 6.4 Hz, -OCH<sub>2</sub>CH<sub>2</sub>-), 3.86 (6 H, s, -OCH<sub>3</sub>), 1.85–1.80 (4 H, m, -OCH<sub>2</sub>CH<sub>2</sub>-), 1.56–1.33 (28 H, m, -CH<sub>2</sub>-), 0.94 (6 H, t,  $J$  = 6.8 Hz, -CH<sub>3</sub>).  $\delta_{\text{C}}$ (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 183.52, 180.93, 160.47, 160.12, 134.08, 130.35, 114.30, 113.81, 68.22, 55.36, 31.89, 29.56, 29.55, 29.37, 29.31, 29.19, 25.98, 22.67, 13.86. HRMS(CI): found 915.3100, [M + H]<sup>+</sup> requires 915.3119.

#### Nickel bis[1-(4-(2-ethylhexyloxy)phenyl)-2-(4-methoxyphenyl)ethene-1,2-dithiolene] complex ([Ni((4-OC<sub>1</sub>,4'-OC<sub>8B</sub>)dpdtt)<sub>2</sub>])

Brown powder (0.64 g, 45%, mp 199.1 °C). Elemental analysis: found C, 64.11; H, 6.44; Ni, 6.61; S, 15.20. C<sub>46</sub>H<sub>56</sub>NiO<sub>4</sub>S<sub>4</sub> requires C, 64.25; H, 6.56; Ni, 6.83; S, 14.92%.  $\delta_{\text{H}}$ (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.39 (8 H, m, aromatic H), 6.88 (8 H, m, aromatic H), 3.92 (4 H, d,  $J$  = 5.6 Hz, -OCH<sub>2</sub>CH-), 3.86 (6 H, s, -OCH<sub>3</sub>), 1.79–1.71 (2 H, m, -OCH<sub>2</sub>CH-), 1.57–1.39 (16 H, m, -CH<sub>2</sub>-), 1.00 (12 H, t,  $J$  = 7.6 Hz, -CH<sub>3</sub>).  $\delta_{\text{C}}$ (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 180.75, 180.50, 160.43, 160.32, 134.37, 134.03, 130.35, 130.33, 114.33, 113.80, 70.66, 55.34, 39.39, 30.47, 29.07, 23.83, 23.05, 13.85, 10.88. HRMS(CI): found 859.2512, [M + H]<sup>+</sup> requires 859.2493.

#### Nickel bis[1-(4-(3,7-dimethyloctyloxy)phenyl)-2-(4-methoxyphenyl)ethene-1,2-dithiolene] complex ([Ni((4-OC<sub>1</sub>,4'-OC<sub>10B</sub>)dpdtt)<sub>2</sub>])

Black powder (1.08 g, 53%, mp 170.3 °C). Elemental analysis: found C, 65.64; H, 6.91; Ni, 6.32; S, 14.63. C<sub>50</sub>H<sub>64</sub>NiO<sub>4</sub>S<sub>4</sub> requires C, 65.56; H, 7.04; Ni, 6.41; S, 14.00%.  $\delta_{\text{H}}$ (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.38 (8 H, m, aromatic H), 6.87 (8 H, m, aromatic H), 4.07 (4 H, m, -OCH<sub>2</sub>CH<sub>2</sub>-), 3.85 (6 H, s, -OCH<sub>3</sub>), 1.88–1.20 (20 H, m), 1.00 (6 H, d,  $J$  = 6.3 Hz, -CH<sub>3</sub>), 0.93 (12 H, d,  $J$  = 6.6 Hz, -CH<sub>3</sub>).  $\delta_{\text{C}}$ (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 180.72, 180.53, 160.43, 160.07, 134.34, 134.07, 130.35, 114.30, 113.80, 66.55, 55.34, 39.23, 37.25, 36.11, 29.87, 27.98, 24.65, 22.45, 22.35, 19.41. HRMS(CI): found 915.3079 and 943.3484, [M + H]<sup>+</sup> requires 915.3119 and [M + C<sub>2</sub>H<sub>5</sub>]<sup>+</sup> requires 943.3432.

#### Nickel bis[1-(4-(2-butyloctyloxy)phenyl)-2-(4-methoxyphenyl)ethene-1,2-dithiolene] complex ([Ni((4-OC<sub>1</sub>,4'-OC<sub>12B</sub>)dpdtt)<sub>2</sub>])

Black powder (1.06 g, 49%, mp 154.8 °C). Elemental analysis: found C, 66.93; H, 7.36; Ni, 5.86; S, 13.02. C<sub>54</sub>H<sub>72</sub>NiO<sub>4</sub>S<sub>4</sub> requires C, 66.72; H, 7.47; Ni, 6.04; S, 13.19%.  $\delta_{\text{H}}$ (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.40 (8 H, m, aromatic H), 6.89 (8 H, m, aromatic H), 3.91 (4 H, d,  $J$  = 5.7 Hz, -OCH<sub>2</sub>CH-), 3.86 (6 H, s, -OCH<sub>3</sub>), 1.84 (2 H, m, -OCH<sub>2</sub>CH-), 1.57–1.32 (32 H, m), 0.97–0.90 (12 H, m, -CH<sub>3</sub>).  $\delta_{\text{C}}$ (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 180.93, 180.68, 160.45, 160.34, 134.40, 134.06, 130.32, 130.30, 114.34, 113.80, 71.07,

55.34, 37.90, 31.85, 31.30, 30.99, 29.66, 29.04, 26.78, 23.04, 22.66, 13.86, 13.84. HRMS(CI): found 971.3742,  $[M + H]^+$  requires 971.3745.

**Nickel bis[1-(4-(2-hexyldecyloxy)phenyl)-2-(4-methoxyphenyl)-ethene-1,2-dithiolene] complex ( $[Ni((4-OC_{12B}, 4'-OC_{16B})dpedt)_2]$ )**

Black powder (1.47 g, 50%, mp 147.4 °C). Elemental analysis: found C, 68.43; H, 8.18; Ni, 5.17; S, 12.08.  $C_{62}H_{88}NiO_4S_4$  requires C, 68.68; H, 8.18; Ni, 5.41; S, 11.83.  $\delta_H$ (400 MHz,  $CD_2Cl_2$ ) 7.39 (8 H, m, aromatic H), 6.87 (8 H, m, aromatic H), 3.90 (4 H, d,  $J = 5.2$  Hz,  $-OCH_2CH-$ ), 3.86 (6 H, s,  $-OCH_3$ ), 1.84 (2 H, m,  $-OCH_2CH-$ ), 1.50–1.35 (48 H, m), 0.94 (12 H, m,  $-CH_3$ ).  $\delta_C$ (100 MHz,  $CD_2Cl_2$ ) 180.66, 180.40, 160.42, 160.31, 134.40, 130.38, 130.35, 114.34, 113.80, 71.10, 55.33, 37.96, 31.93, 31.88, 31.33, 30.03, 29.70, 29.61, 29.35, 26.84, 26.82, 22.70, 13.91. HRMS(CI): found 1083.5101,  $[M + H]^+$  requires 1083.4997.

**Nickel bis[1,2-di(4-(2-ethylhexyloxy)phenyl)ethene-1,2-dithiolene] complex ( $[Ni((4-OC_{8B}, 4'-OC_{8B})dpedt)_2]$ )**

Brown powder (2 g, 47%, mp 163.7 °C). Elemental analysis: found C, 68.55; H, 8.07; Ni, 5.42; S, 12.10.  $C_{60}H_{84}NiO_4S_4$  requires C, 68.23; H, 8.02; Ni, 5.56; S, 12.14.  $\delta_H$ (400 MHz,  $CD_2Cl_2$ ) 7.38 (8 H, d,  $J = 8.4$  Hz, aromatic H), 6.88 (8 H, d,  $J = 8.4$  Hz, aromatic H), 3.92 (8 H, d,  $J = 5.6$  Hz,  $-OCH_2CH-$ ), 1.80 (4 H, m,  $-OCH_2CH-$ ), 1.57–1.37 (32 H, m,  $-CH_2-$ ), 0.99–0.95 (24 H, m,  $-CH_3$ ).  $\delta_C$ (100 MHz,  $CD_2Cl_2$ ) 180.78, 160.34, 134.07, 130.33, 114.33, 70.67, 39.38, 30.46, 29.06, 23.82, 23.04, 13.83, 10.87. HRMS(CI): found 1055.4709,  $[M + H]^+$  requires 1055.4684.

**Nickel bis[1,2-di(4-dodecyloxyphenyl)ethene-1,2-dithiolene] complex ( $[Ni((4-OC_{12L}, 4'-OC_{12L})dpedt)_2]$ )**

Brown powder (1.6 g, 48%, mp 168.8 °C). Elemental analysis: found C, 71.62; H, 9.08; Ni, 4.46; S, 9.32.  $C_{76}H_{116}NiO_4S_4$  requires C, 71.28; H, 9.13; Ni, 4.58; S, 10.01%.  $\delta_H$ (300 MHz,  $CD_2Cl_2$ ) 7.37 (8 H, dd,  $J = 2.0$ –9.0 Hz, aromatic H), 6.86 (8 H, dd,  $J = 2.0$ –9.0 Hz, aromatic H), 4.00 (8 H, t,  $J = 6.6$  Hz,  $-OCH_2CH_2-$ ), 1.86–1.77 (8 H, m,  $-OCH_2CH_2-$ ), 1.51–1.42 (72 H, m), 0.92 (12 H, t,  $J = 6.3$  Hz,  $-CH_3$ ).  $\delta_C$ (75 MHz,  $CD_2Cl_2$ ) 180.73, 160.09, 134.11, 130.33, 114.29, 68.21, 31.94, 29.65, 29.61, 29.40, 29.36, 29.30, 29.21, 26.01, 22.71, 13.89. HRMS(CI): found 1279.7148,  $[M + H]^+$  requires 1279.7188.

**Nickel bis[1,2-di(4-(3,7-dimethyloctyloxy)phenyl)ethene-1,2-dithiolene] complex ( $[Ni((4-OC_{10B}, 4'-OC_{10B})dpedt)_2]$ )**

Black powder (1.44 g, 59%, mp 129.9 °C). Elemental analysis: found C, 69.85; H, 8.74; Ni, 4.78; S, 11.25.  $C_{68}H_{100}NiO_4S_4$  requires C, 69.90; H, 8.63; Ni, 5.02; S, 10.98%.  $\delta_H$ (400 MHz,  $CD_2Cl_2$ ) 7.37 (8 H, d,  $J = 8.4$  Hz, aromatic H), 6.86 (8 H, d,  $J = 8.4$  Hz, aromatic H), 4.07 (8 H, m,  $-OCH_2CH_2-$ ), 1.90–1.84 (8 H, m,  $-OCH_2CH_2-$ ), 1.73–1.21 (32 H, m), 1.01 (12 H, d,  $J = 6.4$  Hz,  $-CH_3$ ), 0.94 (24 H, d,  $J = 6.4$  Hz,  $-CH_3$ ).  $\delta_C$ (100 MHz,  $CD_2Cl_2$ ) 180.58, 160.05, 134.14, 130.35, 114.30, 66.55, 39.24, 37.27, 36.14, 29.88, 28.00, 24.66, 22.47, 22.37, 19.43. HRMS(CI): found 1167.5953,  $[M + H]^+$  requires 1167.5936.

**Nickel bis[1,2-di(4-(2-butyloctyloxy)phenyl)ethene-1,2-dithiolene] complex ( $[Ni((4-OC_{12B}, 4'-OC_{12B})dpedt)_2]$ )**

Black powder (2.36 g, 51%, mp 103.2 °C). Elemental analysis: found C, 71.57; H, 9.14; Ni, 4.32; S, 10.06.  $C_{76}H_{116}NiO_4S_4$  requires C, 71.28; H, 9.13; Ni, 4.58; S, 10.01%.  $\delta_H$ (300 MHz,  $CD_2Cl_2$ ) 7.39 (8 H, m, aromatic H), 6.88 (8 H, m, aromatic H), 3.91 (8 H, d,  $J = 5.7$  Hz,  $-OCH_2CH-$ ), 1.85–1.79 (4 H, m,  $-OCH_2CH-$ ), 1.54–1.34 (64 H, m,  $-CH_2-$ ), 0.97–0.91 (24 H, m,  $-CH_3$ ).  $\delta_C$ (75 MHz,  $CD_2Cl_2$ ) 180.71, 160.32, 134.07, 130.29, 114.33, 71.05, 37.91, 31.85, 31.30, 31.00, 29.67, 29.05, 26.78, 23.05, 22.67, 13.87, 13.85. HRMS(CI): found 1279.7188,  $[M + H]^+$  requires 1279.7188.

**Nickel bis[1,2-bis(4-(2-hexyldecyloxy)phenyl)ethene-1,2-dithiolene] complex ( $[Ni(4-OC_{16B}, 4-OC_{16B})dpedt)_2]$ )**

Black pasty powder (2.03 g, 49%). Elemental analysis: found C, 73.75; H, 9.96; Ni, 3.58; S, 8.18.  $C_{92}H_{148}NiO_4S_4$  requires C, 73.42; H, 9.91; Ni, 3.90; S, 8.52%.  $\delta_H$ (300 MHz,  $CD_2Cl_2$ ) 7.38 (8 H, d,  $J = 8.7$  Hz, aromatic H), 6.87 (8 H, d,  $J = 8.7$  Hz, aromatic H), 3.91 (8 H, d,  $J = 5.7$  Hz,  $-OCH_2CH-$ ), 1.83–1.80 (4 H, m,  $-OCH_2CH-$ ), 1.56–1.34 (96 H, m,  $-CH_2-$ ), 0.93–0.91 (24 H, m,  $-CH_3$ ).  $\delta_C$ (75 MHz,  $CD_2Cl_2$ ) 180.69, 160.32, 134.07, 130.29, 114.65, 114.33, 71.06, 37.94, 31.91, 31.86, 31.30, 30.00, 29.67, 29.58, 29.32, 26.81, 26.79, 22.68, 13.88. HRMS(CI): found 1503.9624,  $[M + H]^+$  requires 1503.9692.

**Nickel bis[1,2-bis(4-(2-octyldodecyloxy)phenyl)ethene-1,2-dithiolene] complex ( $[Ni((4-OC_{20B}, 4'-OC_{20B})dpedt)_2]$ )**

Black pasty powder (2.28 g, 43%). Elemental analysis: found C, 75.19; H, 10.64; Ni, 3.16; S, 6.72.  $C_{108}H_{180}NiO_4S_4$  requires C, 75.00; H, 10.49; Ni, 3.39; S, 7.42%.  $\delta_H$ (400 MHz,  $CD_2Cl_2$ ) 7.38 (8 H, d,  $J = 8.8$  Hz, aromatic H), 6.87 (8 H, d,  $J = 8.8$  Hz, aromatic H), 3.91 (8 H, d,  $J = 5.2$  Hz,  $-OCH_2CH-$ ), 1.84 (4 H, m,  $-OCH_2CH-$ ), 1.50–1.34 (128 H, m,  $-CH_2-$ ), 0.95 (24 H, m,  $-CH_3$ ).  $\delta_C$ (100 MHz,  $CD_2Cl_2$ ) 180.60, 160.31, 134.11, 130.32, 114.33, 71.09, 37.97, 31.95, 31.32, 30.03, 29.70, 29.67, 29.66, 29.61, 29.38, 29.36, 26.85, 22.71, 13.92. MS(CI): found 1729.10,  $[M + H]^+$  requires 1729.21.

**Nickel bis[1,2-bis(4-(2-decyltetradecyloxy)phenyl)ethene-1,2-dithiolene] complex ( $[Ni((4-OC_{24B}, 4'-OC_{24B})dpedt)_2]$ )**

Black pasty powder (3.74 g, 57%). Elemental analysis: found C, 76.79; H, 11.11; Ni, 2.86; S, 6.91.  $C_{124}H_{212}NiO_4S_4$  requires C, 76.22; H, 10.94; Ni, 3.00; S, 6.56.  $\delta_H$ (300 MHz,  $CD_2Cl_2$ ) 7.38 (8 H, d,  $J = 8.7$  Hz, aromatic H), 6.87 (8 H, d,  $J = 8.7$  Hz, aromatic H), 3.90 (8 H, d,  $J = 5.7$  Hz,  $-OCH_2CH-$ ), 1.82 (4 H, m,  $-OCH_2CH-$ ), 1.56–1.30 (160 H, m,  $-CH_2-$ ), 0.94–0.85 (24 H, m,  $-CH_3$ ).  $\delta_C$ (75 MHz,  $CD_2Cl_2$ ) 180.72, 160.32, 134.07, 130.28, 114.33, 71.07, 37.91, 31.92, 31.27, 29.99, 29.66, 29.62, 29.35, 26.80, 22.69, 13.88. MS(CI): found 1953.57,  $[M + H]^+$  requires 1953.47.

**Nickel bis[1-(4-(2-ethylhexyloxy)phenyl)-2-(4-decyloxyphenyl)-ethene-1,2-dithiolene] complex ( $[Ni((4-OC_{10L}, 4'-OC_{8B})dpedt)_2]$ )**

Black powder (1.24 g, 73%, mp 153.2 °C). Elemental analysis: found C, 68.80; H, 8.23; Ni, 5.06; S, 11.57.  $C_{64}H_{92}NiO_4S_4$  requires C, 69.10; H, 8.34; Ni, 5.28; S, 11.53%.  $\delta_H$ (400 MHz,  $CD_2Cl_2$ ) 7.37 (8 H, d,  $J = 8.4$  Hz, aromatic H), 6.86 (8 H, m,

aromatic H), 4.02 (4 H, t,  $J = 6.4$  Hz,  $-\text{OCH}_2\text{CH}_2-$ ), 3.92 (4 H, d,  $J = 5.2$  Hz,  $-\text{OCH}_2\text{CH}-$ ), 1.84–1.75 (6 H, m), 1.57–1.34 (44 H, m), 1.00–0.92 (18 H, m,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (100 MHz,  $\text{CD}_2\text{Cl}_2$ ) 180.59, 180.55, 160.29, 160.05, 134.16, 134.10, 130.35, 114.32, 114.28, 70.65, 68.20, 39.40, 31.92, 30.48, 29.60, 29.58, 29.41, 29.34, 29.23, 29.08, 26.02, 23.84, 23.06, 22.70, 13.89, 13.87, 10.90. HRMS(CI): found 1111.5359,  $[\text{M} + \text{H}]^+$  requires 1111.5310.

**Nickel bis[1-(4-(3,7-dimethyloctyloxy)phenyl)-2-(4-decyloxyphenyl)-ethene-1,2-dithiolene] complex ( $[\text{Ni}((4\text{-OC}_{10\text{L}}, 4'\text{-OC}_{10\text{B}})\text{dpedt})_2]$ )**

Black powder (1.7 g, 59%, mp 158.5 °C). Elemental analysis: found C, 70.04; H, 8.68; Ni, 4.94; S, 11.11.  $\text{C}_{68}\text{H}_{100}\text{NiO}_4\text{S}_4$  requires C, 69.90; H, 8.63; Ni, 5.02; S, 10.98%.  $\delta_{\text{H}}$ (300 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.37 (8 H, m, aromatic H), 6.86 (8 H, m, aromatic H), 4.04 (8 H, m,  $-\text{OCH}_2\text{CH}_2-$ ), 1.90–1.20 (52 H, m), 1.00–0.90 (24 H, m,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) 180.61, 160.05, 134.12, 130.34, 114.28, 68.20, 66.54, 39.23, 37.25, 36.12, 31.91, 29.87, 29.59, 29.57, 29.39, 29.33, 29.21, 27.99, 26.01, 24.65, 22.69, 22.45, 22.35, 19.41, 13.89. HRMS(CI): found 1167.5985,  $[\text{M} + \text{H}]^+$  requires 1167.5936.

**Nickel bis[1-(4-dodecyloxyphenyl)-2-(4-tetradecyloxyphenyl)-ethene-1,2-dithiolene] complex ( $[\text{Ni}((4\text{-OC}_{12\text{L}}, 4'\text{-OC}_{14\text{L}})\text{dpedt})_2]$ )**

Brown powder (0.67 g, 52%, Mp 163.7 °C). Elemental analysis: found C, 71.82; H, 9.42; Ni, 4.21; S, 8.68.  $\text{C}_{80}\text{H}_{124}\text{NiO}_4\text{S}_4$  requires C, 71.88; H, 9.35; Ni, 4.39; S, 9.59%.  $\delta_{\text{H}}$ (300 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.37 (8 H, dd,  $J = 2.0$ –9.0 Hz, aromatic H), 6.86 (8 H, dd,  $J = 2.0$ –9.0 Hz, aromatic H), 4.00 (8 H, t,  $J = 6.6$  Hz,  $-\text{OCH}_2\text{CH}_2-$ ), 1.88–1.75 (8 H, m,  $-\text{OCH}_2\text{CH}_2-$ ), 1.54–1.31 (80 H, m), 0.92 (12 H, t,  $J = 6.3$  Hz,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) 180.98, 160.08, 134.10, 130.31, 114.28, 68.20, 31.92, 29.65, 29.59, 29.57, 29.37, 29.34, 29.19, 25.98, 22.68, 13.86. HRMS(CI): found 1335.7930,  $[\text{M} + \text{H}]^+$  requires 1335.7814.

**Nickel bis[1-(4-dodecyloxyphenyl)-2-(4-undecyloxyphenyl)-ethene-1,2-dithiolene] complex ( $[\text{Ni}((4\text{-OC}_{12\text{L}}, 4'\text{-OC}_{11\text{L}})\text{dpedt})_2]$ )**

Brown powder (0.79 g, 68%, mp 171.9 °C). Elemental analysis: found C, 70.68; H, 9.12; Ni, 4.52; S, 9.06.  $\text{C}_{74}\text{H}_{112}\text{NiO}_4\text{S}_4$  requires C, 70.95; H, 9.01; Ni, 4.69; S, 10.24%.  $\delta_{\text{H}}$ (300 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.38 (8 H, dd,  $J = 2.0$ –9.0 Hz, aromatic H), 6.86 (8 H, dd,  $J = 2.0$ –9.0 Hz, aromatic H), 4.00 (8 H, t,  $J = 6.6$  Hz,  $-\text{OCH}_2\text{CH}_2-$ ), 1.84–1.77 (8 H, m,  $-\text{OCH}_2\text{CH}_2-$ ), 1.56–1.32 (68 H, m), 0.92 (12 H, t,  $J = 6.6$  Hz,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) 180.72, 160.08, 134.10, 130.31, 114.28, 68.20, 31.91, 29.65, 29.63, 29.60, 29.57, 29.38, 29.34, 29.19, 25.99, 22.68, 13.87. HRMS(CI): found 1251.6968,  $[\text{M} + \text{H}]^+$  requires 1251.6875.

**Nickel bis[1-(4-(2-butyloctyloxy)phenyl)-2-(4-dodecyloxyphenyl)-ethene-1,2-dithiolene] complex ( $[\text{Ni}((4\text{-OC}_{12\text{L}}, 4'\text{-OC}_{12\text{B}})\text{dpedt})_2]$ )**

Black powder (1.48 g, 71%, mp 99.0 °C). Elemental analysis: found C, 70.98; H, 9.17; Ni, 4.33; S, 9.59.  $\text{C}_{76}\text{H}_{116}\text{NiO}_4\text{S}_4$  requires C, 71.28; H, 9.13; Ni, 4.58; S, 10.01%.  $\delta_{\text{H}}$ (300 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.38 (8 H, d,  $J = 8.7$  Hz, aromatic H), 6.87 (8 H, dd,  $J = 1.5$ –8.7 Hz, aromatic H), 4.00 (4 H, t,  $J = 6.6$  Hz,  $-\text{OCH}_2\text{CH}_2-$ ), 3.90 (4 H, d,  $J = 5.7$  Hz,  $-\text{OCH}_2\text{CH}-$ ),

1.87–1.78 (6 H, m), 1.57–1.32 (68 H, m), 0.97–0.90 (18 H, m,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) 180.71, 180.65, 160.31, 160.07, 134.13, 134.05, 130.32, 130.30, 114.32, 114.28, 71.05, 68.20, 37.91, 31.92, 31.86, 31.30, 31.00, 29.67, 29.64, 29.60, 29.58, 29.39, 29.35, 29.21, 29.05, 26.79, 26.00, 23.05, 22.69, 22.67, 13.88, 13.86. HRMS(CI): found 1279.7188,  $[\text{M} + \text{H}]^+$  requires 1279.7188.

**Nickel bis[1-(4-(3,7-dimethyloctyloxy)phenyl)-2-(4-dodecyloxyphenyl)ethene-1,2-dithiolene] complex ( $[\text{Ni}((4\text{-OC}_{12\text{L}}, 4'\text{-OC}_{10\text{B}})\text{dpedt})_2]$ )**

Brown powder (1.13 g, 55%, mp 149.7 °C). Elemental analysis: found C, 70.80; H, 8.88; Ni, 4.64; S, 10.20.  $\text{C}_{72}\text{H}_{108}\text{NiO}_4\text{S}_4$  requires C, 70.62; H, 8.89; Ni, 4.79; S, 10.47%.  $\delta_{\text{H}}$ (300 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.38 (8 H, d,  $J = 9.0$  Hz, aromatic H), 6.87 (8 H, dd,  $J = 1.5$ –9.0 Hz, aromatic H), 4.08–3.99 (8 H, m,  $-\text{OCH}_2-$ ), 1.85–1.20 (60 H, m), 1.00–0.90 (24 H, m,  $-\text{CH}_3$ ).  $\delta_{\text{C}}$ (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) 180.71, 160.07, 134.10, 130.31, 114.29, 68.20, 66.54, 39.22, 37.23, 36.10, 31.92, 29.86, 29.65, 29.63, 29.59, 29.57, 29.38, 29.34, 29.19, 27.98, 25.99, 24.64, 22.68, 22.43, 22.34, 19.39, 13.89. HRMS(CI): found 1223.6636,  $[\text{M} + \text{H}]^+$  requires 1223.6562.

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