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## Synthesis and Characterization of Novel Dibenz[a,c]anthracenedicarboxythioimides: The Effect of Thionation on Self-Assembly

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We report the synthesis and properties of a series of novel dibenzanthracenedicarboxythioimides and an investigation of the effects of thionation on self-assembly in these systems. These compounds all display columnar mesophases over broad temperature ranges and self-associate to form dimers in solution. Overall, thionation slightly improves self-assembly in these systems. Furthermore, increasing the thionation of these materials leads to a lowering of the LUMO energy and a narrowing of the HOMO-LUMO band gap.

### Introduction

With increased demand for green energy sources and an increased interest in photovoltaic solar cell technologies, new materials that can efficiently transport charge are highly desired. Due to this,  $\pi$ -conjugated organic semiconductors are attractive due to their low cost and ease of processability.<sup>1</sup> The development of materials with efficient charge transport requires not only optimal frontier molecular orbital energies, but also effective intermolecular interactions that facilitate charge transport. As such, control over self-assembly through  $\pi$ -stacking interactions is important for the design of materials for organic electronics. Furthermore, in order to be useful for device applications,  $\pi$ -conjugated n-type materials should display low LUMO energy levels and efficient charge transport.<sup>2,3</sup>

Imide-based materials, particularly perylenebisimides<sup>4</sup> and naphthalene diimides,<sup>5</sup> are widely used as electron deficient materials due to their high photochemical stability, ease of synthetic modification, and their charge transmission ability.<sup>6-11</sup>

Both perylenebisimides and naphthalene diimides self-assemble both in the solid phase and in solution.<sup>12-16</sup> Perylene bisimides, in particular, have been an active area of research due to their propensity to form varied supramolecular organizations as a result of hydrogen-bonding, metal coordination, and  $\pi$ - $\pi$  stacking resulting in an improvement in their photochemical and charge transport properties.<sup>12-14</sup>

Recently, several studies have illustrated the importance of thioimides in improving the electron-accepting ability of these n-type materials by lowering the LUMO energy even

further.<sup>17-23</sup> For example, Seferos and co-workers recently prepared a series of perylenebisimides where the carbonyl groups were systematically replaced by thiocarbonyls and showed that increasing thionation led to lower LUMO levels and increased electron mobilities.<sup>17</sup> Furthermore, their work demonstrated that the thionated materials displayed increased surface roughness (due to increased aggregation) and more continuous grain boundaries than the parent imide materials.<sup>17</sup> This study suggests that thionation not only affects the electron-accepting ability of these compounds, but may influence the self-assembly. Despite this promising approach, little work has been done to systematically explore the effect of thionation on self-assembly. In particular, the effect of thionation on the formation of columnar liquid crystalline phases has not been explored.

Discotic liquid crystals have potential as organic semiconductors because they self-assembly into extended  $\pi$ -stacked arrays that allow effective charge transport.<sup>24-27</sup>

Typically, discotic liquid crystalline phases are formed from compounds that consist of a rigid aromatic core and several peripheral side chains. Several studies have shown that electron withdrawing substituents on the aromatic core can promote self-assembly to form columnar mesophases over broad temperature ranges.<sup>28-34</sup> Thionation, which renders the core more electron deficient, may provide a novel approach to tuning self-assembly in this class of materials as well as presenting a potential approach for the design of electron-accepting columnar liquid crystals.

Recent work by our group had focused on substituted dibenzanthracenes and how changes to their molecular structure affect their liquid crystalline temperature range.<sup>33-35</sup>

One previously prepared series of dibenzanthracenedicarboximides (**1a,b**) (Figure 1), which feature electron-withdrawing *N*-alkyl imide groups attached to the polycyclic aromatic core, exhibit hexagonal columnar mesophases over broad temperature ranges.<sup>35</sup> However,

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Electronic Supplementary Information (ESI) available: <sup>1</sup>H and <sup>13</sup>C NMR Spectra, DSC Traces, and details of  $K_{dim}$  determination. See DOI: 10.1039/x0xx00000x

despite their electron-withdrawing imide groups, the compounds in this series do not appear to be effective electron-accepting materials; likely the result of the electron-rich aromatic core and four electron-donating alkoxy groups.<sup>35</sup> This study aims to investigate the effect of thionation of imide groups on columnar mesophase formation as well as self-association in solution. Herein we describe the synthesis and characterization of a series of novel dibenzanthracenedicarboxythioimides **2** and **3** (Figure 1). We anticipated that, by replacing one or both of the imide functionalities with thioimides, we could tune the self-assembly and mesomorphic properties in these systems and prepare materials with low LUMO energy levels attractive for potential device applications in organic semiconductors.

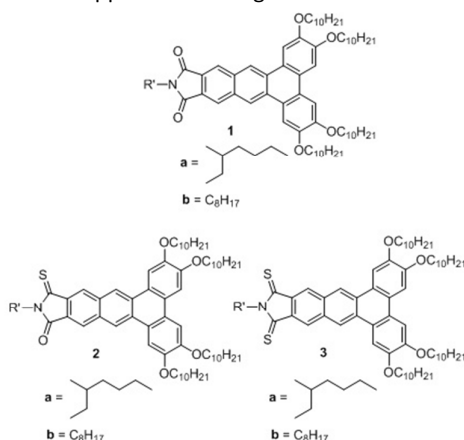


Fig. 1: Dibenzanthracenedicarboximide series (**1**) and target dibenzanthracenedicarboxythioimide compounds (**2**, **3**)

## Experimental

### Materials and Methods

All reagents and starting materials were purchased from Sigma-Aldrich and used as purchased. Anhydrous solvents were dispensed using a custom-built solvent system from Glasscontour (Irvine, CA) which used purification columns packed with activated alumina and supported copper catalyst. Oven-dried glassware was used for all reactions that were performed under nitrogen.

High resolution mass spectra were recorded at the Centre Régional de Spectrométrie de Masse à l'Université de Montréal using an Agilent LC-MSD TOF spectrometer. <sup>1</sup>H and <sup>13</sup>C spectra were recorded on an Agilent Technologies 400 MHz Spectrometer using deuterated chloroform purchased from CIL Int. Chemical shifts are reported in  $\delta$  scale downfield from the peak for tetramethylsilane. In some cases not all aliphatic and/or aromatic <sup>13</sup>C peaks are observed in the *N*-substituted dibenzanthracenedicarboxythioimides due to overlapping signals. For the variable concentration studies, a 0.05 M stock solution of each compound was prepared. Subsequent dilutions were performed and the chemical shift of each of the aromatic signals was recorded. The association constant was

determined using each of the aromatic resonances by fitting the data to the following equation<sup>36</sup>:

$$P = (P_d - P_m) \left(1 + \frac{1 - \sqrt{8K_E C + 1}}{4K_E C}\right) + P_m$$

Where *P* is the measured chemical shift, *P<sub>d</sub>* is the theoretical shift of the dimer, *P<sub>m</sub>* is the theoretical shift of the monomer, *C* is the concentration, and *K<sub>E</sub>* is the equilibrium constant for dimerization.

Dynamic Light Scattering was carried out using a Zetasizer Nano-ZS ZEN3600. A 0.05 M stock solution of each compound in chloroform were prepared. Subsequent dilutions were performed to generate measurements over the desired concentration range.

Phase transition temperatures and enthalpies were investigated using differential scanning calorimetry (DSC) on a TA Instruments DSC Q200 with a scanning rate of 5 °C/min. Texture analysis was carried out using polarized optical microscopy on an Olympus BX-51 polarized optical microscope equipped with a Linkam LTS 350 heating stage and a digital camera.

Cyclic Voltammetry was carried out using a Basi EC Epsilon Voltammeter using a Pt disk as the working electrode, a Pt wire auxiliary electrode, and an Ag wire as a pseudo-reference electrode. A 2.0 mM solution in anhydrous DCM was used with Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) as the electrolyte and ferrocene as the internal reference. The potential was scanned from -2.0 to 2.0 V. The HOMO and LUMO energies of **1a**, **2a**, and **3a** were determined using -4.80 eV as the HOMO energy of ferrocene.

### Synthesis

**General procedure for the synthesis of Series 2a,b:** The desired *N*-substituted dibenzanthracenedicarboximide (**1a,b**) (1 eq) and Lawesson's Reagent (0.5 eq) were dissolved in 50.0 mL of dry toluene. The solution was heated at reflux under N<sub>2</sub> for 4 hours. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The crude products were purified according to the conditions listed.

**Compound 2a:** Lawesson's Reagent (0.07 g, 0.16 mmol), *N*-2-ethyl-1-hexyl-2,3,6,7-tetrakis(decyloxy)-11,12-dibenz[*a,c*]anthracenedicarboximide (**1a**) (0.36 g, 0.33 mmol), and toluene (50.0 mL) were used. The crude product was purified via column chromatography (1:1 hexanes/chloroform) and the resulting material was recrystallized from chloroform/ethanol to yield the desired product as an orange solid (0.20 g, 54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 0.89 (m, 20H), 1.38 (m, 50H), 1.62 (m, 12H), 1.97 (m, 8H), 2.13 (m, 1H), 4.00 (m, 2H), 4.26 (m, 8H), 7.71 (s, 2H), 7.98 (s, 2H), 8.31 (s, 1H), 8.51 (s, 1H), 8.81 (s, 1H), 8.87 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 14.0, 14.1, 22.6, 23.0, 24.0, 26.2, 28.5, 29.3, 29.40, 29.43, 29.5, 29.6, 29.7, 30.7, 31.9, 37.7, 45.4, 69.3, 69.5, 106.9, 107.2, 107.4, 122.5, 123.5, 123.7, 124.0, 124.5, 124.8, 124.9, 125.4, 130.1, 130.2, 131.9, 132.5, 132.9, 149.2, 150.43, 150.49, 169.5, 196.6; HRMS (ASAP) calc'd for C<sub>72</sub>H<sub>110</sub>NO<sub>5</sub>S+H *m/z* 1100.8105, found 1100.8131.

**Compound 2b:** Lawesson's Reagent (0.06 g, 0.14 mmol), *N*-octyl-2,3,6,7-tetrakis(decyloxy)-11,12-dibenz[*a,c*]anthracenedicarboximide (**1b**) (0.30 g, 0.28 mmol), and toluene (50.0 mL) were used. The crude product was purified via column chromatography (1:1 hexanes/chloroform) and the resulting material was recrystallized from chloroform/ethanol to yield the desired product as an orange solid (0.12 g, 51%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.88 (m, 20H), 1.43 (m, 50H), 1.61 (m, 10H), 1.82 (m, 2H), 1.97 (m, 9H), 4.13 (m, 2H), 4.28 (m, 8H), 7.79 (s, 2H), 8.11 (s, 2H), 8.46 (s, 1H), 8.66 (s, 1H), 9.01 (s, 1H), 9.07 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 14.1, 22.64, 22.69, 26.20, 26.21, 27.0, 27.8, 29.21, 29.24, 29.40, 29.41, 29.45, 29.53, 29.59, 29.65, 29.66, 29.72, 29.74, 31.8, 31.9, 41.4, 69.2, 69.3, 69.4, 106.8, 107.2, 122.44, 122.48, 123.5, 123.6, 123.8, 124.4, 124.7, 124.8, 125.3, 129.9, 130.1, 131.8, 132.4, 132.8, 149.1, 150.3, 150.4, 169.0, 196.1. HRMS (ASAP) calc'd for C<sub>72</sub>H<sub>110</sub>NO<sub>5</sub>S+H *m/z* 1100.8105, found 1100.811.

**General procedure for the synthesis of Compounds 3a,b:** The desired *N*-substituted dibenzanthracenedicarboximide (**1a,b**) (1 eq) and Lawesson's Reagent (1 eq) were dissolved in 50.0 mL of dry toluene (excess). The solution was heated at reflux under N<sub>2</sub> overnight. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The crude products were purified according to the conditions listed.

**Compound 3a:** Lawesson's Reagent (0.09 g, 0.23 mmol), *N*-2-ethyl-1-hexyl-2,3,6,7-tetrakis(decyloxy)-11,12-dibenz[*a,c*]anthracenedicarboximide (**1a**) (0.25 g, 0.23 mmol), and toluene (50.0 mL) were used. The crude product was purified via column chromatography (60:40 hexanes/dichloromethane) and the resulting material was recrystallized from chloroform/ethanol to yield the desired product as a purple solid (0.21 g, 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.90 (m, 20H), 1.31 (m, 50H), 1.61 (m, 12H), 1.97 (m, 8H), 2.26 (m, 1H), 4.22 (m, 8H), 4.36 (m, 2H), 7.65 (s, 2H), 7.90 (s, 2H), 8.28 (s, 2H), 8.72 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 10.8, 14.1, 22.6, 23.0, 24.1, 26.2, 28.5, 29.40, 29.42, 29.45, 29.62, 29.65, 29.67, 29.71, 29.73, 29.75, 30.7, 31.93, 31.95, 38.0, 48.3, 69.3, 69.4, 106.8, 107.1, 122.5, 123.9, 124.8, 125.0, 129.9, 132.04, 132.06, 149.1, 150.3, 197.0. HRMS (ASAP) calc'd for C<sub>72</sub>H<sub>109</sub>NO<sub>4</sub>S<sub>2</sub> *m/z* 1115.7750, found 1115.7798.

**Compound 3b:** Lawesson's Reagent (0.09 g, 0.23 mmol), *N*-octyl-2,3,6,7-tetrakis(decyloxy)-11,12-dibenz[*a,c*]anthracenedicarboximide (**1b**) (0.25 g, 0.23 mmol), and toluene (50.0 mL) were used. The crude product was purified via column chromatography (60:40 hexanes/chloroform) and the resulting material was recrystallized from chloroform/ethanol to yield the desired product as a purple solid (0.18 g, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 0.87 (m, 16H), 1.40 (m, 45H), 1.60 (m, 20H), 1.79 (m, 2H), 1.97 (m, 8H), 4.22 (m, 8H), 4.46 (t, 2H), 7.66 (s, 2H), 7.93 (s, 2H), 8.37 (s, 2H), 8.82 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 11.5, 20.0, 20.1, 23.5, 24.4, 24.8, 26.6, 26.7, 26.81, 26.84, 26.9, 27.04, 27.06, 27.1, 29.2, 29.3, 66.8, 67.0, 104.4, 104.7, 120.0, 121.6, 122.3, 122.5, 127.6, 129.6, 129.8, 146.7, 147.9, 193.5.

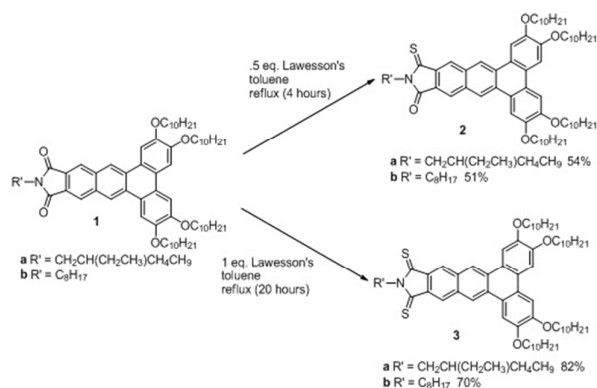
HRMS (ASAP) calc'd for C<sub>72</sub>H<sub>109</sub>NO<sub>4</sub>S<sub>2</sub>+H *m/z* 1116.789, found 1116.788.

## Results and Discussion

The desired dibenzanthracenedicarboxythioimides (**2a,b** and **3a,b**) were prepared from compounds **1a**<sup>33</sup> and **1b**<sup>33</sup> using Lawesson's Reagent in toluene via a procedure adapted from Tilley and co-workers.<sup>18</sup> To generate the dithionated derivatives (**3a,b**), 1 equivalent of the *N*-alkyl dibenzanthracenedicarboximide (**1a,b**) and 1 equivalent of Lawesson's Reagent were combined in toluene. The reaction mixture was heated to reflux overnight, during which the solution turned from yellow to dark purple. The crude material was easily purified via column chromatography and recrystallization to generate compounds **3a-b** as purple solids in yields of 82% and 70% respectively. To achieve the monothionated derivatives (**2a,b**), 1 equivalent of the imide (**1a,b**) and 0.5 equivalents of Lawesson's Reagent were combined in toluene. The reactions were heated to reflux and monitored by thin layer chromatography for a period of 4 hours. In each case, the crude material contained the desired monothionated material as the major product as well as small amounts of both the respective starting material and dithionated derivative (**3a,b**). Fortunately, the desired monothionated products (**2a,b**) were readily separated from the side-products via column chromatography. Subsequent recrystallization generated compounds **2a-b** as orange solids in yields of 54% and 51% respectively.

Once purified, the liquid crystalline properties of compounds **2a,b** and **3a,b** were investigated by polarized optical microscopy and differential scanning calorimetry (DSC). The results are summarized in Table 1.

Compounds **1a** and **1b** were previously shown to exhibit columnar hexagonal mesophases.<sup>35</sup> Polarized optical microscopy studies of **2** and **3** also show dendritic textures with homeotropically aligned domains that are consistent with a uniaxial hexagonal columnar mesophase (Figure 2). All of these compounds exhibit columnar mesophases over broad temperature ranges, as summarized in Table 1. In this series of compounds, there is a slight increase in the melting transition temperature (the crystalline to columnar mesophase transition) with increasing thionation (Table 1). For example, imide **1a** has a melting transition at 28 °C, while the corresponding dithioimide melts at 50 °C. A similar trend is



**Scheme 1:** Synthesis of series 2 and 3.

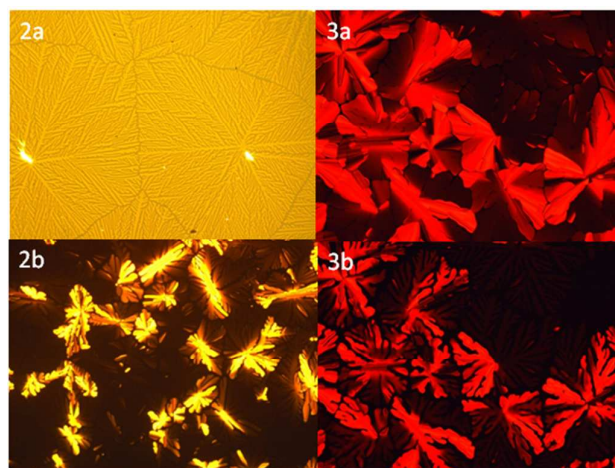
**Table 1:** Phase behaviour of compounds based on DSC with a scan rate of 5°C·min<sup>-1</sup> on heating.

Compound	X, Y, R	Phase Transition Temperature in °C (Enthalpies of transitions in kJ/mol)
<b>1a</b> <sup>35</sup>	X = Y = O R = branched	Cr 28 (28.4) Col <sub>h</sub> 223 (2.9) I
<b>2a</b>	X = O, Y = S R = branched	Cr 46 (13.8) Col <sub>h</sub> 221 (3.9) I
<b>3a</b>	X = Y = S R = branched	Cr 50 (50.7) Col <sub>h</sub> 216 (2.6) I
<b>1b</b> <sup>35</sup>	X = Y = O R = linear	Cr 64 (29.9) Col <sub>h</sub> 222 (2.1) I
<b>2b</b>	X = O, Y = S R = linear	Cr 67 (44.8) Col <sub>h</sub> 224 (3.2) I
<b>3b</b>	X = Y = S R = linear	Cr 79 (54.3) Col <sub>h</sub> 226 (3.3) I

observed when compound **1b** is compared with **3b**. These results suggest that increasing thionation may stabilize the crystalline phase of these compounds, presumably because of improved intermolecular interactions involving the polarizable sulfur atom. It is also noteworthy that the compounds with the linear *N*-octyl side-chains (**1b-3b**) all exhibit higher melting transitions than the corresponding branched *N*-alkyl derivatives (**1a-3a**). This trend can be attributed to the branched side chains destabilizing the crystalline phase, presumably because the branching prevents effective packing. The effect of thionation on the phase transition from the columnar phase to the liquid (the clearing point) is more subtle, with all six derivatives compounds showing similar phase transition temperatures. These results demonstrate that thionation has a relatively small effect on mesophase stability. A closer examination of the clearing transition temperatures does, however, reveal some interesting trends. In particular, the clearing point for the branched-chain (**1a-3a**) derivatives shows a slight decrease with increasing thionation while the clearing point for the linear-chain derivatives (**1b-3b**) shows a slight increase with increasing thionation. We believe this may be the result of the longer carbon-sulfur bond influencing the conformational distribution of the branched side chain and slightly disrupting the packing in the mesophase. In contrast, for the derivatives with linear *N*-alkyl chains (**1a-1b**) the conformation of the alkyl chain is not

significantly influenced by thionation. Rather, the slight increase in clearing points with increasing thionation may be the result of a slight stabilization of the mesophase by virtue of the electron-withdrawing thioimides.

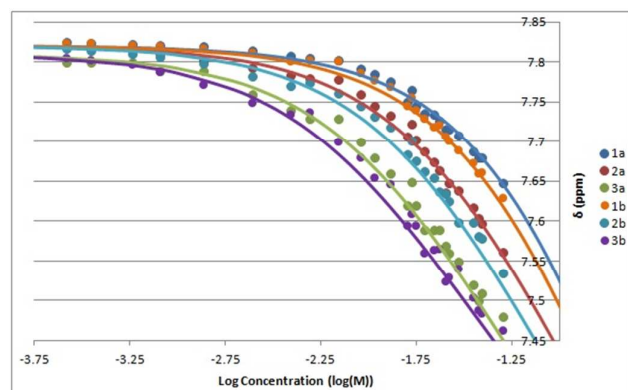
In order to further study the self-assembly in these dibenzanthracenedicarboximides and their thionated derivatives, self-association in solution was investigated. Other discotic aromatic systems such as hexabenzocoronenes,<sup>37</sup> phthalocyanines,<sup>38</sup> porphyrins,<sup>39</sup> and helicenes<sup>40</sup> can often self-assemble in solution to form dimers or higher aggregates. Solution self-assembly can be probed by variable



**Fig. 2:** Representative polarized optical micrographs of compounds **2a,b** and **3a,b**, obtained on cooling near the isotropic-columnar mesophase transition. All micrographs were taken at 200x magnification.

concentration NMR because  $\pi$ -stacked aggregates will often exhibit different chemical shifts than the corresponding monomers in solution and the observed peaks will shift as the proportion of the monomer decreases.<sup>41-45</sup> Based on this, variable concentration <sup>1</sup>H NMR studies were performed on both the imides (**1a, b**) and the thionated derivatives (**2a,b** and **3a,b**), and showed that the chemical shift of the aromatic protons changed as a function of concentration. Solutions of all six derivatives in CDCl<sub>3</sub> displayed upfield chemical shifts with increasing concentration. This observation is consistent with aggregation through  $\pi$ - $\pi$  stacking interactions. A plot of chemical shift of the aromatic <sup>1</sup>H NMR signals as a function of concentration for each derivative was fitted to a curve for monomer-dimer aggregation<sup>36</sup> (Figure 3) and yielded dimerization constants, *K*, for each of the six derivatives (Table 2). Refer to Electronic Supplementary Information for more detailed on the calculation of dimerization constants. Both the branched chain (**1a, 2a, 3a**) and linear chain (**1b, 2b, 3b**) derivatives display very similar dimerization constants for the parent imides (**1a-b**), monothionated (**2a-b**) and dithionated derivatives (**3a-b**). The results are consistent with dimerization in solution and both series show a general trend of increasing self-association with increasing thionation. In each case, however, the linear chain derivative shows a slightly higher *K* for dimerization than the corresponding branched derivative. The branched side chains appear to have a slight influence on

self-association in solution, which is consistent with the idea that the branched *N*-alkyl chains slightly disrupt  $\pi$ -stacking in solution. In contrast, increasing thionation increases self-association in solution, as shown by the gradual increase in



**Fig. 3:** Plot of **1a,b**, **2a,b**, and **3a,b** of  $^1\text{H}$  NMR shift of aromatic signal vs. log concentration (dots) fitted to a curve using a monomer-dimer model (lines).

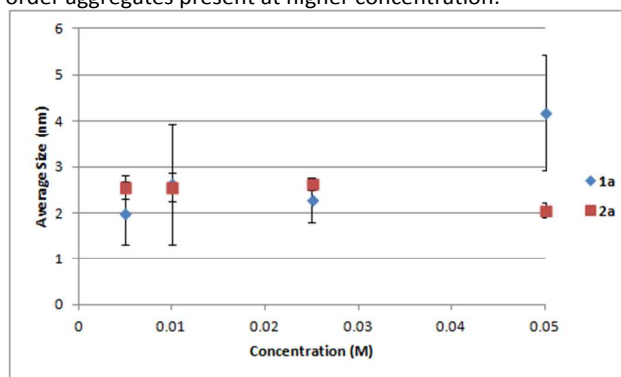
**Table 2:** Dimerization constants ( $K_{\text{dim}}$ ) for compounds **2a,b** and **3a,b**.

Compound	X, Y, R	$K_{\text{dim}}$ ( $\text{M}^{-1}$ )
<b>1a</b>	X = Y = O R = branched	$1.07 \pm 0.31$
<b>2a</b>	X = O, Y = S R = branched	$4.61 \pm 0.43$
<b>3a</b>	X = Y = S R = branched	$10.29 \pm 1.33$
<b>1b</b>	X = Y = O R = linear	$2.15 \pm 0.24$
<b>2b</b>	X = O, Y = O R = linear	$6.07 \pm 0.44$
<b>3b</b>	X = Y = S R = linear	$15.43 \pm 1.31$

dimerization constants going from compounds **1** to **3**. Overall, the differences in solution self-assembly correspond reasonably with the mesomorphic behaviour, underscoring the importance of thionation for improving self-assembly, which is in part counteracted by the branched side chains.

The relatively small *K* values, combined with the small change in chemical shift as a function of concentration ( $< 1\text{ ppm}$ ),<sup>36</sup> strongly suggest that the aggregation is simple dimerization and not the formation of higher aggregates. However, the while the data fit well to the model for dimerization, the model does not allow us to rule out extended aggregation by isodesmic indefinite association.<sup>46</sup> We therefore performed dynamic light scattering measurements as a function of concentration. Hydrodynamic diameters were measured for both the parent imide (**1a**) and monothionated (**2a**) derivatives at various concentrations (Figure 4). Unfortunately, the absorbance of the dithionated derivative (**3a**) was too high for similar measurements to be calculated. Because these molecules are disc-shaped, the measured sizes correspond to the diameter of a sphere having the same translational diffusion speed.<sup>47,48</sup> There is no significant difference in the sizes measured at increased concentrations. The proposed dimer is expected to have only a slightly higher diameter than the monomer. The measured hydrodynamic diameters are consistent with the expected size of the monomers and dimers, and we do not see any evidence of higher order

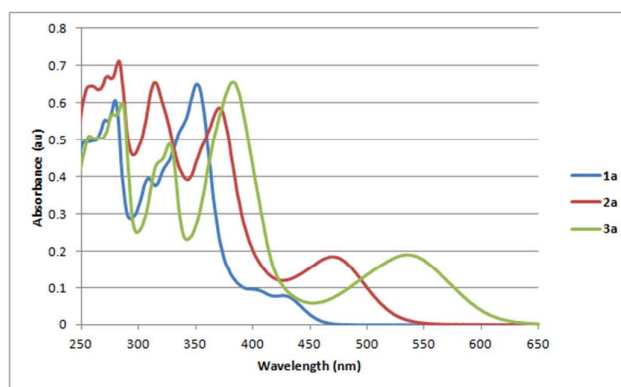
aggregates by dynamic light scattering. Therefore, this result further supports our dimer model as opposed to having higher order aggregates present at higher concentration.



**Fig. 4:** Hydrodynamic diameters of **1a** and **2a** measured by DLS in  $\text{CHCl}_3$ . Error bars show the standard deviation in the measurements after 3 trials of 17 measurements each.

The spectroscopic properties of series **2a** and **3a** (bearing branched *N*-alkyl chains) were also examined. The absorbance spectra of **1a**, **2a**, and **3a** show absorbance maxima close to 350 nm as well as some weak absorption bands at longer wavelengths consistent with intramolecular charge transfer bands (Figure 5). The absorption bands near 350 nm show a distinct bathochromic shift from with increasing thionation with an absorption maximum of 349 nm for **1a**, 369 nm for **2a**, and 381 nm for **3a**. These results suggest a reduction in the HOMO-LUMO gap with increasing sulfur content, which is consistent with previously reported imides and their thionated derivatives.<sup>17-23</sup> The weaker intramolecular charge transfer absorption bands show a similar bathochromic shift: 423 nm for **1a**, 469 nm for **2a**, and 541 nm for **3a**. The series also shows fluorescence quenching with increasing thionation (Figure 6). This result is consistent with our expectations due to the heavy atom effects<sup>49</sup> from the sulfur atoms on the thionated derivatives.

The electrochemical properties of these compounds were investigated using cyclic voltammetry (Figure 7). Cyclic voltammetry of **1a**, **2a**, and **3a** in DCM with  $\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte showed quasireversible oxidation peaks at



**Fig. 5:** UV-Vis spectra of  $1 \times 10^{-5}\text{ M}$  solutions of **1a**, **2a**, and **3a** in  $\text{CHCl}_3$ .



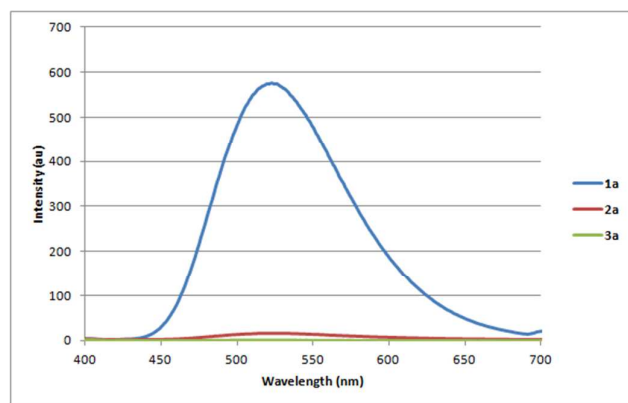


Fig. 6: Emission spectra of  $2 \times 10^{-6}$  M solutions of **1a**, **2a**, and **3a** in  $\text{CHCl}_3$  (excitation at 350 nm).

approximately 0.67 V vs  $\text{Fc}/\text{Fc}^+$ , from which an estimated HOMO of -5.48 eV for the parent imide (**1a**) and -5.47 eV for the monothionated (**2a**) and dithionated (**3a**) derivatives were obtained. Reduction peaks for the three derivatives were also observed between -1.48 V and -1.90 V vs  $\text{Fc}/\text{Fc}^+$ . The LUMO energies were therefore estimated to be -2.89 eV for the parent imide (**1a**), -2.91 eV for the monothionated derivative (**2a**) and -3.30 eV for the dithionated derivative (**3a**). These results show that there is a decrease in the HOMO-LUMO gap with increasing thionation, and that the changes in the band gap are primarily driven by a lowering of the LUMO energy. These observations are consistent with previous studies<sup>16-22</sup> and are also consistent with the observations by UV-visible spectroscopy, although the presence of an intramolecular charge transfer band in the UV-visible spectra makes it difficult to reliably estimate the optical band gap.

Density functional theory calculations on truncated model compounds where the alkyl chains are removed were carried out at the B3LYP/6-31G\* level using Spartan. These results show HOMO energies change little upon thionation, giving values of -5.43 eV for **1**, -5.46 eV for **2**, and -5.49 eV for **3**. In contrast, the LUMO energies change significantly upon thionation: -2.07 eV for **1**, -2.57 eV for **2**, and -3.01 eV for **3**. Although the calculated LUMO energies do not match those estimated from the CV experiments, the overall trend of decreasing LUMO energy with increasing thionation is consistently observed.

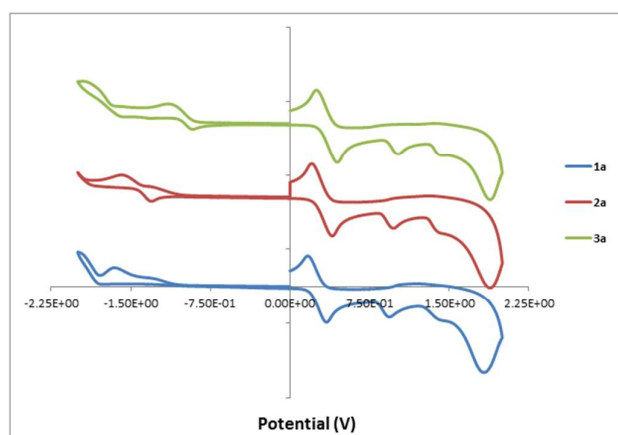


Fig. 7: Cyclic voltammetry spectra of **1a**, **2a**, and **3a** using Ferrocene as a reference.

## Conclusions

In summary, we have for the first time investigated the effect of thionation on self-assembly in solution and in the columnar mesophase and shown that increasing thionation does not disrupt the self-assembly in a series of dibenzanthracenedicarboxythioimides (**2a,b** and **3a,b**). This series demonstrated broad liquid crystalline phases and increased aggregation in solution with increasing thionation. Furthermore, when compared to the parent imides, the thionated derivatives possess lower LUMO energy levels and a narrower HOMO-LUMO gap that is attractive for potential

device applications in organic semiconductors. These results show that thionation can be used to tune the electronic properties of imide-containing columnar liquid crystals without having a significant effect on mesomorphic properties. When combined with the relative ease of the synthetic transformation, these findings suggest that thionation may be a promising method for the design of novel electron-deficient discotic liquid crystalline materials.

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## Table of Contents Entry



The effect of thionation on the formation of columnar liquid crystalline phases of dibenzanthracenedicarboximides as well as their self-association in solution is described.