

## Synthesis and aggregation study of optically active tetra- $\beta$ -[(*S*)-2-octanyloxy]-substituted copper and nickel phthalocyanines

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**Abstract.** The optically active tetra- $\beta$ -[(*S*)-2-octanyloxy]-substituted copper and nickel phthalocyanines were synthesized via a two-step route with 4-nitro-phthalonitrile and (*S*)-2-octanol as the starting materials. Both compounds are fully characterized by MS, <sup>1</sup>H NMR, UV-Vis, IR, CD and elemental analysis, and soluble in common organic solvents except methanol. The results showed that they were dispersed into single molecules in chloroform and dichloromethane, but prone to congregate into H-type aggregates in ethanol and diethyl ether. They assembled to H-type aggregates with left-handed helix when deposited as thin films.

**Keywords.** Synthesis; spectra; aggregation; chirality.

### 1. Introduction

Phthalocyanine (Pc) compounds have received much attention for their potential applications in optoelectronic technologies,<sup>1</sup> catalytic materials<sup>2</sup> and film materials<sup>3</sup>, etc. All these applications were attributed to the largely flat 18-electron  $\pi$ -conjugated system and the central metal of them.<sup>4</sup> Moreover, they could be modified by introducing various substituents on the periphery moiety of Pc ring to generate new derivatives with enhanced solubility<sup>5</sup> or novel functionality.<sup>6</sup> Hence, a considerable effort has been made to obtain structurally desired Pc compounds for practicality.<sup>7</sup> Among them, optically active Pcs have attracted chemists in the last ten years for their special chiral stacking.<sup>8,9</sup>

Optically active Pcs reported to date, could fall mainly into three groups: (i) Pcs containing chiral carbons in the side chain; (ii) Pcs with optically active aromatic molecules; (iii) Pcs with planar asymmetry.<sup>8–10</sup> More attention was given to the first group of optically active Pcs usually behaved multiple liquid crystal mesophases.<sup>10</sup> However, this kind of

optically active Pcs were too less to meet requirement of investigation on chiral stacking due to racemization of chiral chain substrates at reaction temperature even if some of them were commercially available. In order to obtain new optically active Pcs, here (*S*)-2-octanol was selected as the original chiral molecules to synthesize optically active tetra- $\beta$ -[(*S*)-2-octanyloxy]-substituted copper and nickel phthalocyanines (**4a** and **4b**) at 135°C by a modified synthetic method<sup>11</sup> and for that no racemization was found for (*S*)-2-octanol at more than 140°C.<sup>12</sup> The characterization on them showed that they were optically active and had strong intermolecular forces in some organic solvents though they had excellent solubility, which compelled Pc molecules to form H-type aggregates.

### 2. Experimental

#### 2.1 Materials and methods

2-(Dimethylamino)ethanol (DMAE) was distilled from Na prior to use. DMSO was pre-dried over BaO and distilled under reduced pressure. (*S*)-2-octanol (99% ee) was bought from Sigma-Aldrich

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(St. Louis, MO). Column chromatography purification was performed on silica gel. All other reagents and solvents were of commercial grade and used without further purification.

$^1\text{H}$  NMR spectra were recorded on an INOVA-500 spectrometer. IR spectra were measured on a Magna 560 FT-IR spectrometer. UV-Vis spectra were taken on a Cary 500 UV-VIS-NIR spectrophotometer. MS spectra were obtained on a LDI-1700-TOF mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 Elemental Analyzer. Circular dichroism (CD) spectra were measured at room temperature on a JASCO-810 system. Optical rotation was measured with a WZZ-1S digital automatic polarimeter.

## 2.2 Synthesis of 4-[(S)-2-octanyloxy]phthalonitrile **3**

10.39 g **1** (60 mmol) and 7.81 g **2** (60 mmol) were added to 100 mL anhydrous DMSO at room temperature. The reaction mixture was stirred and then 3.6 g LiOH (150 mmol) was interfused over 2 h. The mixture was continually stirred and monitored by TLC. After 24 h, the mixture was then poured into 300 mL 10% NaCl solution and extracted with 100 mL chloroform twice. The combined organic layer was washed by 100 mL water and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The product was collected by removing solvent and further purified by flash column chromatography with chloroform as mobile phase to afford light yellow adhered liquid **3**: 12.46 g, yield: 81%; b.p.  $>200^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69 (*d*,  $J = 9$ , 1H, ArH), 7.22 (*s*, 1H, ArH), 7.14 (*d*,  $J = 9$ , 1H, ArH), 4.45 (*m*, 1H, OCH), 1.75 (*m*, 2H,  $\text{CH}_2$ ), 1.62 (*m*, 3H,  $\text{CH}_3$ ), 1.42 (*m*, 2H,  $\text{CH}_2$ ), 1.28–1.35 (*m*, 6H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 0.88 (*m*, 3H,  $\text{CH}_3$ ); MS ( $\text{CHCl}_3$ ):  $m/z$  calcd. for  $[\text{M} + \text{Na}]^+$ : 279.3, found: 279.6 (an isotopic cluster peak)  $[\text{M} + \text{Na}]^+$ ; IR (KBr): 2231 vs  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$ ), 1253 vs  $\text{cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ); UV-Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 264, 302, 310$  nm.  $[\alpha]_{\text{D}}^{20}$  (0.69%,  $\text{CHCl}_3$ ) +15.6; Anal. Calcd. for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}$  (256.3): C 74.97, H 7.86, N 10.93, Found: C 74.93, H 7.63, N 10.85.

## 2.3 Synthesis of **4a** and **4b**

4.10 g Phthalonitrile derivative **3** (16.0 mmol) and 0.87 g  $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (4.0 mmol) were added to a stirred DMAE (15 mL) in a 50 mL one-neck round-bottomed flask equipped with an air condenser. The resulting solution was stirred and heated at  $135^\circ\text{C}$

under nitrogen for 24 h. After cooling under nitrogen to room temperature, the dark solution was diluted with methanol and filtered in vacuo to afford a solid, which was extracted with a Soxhlet apparatus using methanol as the solvent and then further purified by silica gel column chromatography with chloroform as mobile phase to give pure blue solid **4a**: 2.26 g, Yield: 52%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.22–8.47 (*s*, broad, 12H, ArH), 4.38–4.85 (*s*, broad, 4H, 4OCH), 2.01–0.88 (*m*, broad, 64H,  $4\text{CH}_3(\text{CH}_2)_5$  and  $4\text{CH}_3$ ); MS ( $\text{CHCl}_3$ ):  $m/z$  calcd. for  $[\text{M}]$ : 1088.9, found: 1088.4  $[\text{M}]$ ; UV-Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 288, 339, 384, 617, 685$  nm; IR (KBr): 1234 vs  $\text{cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ); Anal. Calcd. for  $\text{C}_{64}\text{H}_{80}\text{N}_8\text{O}_4\text{Cu}$  (1088.9): C 70.59, H 7.41, N 10.29, Found: C 70.62, H 7.53, N 10.22.

The compound **4b** obtained by the aforesaid procedure gave: 2.95 g, yield: 68%;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.09–6.05 (*m*, broad, 12H, ArH), 4.77–4.93 (*m*, broad, 4H, 4OCH), 2.14–1.04 (*m*, broad, 64H,  $4\text{CH}_3(\text{CH}_2)_5$  and  $4\text{CH}_3$ ); MS ( $\text{CHCl}_3$ ):  $m/z$  calcd. for  $[\text{M}]$ : 1084.1, found: 1083.7  $[\text{M}]$ ; UV-Vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 302, 328, 385, 610, 678$  nm; IR (KBr): 1235 vs  $\text{cm}^{-1}$  ( $\text{C}-\text{O}-\text{C}$ ); Anal. Calcd. for  $\text{C}_{64}\text{H}_{80}\text{N}_8\text{O}_4\text{Ni}$  (1084.1): C 70.91, H 7.44, N 10.34, Found: C 70.87, H 7.47, N 10.26.

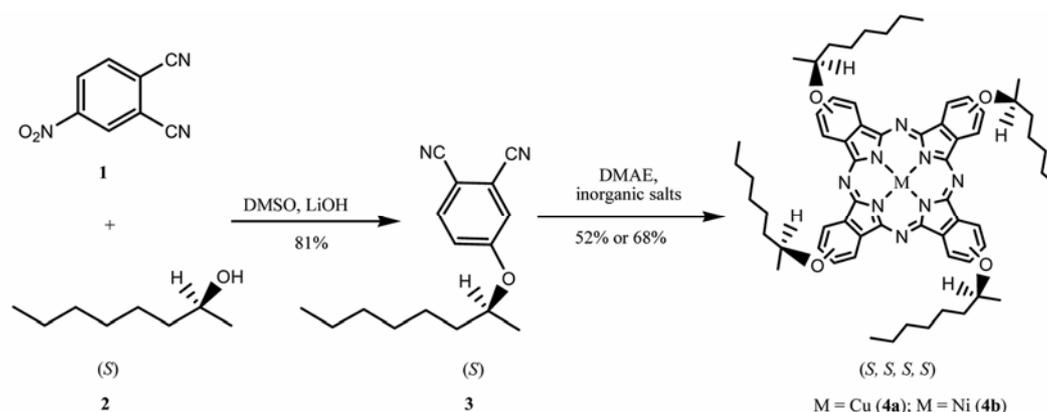
## 2.4 Preparation of depositing films

The preparation of films of **4a** and **4b** deposited on quartz glass was carried out as follows. A piece of thin quartz glass ( $10 \times 10 \times 0.2$  mm) was pre-cleaned with acetone and dried in air, and then immersed in 10 mL solution of **4a** or **4b** in  $\text{CHCl}_3$  ( $1.0 \times 10^{-5}$  mol/L) in a 50 mL beaker. Subsequently, the beaker was covered by a filter paper and set aside for one day to let chloroform evaporate to leave behind the blue film deposited on quartz glass.

## 3. Results and discussion

### 3.1 Synthesis and characterization

Following the general synthetic route for tetra-substituted Pcs involving the aromatic nucleophilic substitution reaction between nitrophthalonitriles and a suitable oxygen nucleophile followed by cyclotetramerization of the resultant phthalonitrile derivatives,<sup>11</sup> a modified procedure was employed to synthesize Pc compounds **4a** and **4b** (scheme 1). Phthalonitrile (**1**) and optically active (S)-2-octanol



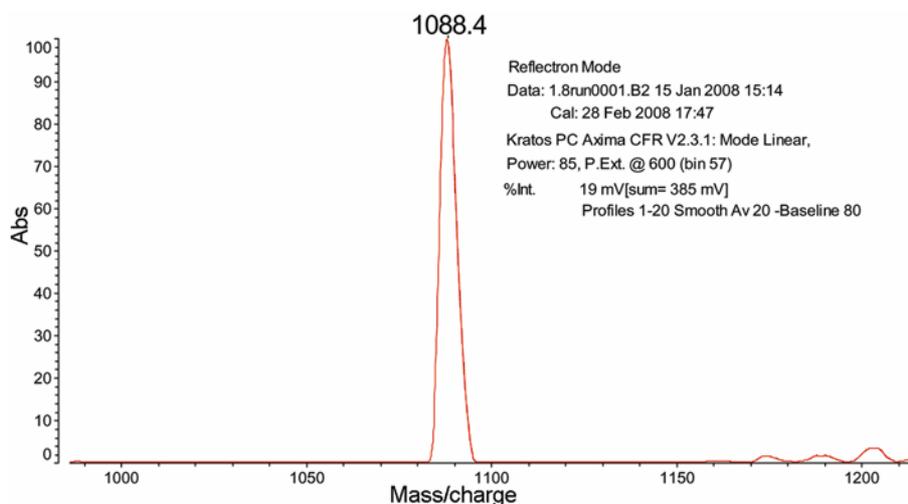
Scheme 1.

(**2**) were chosen as starting materials to synthesize phthalonitrile derivative **3** with good yield in the presence of LiOH and anhydrous DMSO at room temperature. Because phthalonitrile (**3**) was a light yellow viscous liquid, so it was firstly separated from the reaction mixtures by extraction with chloroform and then purified by flash column chromatography. Upon treatment with  $\text{Cu}(\text{OAc})_2$  or  $\text{NiCl}_2$  in DMAE under nitrogen at  $135^\circ\text{C}$ , **4a** and **4b** were synthesized from phthalonitrile (**3**), respectively. They could be first washed by Soxhlet extraction with methanol to remove most of impurities, and further purified by flash column chromatography with chloroform as mobile phase. The synthesized Pc compounds were characterized by MS,  $^1\text{H}$  NMR, UV-Vis, IR, CD and elemental analysis, which were consistent with the proposed structures (scheme 1). In their mass spectra, the peaks of singly charged molecular ions were obvious, e.g. mass spectrum of **4a** (figure 1). The  $^1\text{H}$  NMR spectra of them were strongly impacted by paramagnetism of the center Cu (II) and Ni (II) in a square planar environment,<sup>13</sup> which resulted in that both **4a** and **4b** displayed three broad bands in  $^1\text{H}$  NMR spectra: **4a**,  $\delta$  11.22–8.47 (H bonding with aromatic ring), 4.38–4.85 (H bonding with chiral carbon), 2.01–0.88 (H bonding with non-chiral carbons in (*S*)-2-octanyloxy); **4b**,  $\delta$  8.09–6.05, 4.77–4.93, 2.14–1.04 (corresponding to the aforementioned three kinds of hydrogen, respectively). The IR absorptions at  $1234\text{ cm}^{-1}$  (C–O–C) for **4a** and at  $1235\text{ cm}^{-1}$  (C–O–C) for **4b** meant the characteristic vibration of chemical bond linking (*S*)-2-octanyloxy group and Pc ring. From the UV-vis spectra of **4a** and **4b** in chloroform, it was found that the typical Q-band absorptions were at 685 nm and 678 nm, respectively (figure 2). The only differ-

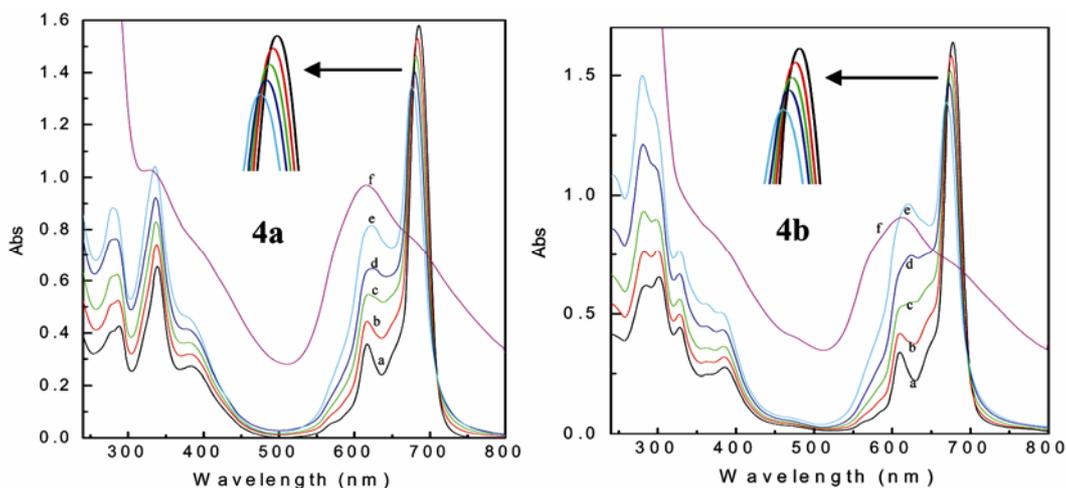
ence was that the Q band of **4b** shifted blue 7 nm than **4a**, which was caused by much electron-pulling power of Ni (II) for its less *d* electrons relative to Cu (II), to decrease electron cloud of Pc ring and bring blue shift of Q band.<sup>14</sup>

### 3.2 Understanding UV-Vis spectra

Besides methanol, both **4a** and **4b** could be dissolved in common organic solvents. Especially in chloroform and diethyl ether, they showed excellent solubility. But the dispersed states of them in two organic solvents were very different, which could be understood by UV-Vis spectra analysis (figure 2 and table 1). For example **4a**, in chloroform, a high Q band (685 nm) and a little shoulder peak (617 nm) were observed, which shows that Pc molecules were dispersed well.<sup>15</sup> But in ethyl ether, the shoulder peak increased greatly and the Q band lowered some. Moreover, when the volume ratio of chloroform/diethyl ether changed from 1 : 0 to 0 : 1, the Q band gradually shifted blue from 685 to 676 nm and the logarithm of molar extinction coefficient ( $\log \epsilon$ ) decreased from 5.20 to 5.13. Synchronously the shoulder peak shifted red from 617 to 623 nm and the  $\log \epsilon$  increased from 4.55 to 4.91. Accordingly, the colour of solution changed from primal cyan to final blue. The phenomena implied that H-aggregates gradually formed from Pc molecules according to a co-facial method,<sup>16</sup> namely **4a** was inclined to form H-aggregates in ethyl ether. Further the same aggregation tendency was found for **4a** and **4b** in some molecule-oxygenic solvents, such as ethanol, acetic ether, tetrahydrofuran, etc. Contrarily, no similar phenomena were observed for them in



**Figure 1.** MS of synthesized Pc **4a**.



**Figure 2.** The UV-Vis spectra of solutions of **4a** and **4b** in chloroform/ethyl ether ( $1.0 \times 10^{-5}$  mol/L, v/v, 1:0 (a); 2:1 (b); 1:1 (c); 1:2 (d); 0:1 (e)), and films of them (f) prepared by deposition of them on thin quartz glass.

molecule-oxygen-free solvents, e.g. chloroform and dichloromethane.

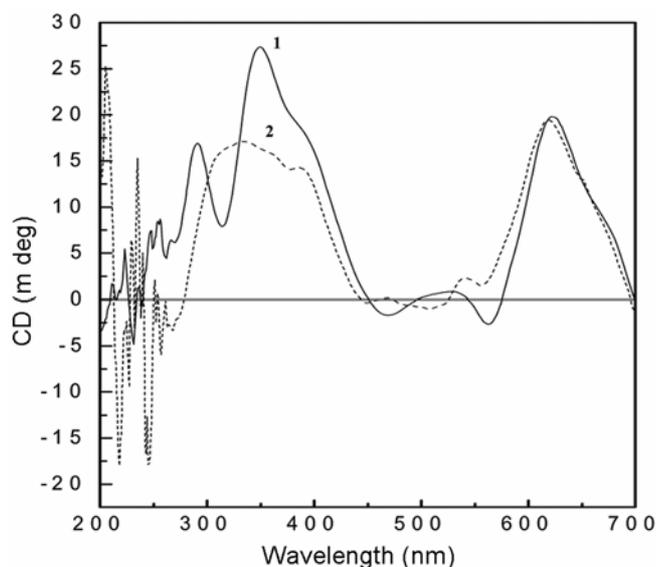
The aforementioned phenomena might be understood through following points. There were two main intermolecular actions between solvent and Pc molecules. One was the strong affinity between solvent and 2-octanyloxy groups around Pc rings, which prevented Pc molecules from depositing and caused them to show excellent solubility in chloroform or ethyl ether. The other one was the weak action between solvents and 18-electron  $\pi$ -conjugated systems of Pcs, which led to different dispersed states for them in two kinds of solvents. The chloroform molecules could readily insert into the hydro-

phobic regions between Pc molecules and disperse them nicely. But it was not easy for ethyl ether molecules to approach Pc ring owing to the existence of hydrophilic ether-oxygen atom. Accordingly the coordination of the ether-oxygen atom with the center metals Cu (II) or Ni (II) was also too weak to disperse **4a** or **4b**.<sup>17</sup> The result was that the intermolecular action compelled them to congregate to some H-aggregates. The phenomenon is similar to the water-soluble Pc compounds, which usually formed H-aggregates and generated broad Q bands in water in which though they could be easily dissolved.<sup>18</sup> The excellent solubility of water-soluble Pcs is mainly derived from the affinity between water

**Table 1.** UV-Vis spectral parameters of **4a** and **4b** in chloroform/ethyl ether ( $1.0 \times 10^{-5}$  mol/L), and the solid films.

Samples $\lambda$ (nm), log $\epsilon$	Chloroform/ethyl ether (v/v)					Films
	1:0	2:1	1:1	1:2	0:1	
Q <sub>4a</sub>	685, 5.20	683, 5.19	681, 5.17	679, 5.15	676, 5.13	618
S <sub>4a</sub> *	617, 4.55	617, 4.65	618, 4.74	623, 4.81	623, 4.91	–
Q <sub>4b</sub>	678, 5.22	676, 5.20	674, 5.18	673, 5.17	669, 5.14	615
S <sub>4b</sub> *	610, 4.53	610, 4.62	622, 4.73	622, 4.87	622, 4.98	–

\*‘S’ represents the shoulder peak near left of Q band. –, means unobvious peak.

**Figure 3.** CD spectra of films for **4a** (1) and **4b** (2).

and hydrophilic substituents around Pc ring, but the water molecules could not effectively insert in-between hydrophobic Pc rings to prevent them from forming H-aggregates.

The transmission UV-Vis spectra of solid films of **4a** and **4b** deposited on thin quartz glasses all displayed broad and shift-blue Q bands relative to the liquid UV-Vis spectra. For example **4a**, there were a main absorption band around 618 nm and an unobvious absorption band at around 680 nm (figure 2). The main band shifted blue 67 nm relative to the Q band in chloroform, which meant that **4a** mainly existed in the form of H-aggregates in solid state for that, as a rule, the Q bands of Pc H-aggregates in solid markedly shifted blue relative to Pc molecules in solutions.<sup>19</sup>

### 3.3 Chirality and CD spectra

The optical rotation of **4a** and **4b** could not be obtained on a WZZ-1S digital automatic polarimeter since the wavelength (589 nm) of sodium lamp in

the instrument fell in the range of the great Q absorbance (550–750 nm) of Pc compounds. But they could be indirectly estimated to be optical active by measuring the optical rotation of unreacted **3** separated from remnants, which showed that **3** was not racemized after undergoing the reaction conditions under which to synthesize **4a** and **4b**. Thereby the optical activity of **3** was concluded to be kept in the synthesized Pc compounds.

As we all know, CD spectra were from a chiral stacking of large numbers of optically active molecules or were induced by enough big chiral molecules, e.g. protein and nucleic acid.<sup>9</sup> It was found **4a** and **4b** in chloroform or ethyl ether did not offer any CD activity. This accounted for that **4a** and **4b** mainly existed in the form of single molecules or small H-type dimmers and oligomers in solution. H-type aggregates formed were not enough in solution to bring CD activity for excellent solubility of them. However, the deposition films of **4a** and **4b** on thin quartz glass displayed characteristic CD spectra (figure 3). It was deduced that the films must result from a stacking of large numbers of chiral molecules. According to a chiral exciton coupling theory attested in the literature,<sup>20</sup> the positive CD patterns corresponding to the main Q bands (at around 620 nm) suggested that the molecules stacked mainly in the form of a left-handed helix in solid films. Contrarily, the deposition films of metal Pcs substituted by racemic 2-octanyloxy groups synthesized by same method did not show any CD activity, which implied that the racemic molecules in films did not stack by chiral method. Combining the UV-Vis with CD spectra of solid films, it was known that the molecules of **4a** and **4b** mainly existed in the form of H-aggregates with left-handed helix in films.

## 4. Conclusions

In summary, two optically active Pc derivatives **4a** and **4b** have been successfully synthesized from

4-nitro-phthalonitrile and (*S*)-2-octanol, and characterized by MS, <sup>1</sup>H NMR, UV-Vis, IR and CD spectra. They have excellent solubility in common organic solvents except methanol, but show different aggregate states in different solvents. In solid films, they exist mainly as H-type aggregates forming a left-handed helix.

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