



# Tetrakis(phthalocyaninato) terbium–cadmium quadruple-decker liquid crystals with good semiconducting properties

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## ABSTRACT

Neutral and mono-oxidized states of novel sandwich-type tetrakis[2,3,9,10,16,17,23,24-octa(dodecanoyloxy)phthalocyaninato] terbium–cadmium quadruple-decker complex  $\{[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Cd}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\}$  (**1**) and  $\{[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Cd}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\}$ - $\text{SbCl}_6$  (**2**) were synthesized and spectroscopically characterized. Polarized optical microscope (POM) together with differential scanning calorimeter (DSC) measurement revealed their similar two rectangular columnar mesophases over a relatively lower temperature range and higher temperature range, respectively, within their wide liquid crystal temperature range of 19–266 °C for **1** and 4–249 °C for **2**. Temperature-dependent X-ray diffraction (XRD) analysis result disclosed the slight difference in terms of the neighboring quadruple-decker  $\pi$ – $\pi$  stacking between these two mesophases, which in turn accounts for their electric conducting behavior along with the change in temperature. In addition, due to the ionic conductive nature, the mono-oxidized liquid crystals of **2** display more than 2 order of magnitude higher electric conductivity than that for **1**, with the highest value  $4.1 \times 10^{-4} \text{ S cm}^{-1}$  achieved at 140 °C.

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## 1. Introduction

Liquid crystals (LCs), as an important self-organized functional soft materials, have found a wide range of applications such as liquid–crystal display technology, single-molecule magnets, and biomaterials [1]. In recent years, the aromatic core-based liquid crystals, which are also known as discotic liquid crystals, have received increasing research interest due to their good semiconductivity in the mesophase associated with effective  $\pi$ – $\pi$  intermolecular

stacking among their self-organized liquid crystal molecules [2]. As one of the most important functional molecular materials with large  $\pi$ -conjugated electronic structure and extraordinary thermal and photochemical stability [3], phthalocyanine derivatives have been among the most intensively studied discotic liquid crystal materials due to their strong absorption in the visible and NIR regions, which enables their applications in optoelectronic devices [4].

Monomeric phthalocyanine derivatives with discotic liquid crystal behavior were first reported in 1982 [5]. In the following years, more extensive studies have been carried out in this direction, leading to the report of a large number of various phthalocyanine liquid crystals with

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good stability and electric conductivity [6]. Due also to the good semiconducting properties revealed for the sandwich-type bis(phthalocyaninato) rare earth complexes, the phase behaviors of quite a number of such kind of double-deckers have been systematically studied for potential applications in various organic electronic devices [7]. Quite recently, the mesophase behavior of tris(phthalocyaninato) rare earth complexes was also investigated by this group [8]. However, despite the quite systematic studies of the semiconducting properties of both monomeric phthalocyanine and bis(phthalocyaninato) rare earth liquid crystals, the electric conductivity for the liquid crystals based on the tris(phthalocyaninato) rare earth triple-decker or sandwiches with more than three phthalocyanine decks has not yet been reported thus far.

Very recently, novel sandwich-type tetrakis(phthalocyaninato) rare earth-cadmium quadruple-decker complexes were synthesized on the basis of the capability of phthalocyanine to coordinate with divalent transition metal of cadmium in the formation of stacked tetrapyrrole metal oligomers. The tetrapyrrole rare earth-cadmium quadruple-decker analogs have aroused increasing attention because of the extension of the  $\pi$  networks along the axis perpendicular to the macrocycle plane, which makes them even more promising as active materials for efficient charge transport compared with their double-/triple-decker counterparts [9]. For the purpose of introducing the mesophase behavior into this new species of sandwich compounds with large fraction of aromatic discotic core, long dodecanoyloxy chains were incorporated onto the phthalocyanine periphery in the quadruple-decker molecule, yielding tetrakis[2,3,9,10,16,17,23,24-octa(dodecanoyloxy)phthalocyaninato] terbium–cadmium quadruple-decker complex  $\{[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Cd}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\}$  (**1**), **Scheme 1**. Oxidation with phenoxathiin hexachloroantimonate afforded the mono-oxidized derivative  $\{[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Cd}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\}$ · $\text{SbCl}_6$  (**2**). Both neutral and mono-oxidized states exhibited two similar rectangular columnar LC mesophases within their wide liquid crystal temperature range from 19 to 266 °C for **1** and 4 to 249 °C for **2**, respectively, with slight differences in terms of the neighboring quadruple-decker  $\pi$ – $\pi$  stacking between these two mesophases. This in turn rationalizes their electric conducting behavior as a function of temperature. In addition, due to the ionic conductive nature [10], the mono-oxidized liquid crystals of **2**

display more than 2 order of magnitude higher electric conductivity than that for **1**, with the highest value  $4.1 \times 10^{-4} \text{ S cm}^{-1}$  achieved at 140 °C.

## 2. Experimental section

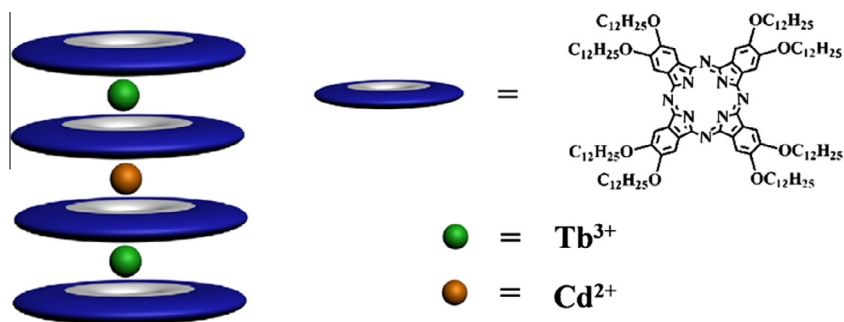
### 2.1. General remarks

All the reagents and solvents were used as received. The compounds of  $\{[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\}$  [11] and phenoxathiin hexachloroantimonate [12] were prepared according to published procedure.

Electronic absorption spectra were recorded on a PerkinElmer Lambda 750 UV/VIS Spectrophotometer. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high-resolution Fourier-transform ion-cyclotron-resonance (FT-ICR) mass spectrometer with alpha-cyano-4-hydroxycinnamic acid as matrix. Elemental analysis was performed on an Elementar Vavio El III. Phase transition behavior was observed using a Carl Zeiss Axio Cscope. A1 polarized optical microscope (POM) with a Linkam LTS420 liquid crystal freezing and heating stage system. Differential scanning calorimeter (DSC) measurements were performed on a Perkin Elmer DSC8000. The X-ray diffraction measurements were carried out using Rigaku D-Max (Cu  $K\alpha$  radiation) equipped with a heating plate controlled by a thermoregulator.

### 2.2. Synthesis of $\{[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Cd}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\}$ (**1**)

A mixture of  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (5.3 mg, 0.02 mmol) and neutral bis(phthalocyaninato) terbium double-decker  $\{[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\}$  (42.5 mg, 0.01 mmol) in 1,2,4-trichlorobenzene (TCB) (4 mL) was heated to reflux under nitrogen for 2.5 h. After being cooled to room temperature, the volatiles were removed under reduced pressure. The residue was chromatographed on a silica gel column using  $\text{CHCl}_3$  as the eluent to give a green band, which contained mainly the unreacted  $\{[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\}$ . Further elution with  $\text{CHCl}_3$  gave a blue band containing the target quadruple-decker complex  $\{[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Cd}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\text{Tb}[\text{Pc}(\text{OC}_{12}\text{H}_{25})_8]\}$  (**1**). Repeated chromatography gave the pure homoleptic quadruple-decker complex **1** in the yield of 18.1 mg, 43%.



**Scheme 1.** Schematic molecular structure of tetrakis(phthalocyaninato) Tb(III)–Cd(II) quadruple-decker complex.

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