The first liquid crystalline phthalocyanine derivative capable of edge-on alignment for solution processed organic thin-film transistors†

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Tetraoctyl-substituted vanadyl phthalocyanine (OVPc4C8) as a new NIR-absorbing discotic liquid crystalline material can form highly ordered thin films with edge-on alignment of the molecules and molecular packing mode identical to that in the phase II of OVPc for solution processed OTFTs with mobility up to 0.017 cm² V⁻¹ s⁻¹.

Over the past two decades, considerable interest has been shown in the use of organic semiconductors as active materials in optoelectronic devices such as organic thin-film transistors (OTFTs) and organic solar cells (OSCs). In order to fully explore the advantages of organic semiconductors, i.e., mechanical flexibility and low-cost for large-area optoelectronic devices, it is important to develop solution-processable materials for device fabrication.5

Metal phthalocyanines (MPcs) have become one of the most important classes of organic semiconductors because of (1) their easy synthesis and adjustment of physical properties by selecting the appropriate central metal atom; (2) high field-effect mobility of vacuum-deposited thin films; (3) intense absorption in the near-infrared (NIR) region; and (4) extraordinary thermal and photochemical stability.4 Actually, MPcs have successfully been used in the fabrication of high performance optoelectronic devices such as OTFTs5–8 and OSCs9–11 both by vacuum-deposition. Particularly, OTFTs with field-effect mobility (μFFET) up to 1.2 cm² V⁻¹ s⁻¹ for holes and 0.3 cm² V⁻¹ s⁻¹ for electrons have been demonstrated with vanadyl phthalocyanine (OVPC)7 and phthalocyaninato tin(iv) dichloride (SnCl₂Pc),9 respectively. On the other hand, many soluble phthalocyanines (Pcs) have been prepared via peripheral substitution, and some of them are discotic liquid crystals which can form highly ordered columnar mesophases (e.g., hexagonal and rectangular mesophases) comprising one-dimensional charge transport channels. Moreover, mobility up to 0.6 cm² V⁻¹ s⁻¹ for a Pc derivative as measured by the pulse-radiolysis time-resolved microwave conductivity technique has been reported.15 However, soluble Pc-based OTFT devices with reasonably high mobility (> 10⁻³ cm² V⁻¹ s⁻¹) have not been demonstrated yet by common solution process (such as spin-coating), although Langmuir–Blodgett or layer-by-layer deposition techniques could afford OTFT devices with μFFET up to 0.46 cm² V⁻¹ s⁻¹.14–16 Ono recently reported OTFT devices based on soluble PCs with μFFET up to 6 × 10⁻² cm² V⁻¹ s⁻¹, but high temperature (350 °C) had to be applied to convert the precursor to the high mobility form.17 One of the main reasons leading to this situation may be the difficult edge-on alignment of disc-like molecules of liquid crystalline (LC) PCs for formation of charge transport channels along the source-drain direction18 and molecular arrangement like that in the high mobility phase II of OVPc.4 In the current communication, we report a tetraoctyl-substituted LC MPC, OVPc4C8 (Fig. 1). It exhibits a rectangular columnar LC mesophase with a LC isotropic transition temperature (Tc) of 175 °C. Most importantly, the film comprising edge-on aligned molecules can be easily prepared by annealing the spin-cast film at a relative low temperature of 120 °C for preparation of high performance OTFTs. A μFFET up to 0.017 cm² V⁻¹ s⁻¹ along with a low threshold voltage (VT ~0 V) has been demonstrated. To our best knowledge, this is the first Pc derivative for common solution processed OTFTs with high field-effect mobility. High solubility, high mobility and strong NIR-absorption will make this type of materials promising solution-processible organic semiconductors.

OVPc4C8 is highly soluble in common organic solvents, such as chloroform, tetrahydrofuran and toluene. More than 100 mg of OVPc4C8 can be dissolved in 1 mL chloroform. Alkyl substituents instead of alkoxyl ones were used in order to exclude the effect of oxygen atoms in the flexible side chains on alignment behavior of the discotic molecules on the substrate.19 Randomly arranged alkyl chains can render OVPc4C8 with high solubility and lower Tc for ease of preparation of highly ordered film via thermal annealing in LC state.

![Molecular structure of tetraoctyl-substituted vanadyl phthalocyanine OVPc4C8.](Fig. 1 Molecular structure of tetraoctyl-substituted vanadyl phthalocyanine OVPc4C8.)
Thermotropic LC properties of OVPc4C8 were studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD). As shown in Fig. 2(a), only one phase transition at 175 °C with a transition enthalpy value \( (\Delta H) \) of 12.3 J g\(^{-1}\) corresponding to \( T_c \) was observed upon heating. “Branched” textures typical for highly ordered columnar mesophases were observed under POM upon cooling OVPc4C8 from the isotropic state (see ESI†). Fig. 2(b) shows the XRD patterns of OVPc4C8 at different temperatures. At 40 °C, the extinction of all the reflections with \( h + k \neq 2n \) allows us to assign the \( c2mm \) symmetry to the rectangular two-dimensional lattices,\(^{20,21}\) with a quasi-square lattice parameters \( a = 32.2 \) Å and \( b = 31.4 \) Å. A shoulder at \( 2\theta = 24.4^\circ \) suggests an average \( \pi-\pi \) stacking distance of about 3.6 Å in the columns. The molecules in the column form slipped \( \pi-\pi \) stacking. The tilt angle of the molecules with respect to the columnar axis is about 54° due to the presence of axial substituents (see ESI†).

At 140 °C, a similar pattern can be observed but with broader peaks, reduced intensity and disappearance of the 20 and 40 reflection peaks, indicating the lower order of the molecules in the columns. When OVPc4C8 is heated to an isotropic liquid at 195 °C, a diffuse small-angle reflection peak appears at \( 2\theta = 4.5^\circ \). This type of reflection was also observed in hexabenzocoronene derivatives, which was ascribed to the positional correlation of molecular aggregates possessing different electron density between the discotic core stacks and the alkyl chains.\(^{22}\)

The self-organization process of OVPc4C8 on quartz and SiO\(_2\)/Si substrates upon thermal annealing was monitored by UV-vis-NIR absorption spectroscopy and the thin-film XRD technique, respectively. As shown in Fig. 3(a), the pristine film of OVPc4C8 shows a broad absorption band in 500-900 nm. Upon annealing, the long-wavelength absorption peak becomes stronger and red-shifted, and meanwhile the two short-wavelength absorption peaks become weaker, indicative of a self-organization process of the molecules. With a given annealing time of 20 min, the spectral change becomes more pronounced with an increase of the annealing temperature, and achieves a saturated state at 120 °C. The spectrum is identical to that of the high mobility phase II of OVPc, indicative of a similar molecular arrangement.\(^{4,23,24}\) To characterize the orientation of the molecules by thin film XRD, SiO\(_2\)/Si substrates were treated with a phenyltrichlorosilane (PTS) monolayer for spin-coating 40 nm films of OVPc4C8. As shown in Fig. 3(b), the pristine film of OVPc4C8 only shows a broad diffraction peak at \( 2\theta = 3.96^\circ \), corresponding to a \( d \)-spacing of 2.23 nm, indicating a low-ordered edge-on alignment of molecules. After the film is annealed at 120 °C for 20 min, the diffraction peak becomes stronger and sharper with second- and third-order diffraction peaks at \( 2\theta = 7.90^\circ \) \((d\)-spacing of 1.12 nm\) and \( 11.9^\circ \) \((d\)-spacing of 0.74 nm\), respectively, indicating highly ordered edge-on alignment of molecules and the formation of the film with layered nanostructures. These diffractions are well consistent with those in powder XRD, revealing that the molecules in the films should pack in a manner similar to that in the bulk state. Consistent with absorption spectroscopic observation, further increasing the annealing temperature to 150 °C afforded identical XRD patterns.

Top-contact OTFT devices were fabricated on SiO\(_2\)/Si substrate to study charge carrier transport properties of...
calculated from the saturation regime along with an 

saturation regions. The source–drain current scales up with an 

The current–voltage characteristics exhibit standard linear and 

shows the typical OTFT output and transfer characteristics. 

respectively, were realized. Modification with a 100 nm poly-

processible organic semiconductors. 

High mobility, strong NIR-absorption and ease of preparation 
demonstrated with a top-contact OTFT device configuration. 

V$_{off}$ of 4$	imes$10$^{-3}$ and (6.8$	imes$10$^{-3}$) cm$^2$V$^{-1}$s$^{-1}$, respectively, were realized. Modification with a 100 nm poly-
imide layer resulted in the best device performance. Fig. 4 

showing the typical OTFT output and transfer characteristics. 

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Notes and references


Fig. 4 Output (a) and transfer (b) characteristics of OTFTs based on OVPc4C8 on polyimide-modified SiO2/Si substrate with an annealing temperature of 120 °C.