

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).^{1,2} 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-processible materials for device fabrication.³

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 OTFTs^{5–8} and OSCs^{9–11} both by vacuum-deposition. Particularly, OTFTs with field-effect mobility (μ_{TFT}) 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 phthalocyanato tin(IV) dichloride (SnCl₂Pc),⁸ 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.¹² 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.¹³ 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 μ_{TFT} up to 0.46 cm² V⁻¹ s⁻¹.^{14–16} Ono recently reported OTFT devices based on soluble Pcs with μ_{TFT} 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 (T_c) 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 μ_{TFT} up to 0.017 cm² V⁻¹ s⁻¹ along with a low threshold voltage ($V_T \sim 0$ 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 alkoxy 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 T_c for ease of preparation of highly ordered film *via* thermal annealing in LC state.

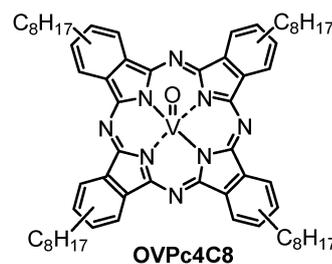


Fig. 1 Molecular structure of tetraoctyl-substituted vanadyl phthalocyanine **OVPC4C8**.

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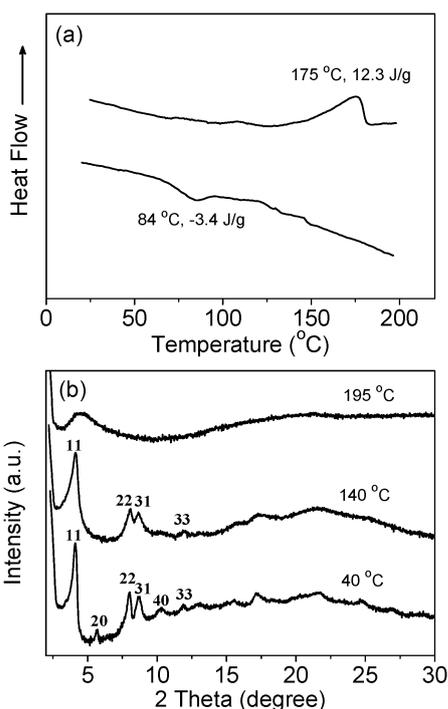


Fig. 2 DSC second-heating and cooling traces of **OVPe4C8** under nitrogen with a heating rate of $\pm 10\text{ }^{\circ}\text{C min}^{-1}$ (a) and powder XRD patterns of **OVPe4C8** at different temperatures (b).

Thermotropic LC properties of **OVPe4C8** 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 $175\text{ }^{\circ}\text{C}$ with a transition enthalpy value (ΔH) 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 **OVPe4C8** from the isotropic state (see ESI†). Fig. 2(b) shows the XRD patterns of **OVPe4C8** at different temperatures. At $40\text{ }^{\circ}\text{C}$, 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 $a = 32.2\text{ \AA}$ and $b = 31.4\text{ \AA}$. A shoulder at $2\theta = 24.4^{\circ}$ suggests an average π - π stacking distance of about 3.6 \AA in the columns. The molecules in the column form slipped π - π 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 $140\text{ }^{\circ}\text{C}$, 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 **OVPe4C8** is heated to an isotropic liquid at $195\text{ }^{\circ}\text{C}$, 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 **OVPe4C8** on quartz and SiO_2/Si substrates upon thermal annealing was monitored by UV-vis-NIR absorption spectroscopy and the thin-film XRD

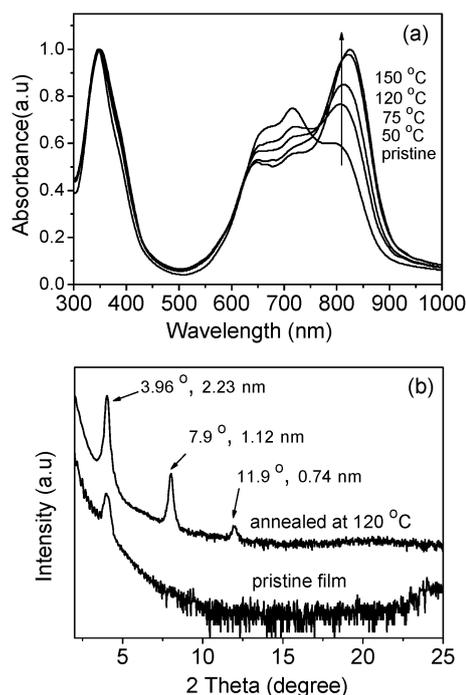


Fig. 3 Film UV-vis-NIR absorption spectra of **OVPe4C8** upon annealing at different temperature (a) and the thin-film XRD patterns of **OVPe4C8** before and after annealing at $120\text{ }^{\circ}\text{C}$ (b).

technique, respectively. As shown in Fig. 3(a), the pristine film of **OVPe4C8** shows a broad absorption band in $500\text{--}900\text{ nm}$. 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 $120\text{ }^{\circ}\text{C}$. The spectrum is identical to that of the high mobility phase II of **OVPe**, 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 **OVPe4C8**. As shown in Fig. 3(b), the pristine film of **OVPe4C8** 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 $120\text{ }^{\circ}\text{C}$ 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° (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 $150\text{ }^{\circ}\text{C}$ afforded identical XRD patterns.

Top-contact OTFT devices were fabricated on SiO_2/Si substrate to study charge carrier transport properties of

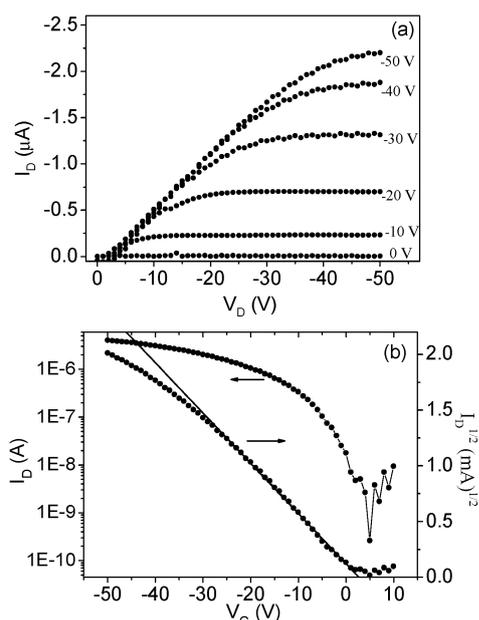


Fig. 4 Output (a) and transfer (b) characteristics of OTFTs based on **OVPc4C8** on polyimide-modified SiO₂/Si substrate with an annealing temperature of 120 °C.

OVPc4C8. Au (40 nm) source and drain electrodes were deposited on the organic semiconductor layer through a shadow mask with a channel width (W) of 4000 μm and a channel length (L) of 150 μm , respectively. Fabrication and characterization of OTFT devices were both carried out in ambient conditions. It was found that device performance of **OVPc4C8** depended on dielectric layer modification and annealing temperature. Thermal annealing at 120 °C gave the best device performance, consistent with absorption spectral and thin-film XRD monitoring. With the substrates modified with octadecyltrichlorosilane (OTS) and PTS, μ_{TFT} values of $(2.5 \pm 0.5) \times 10^{-3}$ and $(6.8 \pm 0.4) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, were realized. Modification with a 100 nm polyimide layer resulted in the best device performance. Fig. 4 shows the typical OTFT output and transfer characteristics. The current–voltage characteristics exhibit standard linear and saturation regions. The source–drain current scales up with an increase of the gate voltage (V_{G}). A μ_{TFT} up to 0.017 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, calculated from the saturation regime along with an $I_{\text{on}}/I_{\text{off}}$ of 4×10^3 and a V_{T} of 2 V have been realized.

In summary, we have designed and synthesized a tetraalkyl-substituted LC Pc derivative, *i.e.*, **OVPc4C8**, which is capable of forming highly ordered thin films by simply annealing the spin-cast films at 120 °C. A μ_{TFT} up to 0.017 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ along with a low threshold voltage ($V_{\text{T}} \sim 0$ V) has been demonstrated with a top-contact OTFT device configuration. High mobility, strong NIR-absorption and ease of preparation and processing make this class of materials attractive solution processible organic semiconductors.

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