Electronic Supplementary Information for

The First Liquid Crystalline Phthalocyanine Derivative Capable of Edge-On Alignment for Solution Processed Organic Thin-Film Transistors

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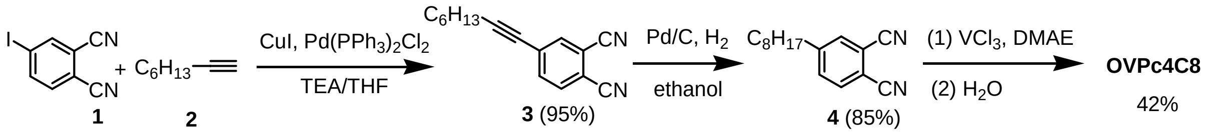
1. Synthesis and characterization of OVPc4C8

General Information. All reactions were carried out under argon unless stated otherwise. Tetrahydrofuran (THF) was distilled over Na/benzophenone. Triethylamine (TEA) was distilled over CaH_2. Dimethylaminoethanol (DMAE) was dried with K_2CO_3 and then distilled. Other reagents were obtained from commercial resources and used without further purification. ^1H NMR spectra were recorded on Bruker AV 300-MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Elemental analysis was carried out on a FlashEA1112 elemental analyzer. MALDI-TOF mass spectra were recorded on Kratos AXIMA-CFR Kompact MALDI Mass Spectrometer with anthracene-1,8,9-triol as the matrix. GC/MS were recorded on an Agilent 5975/6890N gas chromatography-mass spectrometer. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA7 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} in nitrogen. Differential scanning calorimetry (DSC) was run on a Perkin-Elmer DSC7 at a heating/cooling rate of 10/-10 °C min^{-1} in nitrogen. POM observation was done on an Olympus BX51 polarizing optical microscope equipped with a LTS 350 hot stage and a TMS 94 temperature programmer (Linkam). Temperature-dependent powder XRD were carried out on D\Max 2500V X-ray diffractometer. Thin-film XRD were recorded on a Bruker D8 Discover thin-film diffractometer with Cu Kα radiation (λ = 1.54056 Å) operated at 40 keV and 40 mA. UV-vis-NIR absorption was recorded on Shimadzu UV3600 spectrometer.



Scheme S1. Synthesis route of **OVPc4C8**.

4-Octynylphthalonitrile (3). Into the mixture of 4-iodophthanitrile (**1**, 10.3 g, 40.0 mmol), CuI (2.86 g, 15.0 mmol) and $Pd(PPh_3)_2Cl_2$ (1.12 g, 1.6 mmol) in 320 mL of TEA and 80 mL of THF was added 1-octyne (**2**, 7.20 mL, 48.0 mmol) by syringe. The reaction mixture was stirred at room temperature and monitored by TLC. No trace of **1** was found after 17 hours.

The reaction mixture was then filtered and dissolved in 500 mL of Et_2O. The organic solution was washed with water, saturated NH_4Cl aqueous solution and then brine. Upon evaporating off the solvent, the residue was purified by column chromatography on silica gel with petroleum ether and dichloromethane (1:1 v/v) as eluent to give 8.98 g **3** as colorless oil in a yield of 95%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.75 (d, *J* = 1.23 Hz, 1H), 7.70 (d, *J* = 8.16 Hz, 1H), 7.66 (dd, *J* = 8.16 Hz, *J* = 1.50 Hz, 1H), 2.44 (t, *J* = 7.05 Hz, 2H), 1.59 (2H), 1.42 (2H), 1.31 (4H), 0.90 (t, *J* = 6.90 Hz, 3H).

4-Octylphthalonitrile (4). Into a **3** (1.89 g, 8.0 mmol) solution in 400 mL absolute ethanol was added Pd/C catalyst (weigh ratio 10%, 425 mg). The reaction mixture was stirred at room temperature under H_2 (about 2 atm). After 21 hrs the reaction was completed and the catalyst was carefully filtered. Upon evaporating off the solvent, the residue was purified by column chromatography on silica gel with petroleum ether and chloroform (1:1 v/v) as eluent to give 1.63 g **4** as colorless oil in a yield of 85%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.70 (d, *J* = 8.04 Hz, 1H), 7.60 (d, *J* = 1.38 Hz, 1H), 7.52 (dd, *J* = 8.04 Hz, *J* = 1.56 Hz, 1H), 2.73 (t, *J* = 7.80 Hz, 2H), 1.62 (2H), 1.28 (10H), 0.87 (t, *J* = 6.75 Hz, 3H). m/z (GC/MS-basic EI): 240 (M^+) (theoretical mass for $C_{16}H_{20}N_2$: 240.34).

2(3),9(10),16(17),23(24)-Tetraoctyl phthalocyaninatovanadyl (OVPc4C8).

4 (577 mg, 2.40 mmol) and vanadium (III) chloride (190 mg, 1.20 mmol) was dissolved in 4.0 mL of DMAE. The mixture was stirred at room temperature for 5 mins and then refluxed for 21 hrs under argon. The reaction mixture was cooled to room temperature. 10 mL of water was added and further refluxed for 6 hrs. The precipitate was filtered and washed with water until the filtrate became clear. The precipitate was dissolved in 50 mL of chloroform and dried with anhydrous $MgSO_4$. The solution was further condensed to 3 mL and reprecipitated in 30 mL of methanol. The resulting precipitate was purified by column chromatography on silica gel with toluene and methylene chloride (1:1) as eluent to give 260 mg **OVPc4C8** in a yield of 42%. IR (υ_{max}/cm^{-1}) (KBr): 734, 753, 826, 1003 (V=O), 1056, 1084 (C-N), 1135, 1161, 1337, 1404, 1457, 1503, 1614 (C=C ring), 2853, 2923, 2953. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.28 (b, 12H), 3.42 (b, 8H), 2.12 (b, 8H), 1.41 (b, 40H), 0.95 (b, 12H). m/z (MALDI-TOF): 1028.16 (MH^+) (theoretical mass: 1027.59). UV–vis ($CHCl_3$): 701, 666, 632, 346 nm. Anal. calcd. For $C_{64}H_{80}N_8OV$: C, 74.75; H, 7.84; N, 10.90. Found: C, 74.29; H, 8.25; N, 11.11.

2. Thermotropic Liquid Crystalline Properties

Table S1. Temperature-dependent X-ray diffraction data on **OVPc4C8**.

	d_{exp} (Å)	hk	d_{calc} (Å)	Lattice parameters (Å)
OVPc4C8	22.5	11	22.5	$a = 32.2$
Col_r	16.1	20	16.1	$b = 31.4$
(40 °C)	11.3	22	11.2	
	10.4	31	10.2	
	8.3	40	8.1	
	7.5	33	7.5	
	3.6 (π-π stacking)			
OVPc4C8	22.4	11	22.4	$a = 32.2$
Col_r	11.2	22	11.2	$b = 31.3$
(140 °C)	10.4	31	10.2	
	7.6	33	7.5	
	3.6 (π-π stacking)			

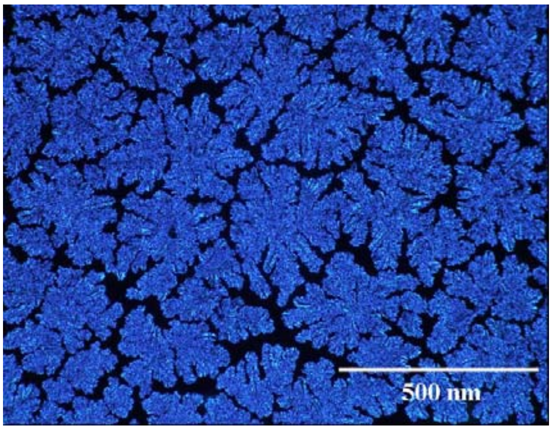


Figure S1. POM texture of **OVPc4C8** at 150 ^{o}C upon cooling from isotropic state.

3. Possible Model of the Molecular Arrangement in the Column

Form the temperature-XRD results of **OVPc4C8**, the molecules can form columnar rectangular mesophase with quasi-square lattice parameters a = 32.2 Å and b = 31.4 Å, indicating the intercolumnar distance is about 32 Å and the theoretical title angle of the molecules with respect to the columnar axis was about 54^{o} according the formula: $\Phi = \arccos\left(\frac{a}{b\sqrt{3}}\right)$.[2] The simple calculated molecular diameter of the **OVPc4C8** is about 33 Å, including the diameter of **OVPc** core about 15 Å from single crystal structure and the length of octyl chain with all-trans conformation about 9 Å. Since **OVPc4C8** has the axial substituent, it is not possible to form a simple face-to-face stacking column observed in liquid crystals of planar Pc, the **OVPc4C8** molecules must form a slipped π-π stacking concave and convex pairs and with a distance of 7 Å between the convex pairs along the columnar axis, i.e. the half diameter of **OVPc** core, as observed in the **OVPc** phase II.[3] The larger title angle is accorded with this packing model. So, the possible schematic representation of the 2D lattice is shown in figure S2a. Based on the above analysis, the discotic dimension (about 40 Å) are significantly larger than the intercolumnar distance (about 32 Å) derived form the X-ray measurements. A possible explanation of this discrepancy is the interdigitation of the regiorandom peripheral chains belonging to the molecules in the neighboring columns and strongly twisted form the plane of the **OVPc** core. As shown in figure S2b, the intracolumnar molecules should tilt along the *b* direction in order to keep the elliptical shape of the column in agreement with the *c*2mm symmetry.

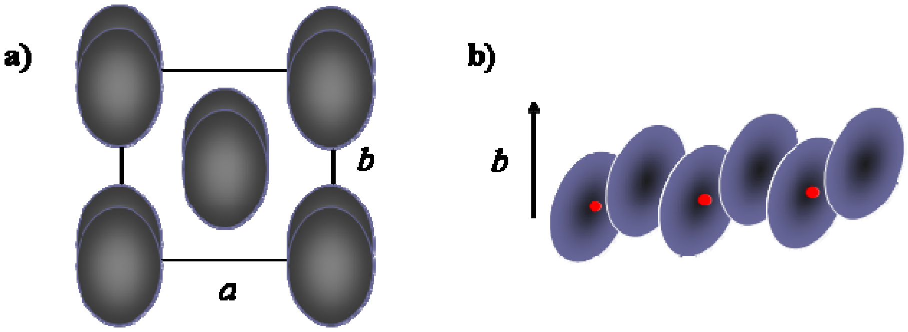


Figure S2. Schematic representation of staking of the **OVPc4C8** along the columnar axis from top (a) and side (b) view of the column.

4. Device Fabrication and Characterization

Top-contact OTFTs were constructed on the heavily n-doped Si substrates with 330 nm SiO_2 layer and a capacitance of 10 nF/cm^2. The SiO_2/Si substrates were modified by the self-assemble monolayer (SAMs) of PTS or OTS.[2] The PI dielectric layer (~ 100 nm) were prepared according to the reference.[4] The capacitance of resulting dielectric layer is about 8 nF/cm^2. Organic semiconductor layers (~40 nm) were deposited by spin-casting 7 mg/ml solution in chloroform at 1000 rpm for 60 sec under ambient atmosphere. After spin-coating, the samples were then annealed in a hot plate at 120 ^{o}C for 20 min. Finally, 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. The devices were post-annealed at 120 ^{o}C for 20 min. The electrical measurements were performed with two Keithley 236 measurement units at room temperature under ambient conditions.

Table S2. OTFTs device performance of **OVPc4C8** with different dielectric layer modification at an annealing temperature of 120 °C.

compound		μ_{TFT} (cm^2/V·s)	V_T (V)	I_{on}/I_{off}
OVPc4C8	OTS	$(2.5 \pm 0.5) \times 10^{-3}$	-2 – 2	$(1\text{-}2) \times 10^4$
	PTS	$(6.8 \pm 0.4) \times 10^{-3}$	-1 – 2	$(1\text{-}3) \times 10^4$
	PI	0.014 ± 0.003	0– 3	$(1\text{-}4) \times 10^3$

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