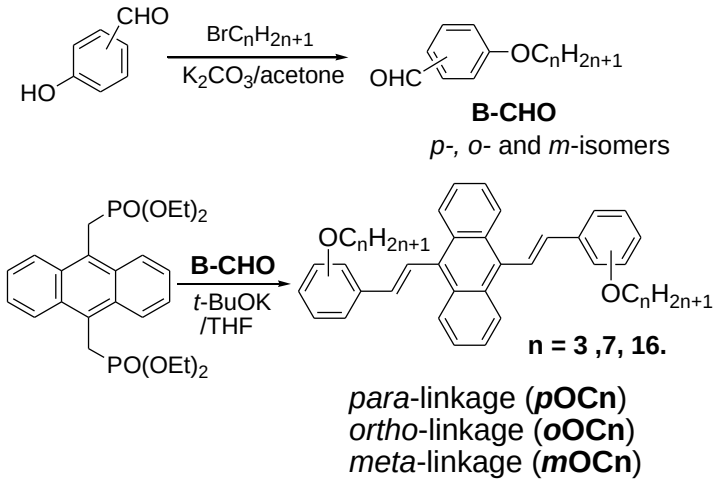
# Supporting Information

# Effect of Linking positions of Alkyloxy Chains on Piezochromic Luminescence of 9,10-Bis(alkoxystyryl)anthracenes

Wei Liu, Yalong Wang, Mingxiao Sun, Deteng Zhang, Meng Zheng and Wenjun Yang*

## Table of Content




**Scheme S1** Synthesis and structure of **OC*n*** isomers.

## Experimental section

**9,10-Bis(chloromethyl)anthracene.** To a stirred solution of anthracene (1.78 g, 10 mmol), dry $ZnCl_2$ (1.64 g, 12 mmol), paraformaldehyde (1.50 g, 50 mmol) in dioxane (20 mL) was slowly added concentrated aqueous hydrochloric acid (40 mL) at room temperature. After stirring slowly at gentle reflux for 3 h, heating was stopped and the mixture was allowed to stand for 16 h. The fine granular yellow solid was separated by filtration, and washed with $H_2O$ and dioxane to give a crude product. The crude product was recrystallized from toluene to give a yellowish solid (1.8 g, 64 %). $^1$H NMR (500 MHz, $CDCl_3$, ppm) δ 8.4 (m, 4H), 7.62 (m, 4H), 5.6 (s, 4H)

**9,10-bis(diethylphosphorylmethyl)anthracene.** A solution of 9,10-bis(chloromethyl)anthracene (7.8 g, 28.3 mmol) and triethyl phosphate 30 ml was stirred vigorously at gentle reflux for a night, cooling down and removed excess triethyl phosphate with reduced pressure distillation. The crude product was separated by silica gel column chromatography (ethyl acetate/petroleum ether, 1/1, v/v). A yellowish solid (9.3 g, 68.7 %) was obtained. $^1$H NMR (500 MHz, $CDCl_3$, ppm) δ 8.32 (d, 4H), 7.5 (d, 4H), 4.2 (d, 8H), 3.78 (d, 4H), 1.1 (t, 12H)

**4-Propoxybenzaldehyde.** $K_2CO_3$ (2.12 g, 19.64 mmol) and KI (catalytic amount) were added to a solution of 4-Hydroxy-benzaldehyde (2 g, 16.37 mmol) in dry DMF (20 mL), and the mixture was stirred at 80 °C. 1-Bromopropane (1.6 ml, 18.02 mmol) was slowly dropped into the mixture. The reaction lasted overnight at 80 °C. After cooling to room temperature, the mixture was poured into brine and extracted with dichloromethane. The organic phase was dried over $MgSO_4$ and the solvent was evaporated in vacuo. The product (2.00 g, 89.4 %) was obtained by silica gel column chromatography (ethyl acetate/ n-hexane, 1/10, v/v).

Other 4-alkoxybenzaldehyde, 3-alkoxybenzaldehyde and 2-alkoxybenzaldehyde were synthesized by the same procedure as described for 4-Propoxybenzaldehyde.

**9,10-Di(*p*-propoxystyryl)anthracenes (DSA-*p*-OC3).** 9,10-Bis(diethylphosphorylmethyl)anthracene (0.3 g, 0.63 mmol) and 4-Propoxy-benzaldehyde (0.20 g, 1.38 mmol) was dissolved in 20 mL of dry THF. Potassium tert-butoxide (0.15 g, 1.38 mmol) was added and the suspension was stirred at room temperature for 8 h. After added methyl alcohol into the mixture and a yellow-green solid separated out immediately, the THF was rotary evaporated, the residue was washing with methyl alcohol and the crude product was separated by silica gel column chromatography (petroleum ether/methylene chloride, 4/1, v/v). This afforded 0.23 g of compound **DSA-*p*-OC3** as a yellow-green solid with a yield of 82.5 %. $^{1}$H NMR (500 MHz, $CDCl_3$, ppm) δ 8.39 (m, 4H), 7.80, 7.76 (d, 2H), 7.62, 7.60 (d, 4H), 7.45 (m, 4H), 6.99, 6.97 (d, 4H), 6.85, 6.84 (d, 2H), 4.00, 3.99, 3.98 (t, 4H), 1.85 (m, 4H), 1.09, 1.07, 1.06 (t, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$, ppm) δ 159.21, 136.92, 132.81, 130.06, 129.66, 127.78, 126.55, 125.07, 122.79, 114.88, 69.71, 22.62, 10.56. Anal. Calcd for $C_{36}H_{34}O_2$: C, 86.71; H, 6.87; O, 6.42. Found: C, 86.65; H, 6.93.

Other 9,10-bis(*p*-alkyloxystyryl)anthracenes (**DSA-*p*-OC*n***), 9,10-bis(*m*-alkyloxystyryl)anthracenes (**DSA-*m*-OC*n***) and 9,10-bis(*o*-alkyloxystyryl)anthracenes (**DSA-*o*-OC*n***)were synthesized by the same procedure as described for **DSA-*p*-OC3**. All compounds only display one spot on TLC plate, and other samples are characterized only by $^{1}$H NMR, and the corresponding data are listed as follows：

**DSA-*p*-OC7**: $^{1}$H NMR (500 MHz, $CDCl_3$, ppm) δ 8.39(m, 4H), 7.78, 7.75(d, 2H), 7.61, 7.59 (d, 4H), 7.44 (m, 4H), 6.98, 6.97 (d, 4H), 6.87, 6.84 (d, 2H), 4.04, 4.02, 4.01 (t, 4H), 1.82 (m, 4H), 1.33 (m, 16H), 0.91, 0.90, 0.89 (t, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$, ppm) δ 159.23, 136.94, 132.82, 130.05, 129.67, 127.78, 126.55, 125.07, 122.79, 114.89, 68.23, 31.81, 29.31, 29.09, 26.04, 22.63, 14.06. Anal. Calcd for $C_{44}H_{50}O_2$: C, 86.51; H, 8.25; O, 5.24. Found: C, 86.39; H, 8.29.

**DSA-*p*-OC16**: $^{1}$H NMR (500 MHz, $CDCl_3$, ppm) δ 8.38 (m, 4H), 7.76 (d, 2H), 7.60 (d, 4H), 7.44 (m, 4H), 6.97 (d, 4H), 6.85 (d, 2H), 4.02 (t, 4H), 1.81 (m, 4H), 1.33 (m, 52H), 0.86 (t, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$, ppm) δ 159.74, 136.92, 132.80, 130.35, 129.77, 127.83, 126.54, 125.11, 123.05, 114.37, 68.95, 31.83, 31.46, 29.68, 29.63, 29.55, 29.43, 29.39, 29.31, 29.28, 29.23, 29,12, 29.02, 25.86, 22.78, 14.20. Anal. Calcd for $C_{62}H_{86}O_2$: C, 86.25; H, 10.04; O, 3.71. Found: C, 86.09; H, 10.13.

**DSA-*m*-OC3**: $^{1}$H NMR (500 MHz, $CDCl_3$, ppm) δ 8.38 (m, 4H), 7.93, 7.90 (d, 2H), 7.46 (m, 4H), 7.37, 7.35 (d, 2H), 7.26, 7.24 (d, 4H), 6.91, 6.90, 6.88 (t, 4H), 4.03,

4.01, 4.00 (t, 4H), 1.85 (m, 4H), 1.09, 1.07, 1.06 (t, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$, ppm) δ 159.66, 138.72, 137.45, 132.65, 129.79, 129.57, 126.47, 125.39, 125.25, 119.16, 114.14, 112.63, 69.63, 22.68, 10.60. Anal. Calcd for $C_{36}H_{34}O_2$: C, 86.71; H, 6.87; O, 6.42. Found: C, 86.64; H, 6.92.

**DSA-*m*-OC7**: $^1$H NMR (500 MHz, $CDCl_3$, ppm) δ 8.39 (m, 4H), 7.94, 7.91 (d, 2H), 7.47 (m, 4H), 7.38, 7.37 (d, 2H), 7.27, 7.26 (d, 4H), 6.92, 6.91, 6.89 (t, 4H), 4.07, 4.06, 4.04 (t, 4H), 1.84 (m, 4H), 0.92, 0.90, 0.89 (t, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$, ppm) δ 159.71, 138.75, 137.49, 132.69, 129.81, 129.62, 126.50, 125.28, 125.11, 119.17, 114.18, 112.66, 68.17, 31.83, 29.40, 29.12, 26.10, 22.64, 14.12. Anal. Calcd for $C_{44}H_{50}O_2$: C, 86.51; H, 8.25; O, 5.24. Found: C, 86.42; H, 8.30.

**DSA-*m*-OC16**: $^1$H NMR (500 MHz, $CDCl_3$, ppm) δ 8.39 (m, 4H), 7.94, 7.91 (d, 2H), 7.47 (m, 4H), 7.38, 7.35 (d, 2H), 7.24, 7.22 (d, 4H), 6.92, 6.90, 6.89 (t, 4H), 4.07, 4.05, 4.04 (t, 4H), 1.84 (m, 4H), 0.89, 0.87, 0.86 (t, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$, ppm) δ 159.67, 138.72, 137.46, 132.65, 129.77, 129.58, 126.46, 125.25, 124.97, 119.14, 114.14, 112.61, 68.14, 31.92, 31.44, 29.66, 29.61, 29.55, 29.42, 29.37, 29.29, 29.25, 29.21, 29,11, 28.97, 26.11, 22.68, 14.09. Anal. Calcd for $C_{62}H_{86}O_2$: C, 86.25; H, 10.04; O, 3.71. Found: C, 86.09; H, 10.12.

**DSA-*o*-OC3**: $^1$H NMR (500 MHz, $CDCl_3$, ppm) δ 8.48 (m, 4H), 7.98, 7.96 (d, 2H), 7.82, 7.80 (d, 2H), 7.47 (m, 4H), 7.32, 7.31 (d, 4H), 7.07, 7.06, 7.04 (t, 2H), 6.99, 6.98 (d, 2H), 4.02, 4.01, 4.00 (t, 4H), 1.82 (m, 4H), 1.03, 1.01, 1.00 (t, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$, ppm) δ 156.72, 133.33, 132.91, 129.55, 128.91, 127.17, 126.64, 125.78, 125.02, 120.59, 111.96, 69.84, 22.68, 10.75. Anal. Calcd for $C_{36}H_{34}O_2$: C, 86.71; H, 6.87; O, 6.42. Found: C, 86.67; H, 6.93.

**DSA-*o*-OC7**: $^1$H NMR (500 MHz, $CDCl_3$, ppm) δ 8.48 (m, 4H), 7.99, 7.96 (d, 2H), 7.81, 7.80 (d, 2H), 7.47 (m, 4H), 7.32, 7.30 (d, 4H), 7.08, 7.07, 7.05 (t, 2H), 6.99, 6.97 (d, 2H), 4.06, 4.05, 4.04 (t, 4H), 1.81 (m, 4H), 1.35 (m,16H), 0.81, 0.79, 0.78 (t, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$, ppm) δ 156.81, 133.34, 132.97, 129.60, 128.88, 127.23, 126.64, 125.85, 125.01, 120.01, 112.09, 68.43, 31.72, 29.37, 29.02, 26.13, 22.54, 14.03. Anal. Calcd for $C_{62}H_{86}O_2$: C, 86.51; H, 8.25; O, 5.24. Found: C, 86.41; H, 8.32.

**DSA-*o*-OC16**: $^1$H NMR (500 MHz, $CDCl_3$, ppm) δ 8.47 (m, 4H), 7.99, 7.96 (d, 2H), 7.82, 7.81 (d, 2H), 7.46 (m, 4H), 7.31, 7.29 (d, 4H), 7.08, 7.06, 7.05 (t, 2H), 6.98, 6.97 (d, 2H), 4.06, 4.05, 4.04 (t, 4H), 1.81 (m, 4H), 1.35 (m, 52H), 0.88, 0.87, 0.85 (t, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$, ppm) δ 156.74, 133.31, 132.95, 129.53, 128.88, 127.23, 126.62, 125.81, 125.00, 120.56, 111.98, 68.35, 31.92, 31.46, 29.68, 29.63,

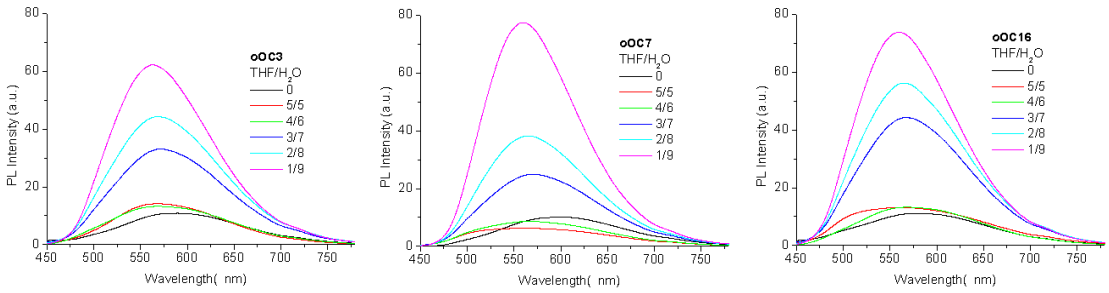
29.55, 29.43, 29.39, 29.31, 29.28, 29.23, 29,12, 29.02, 26.15, 22.69, 14.11. Anal. Calcd for $C_{62}H_{86}O_2$: C, 86.25; H, 10.04; O, 3.71. Found: C, 86.10; H, 10.12.

## Measurement

NMR spectra were recorded in $CDCl_3$ on a Bruker-AC500 spectrometer (500 MHz for $^1H$ NMR and 125 MHz for $^{13}C$ NMR) with tetramethylsilane (TMS) as the internal standard. The elemental analysis was performed on Perkin–Elmer 2400. UV-vis absorption and diffuse reflectance absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Fluorescence measurements were carried out with Hitachi F-4600 spectrophotometer. The fluorescence quantum yield (Φ) was determined by the dilution method using fluorescein in water (pH = 11) as the reference in which the absolute absorption maxima are less than 0.1. Powder wide-angle X-ray diffraction experiment was performed on a Powder X-ray Diffractometry (INCA Energy, Oxford Instruments) operating at 3 kW. Differential scanning calorimetry (DSC) curves were determined on a Netzsch DSC 204F1 at a heating rate of 10 °C /min.

Grinding experiment: Pristine solid was put on a glass plate and then ground with a metal spatula at room temperature. Pressing experiment: A quantity of fluorophore and KBr powder was simply mixed in a mortar and then pressed with IR pellet press for 1 min at room temperature under the pressure of 1500 psi. Annealing experiments: the ground sample was put into an oven with the temperature $T_m - 30$ ($T_m$ is the isotropic melt point of each compound) for 3 min. Solvent- fuming experiment: The ground sample was exposed to the dichloromethane vapor for 1 min in a sealed beaker at room temperature.

Aqueous dispersion was prepared by adding slowly different amount of deionized water to the THF solution of fluorophore with the concentration of $1.0 \times 10^{-4}$ M under vigorous stirring. The apparent concentration of aqueous dispersion was kept at $1.0 \times 10^{-5}$ M.



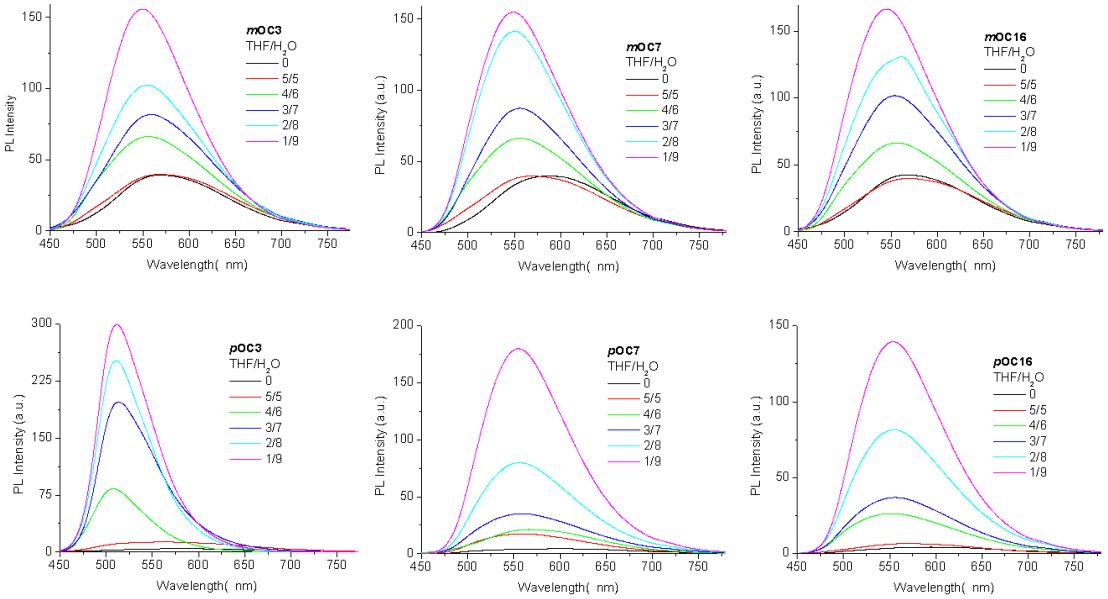



**Fig. S1** Emission spectra of **OC*n*** in different ratio of THF/water mixture.

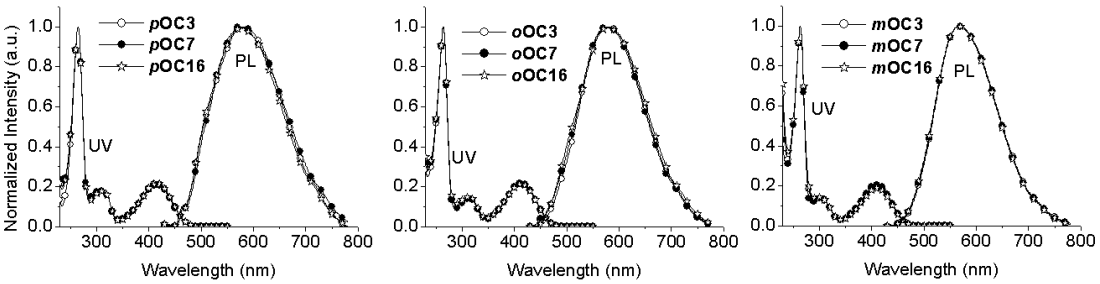



**Fig. S2** Normalized emission (PL) and absorption (UV) spectra of **OC*n*** in THF.

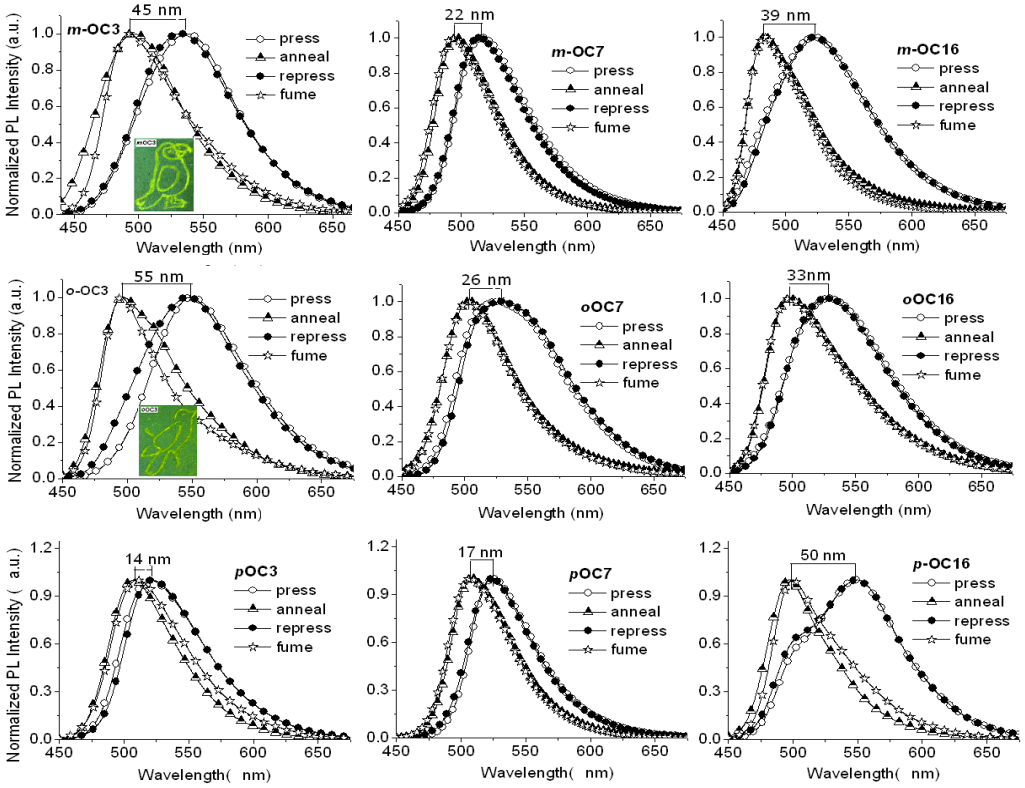


**Fig. S3** Normalized fluorescence emission spectra of **OC*n*** upon brief pressing, thermal-annealing, re-pressing and solvent-fuming. Inset: A piece of filter paper soaked with ***m*OC3** or ***o*OC3** is drawn a bird using a metal spatula and illuminated under a 365 nm UV lamp.

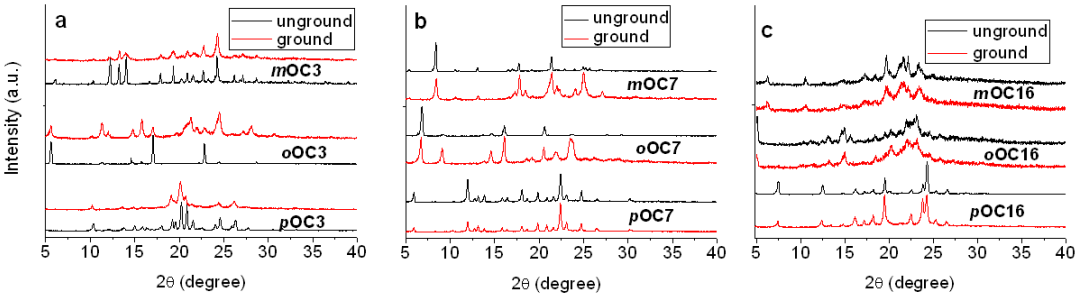



**Fig. S4** Powder X-ray diffraction patterns of pristine and ground **OC*n*** samples at room temperature.

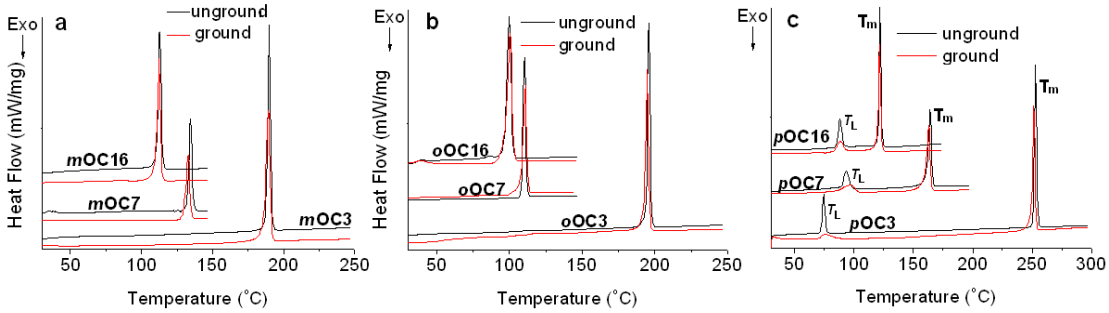
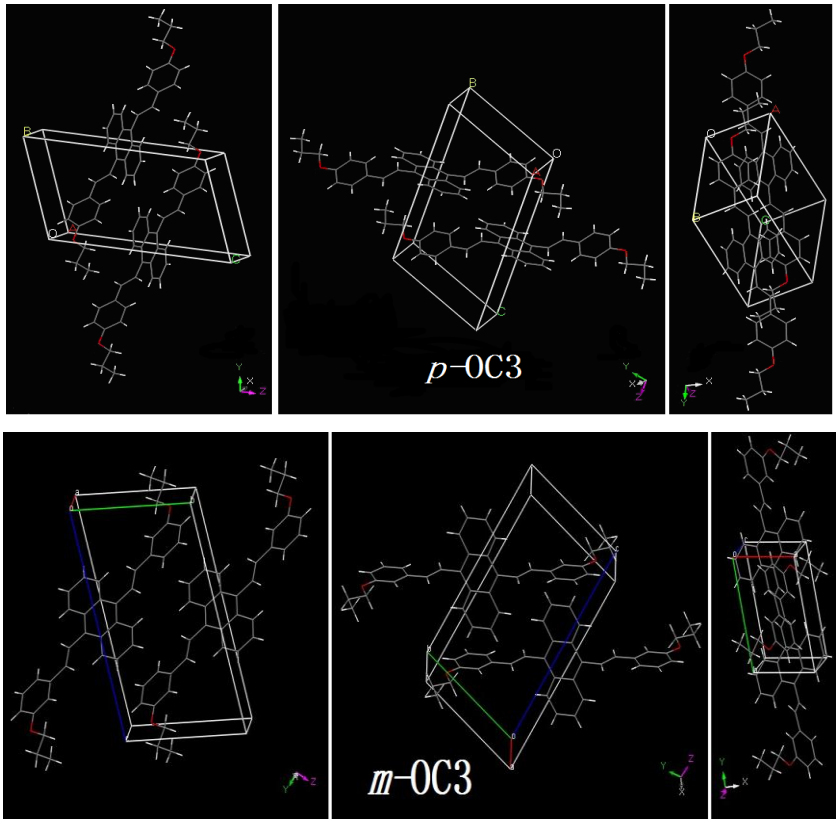



**Fig. S5** DSC curves of pristine and ground **OC*n*** samples.



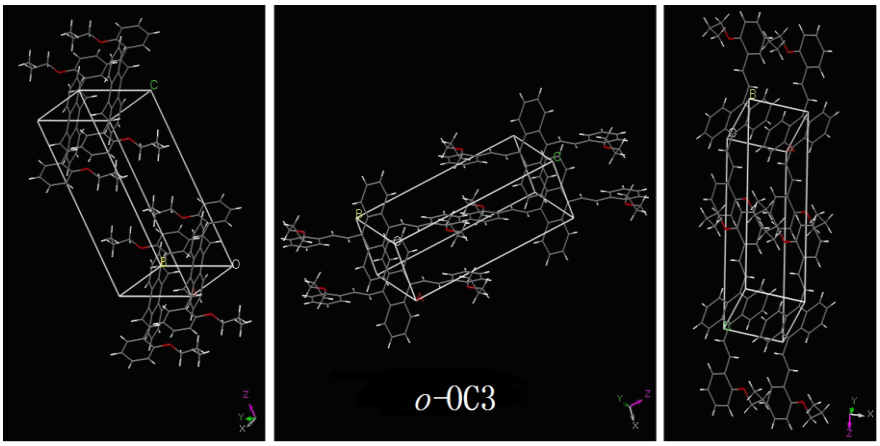



**Fig. S6** Unit cell structures of 9,10-bis(*p*-/*m*-/*o*-propoxystyryl)anthracenes (***p*OC3**, ***m*OC3** and ***o*OC3**) in the crystal.

**Table S1** Crystal Data and Structure Refinement for ***p*-OC3, *m*-OC3** and ***o*-OC3**

| Identification code | ***p*-OC3** | ***m*-OC3** | ***o*-OC3** |
|---|---|---|---|
| Empirical formula | $C_{36}$ $H_{34}$ $O_2$ | $C_{36}$ $H_{34}$ $O_2$ | $C_{36}$ $H_{34}$ $O_2$ |
| Formula weight | 498.63 | 498.63 | 498.63 |
| Temperature | 291(2) K | 291(2) K | 296(2)K |
| Wavelength | 0.71 073 Å | 0.71073 Å | 0.71073 Å |
| Crystal system, space group | Triclinic, P-1 | Triclinic, P-1 | Triclinic, P-1 |
| a, Å | 5.4312(11) | 5.4269(11) | 5.105(12) |
| b, Å | 8.8724(18) | 8.9384(18) | 8.65(2) |
| b, Å | 15.066(3) | 14.968(3) | 15.66(4) |
| Alpha, deg | 102.61(3) | 74.64(3) | 85.57 (3) |
| Beta, deg | 98.34(3) | 81.57(3) | 82.78(3) |
| Gamma, deg | 101.81(3) | 77.00(3) | 85.67(3) |
| Volume | 679.6(2) $Å^3$ | 679.3(2) $Å^3$ | 683(3) $Å^3$ |
| Z | 1 | 1 | 1 |
| Calculated density | 1.218 $Mg/m^3$ | 1.219 $Mg/m^3$ | 1.213 $Mg/m^3$ |
| F(000) | 266 | 266 | 266 |
| Absorption coefficient | 0.074$mm^{-1}$ | 0.074$mm^{-1}$ | 0.073$mm^{-1}$ |