Supporting Information

Supramolecular Organization and Photovoltaics of Triangle-shaped Discotic Graphenes with Swallow-tailed Alkyl Substituents**

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Experimental Section:

^1H NMR and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker DPX 250, and Bruker DRX 500. UV-visible spectra were measured on a Perkin-Elmer Lambda 9 spectrophotometer at room temperature. Fluorescence spectra were determined on a Spex Fluorolog II (212). FD mass measurements were carried out on a VG instruments ZAB 2-SE-FPD. High-resolution MALDI-TOF mass spectra were recorded on a Bruker Reflex II-TOF Spectrometer using a 337 nm nitrogen laser with TCNQ as matrix. DSC was measured by Mettler DSC 30 with a heating rate of 10 K/min from –150 °C to 250°C. The 2D-WAXS experiments were performed by means of a rotating anode (Rigaku 18 kW) X-ray beam with a pinhole collimation and a 2D Siemens detector. A double graphite monochromator for the Cu-Kα radiation (λ=0.154 nm) was used.
Unless otherwise noted, all starting materials were purchased from Aldrich, Acros, ABCR and use as received without further purification.

1,3,5-Tris(2’-(4’’-(4’’’-(2’’’’-hexyl-decyl))phenyl)biphenyl)benzene (2a)

Preparation of Negishi reagent
In a dry flask, 384mg (15.9mmol) Zn powder were initially treated with 60mg (5%) iodine-crystals in 8ml DMA, then 1.15g (3.94mmol) 2-hexyl-decylbromide was added and the resulting mixture was mixed at 80°C for 24 h.
The above Negishi reagent was transferred *via* cannula to the flask which contained with 500mg (0.438mmol) 1,3,5-tris[2’-(4’’-(4’’’-iodophenyl))biphenyl]benzene and 36mg (10mol%) dichloro[1,1’-bis(diphenylphosphino)ferrocene]palladium(II). The mixture was stirred overnight under 50 °C. The reaction was quenched by adding aqueous HCl solution, and extracted with dichloromethane, the organic solvent was removed under vacuum, and purified by column chromatography (silica gel, Hexane to Hexane:DCM=6:1) to afford 270mg (43%) of target compound as a colorless oil. FD-MS (8 KV): m/z 1437.3, calcd.: 1436.25 (M^+). ^1H NMR (250 MHz, CD_2Cl_2): δ ppm 7.38~7.16(m, 27H), 6.94~6.91(m, 9H), 6.78(s, 3H), 2.57(d, 6H, J=6.62Hz), 1.65(m, 3H), 1.40~1.22(m, 72H), 0.84(m, 18H). ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 141.57, 141.53, 140.98, 140.83, 140.64, 139.38, 138.19, 130.74, 130.40, 130.07, 130.43, 130.07, 127.69, 127.57, 126.94, 126.71, 40.62, 40.15, 33.59, 32.31, 30.44, 30.09, 30.04, 29.74, 26.97, 26.94, 23.08, 14.27.

1,3,5-Tris(2’-(4’’-(4’’’-(2’’’’-decyl-tetradecyl))phenyl)biphenyl)benzene (2b)

The above Negishi reagent was transferred *via* cannula to the flask which contained with 500mg (0.438mmol) 1,3,5-tris[2’-(4’’-(4’’’-iodophenyl))biphenyl]benzene and 36mg (10mol%) dichloro[1,1’-bis(diphenylphosphino)ferrocene]palladium(II). The mixture was stirred overnight under 50 °C. The reaction was quenched by adding aqueous HCl solution, and extracted with dichloromethane, the organic solvent was removed under vacuum, and purified by column chromatography (silica gel, Hexane to Hexane:DCM=6:1) to afford 230 mg (30%) of target compound as a colorless oil. FD-MS (8 KV): m/z 1774.0, calcd.: 1772.89 (M^+). ^{1}H NMR (250 MHz, CD_2Cl_2): δ ppm 7.35~7.16(m, 27H), 6.97~6.88(m, 9H), 6.78(s, 3H), 2.58(d, 6H, J=6.62Hz), 1.66(m, 3H), 1.41~1.23(m, 120H), 0.86(m, 18H). ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ ppm 141.59, 141.55,141.02, 140.87, 140.62,139.32, 138.18, 130.70, 130.40, 130.07, 129.99, 127.67, 127.55, 126.94, 126.71, 40.64, 40.16, 33.59, 32.33, 30.45, 30.11, 30.07, 29.78, 26.99, 23.08, 14.27.

Triangle-($C_{10,\,6}$)$_3$ (3a)

156 mg (0.109mmol) **2a** was dissolved in 60ml dichloromethane, the solution was then degassed by bubbling through argon for 20 min, and then 1.58g (5eq/H) $FeCl_3$ in 4ml CH_3NO_2 was added dropwise. After being stirred for 45min, the reaction was quenched by adding 50ml methanol. The yellow precipitate was collected, washed by methanol, and passed through the short column (Silica gel, hot toluene), the most organic solvent was removed under vaccum and methanol was added to precipitate the yellow solid, the final yellow sticky powder was dried under vaccum (89%). MALDITOF-MS (TCNQ as matrix): m/z=1418.2701, calcd. 1418.11 for $C_{108}H_{120}$.

^{1}H NMR can not be measured due to the less solubility.

^{13}H NMR can not be measured due to the large disc core and less solubility.

Elemental Analysis: Calculated: C 91.48, H 8.53; Found: C 90.89, H 8.68.

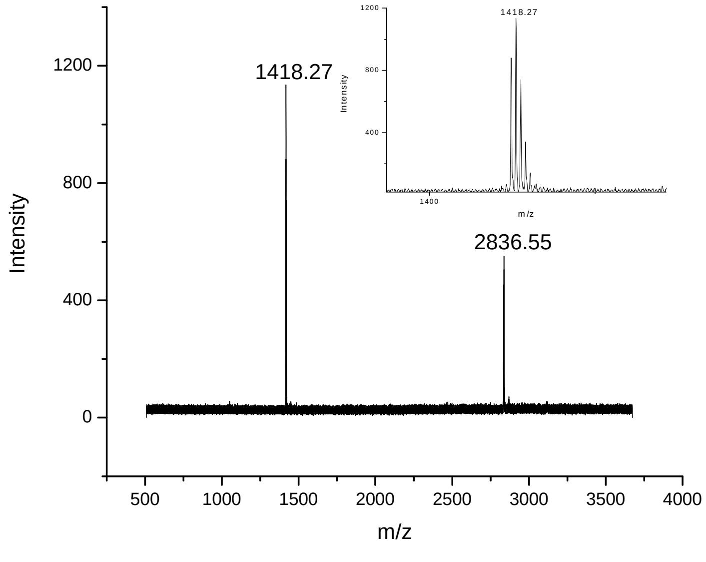

Figure S1. MALDIT-TOF MS spectrum of **3a**.

Triangle-($C_{14,\,10}$)$_3$ (3b)

126 mg (0.0711mmol) **2b** was dissolved in 60ml dichloromethane, the solution was then degassed by bubbling through argon for 20 min, and then 1.04g (5eq/H) $FeCl_3$ in 4ml

CH_3NO_2 was added dropwise. After being stirred for 45min, the reaction was quenched by adding 50ml methanol. The yellow precipitate was collected, washed by methanol, and passed through the short column (Silica gel, hot toluene), the most organic solvent was removed under vaccum and methanol was added to precipitate the yellow solid, the final yellow sticky powder was dried under vaccum (86%). MALDITOF-MS (TCNQ as matrix): m/z=1754.4110, calcd. 1574.75 for $C_{132}H_{168}$.

^{1}H NMR (500MHz, CD_2Cl_2, 140°C) : δ ppm 8.57(br, 18H), 7.70(br, 3H), 3.20(br, 6H), 2.22(m, 3H), 1.75~1.31(m, 120H), 0.89(m, 18H).

^{13}H NMR can not be measured due to the large disc core and less solubility.

Elemental Analysis: Calculated: C 90.35, H 9.65; Found: C 90.12, H 9.81.

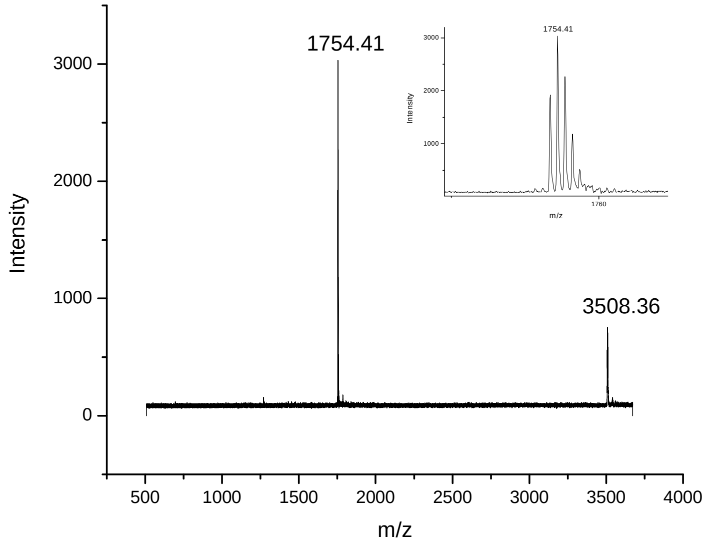

Figure S2. MALDIT-TOF MS spectrum of **3b**.

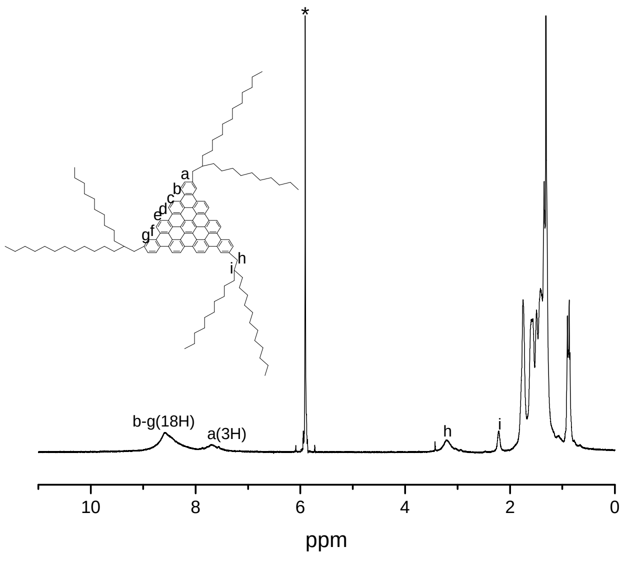

Figure S3. ^{1}H NMR spectrum of **3a** at 140°C in $CDCl_2CDCl_2$ (*).

Fabrication of photovoltics device

The device was fabricated by spin-coating **3a** or **3b**: perylenediimide blend (4:6) solutions (15mg/ml) onto ITO substrates pre-treated with acetone and isopropanol in an ultrasonic bath followed by cleaning for 10 min with oxygen plasma. The blend film was then annealed at 120 ℃ for 1h. 100nm thick silver was subsequently evaporated through a mask on the surface to form the cathode.

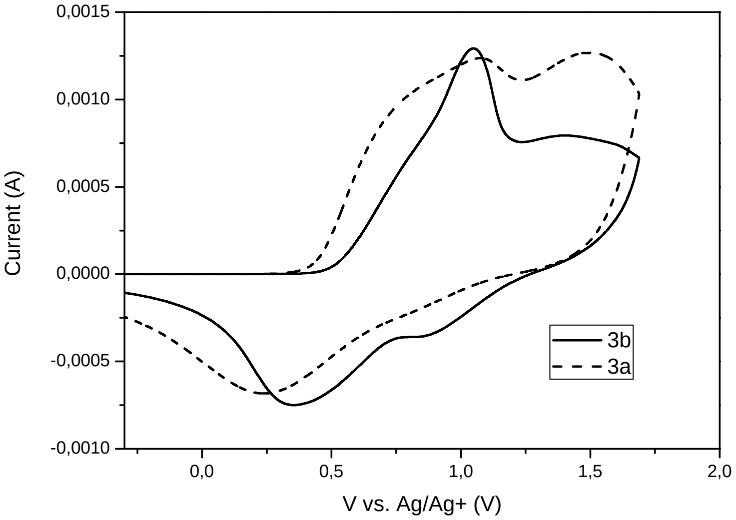

Figure S4. Cyclic voltammetry curve of **3a** and **3b** spin-coated on ITO glass; scanning rate at 25 mVs^{-1}.

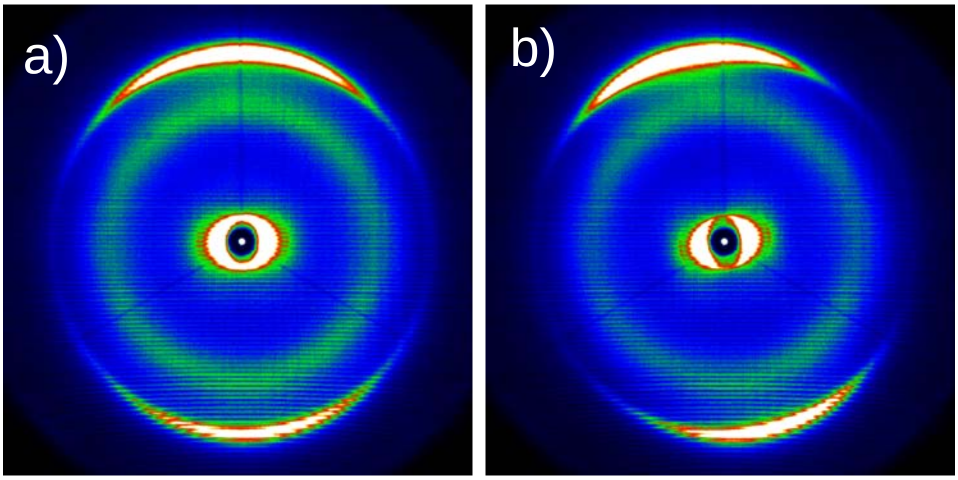

Figure S5. 2D WAXS pattern of **3a** recorded at 30 °C a) before and b) after annealing. Different annealing temperatures have been investigated, but no effect on the order could be observed.

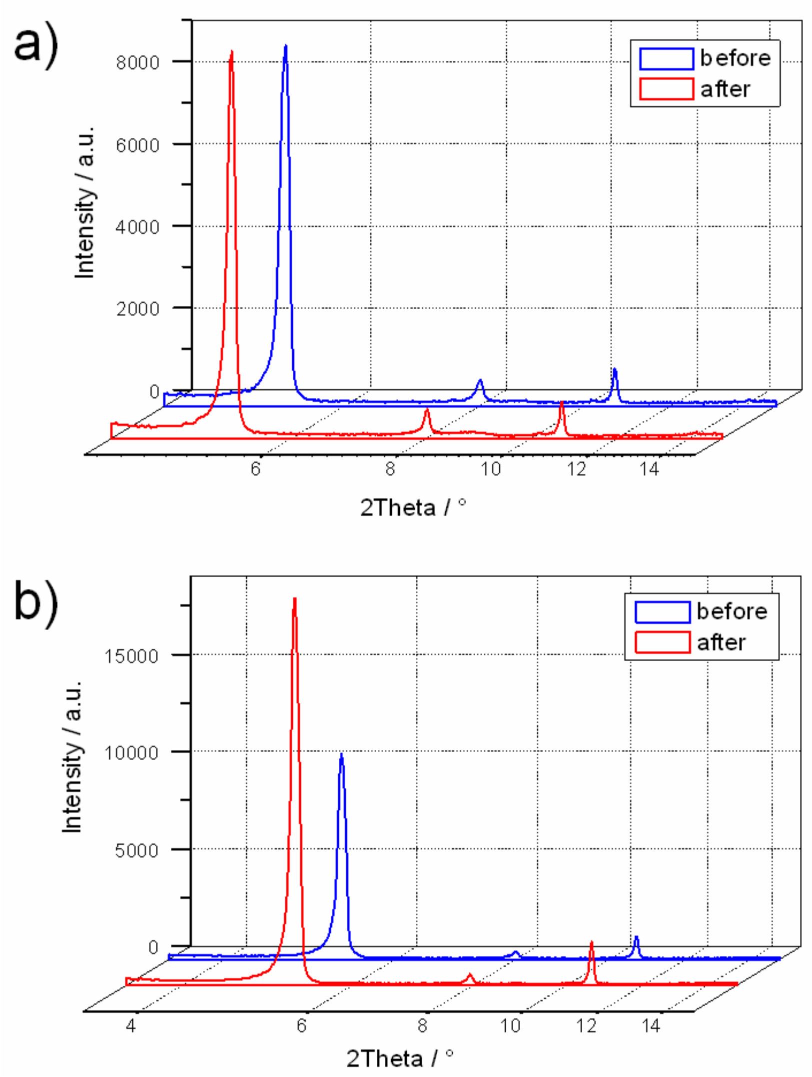

Figure S6. Thin film diffraction of a) **3a** and b) **3b** before and after annealing of spin-coated layers. For comparisons, the diffractorgram before annealing is shifted by 0.5° to lower angles.