Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

# Waveguiding Properties of Perylene Microcrystals Synthesized by Retarding the Growth along π-Stack Direction

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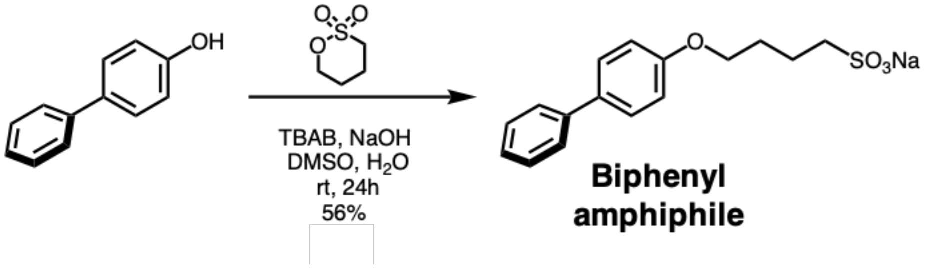
## Table of Contents

# 1.0 General Information

Reagents used for structure directing agent synthesis were purchased from Sigma Aldrich, AK Scientific, Fisher, Acros, Alfa Aesar, TCI and Accela. Perylene was purchased from TCI and used as received. Control molecule sodium dodecyl sulfate was purchased from Sigma Aldrich and used as received. All air or moisture-sensitive manipulations were performed under nitrogen atmosphere using standard schlenk techniques. All glassware was oven-dried prior to use. Unless otherwise stated, all starting materials and reagents were used without further purification. $^1$H and $^{13}$C NMR spectra were recorded on Varian 400-MR NMR. Chemical shifts are reported in $\delta$ (ppm) relative to the residual solvent peak $CD_3OD$: 3.31 for $^1$H, and $CD_3OD$: 49.00 for $^{13}$C. Coupling constants (*J*) are expressed in Hertz (Hz). Splitting patterns are designated as s(singlet), br(broad signal), d(doublet), t(triplet), dd(doublet of doublets), dt(doublet of triplets), dq(doublet of quartets), m(multiplet), and q(quartet). High resolution EI mass spectra were recorded on a Micromass 70-VSE spectrometer. High resolution ESI mass spectra were recorded on a Waters Q-TOF Ultima ESI spectrometer. Scanning Electron Microscope (SEM) images were taken on a Zeiss SUPRA55-VP at an acceleration voltage of 1kV. Transmission Electron Microscope (TEM) images and Selected Area Electron Diffraction (SAED) patterns were taken on a JEM-2100plus with a voltage of 200 kV, using a LaB6 electron source. Powder XRD (PXRD) for microcrystals were recorded in both transmission and reflection mode. The transmission mode PXRD was recorded on a Bruker Apex DUO equipped with an APEXII CCD detector using a Cu IμS source. A series of 360$^o$ phi scans were collected and data were integrated in the $2\theta$ range 5$^o$ to 45$^o$. The reflection mode PXRD was recorded on a Rigaku Ultima IV with Cu-K <α> radiation (40kV, 30mA), and a D/tex Ultra silicon strip detector. Data was collected in the $2\theta$ range 5$^o$ to 45$^o$. UV-vis adsorption spectra were recorded on an Agilent Technologies Cary Series 5000 UV-vis-NIR Spectrophotometer. Fluorescence emission and excitation spectra were recorded on a Horiba Scientific FluoroMax-4 Spectrofluorometer. Computational calculations were carried out using Biovia Materials Studio 2019.[1] The time-resolved photoluminescence date (lifetimes) were obtained with an avalanche photodiode detector (ADP) and time-correlated single photon counting (TCSPC) technique (PicoQuant HydraHarp) with a pulsed 405 nm laser. The samples were placed on an inverted Nikon microscope with a magnification of 60x. The incident laser fluence is 0.3 μJ/cm$^2$ with a repetition rate of 10 MHz. For the photoluminescence, the samples were placed on an inverted Nikon microscope and excited with a fiber-coupled 450 nm cw laser source. The incident fluence is 1.5 μJ/cm$^2$ and the exposure time is 0.1 seconds. For the waveguiding images, the perylene rod was photoexcited at one end and the signals collected from different spots along the nanorod by finely adjusting the fiber position relative to the spectrometer.

# 2.0 Synthesis of Biphenyl Amphiphile

**Scheme S1**: Synthesis of biphenyl amphiphile



Sodium 4-([1,1’-biphenyl]-4-yloxy)butane-1-sulfonate: [1,1’-biphenyl]-4-ol (3 g, 1 equivalent), tetra-n-butylammonium bromide (0.1 equivalent), and sodium hydroxide (10 equivalents) were dissolved in dimethyl sulfoxide (25 mL) and water (10 mL). 1,4-butane sultone (3 equivalents) was added and the reaction was stirred at rt for 24 h. The reaction mixture was neutralized with HCl, then crashed into acetone, the solid was collected via vacuum filtration. The solid was recrystallized from water and dimethyl sulfoxide to yield 3.25 g white solid (56% yield). $^1$H NMR (400 MHz, Methanol-$d_4$): δ 1.90-2.04 (m, 4H), 2.89 (m, 2H), 4.05 (t, $J$ = 5.9 Hz, 2H), 6.98 (d, $J$ = 8.7 Hz, 2H), 7.25 (t, $J$ = 7.4, 1H), 7.38 (t, $J$ = 7.7 Hz, 2H), 7.53 (dd, $J$ = 11.9, 8.3 Hz, 4H). $^{13}$C NMR (400 MHz, Methanol-$d_4$): δ 24.23, 30.73, 53.60, 69.93, 117.13, 128.75, 130.18, 130.95, 136.13, 143.46, 161.34 ppm. High-Res Mass Spec (ESI): M$^+$ 305.0850 (measured), 305.0848 (calculated).

# 3.0 Microcrystal Synthesis

### 3.1 Method of Microcrystal Synthesis

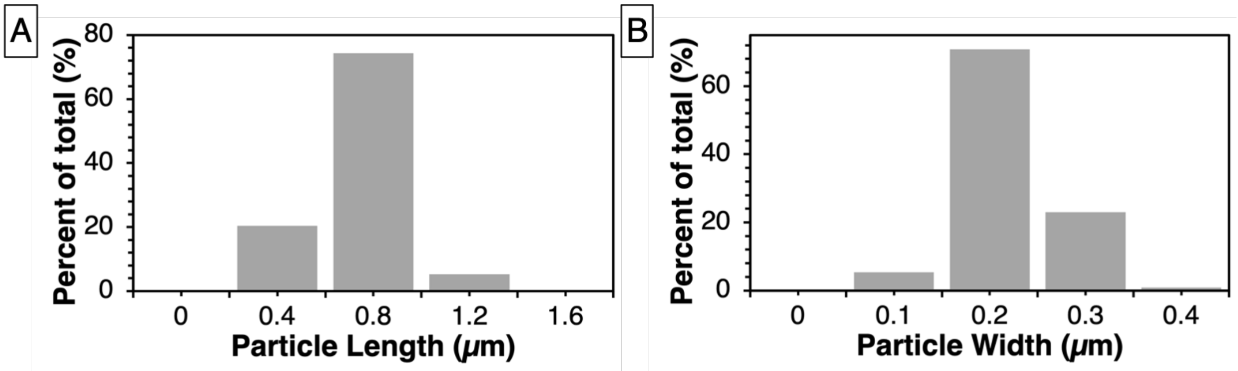
In the typical preparation, 0.5 mL of 0.5 mM perylene in THF were quickly injected into 2.5 mL of 10 mM aqueous amphiphile. The solutions were then rested undisturbed at room temperature for 24 hours. The perylene/THF solutions were heated to 50 °C and then allowed to slowly come to room temperature before use. The samples were protected from light during growth. After the 24 hour growth time, the solutions were centrifuged at 24,000 rpm for 30 minutes, then the supernatant was poured off and the microcrystals were sonicated in fresh water for about 30 seconds. After sonication the samples were then centrifuged again for 30 minutes. The sonication-centrifugation was repeated 3 more times. The microcrystals were re-suspended in fresh water for analysis.

For scanning electron microscope (SEM) imaging, the microcrystals were drop-cast onto aluminum stubs. For transmission electron microscope (TEM) imaging and selected area electron diffraction the microcrystals were drop-cast onto Copper Formvar Carbon grid.

### 3.2 Perylene rod size analysis

MC size was calculated by measuring 200+ MCs across multiple images for each sample. ImageJ[2] was used to measure MC size. Polydispersity was calculated by taking the ratio of the standard deviation over the average.

**Figure S1**: (a) perylene rods length and (b) width distribution



### 3.3 Perylene plates

**Figure S2**: SEM image of perylene plates grown in CTAB

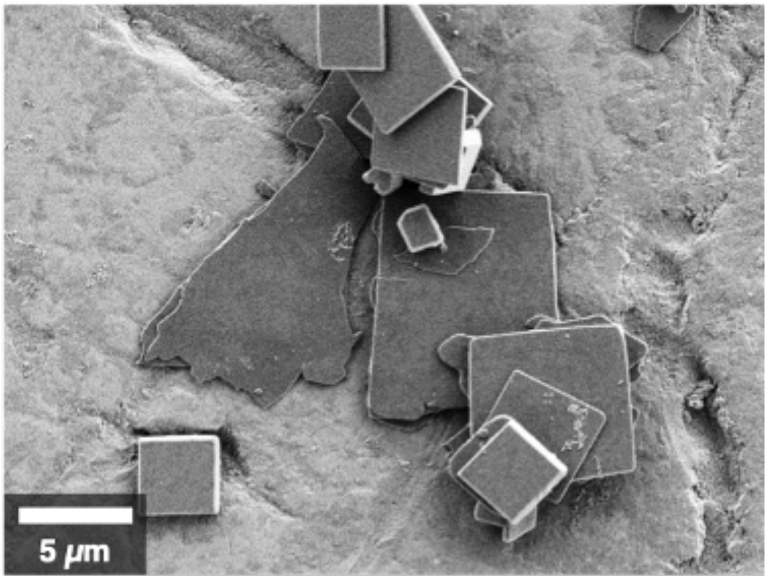
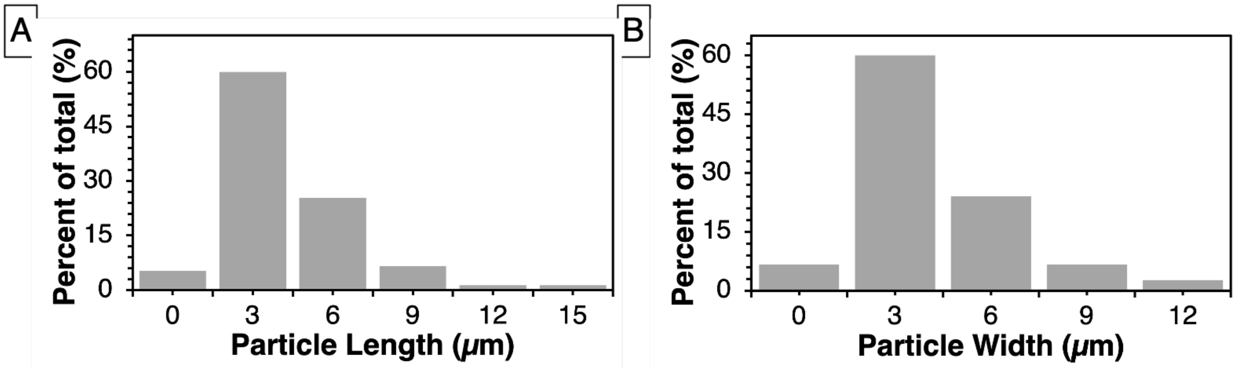
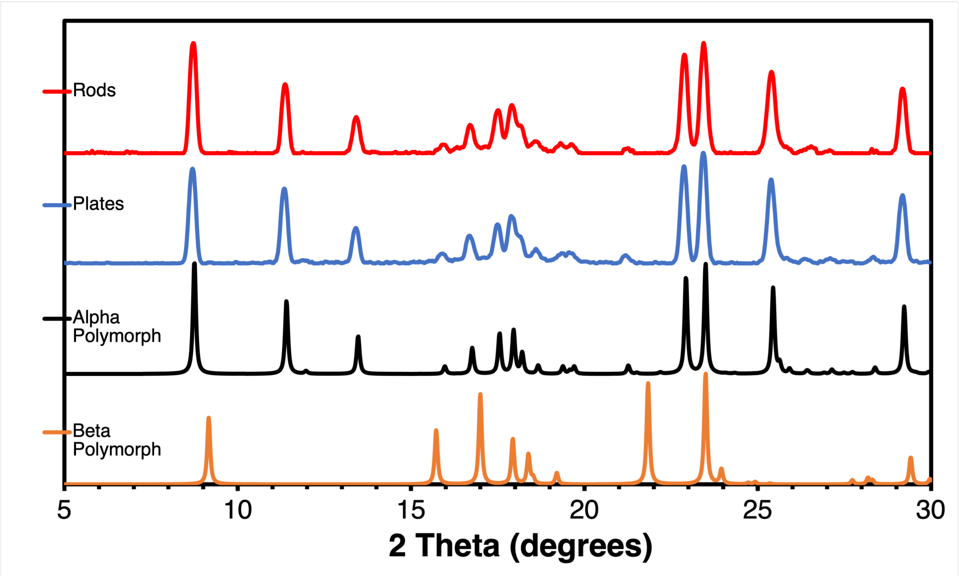


**Figure S3**: (a) perylene plates (grown in CTAB) length and (b) width distribution



# 4.0 Transmission Mode PXRD

**Figure S4**: Transmission mode PXRD of perylene MCs and calculated patterns of $\alpha$ and $\beta$ phases.



## 5.0 Crystal Facets

**Figure S5**: Theoretical and experimental angles on perylene rods with {0 1 1} and {1 0 0} faces blocked. The theoretical rod bound by the {0 1 1} and {1 0 0} faces was generated using the Vesta Software.[3]

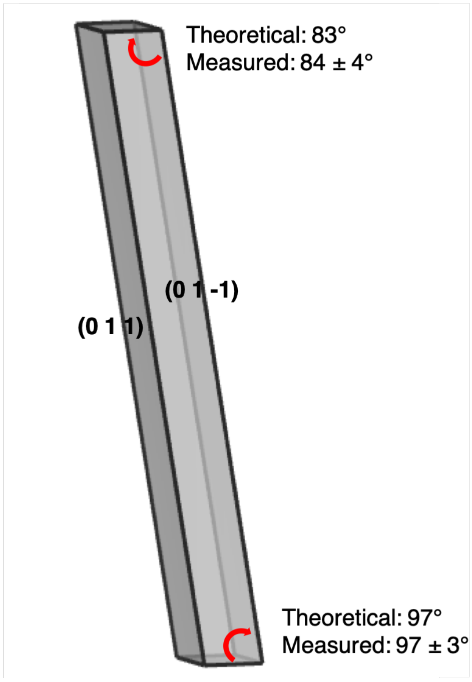


**Figure S6:** Growth and equilibrium morphologies of perylene calculated using Materials Studio

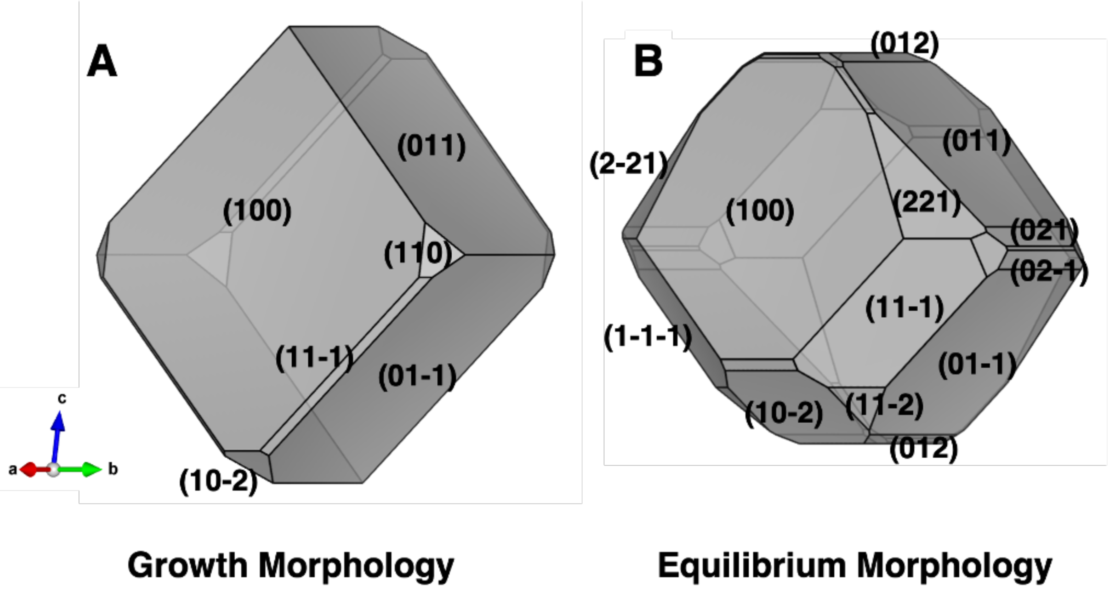
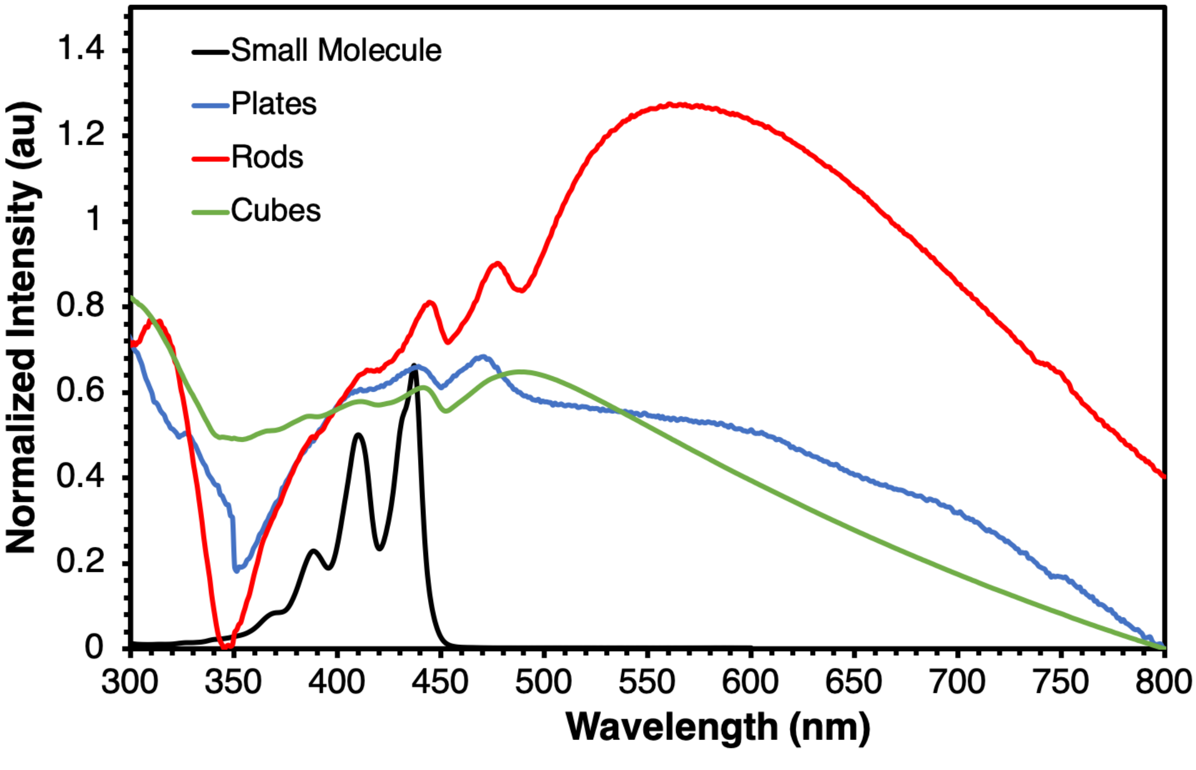


**Table S1:** Surface free energies ($\gamma_{hkl}$) and attachment energies ($E_{hkl}^{attach}$) of the crystal facets calculated using Materials Studio.

| Miller index {hkl} | $\mathbf{d_{hkl}}$ (Å) | $\boldsymbol{\gamma}_{\mathbf{hkl}}$ (mJ m$^{-2}$) | $\mathbf{E_{hkl}^{attach}}$ (kcal mol$^{-1}$) |
|---|---|---|---|
| {1 0 0}s | 10.09 | 119.74 | -44.26 |
| {0 1 1}s | 7.70 | 140.05 | -66.59 |
| {1 1 0}s | 7.37 | 185.56 | -87.05 |
| {1 1 -1}s | 6.55 | 152.13 | -82.95 |
| {1 1 1}s | 5.76 | 168.53 | -93.51 |
| {0 0 2}s | 5.49 | 158.10 | -100.22 |
| {0 2 0}s | 5.40 | 184.03 | -109.57 |

# 6.0 UV-Vis

**Figure S7**: UV-vis full spectral window



# 7.0 Molecular Dipole Orientation

**Figure S8**: Orientation of molecular dipoles and electromagnetic field vectors in perylene plate MCs

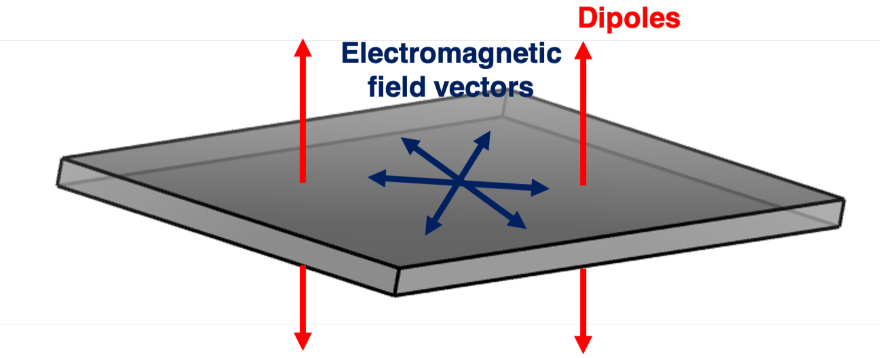
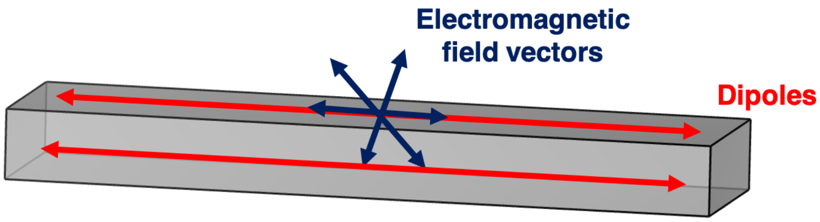
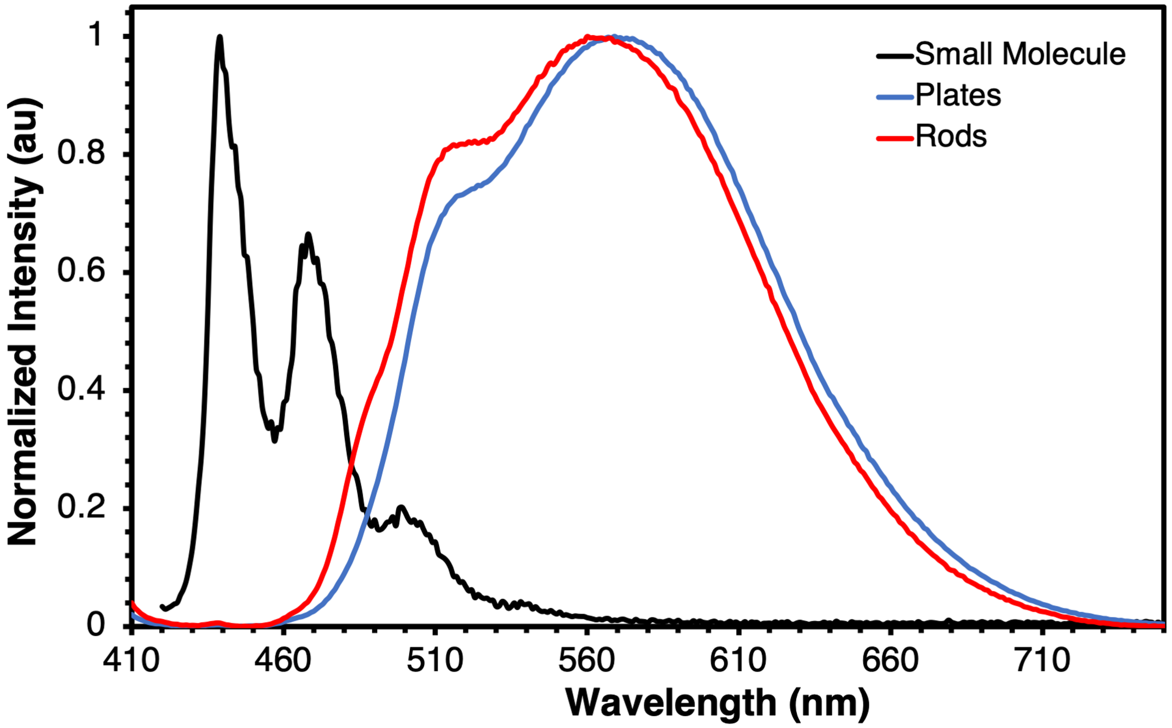


**Figure S9**: Orientation of molecular dipoles and electromagnetic field vectors in perylene rod MCs



## 8.0 Emission Spectrum

**Figure S10**: Emission Spectrum of perylene small molecule in THF (black), and perylene rod and plate MCs

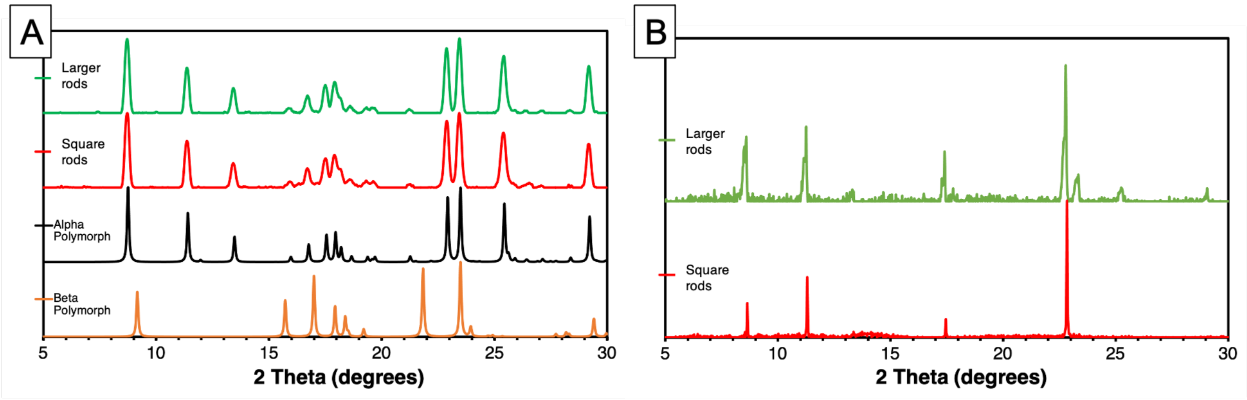


## 9.0 Longer Rods

To achieve the larger perylene rods used for single MC waveguiding studies, the growth conditions were modified slightly. 2 mL of 2 mM perylene in THF was heated to 50 °C, and then the hot solution quickly injected into 2.5 mL of 10 mM aqueous amphiphile which had been heated to 100 °C. The mixture was rested undisturbed at room temperature for 48 hours. The microcrystals were then washed as described above.

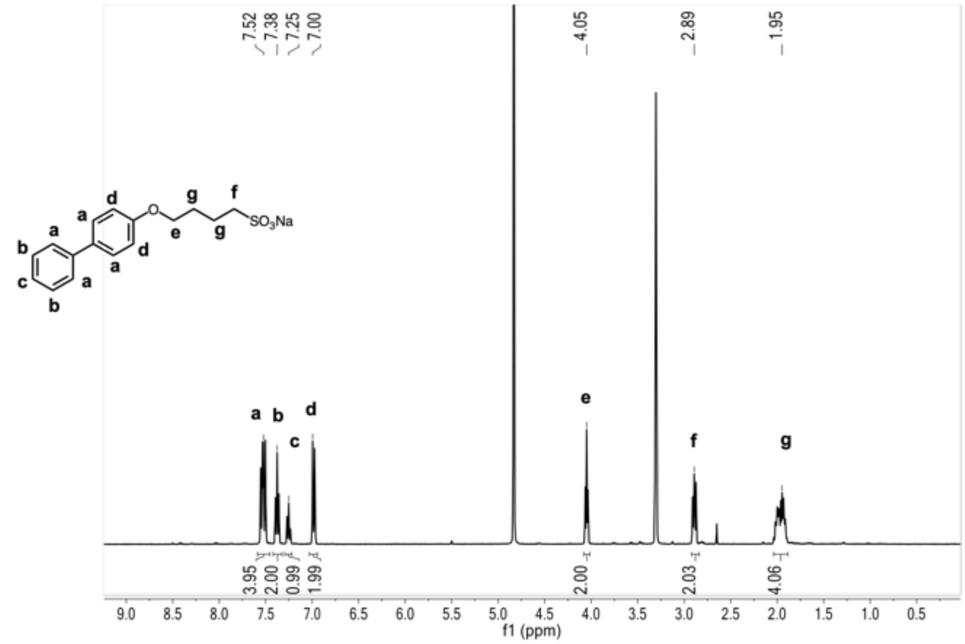
In order to confirm the molecular arrangement of the larger rods, their transmission and reflection mode PXRD spectra were recorded (Figure S10). The transmission mode PXRD (Figure S10A) spectra of the larger rods matched well with that of the square rods and the $\alpha$-polymorph of perylene. Additionally, the reflection mode PXRD spectra (Figure S10B) of the larger rods showed a lower intensity of the (1 0 0) peak relative to the (0 1 1), as was observed in the PXRD spectra of the square rods. This indicates that the larger rods have the same molecular arrangement and same exposed facets as the square rods.

**Figure S11**: (a) Transmission and (B) reflection mode PXRD spectra of longer rods grown according to modified growth conditions.

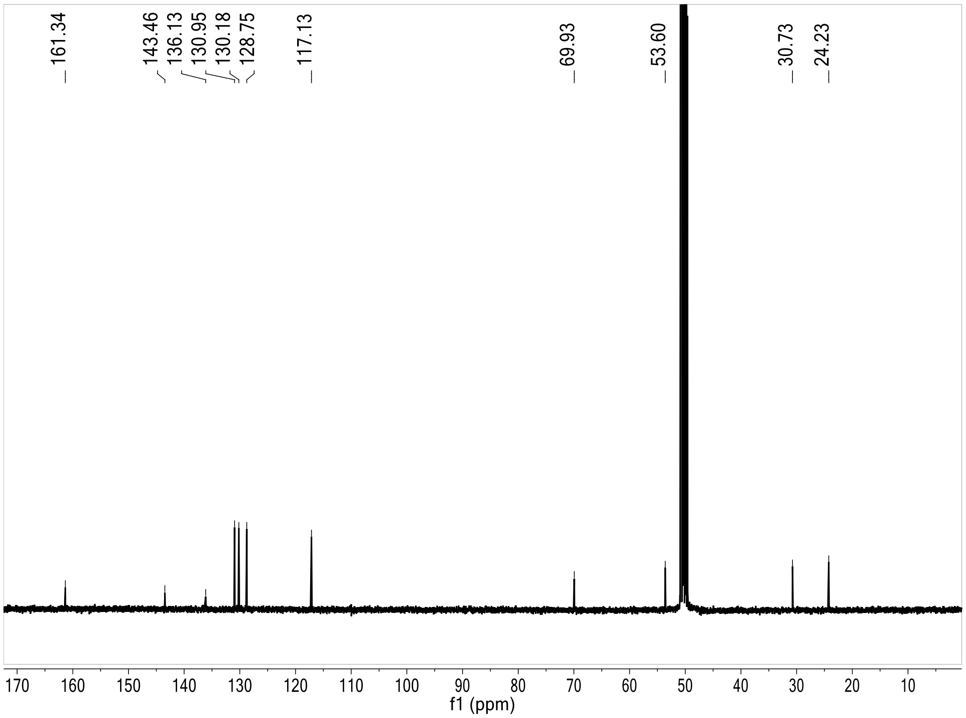


# A.0 $^{1}$H NMR and $^{13}$C NMR of Compound Synthesized

A) $^{1}$H NMR of Sodium 4-([1,1'-biphenyl]-4-yloxy)butane-1-sulfonate



B) $^{13}$C NMR of Sodium 4-([1,1'-biphenyl]-4-yloxy)butane-1-sulfonate



References:

1. *BIOVIA Materials Studio*, Dassault Systèmes BIOVIA: San Diego.
2. Schneider, C. A.; Rasband, W. S.; Eliceiri, K. W., NIH Image to ImageJ: 25 years of image analysis. *Nat Methods* **2012,** *9* (7), 671-5.
3. Momma, K.; Izumi, F., VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Cryst.* **2011,** *44*, 1272-1276.
4. Yao, W.; Yan, Y.; Xue, L.; Zhang, C.; Li, G.; Zheng, Q.; Zhao, Y. S.; Jiang, H.; Yao, J., Controlling the structures and photonic properties of organic nanomaterials by molecular design. *Angew. Chem. Int. Ed.* **2013,** *52* (33), 8713-7.