

Supporting Information

Aryl Amphiphile Shape-Directors for Shape-Controlled Synthesis of Organic Semiconductor Particles

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Table of Contents

1.0 General Information.....	2
2.0 Synthesis	3
2.1 Procedure for Synthesis of ShaD-1.....	3
2.2 Procedure for Synthesis of ShaD-2.....	3
3.0 Particle Synthesis	5
3.1 Method of Particle Synthesis	5
3.2 Attempted Particle Synthesis Conditions	5
4.0 Size Distribution of DPA Particles	6
4.1 Method	6
4.2 Particles grown in ShaD-2.....	6
5.0 SEM Images of DPA Particles Grown in Pure Water.....	7
6.0 SEM Images of Control Experiment (no DPA)	8
7.0 NMR of DPA MCs.....	9
8.0 PXRD of Both DPA Polymorphs.....	10
9.0 Crystal Facets.....	11
9.1 PXRD	11
9.2 Theoretical and Experimental Crystal Angles	11
9.3 Calculated Energies.....	13
A.0 ¹H NMR and ¹³C NMR of Compounds Synthesized	14
References	16

1.0 General Information

Reagents used for structure directing agent synthesis were purchased from Sigma Aldrich, AK Scientific, Fisher, Acros, Alfa Aesar, TCI, Strem, and Accela. Triptycene and 1,3,5-triphenylbenzene were purchased from Sigma Aldrich 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. ^1H and ^{13}C NMR spectra were recorded on Varian 400-MR NMR. Chemical shifts are reported in δ (ppm) relative to the residual solvent peak CDCl_3 : 7.26 for ^1H ; and CDCl_3 : 77.36 for ^{13}C ; MeOD : 3.31 for ^1H , and MeOD : 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. Powder XRD (PXRD) for particles 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 $\text{Cu I}\mu\text{S}$ source. A series of 360° phi scans were collected and data were integrated in the 2θ range 5° to 45° . The reflection mode PXRD was recorded on a Rigaku Ultima IV with $\text{Cu-K } \langle\alpha\rangle$ radiation (40kV, 30mA), and a D/tex Ultra silicon strip detector. Data was collected in the 2θ range 5° to 45° . Conductivity method was used to determine the critical micelle concentration (CMC) of the synthesized surfactants, the conductivity was measured using a Vernier Conductivity Probe. UV-vis adsorption spectra were recorded on an Agilent Technologies Cary Series 5000 UV-vis-NIR Spectrophotometer. Fluorescence emission spectra were recorded on a Horiba Scientific FluoroMax-4 Spectrofluorometer. Computational calculations were carried out using Materials Studio (MS) Accelrys version 6.0.

2.0 Synthesis

2.1 Procedure for Synthesis of ShaD-1

Anthracen-9-ylmethanol: Anthracen-9-ylmethanol was synthesized following the reported procedure.¹ ¹H NMR (400 MHz, Chloroform-*d*): δ 5.69 (s, 2H), 7.51 (m, 2H), 7.58 (m, 2H), 8.03 (d, $J = 8.6$ Hz, 2H), 8.44 (d, $J = 8.8$ Hz, 2H), 8.48 (s, 1H).

Sodium 4-(anthracen-9-ylmethoxy)butane-1-sulfonate (1): Anthracen-9-ylmethanol (1 equivalent) was dissolved in dry THF (20mL) under nitrogen atmosphere. The reaction was stirred over ice and solid sodium hydride (1.2 equivalents) was added. The reaction was brought to room temperature for 1h and then 1,4-butane sultone (1.2 equivalents) was added. The reaction was stirred at rt for 20h. Reaction was quenched with methanol, and solvent was removed under vacuum. The crude was purified by column chromatography on C18 reverse phase column with a gradient from 100% water to 100% MeOH. Solvent was removed under vacuum to yield 3.4g yellow solid (36% yield). ¹H NMR (400 MHz, Methanol-*d*₄): δ 1.77 (m, 2H), 1.88 (m, 2H), 2.80 (m, 2H), 3.75 (t, $J = 6.2$ Hz, 2H), 5.48 (s, 2H), 7.46 (dd, $J = 7.8, 0.2$ Hz, 2H), 7.55 (m, 2H), 8.03 (d, $J = 8.3$ Hz, 2H), 8.39 (d, $J = 8.9$ Hz, 2H), 8.49 (s, 1H). ¹³C NMR (400 MHz, Methanol-*d*₄): δ 23.05, 29.93, 52.38, 65.83, 71.35, 125.45, 126.03, 127.23, 129.26, 129.97, 130.08, 132.26, 132.90 ppm. High-Res Mass Spec (ESI) : M⁺ 389.0785 (measured), 389.0799 (calculated).

2.2 Procedure for Synthesis of ShaD-2

2-carboxy-4,5-dimethoxybenzenediazonium chloride: 2-carboxy-4,5-dimethoxybenzenediazonium chloride was synthesized following the reported procedure.² ¹H NMR (400 MHz, Methanol-*d*₄): δ 4.05 (s, 3H), 4.17 (s, 3H), 7.90 (s, 1H), 8.34 (s, 1H).

(9r,10r)-2,3-dimethoxy-9,10-dihydro-9,10-[1,2]benzoanthracene: (9r,10r)-2,3-dimethoxy-9,10-dihydro-9,10-[1,2]benzoanthracene was synthesized following the reported procedure.³ ¹H NMR (CDCl₃): 3.83 (s, 6H), 5.33 (s, 2H), 6.96 (m, 4H), 7.01 (s, 2H), 7.36 (m, 4H).

(9r,10r)-9,10-dihydro-9,10-[1,2]benzoanthracene-2,3-diol: (9r,10r)-9,10-dihydro-9,10-[1,2]benzoanthracene-2,3-diol was synthesized following the reported procedure.³ ¹H NMR (400 MHz, Chloroform-*d*): 5.36 (s, 2H), 6.95 (s, 2H), 6.95 (dd, $J = 5.3, 3.2$ Hz, 4H), 7.32 (dd, $J = 5.3, 3.2$ Hz, 4H).

Sodium 4,4'-(((9r,10r)-9,10-dihydro-9,10-[1,2]benzoanthracene-2,3-diyl)bis(oxy))bis(butane-1-sulfonate) (2): (9r,10r)-9,10-dihydro-9,10-[1,2]benzoanthracene-2,3-diol (1 equivalent) and tetra-*n*-butylammonium bromide (0.1 equivalent) were dissolved in DMSO (10mL) under nitrogen atmosphere. Sodium hydroxide (10 equivalents) was dissolved in water (2.5mL) and added to the reaction mixture. The reaction was stirred at room temperature for 15m, then 1,4-butane sultone (2.5 equivalents) was added. The reaction was stirred at room temperature overnight. The reaction mixture was precipitated in acetone, and the solid was collected. The crude was purified by column chromatography on C18 reverse phase column with a gradient from 100% water to 100% MeOH.

Solvent was removed under vacuum to yield 0.69g reddish-brown solid (33% yield). ^1H NMR (400 MHz, Methanol- d_4) δ 1.91 (m, 8H), 2.92 – 2.82 (m, 4H), 3.97 (t, $J = 6.2$ Hz, 4H), 5.36 (s, 2H), 7.01 – 6.88 (m, 4H), 7.09 (s, 2H), 7.40 – 7.26 (m, 4H). ^{13}C NMR (400 MHz, Methanol- d_4): δ 22.93, 29.61, 54.79, 70.90, 113.05, 124.19, 125.86, 140.47, 147.41ppm. High-Res Mass Spec (ESI) : M^- 557.1304 (measured), 557.1304 (calculated).

3.0 Particle Synthesis

3.1 Method of Particle Synthesis

In the typical preparation, 0.5 mL of 2 mM 9,10-diphenylanthracene (DPA) in THF were quickly injected into 2.5 mL of 20 mM aqueous surfactant. The solutions were stirred vigorously for 5 minutes then rested undisturbed at room temperature for 24 hours. For the ShaD-1 samples, the DPA/THF solution was heated to 40°C and then allowed to slowly come to room temperature before use, and the samples were protected from light during growth. After 24 hour growth time, the solutions were centrifuged at 4,700 rpm for 20 minutes, then the supernatant was poured off and the micro were sonicated for 1 hour in 30 mL of fresh water. The samples grown in SDS and ShaD-1 were sonicated at room temperature, and the samples grown in ShaD-2 were sonicated at 40°C. After sonication, the samples were then centrifuged for 5 minutes. The sonication-centrifugation was repeated 3 more times. The microparticles were re-suspended in fresh water, and drop-cast on aluminum stubs for scanning electron microscope (SEM) imaging.

3.2 Attempted Particle Synthesis Conditions

Table S1: Results from different crystallization parameters

Parameter Varied	Result
SDS/ShaD concentration	Poor size polydispersity at surfactant concentrations below 20 mM
DPA concentration	Poor size polydispersity and shape yield at DPA concentrations above and below 2 mM
THF: H ₂ O ratio	Poor shape yield with higher water content, fewer particles observed with higher THF content

4.0 Size Distribution of DPA Particles

4.1 Method

Particle size was calculated by measuring 100+ particles across multiple images for each sample. ImageJ⁴ was used to measure particle size. Polydispersity was calculated by taking the ratio of the standard deviation over the average.

4.2 Particles grown in ShaD-2

Table S2: Average, standard deviation and polydispersity of lengths along A for microparticles grown in ShaD-2

Average	3.44 μm
Standard Deviation	1.03 μm
Polydispersity	30%

Table S3: Average, standard deviation and polydispersity of lengths along B for microparticles grown in ShaD-2

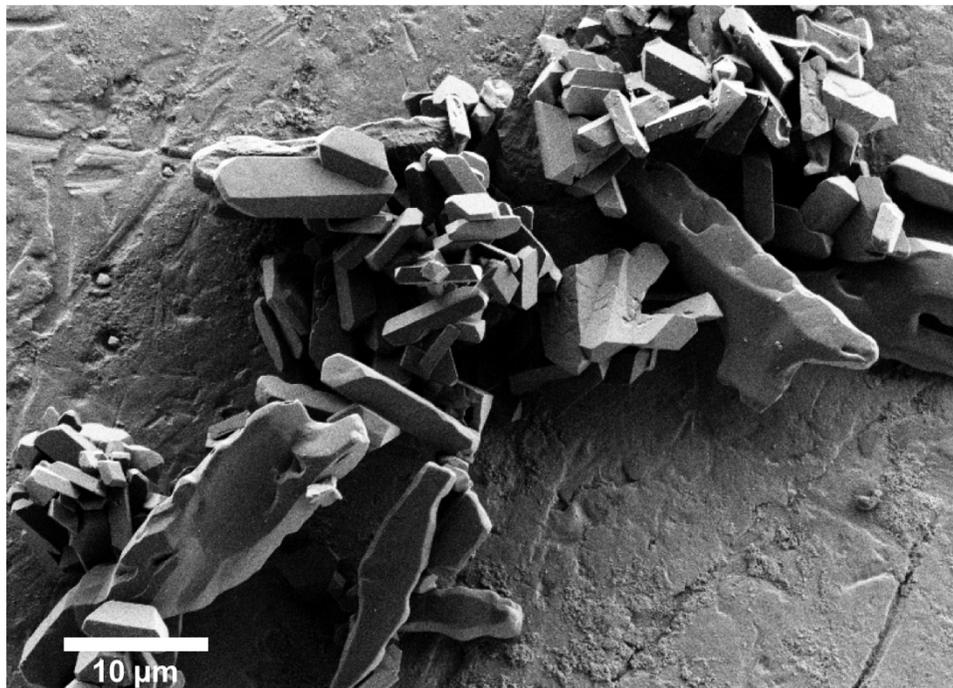
Average	2.63 μm
Standard Deviation	0.88 μm
Polydispersity	33%

Table S4: Average, standard deviation and polydispersity of lengths along C for microparticles grown in ShaD-2

Average	0.79 μm
Standard Deviation	0.29 μm
Polydispersity	36%

5.0 SEM Images of DPA Particles Grown in Pure Water

Figure S1:



6.0 SEM Images of Control Experiment (no DPA)

Figure S2: THF added to ShaD-1

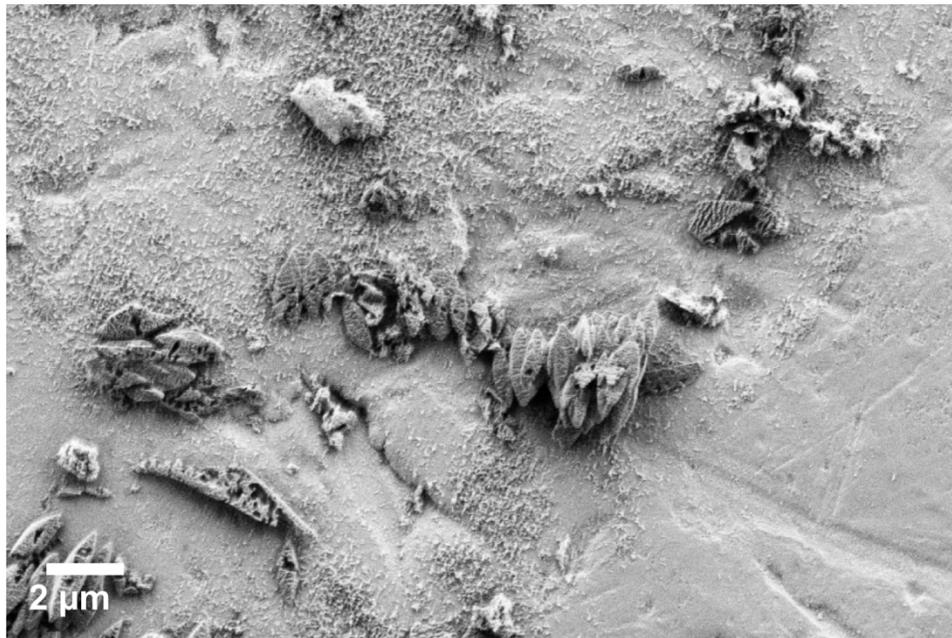
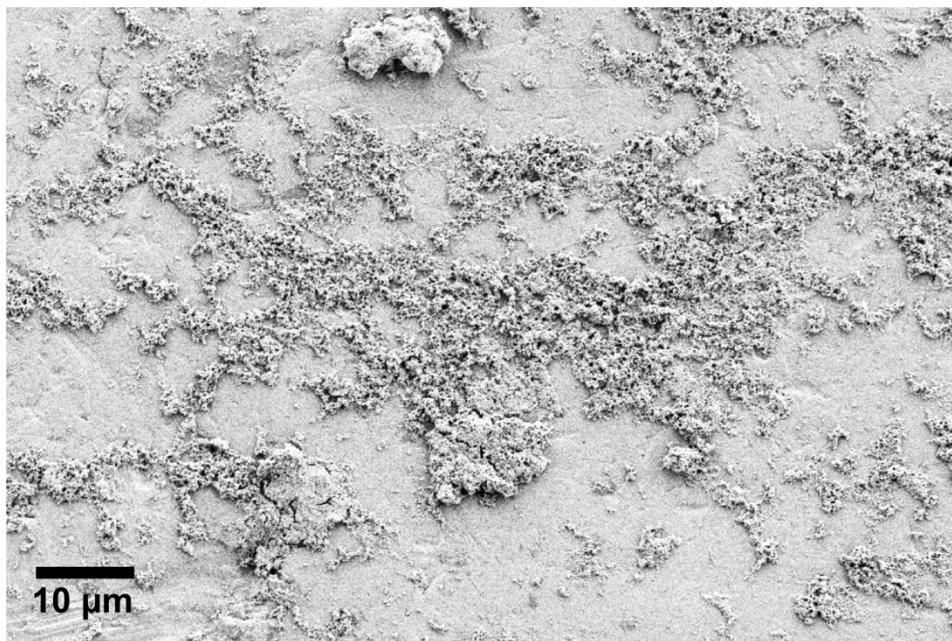
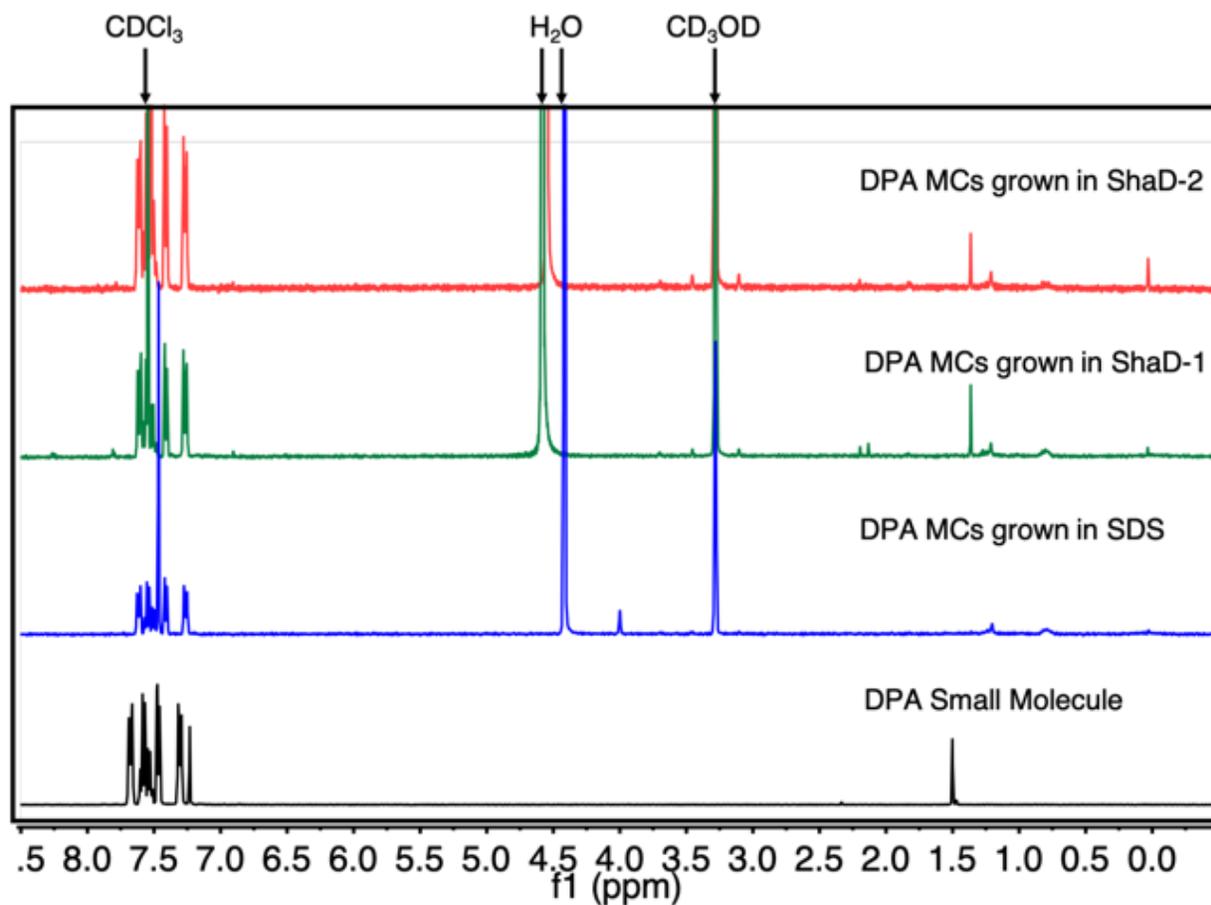


Figure S3: THF added to ShaD-2



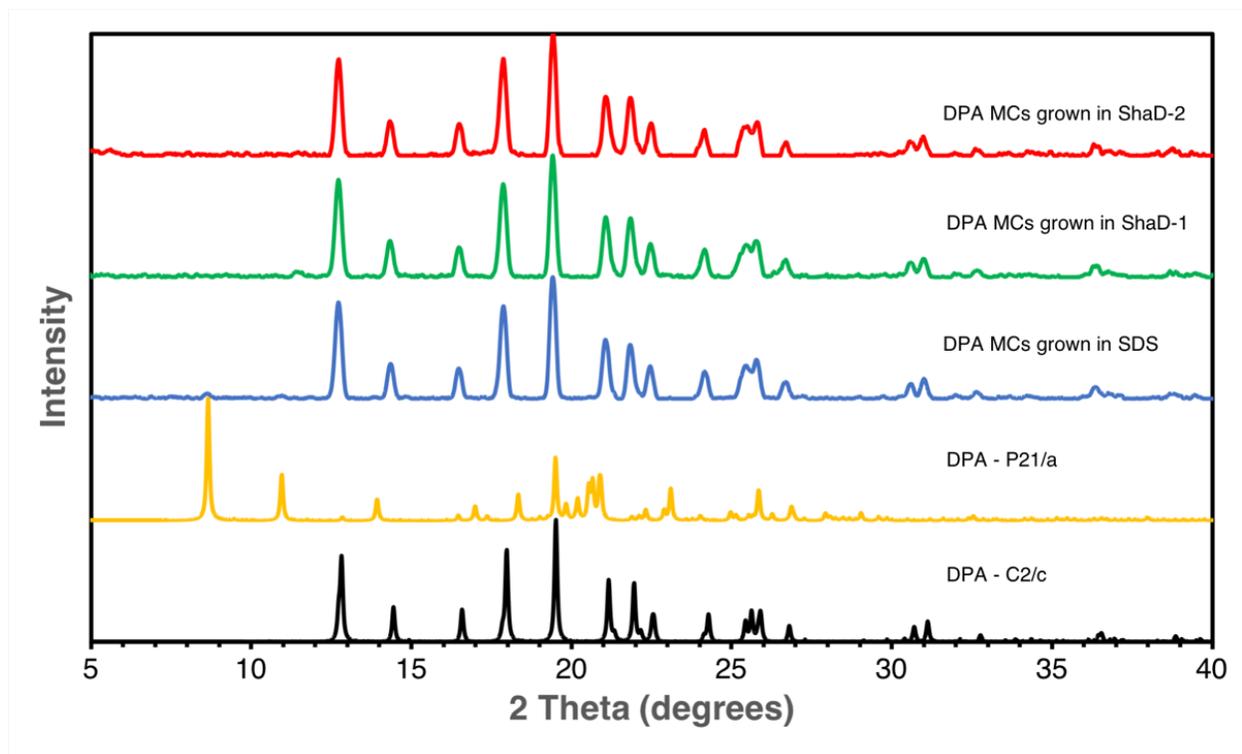
7.0 NMR of DPA MCs

Figure S4: NMR of washed DPA MCs and DP small molecule



8.0 PXRD of Both DPA Polymorphs

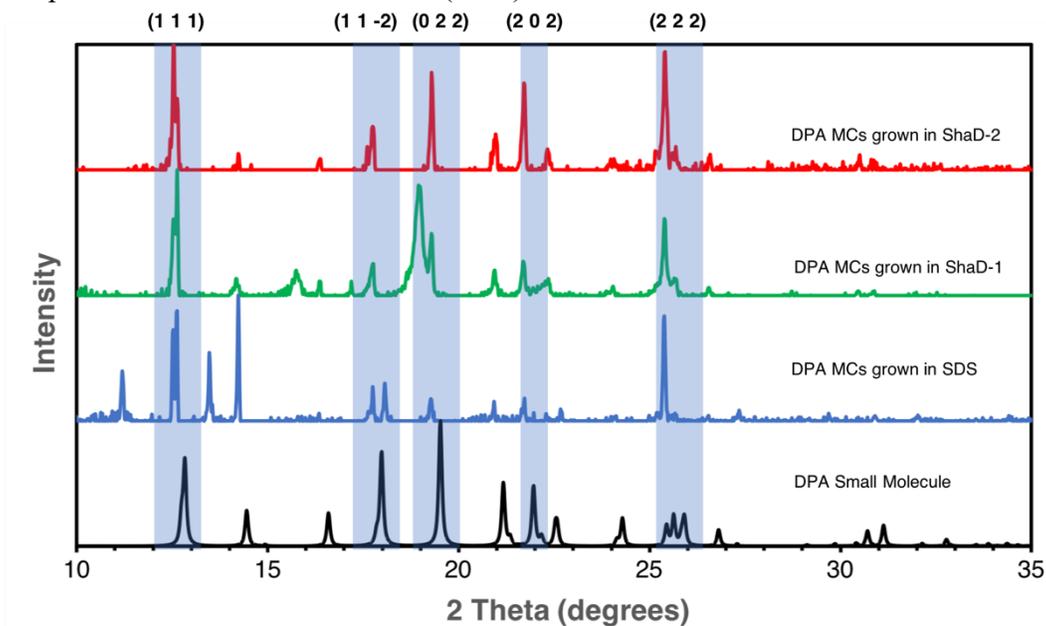
Figure S5: Transmission mode PXRD of DPA MCs grown in SDS, ShaD-1 and ShaD-2 and predicted spectra of both DPA polymorphs



9.0 Crystal Facets

9.1 PXRD

Figure S6: Reflection mode PXRD of DPA MCs grown in SDS, ShaD-1 and ShaD-2 and predicted spectra of DPA small molecule (*C2/c*)



9.2 Theoretical and Experimental Crystal Angles

Figure S7: Theoretical and experimental angles on pseudo-octahedral microcrystals with $\{1 1 1\}$ and $\{1 1 -1\}$ faces blocked

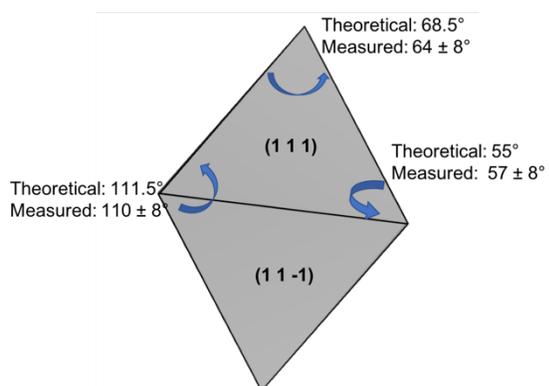


Figure S8: Theoretical and experimental angles on pseudo-octahedral microcrystals with $\{1\ 0\ 1\}$ and $\{1\ 0\ -1\}$ faces blocked

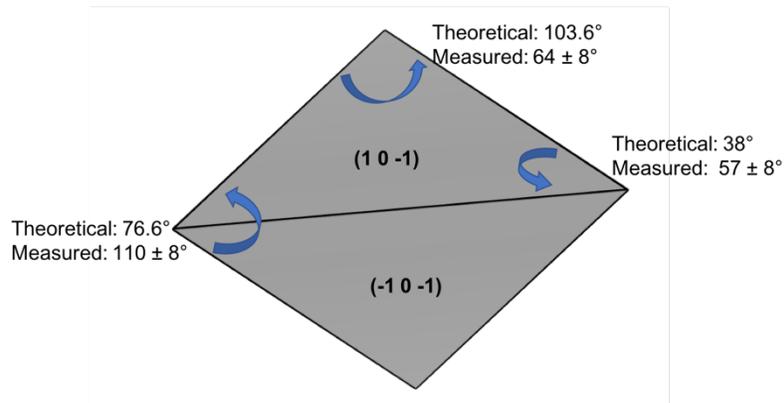
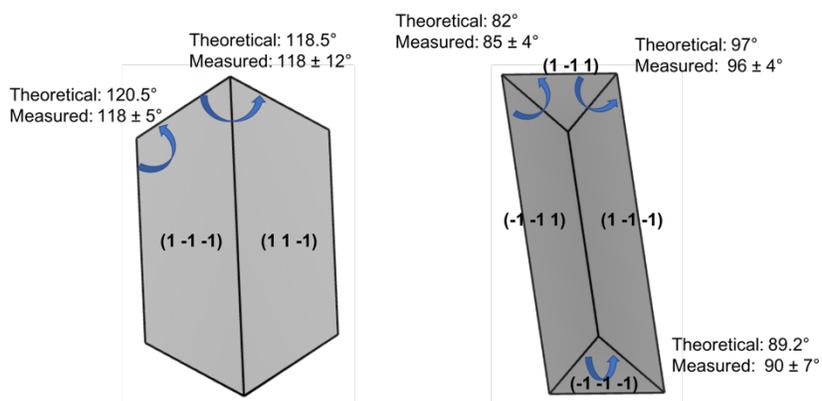


Figure S9: Theoretical and experimental angles on elongated-octahedron microcrystals with $\{1\ 1\ 1\}$ and $\{1\ 1\ -1\}$ faces blocked



9.3 Calculated Energies

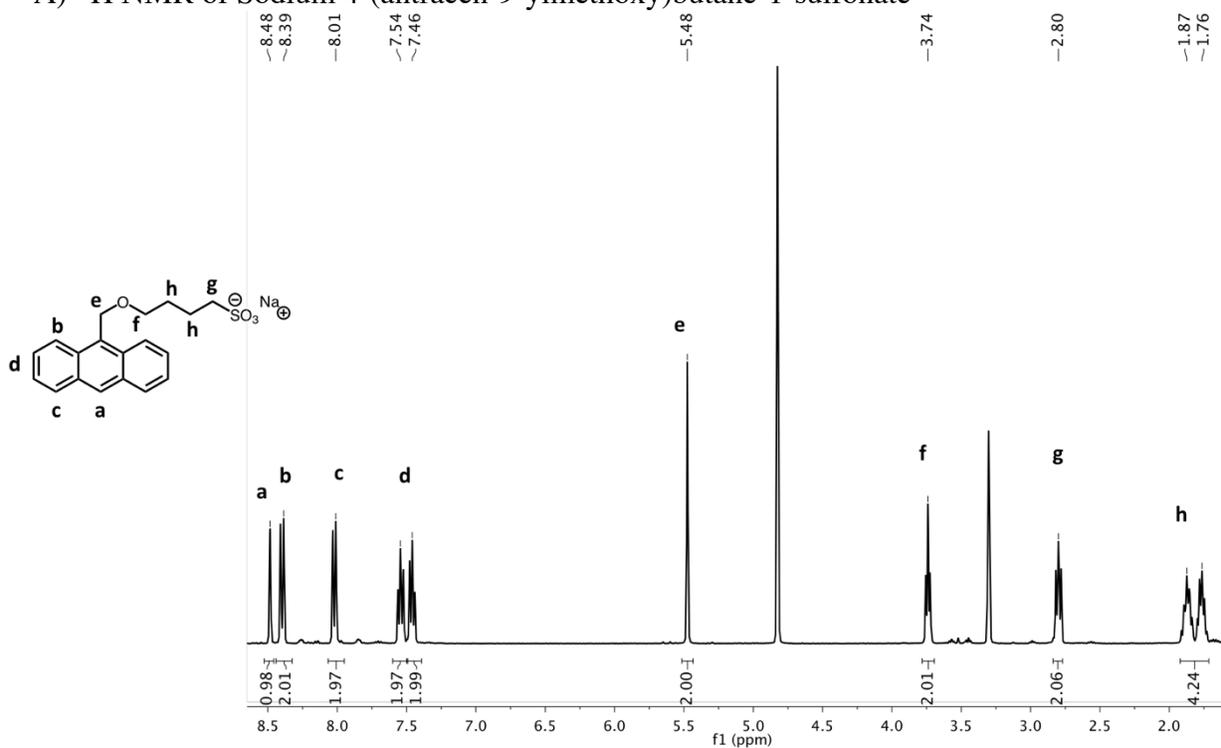
The Attachment Energies (E_{att}) and Surface Free Energies (E_{surface}) were calculated using the Materials Studio Software.⁵ The Morphology Module was used for both calculations; growth morphology was used to calculate E_{att} and equilibrium morphology was used for E_{surface} . The Universal forcefield was used for all calculations. E_{att} is defined as the energy release when a new layer is added to the existing crystal face, and given in units of kcal/mol/unit cell. E_{surface} is the excess energy of the atoms on the surface as compared to in the bulk, and given in units of mJ/m².

Table S5: Attachment Energies (E_{att}) and Surface Free Energies (E_{surface}) of the ten lowest energy facets of a 9,10-diphenylanthracene crystal in the C2/c space group.

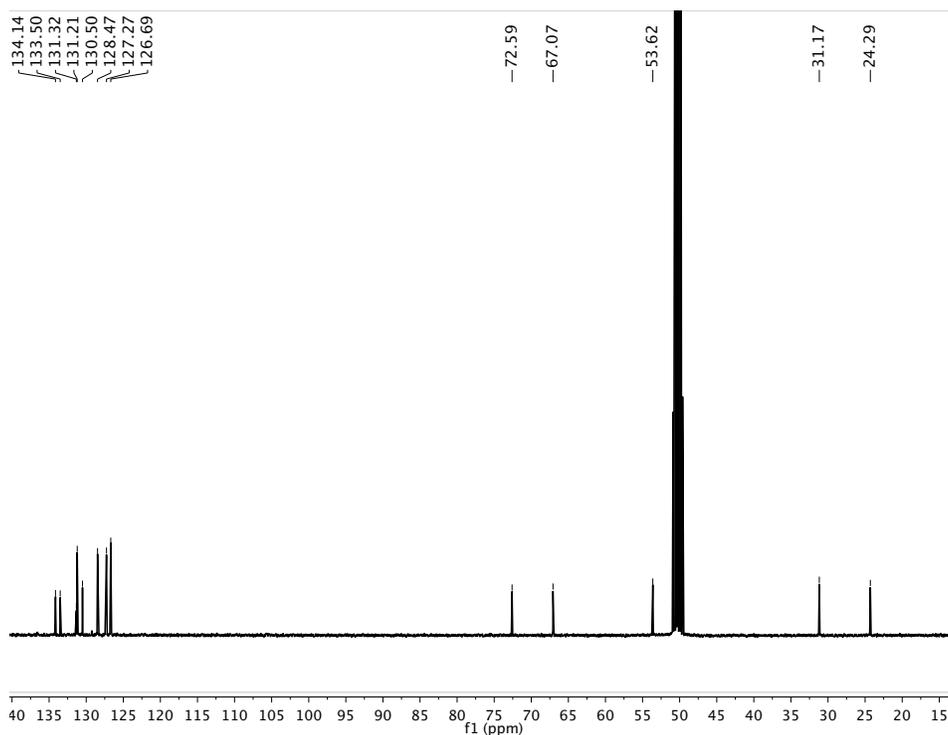
$\{hkl\}$	E_{att} (kcal/mole)	E_{surface} (mJ/m ²)
{ 1 1 1}	-100.2	132.0
{ 1 1 0}	-105.1	168.4
{ 1 1 -1}	-112.4	150.1
{ 0 0 2}	-122.3	145.1
{ 0 2 0}	-128.0	168.8
{ 1 1 2}	-132.3	151.7
{ 1 1 -2}	-138.5	165.5
{ 2 0 0}	-138.6	152.5
{ 0 2 1}	-143.1	182.3
{ 0 2 2}	-158.6	167.5

A.0 ^1H NMR and ^{13}C NMR of Compounds Synthesized

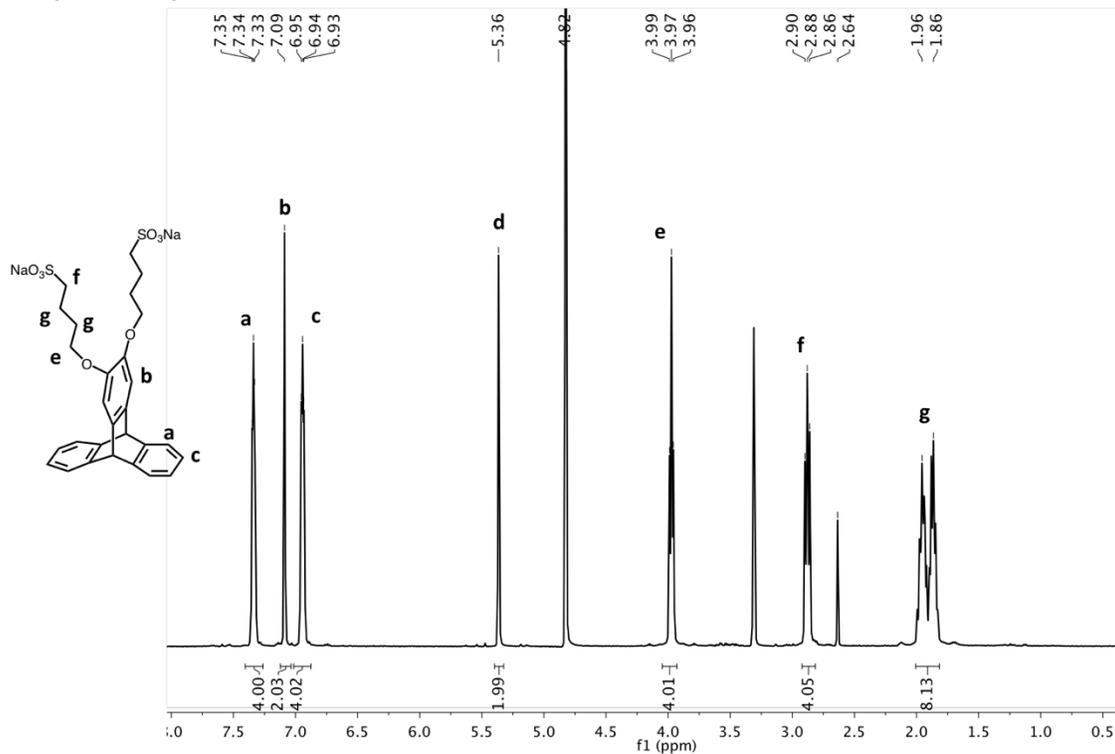
A) ^1H NMR of Sodium 4-(antracen-9-ylmethoxy)butane-1-sulfonate



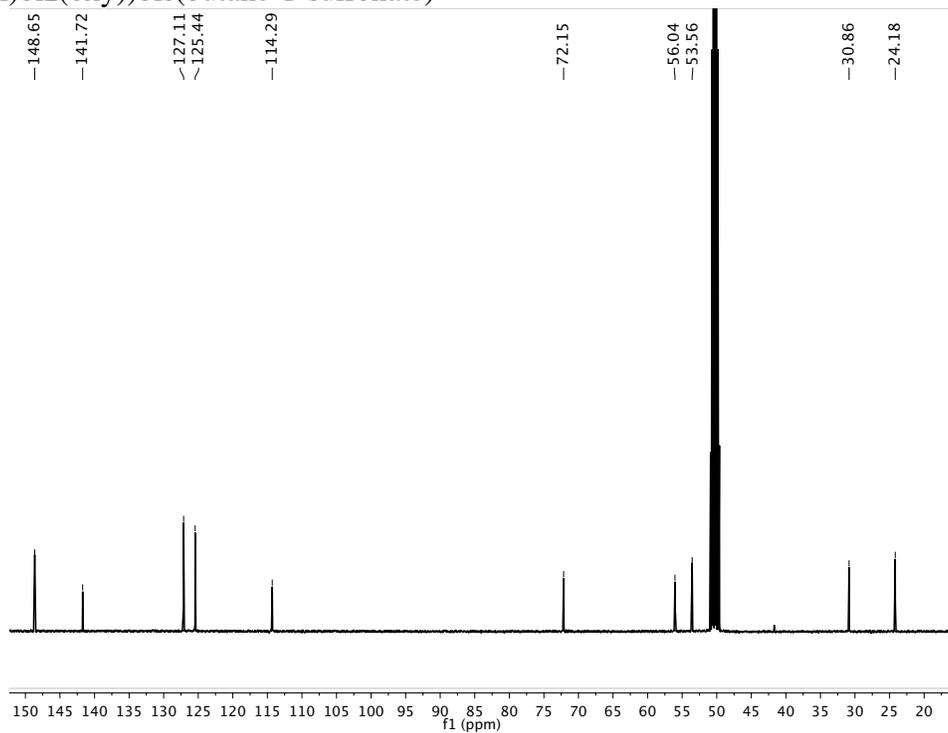
B) ^{13}C NMR of Sodium 4-(antracen-9-ylmethoxy)butane-1-sulfonate



C) ^1H NMR of Sodium 4,4'-(((9r,10r)-9,10-dihydro-9,10-[1,2]benzenoanthracene-2,3-diyl)bis(oxy))bis(butane-1-sulfonate)



D) ^{13}C NMR of Sodium 4,4'-(((9r,10r)-9,10-dihydro-9,10-[1,2]benzenoanthracene-2,3-diyl)bis(oxy))bis(butane-1-sulfonate)



References

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