Electronic Supplementary Information

Understanding molecular self-assembly of a diol compound by considering competitive interactions

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1 Synthesis of the DPD molecule

General Methods

All reactions involving air -or moisture- sensitive reagents or intermediates were carried out in heatgun-dried glassware under an argon atmosphere and were performed using standard Schlenk techniques. All solvents for extraction and flash chromatography (FC) were distilled before use. All chemicals were purchased from Sigma Aldrich, Acros Organics, ABCR, Alfa Aesar, TCI or Fluka and were used as received. Gas chromatography (GC) was performed on an Agilent 7890A chromatograph equipped with a HP-5 column (30 m \times 0.32 mm, film thickness 0.25 μ m) using H₂ (\approx 1 bar) as carrier gas. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker DPX-300 (300 Mhz) or a Bruker AV 400 (400 Mhz). Chemical shifts δ in ppm are referenced to the solvent residual peak (CDCl₃: ¹H, δ = 7.26; ¹³C, δ = (77.0) as an internal standard. Peak multiplicities are given as follows: s, singlet; d, doublet; t, triplet; m, multiplet. HRMS ESI (m/z) spectra were recorded on a Bruker MicroTof or an Orbitrap LTQ XL (Nanospray) from Thermo Scientific. Melting points (MP) were determined on a Stuart SMP10 and are uncorrected. IR spectra were recorded on a Digilab Varian 3100 FT-IR Excalibur Series. IR signals are described as w (weak), m (middle), s (strong), br (broad) in cm⁻¹. This layer chromatography (TLC) was carried out on Merck silica gel 60 F254 plates; detection with UV light or by dipping into a solution of KMnO₄ (1.5 g) and NaHCO₃ (5.0 g) in H₂O (0.40 L) followed by heating. FC was carried out on Merck silica gel 60 (40-63 μ m) with an argon excess pressure of about 0.5 bar.

1,4-Dihexylbenzene (4)



In a three-neck flask equipped with a condenser magnesium (3.65 g, 150 mmol, 2.20 eq) was covered with dry Et₂O (5 mL) under an atmosphere of argon. A few drops of 1-bromohexane were added carefully. After the boiling began the mixture was diluted with Et₂O (45 mL) and 1-bromohexane (21.0 mL, 150 mmol, 2.20 eq) dissolved in Et₂O (50 mL) was added dropwise over a period of 30 min. The resulting mixture was then heated at reflux for 2 h.

Under an atmosphere of argon 1,4-dichlorobenzene (10 g, 68 mmol, 1.0 eq) was dissolved in Et₂O (50 mL). Then NiCl₂·dppp (111 mg, 204 μ mol, 0.30 mol%), followed by the freshly prepared 1-hexylmagnesium bromide solution were added and the resulting mixture was heated at reflux for 15 h. Afterwards the mixture was given into an ice/HCl-solution (aq. 1M, 100 mL), followed by a phase separation. The aqueous layer was extracted with Et₂O (3×100 mL) and the combined organic layers were washed with brine (300 mL), dried over MgSO₄ and concentrated under reduced pressure. Purification by distillation ($T = 121 \,^{\circ}$ C, $p = 3 \times 10^{-1}$ bar) yielded the 1,4-dihexylbenzene (4) (13.9 g, 56.4 mmol, 83%) as a colorless liquid.

¹**H-NMR** (300 MHz, CDCl₃): $\delta = 7.09$ (s, 4H, aryl-H), 2.57 (t, J = 7.8 Hz, 4H, 2 × aryl-CH₂), 1.66–1.53 (m, 4H, 2 × CH₂), 1.42–1.24 (m, 12H, 6 × CH₂), 0.88 (t, J = 6.6 Hz, 6H, 2 × CH₃).

The analytical data is in accordance with the data reported in literature [1].

1,4-Dihexyl-2,5-diiodobenzene (3)



1,4-Dihexylbenzene (4) (10.0 g, 40.6 mmol, 1.00 eq) was dissolved in a solvent mixture consisting of water (25 mL), CCl₄ (50 mL) and acetic acid (230 mL). To this solution H_5IO_6 (4.62 g, 20.3 mmol, 0.500 eq), io-dine (10.3 g, 40.6 mmol, 1.00 eq) and concentrated sulfuric acid (6.9 mL, 0.13 mol, 3.2 eq) were added and the resulting mixture was heated at reflux for 24 h. After cooling to room temperature, water (300 mL) was added and the organic layer was separated. Then the aqueous layer was extracted with pentane (3×200 mL). The combined organic layers were sequentially washed with saturated Na₂S₂O₃-solution (aq.,

150 mL), saturated Na₂CO₃-solution (aq., 150 mL) and saturated Na₂SO₄-solution (aq., 150 mL) before being dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography using pentane as an eluent, which yielded diiodobenzene **3** (17.5 g, 35.1 mmol, 86%) as a colorless solid.

¹**H-NMR** (300 MHz, CDCl₃): $\delta = 7.59$ (s, 2H, aryl-H), 2.59 (t, J = 7.7 Hz, 4H, 2 × aryl-CH₂), 1.67–1.46 (m, 4H, 2 × CH₂), 1.44–1.26 (m, 12H, 6 × CH₂), 0.88 (t, J = 6.6 Hz, 6H, 2 × CH₃).

The analytical data is in accordance with the data reported in literature [1].

2,5-Dihexylterephthalaldehyde (2)



Under an atmosphere of argon diiodobenzene **3** (2.0 g, 4.0 mmol, 1.0 eq) was dissolved in dry THF (20 mL) and cooled down to -78 °C. A solution of *tert*-butyllithium (1.6 M in pentane, 10.5 mL, 16.8 mmol, 4.20 eq) was added dropwise and the resulting reaction mixture was stirred at -78 °C for 2 h. DMF (3.1 mL, 40 mmol, 10 eq) was added slowly and the mixture was stirred for 20 h at room temperature. After addition of saturated NH₄Cl-solution (aq., 30 mL) the organic layer was separated and the aqueous phase was extracted with Et₂O (3×40 mL). The

combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane/Et₂O; 50:1) afforded the dicarbaldehyde **2** (380 mg, 1.26 mmol, 32%) as a pale-yellow solid.

Mp.: 44–46 °C. **IR** (neat): 3345*w*, 3151*w*, 3037*w*, 2920*m*, 2849*w*, 1678*s*, 1609*w*, 1565*w*, 1488*w*, 1400*w*, 1375*w*, 1352*w*, 1313*m*, 1280*w*, 1265*w*, 1241*w*, 1223*w*, 1160*s*, 1115*w*, 911*m*, 886*m*, 860*m*, 796*w*, 777*w*, 717*s*, 620*m*, 530*m*, 472*w* cm⁻¹. ¹**H-NMR** (400 MHz, CDCl₃): $\delta = 10.35$ (*s*, 2H, CHO), 7.72 (*s*, 2H, aryl-H), 3.12–2.93 (*m*, 4H, 2 × aryl-CH₂), 1.66–1.57 (*m*, 4H, 2 × aryl-CH₂CH₂), 1.43–1.24 (*m*, 12H, 6 × CH₂), 0.92–0.84 (*m*, 6H, 2 × CH₃) ppm. ¹³**C-NMR** (100 MHz, CDCl₃): $\delta = 191.8$ (C), 143.5 (C), 136.9 (C), 133.2 (CH), 32.4 (CH₂), 32.0 (CH₂), 31.7 (CH₂), 29.3 (CH₂), 22.7 (CH₂), 14.2 (CH₃) ppm. **Ms** (ESI): m/z: 325 [M+Na]⁺, 357 [M+MeOH+Na]⁺, 691 [2M+Na]⁺. **HRMS** (ESI): m/z: calculated for [M+Na]⁺: 325.2138; found: 325.2136. **EA** in % calculated for C₂₀H₃₀O₂: C: 79.42, H: 10.00; found: C: 79.24, H: 10.02.

2,5-Dihexyl-1,4-phenylene-dimethanol (1)



Terephthalaldehyde (2) (151 mg, 0.500 mmol, 1.00 eq) was dissolved in dry THF (7 mL) under an atmosphere of argon and treated with LiAlH₄ (76 mg, 2.0 mmol, 4.0 eq). The resulting slurry was stirred at 70 °C for 16 h. Afterwards, the reaction mixture was cooled down to 0 °C and carefully H₂O (1.5 mL), aqueous NaOH-solution (15 %, 1.5 mL) and H₂O (2 mL) were added one after the other. The slurry was filtered and rinsed with Et₂O (50 mL). The filtrate was washed with H₂O (2×25 mL) dried over MgSO₄ and concentrated under reduced pressure,

which yielded diol 1 (149 mg, 0.485 mmol, 97%) as a colorless solid.

¹**H-NMR** (300 Mhz, CDCl₃): $\delta = 7.20$ (s, 2 H, aryl-H), 4.70 (s, 4 H, 2 × CH₂-O), 2.68–2.59 (m, 4 H, 2 × aryl-CH₂CH₂), 1.64–1.52 (m, 4 H, 2 × aryl-CH₂CH₂), 1.42–1.25 (m, 12 H, 6 × CH₂), 0.94–0.84 (m, 6 H, 2 × CH₃) ppm. ¹³**C-NMR** (100 MHz, CDCl₃): $\delta = 138.8$ (C), 137.9 (C), 129.4 (CH), 63.1 (CH₂), 32.2 (CH₂), 31.9 (CH₂), 31.6 (CH₂), 29.6 (CH₂), 22.8 (CH₂), 14.2 (CH₃) ppm. **HRMS** (ESI): m/z: calculated for [M+Na]⁺: 329.2451; found: 329.2452.

The analytical data is in accordance with the data reported in literature [2].

2 DFT Calculations for the DPD Adsorption Sites

The DPD molecule can be divided into three different sections: the core benzene ring, the alcohol moieties and the aliphatic chains. To account for the contribution of each of these components to the adsorption energy on the studied silver substrates, we performed DFT calculations for a single benzene ring, p-xylene, p-phenylenedimethanol and dimethyl p-phenylenedimethanol molecules. The latter is a reduced DPD monomer with shorter aliphatic chains (manuscript Fig. 3a). In all positions the molecule is constrained parallel to the underling substrate. On the other hand, since all the studied surfaces have a face-centered cubic crystal structure with a three-layer packing (ABCABC), the monomers can adsorb in four different high symmetric positions [3]. Following detailed information regarding these calculations is presented.

2.1 Configurations on the Ag(111) substrate



HCP A

НСР В

FCC

BR

- Figure S1: High symmetry adsorption positions for benzene on Ag(111). Two different orientations A and B of the TOP position were also analyzed.
 - Figure S2:High symmetry adsorption positions for *p*-xylene and*p*-phenylenedimethanol on the Ag(111) surface. The position of the functional groups is indicated by the gray circles. Seven possible adsorption positions were considered, including different orientations of the TOP and HCP positions.



Figure S3: High symmetry adsorption positions for dimethyl pphenylenedimethanol molecules on Ag(111), labeled as TOP, FCC, HCP, BR.

benzene						
SITO	E_{ads}	d_{MS}				
TOPA	0.51	3.05				
TOPB	0.51	3.05				
HCP	0.62	2.82				
FCC	0.62	3.12				
BR	0.61	2.97				
Miller et al. [4]	0.56 - 0.80	2.70 - 2.90				

p-phenylenedimethanol							
SITO	E_{ads}	d_{MS}					
TOP A	1.0	3.31					
TOPB	0.98	3.31					
TOPC	1.0	3.31	• • •				
HCP A	1.07	3.23	\$4				
HCP B	1.06	3.30	⊶				
FCC	1.07	3.24					
BRA	1.11	3.26					

p-xylene							
SITO	E_{ads}	d_{MS}					
TOP A	0.77	3.31					
TOP B	0.76	3.24	<u> </u>				
TOPC	0.77	3.24					
HCP A	0.81	3.23					
HCP B	0.80	3.17					
FCC	0.83	3.17					
$\operatorname{BR} A$	0.82	3.31	•				

dimethyl <i>p</i> -phenylenedimethanol							
SITO	E_{ads}	d_{MS}					
TOP A	1.21	3.29					
TOP B	1.17	3.31					
TOPC	1.18	3.32					
HCP A	1.21	3.21					
HCP B	1.23	3.21					
FCC	1.25	3.34					
$\operatorname{BR} A$	1.24	3.22	U U				
BRB	1.22	3.27					

Table T1: Calculated adsorption energies E_{ads} for p-xylene, p-phenylenedimethanol and dimethyl pphenylenedimethanol monomers on Ag(111). All adsorption energies are given in eV and all distances in Å.

2.2 Configurations on the Ag(110) substrate



Figure S5: High symmetry adsorption positions for p-xylene and p-phenylenedimethanol on the Ag(110) surface. The position of the functional groups is indicated by the gray circles. Eight possible adsorption positions were considered, including different orientations of the TOP, BR and FH positions.



Figure S6: High symmetry adsorption positions for dimethyl p-phenylenedimethanol molecules on the Ag(110) surface. Nine possible adsorption positions were considered, including different orientations of the TOP, BR and FH positions.

benzene						
SITO	E_{ads}	d_{MS}				
TOPA	0.60	2.81				
TOPB	0.61	2.81				
$_{\mathrm{FH}}$	0.69	—				
BR	0.73	2.80				
BR A	0.73	2.80				
Reckien <i>et al.</i> [5]	0.65 - 1.08	2.74 - 2.91				

SITO	E_{ads}	d_{MS}	
TOP A	0.83	3.15	
TOP B	0.84	3.16	
TOPC	0.75	3.15	
\mathbf{BR}	0.76	2.90	
$\operatorname{BR} \operatorname{A}$	0.91	3.17	
$\mathrm{BR}\mathrm{B}$	0.90	2.87	
FH A	0.89	2.85	U U
FH B	0.74	2.80	

n_{-}	nhenv	lenedi	methanol	dimeth	iyl <i>p</i> -p	henyle	enedimethanol
		d		SITO	E_{ads}	d_{MS}	
5110	Lads	u_{MS}		TOPA	1.14	3.16	
TOPA	1.02	3.20		TOP B	1.30	3 21	
TOPB	1.12	3.20		TODC	1.00	0.21	
TOPC	0.91	3.10		TOPC	1.34	3.15	. <u>.</u>
BB	0.06	3 16	●●● ●●	BRA	1.43	3.12	•••
	1.17	0.10	Ŷ − €) ₽− €₀	BRB	1.38	3.13	<u> </u>
BRA	1.17	3.20	⊶ ∮ ∭en (BBC	1 27	3.25	b-
BRB	1.08	3.19			1.96	0.20 9.10	- ସହୁଁ କ
FH A	1.19	3.10		FII A	1.50	3.12	e
FHB	1 10	3 10		FHB	1.24	3.10	
THD	1.10	5.10		$\rm FHC$	1.26	3.07	

Table T2: Calculated adsorption energies E_{ads} for p-xylene, p-phenylenedimethanol and dimethyl pphenylenedimethanol monomers on Ag(110). All adsorption energies are given in eV and all distances in Å. It should be noted that the preferred adsorption position shown in manuscript Fig. 3b,c corresponds to the BR B site, which is in agreement with the STM observations shown in the manuscript Fig.2c,d. Although the adsorption in the BR A site is the most energetically favoured by a margin of $\Delta E_{ads} < 0.09 \, \text{eV}$, it does not reproduce the experimental results.

3 Adsorption of a *trans*-Hexane Chain on Ag(110)



Figure S7: Adsorption of a trans-hexane chain on Ag(110), calculated for three different configurations. In each case, the dashed black box encircles the unit cell of the substrate, measured between four silver atoms from the 1st layer. The hexane chain is adsorbed (a) on top of the second layer atoms, along the [110] direction; (b) on top of the first layer atoms, along the [110] direction; and (c) orthogonally to the substrate anisotropy. The most energetically favoured adsorption position, with $E_{ads} = 0.30 \text{ eV}$, is depicted in (a), in agreement with previous reports on substrates with similar anisotropy [6].



Figure S8: DFT calculated selfassembled structure of the DPD monomers in the gas phase, taking into consideration hydrogen bonding between the alcohol moieties (encircled in red) and the interdigitation of the aliphatic chains (encircled in blue).

5 Angle Determination for the DPD Self-Assembly on Each Substrate

The values for the different angles reported in the Manuscript are the mean values of multiple measurements in the STM images of each angle of interest^a. An illustrative example of how the measurements were conducted can be observed in Figures S9. Such a measurement was then repeated several times, each with a different set of molecules, *i.e.*, a different unit cell in the DPD SAM.



Figure S9: Illustrative representation of how the reported angles were determined from the STM images from the DPD SAM on Ag(111) (top) and Ag(110) (bottom). Although a single measurement for each angle is here depicted, multiple instances of the same measurement (but involving different molecules) were carried out. The reported values are the mean value among those measurements, and the reported error is the corresponding standard deviation.

The angles α and β on each substrate were measured between the vectors \vec{a} and \vec{b} described in the Manuscript. On the other hand, the angle θ on Ag(111) was measured between a horizontal line parallel to $\vec{L_2}$ and the direction of the vector \vec{b}_{111} . Furthermore, for the measurement of the angle δ , we first measured a 90° angle between two vectors parallel to $\vec{L_1}$ and $\vec{L_2}$ (in agreement with the angle reported for the reference system) and centered on a DPD molecule. Subsequently, the angle δ was measured between the vector parallel to $\vec{L_1}$ and the direction of the vector \vec{a}_{111} . A similar procedure was followed

^aIt should be noted that all images were acquired with the same scanning angle.

to measure the angle ϵ on Ag(110): we first measured a 90° angle (also in agreement with the angle reported for the reference system) starting from a vector parallel to the short axis of the DPD molecule (\vec{a}_{110}) and centered on a DPD molecule. Subsequently, the angle ϵ was measured between the axis orthogonal to \vec{a}_{110} and the direction of the vector \vec{b}_{110} .

The reported errors for the mean angle values are the standard deviation of the distribution of the measured values for each angle. Therefore, it represents the dispersion of the data values and its solely related to how effectively the angles were measured from the STM images. Since the images are acquired at room temperature, artefacts such as thermal and piezo drifts are always present. To minimize their impact, and therefore improve the accuracy of our determination of the unit cell dimensions and all the angles of interest, the same area was scanned multiple consecutive times until drift effects were almost negligible for the given experimental conditions. All the STM images depicted in the Manuscript and ESI were acquired following such a methodology.

6 Coverage of the DPD Self-Assembly on Each Substrate



Figure S10: Constant current STM images depicting the single phase and the submonolayer coverage of the DPD SAM on each substrate. (Left) DPD SAM on Ag(111) (U = -600 mV; I = 50 pA). (Right) DPD SAM on Ag(110) (U = 900 mV; I = 100 pA).

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