Supporting information

One Building Block, Two Different Supramolecular Surface-Confined Patterns: Concentration in Control at the Solid/liquid Interface

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1. Table S1: Parameters referring to the structure and energy characteristics of honeycomb and linear patterns formed by the DBA derivatives.

<table>
<thead>
<tr>
<th></th>
<th>DBA-OC12</th>
<th>DBA-OC14</th>
<th>DBA-OC16</th>
<th>DBA-OC18</th>
<th>DBA-OC20</th>
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<tr>
<td>Repeating period</td>
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<tr>
<td>(honeycomb) /nm</td>
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<td>$^{(1)}$Ah /nm$^2$</td>
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<td>Area of pore /nm$^2$</td>
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<tr>
<td>Pore fraction /%</td>
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<td>$^{(2)}$E_m /meV</td>
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<td>10.03</td>
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<td>$^{(4)}$E_m /meV</td>
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<tr>
<td>$^{(6)}$E_l - $^{(4)}$E_m /meV.nm$^{-2}$</td>
<td>550 (1.7±4.8)</td>
<td>677 (19±3.8)</td>
<td>818 (31±4.7)</td>
<td>910 (45±4.8)</td>
<td>956</td>
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The energies listed in this table are overestimated at the level of maximized alkyl chain – alkyl chain and alkyl chain – substrate interactions. Furthermore, loss of solvation of adsorbed segments is not taken into account. Therefore, this table only reveals trends (as far as the energies are concerned) and should not be used to benchmark the experimental data in a quantitative way. $(1)$ area per unit cell of honeycomb and linear structure, respectively. The number of molecules per unit cell (N) equals 2 for both the honeycomb and linear patterns. $(2)$ adsorption energy per molecule in a honeycomb network, taking into account adsorbate-adsorbate and adsorbate-substrate interactions. $(3)$ adsorption energy per unit of area of honeycomb pattern, $E_h = E_{m,n} N A_h$. $(4)$ adsorption energy per molecule in a linear structure, taking into account adsorbate-adsorbate and adsorbate-substrate interactions. $(5)$ adsorption energy per unit of area of linear pattern, $E_l = E_{m,n} N A_l$. For details on the calculations, see Supporting Information. $(6)$ the values in parentheses correspond to $\hbar/kT \ln K$ calculated from the intercept of the linear fit in Figure 3c. The large difference between the values based upon experimental data and those from theoretical modeling ($E_l - E_h$) demonstrates the significant contribution of the co-adsorbed solvent in stabilizing the porous honeycomb pattern, an aspect which is not taken into account.

**General.** All manipulations were performed in an inert gas (nitrogen or argon) atmosphere. All solvents were distilled before use. All commercially available reagents were used as received. Pd(PPh₃)₄ was prepared following the literature [1].

H (400 MHz, 300 MHz, and 270 MHz) and C (100 MHz, 75 MHz, and 67.5 MHz) NMR spectra were measured on a JEOL JNM AL-400, a Varian Mercury 300, and a JEOL JNM-GSX-270 spectrometers, respectively. The spectra measured in chloroform- d were referenced to residual solvent protons in the H NMR spectra (7.26 ppm) and to solvent carbons in the C NMR spectra (77.0 ppm). Preparative HPLC was undertaken with a JAI LC-908 chromatograph using 600 mm × 20 mm JAIGEL-1H and 2H GPC columns with CHCl₃ as the eluent. Other spectra were recorded using the following instruments: IR spectra, JACSCO FT/IR-410; Mass spectra, JEOL JMS-700 for EI ionization mode and AXIMA-CFR for LD ionization mode.

1,2-Diicosyloxybenzene. A suspension of catechol (1.04 g, 9.44 mmol) and K₂CO₃ (2.87 g, 20.8 mmol) in DMF (50 mL) was stirred for 30 min at room temperature under an argon atmosphere. To the resulting mixture 1-bromoicosane (8.05 g, 22.3 mmol) was added. After stirring for 18 h at 65 °C, CHCl₃ and water was added to the mixture, and the extract was washed with water and brine. The organic phase was dried over MgSO₄, the solvent was evaporated under vacuum, and the product was purified with a silica gel column (hexane/CH₂Cl₂ = 4/1 as an eluent) to afford 1,2-diicosyloxybenzene (3.80 g, 5.67 mmol, 61%) as a white solid. mp 67.9–68.1 °C; H NMR (300 MHz, CDCl₃) δ 6.92–6.84 (m, 4H), 3.99 (t, J = 6.6 Hz, 4H), 1.81 (tt, J = 6.6, 6.6 Hz, 4H), 1.50–1.25 (m, 68H), 0.89 (t, J = 6.6 Hz, 6H); C NMR (75 MHz, CDCl₃) δ 149.4, 121.1, 114.3, 69.4, 31.9, 29.7, 26.0, 22.7, 14.1; IR (KBr) 2917, 2849, 1594, 1508, 1468, 1259, 1122, 724 cm⁻¹; MS (FAB) m/z 670.7 (M⁺); Anal. Calcd for C₄₆H₈₆O₂: C, 82.32; H, 12.92; Found: C, 82.11; H, 13.33.

Synthesis of 1,2-Diicosyloxy-4,5-diiodobenzene. To an EtOH (10 mL) solution of orthoperiodic acid (15.0 mg, 373 mol), 1,2-diicosyloxybenzene (498 mg, 743 mol) and iodine (171 mg, 671 mol) were added at room temperature under an argon atmosphere. After stirring for 17 h at 70 °C, Na₂SO₃ aq. was added to the mixture until the color of the mixture changed from purple to white. White precipitates were filtered off, and the filtrate was washed with water, and dried under vacuum. The filtrate was dissolved in CHCl₃ and purified with a short silica gel column (CH₂Cl₂ as an eluent) giving 1,2-dialkoxy-4,5-diiodobenzene (616 mg, 668 mol, 90%) as a white solid. mp 74.7–75.0 °C; H NMR (300 MHz, CDCl₃) δ 7.25 (s, 2H), 3.92 (t, J = 6.6 Hz, 4H), 1.79 (tt, J = 7.5, 6.6 Hz, 4H), 1.50–1.25 (m, 68H), 0.88 (t, J = 6.6 Hz, 6H); C NMR (75 MHz, CDCl₃) δ 149.9, 124.0, 96.0, 69.5, 31.9, 29.7, 29.3, 29.1, 25.9, 22.7, 14.1; IR (KBr) 2916, 2849, 1547, 1493, 1491, 1254, 1245, 1195, 1016, 857, 719, 636 cm⁻¹; MS (EI) m/z 922.4 (M⁺); Anal. Calcd for C₄₆H₈₄I₂O₂: C, 59.86; H, 9.17; Found: C, 59.91; H, 9.30.

Synthesis of 1,2-Diicosyloxy-4-iodo-5-(trimethylsilyl)ethynylbenzene. Under an argon atmosphere, 1,2-diicosyloxy-4,5-diiodobenzene (1.00 g, 1.08 mmol), CuI (20.6 mg, 108 mol) and Pd(PPh₃)₄ (62.5 mg, 54.0 mol) were placed in a three necked flask. Freshly distilled NEt₃ (50 mL) was added, and then (trimethylsilyl)acetylene (0.184 mL, 1.14 mmol) was slowly added to the reaction mixture via a syringe. After stirring at 50 °C for 3 h, the reaction mixture was filtered and the solvent was evaporated under vacuum. The products were purified with a silica gel column (CH₂Cl₂/hexane = 1/19) to give 1,2-diicosyloxy-4-iodo-5-(trimethylsilyl)ethynylbenzene (472 mg, 529 mol, 49%) as a white solid. mp 51.5–52.5 °C; H NMR (400 MHz, CDCl₃) δ 7.20 (s, 1H), 6.96 (s, 1H), 4.00–3.88 (m, 4H), 1.85–1.73 (m, 4H), 1.50–1.20 (m, 68H), 0.91–0.85 (m, 6H), 0.28 (s, 9H); C NMR (67.5 MHz, CDCl₃) δ 150.1, 148.8, 123.0, 121.7, 117.1, 107.0, 96.4, 90.6, 69.5, 69.4, 32.0, 31.7, 29.81, 29.76, 29.71, 29.5, 29.21, 29.17, 27.0, 26.06, 26.04, 22.8,
22.7, 14.2, 0.1; IR (KBr) 2916, 2849, 2154, 1500, 1470, 1252, 1210, 1177, 840, 719 cm⁻¹; HRMS (EI) calcd for C₅₁H₹₃O₂SiI, 892.5990, found, 892.6024 (M⁺).

**Synthesis of 1,2-Diicosyloxy-4-ethynyl-5-iodobenzene.** Deprotection of the TMS group of 1,2-diicosyloxy-4-iodo-5-(trimethylsilyl)ethynylbenzene (186 mg, 209 mol) was performed with K₂CO₃ (86 mg, 0.62 mmol) in a mixture of MeOH/THF (5 mL/5 mL). After stirring at room temperature for 2 d, water (20 mL) and CHCl₃ (20 mL) were added, and the organic phase was washed with water and brine. The extract was dried over MgSO₄, and the organic phase was washed with water and brine. The extract was dried over MgSO₄, and the solvent was evaporated to afford 1,2-diicosyloxy-4-ethynyl-5-iodobenzene (94 mg, 0.11 mmol, 55%) as a white solid. This material was used for next step without further purification. mp 79.0–79.8 °C; ¹H NMR (270 MHz, CDCl₃) 7.21 (s, 1H), 6.98 (s, 1H), 4.02–3.89 (m, 4H), 3.28 (s, 1H), 1.88–1.71 (m, 4H), 1.55–1.20 (m, 68H), 0.95–0.80 (m, 6H); ¹³C NMR (67.5 MHz, CDCl₃) 150.4, 148.9, 123.0, 120.7, 116.9, 89.6, 85.5, 79.0, 69.5, 32.0, 29.79, 29.75, 29.70, 29.44, 29.42, 29.18, 29.15, 26.1, 26.0, 22.8, 14.2; IR (KBr) 3284, 2916, 2848, 1585, 1497, 1470, 1209, 1166, 867, 718 cm⁻¹; MS (EI) m/z 820.6 (M⁺).

**Synthesis of Hexakis(icosyloxy)hexadehydrotribenzo[12]annulene (1f).** Under a nitrogen atmosphere, 1,2-diicosyloxy-4-ethynyl-5-iodobenzene (90 mg, 0.11 mmol), Cul (6.3 mg, 33 mol), PPh₃ (8.6 mg, 33 mol), K₂CO₃ (42 mg, 33 mol) and DMF (1.0 mL) were placed in a Schlenk tube. After stirring at 160 °C for 16 h, the reaction mixture was poured into aq. NH₄Cl. Products were extracted with CHCl₃ (40 mL), the extract was washed with water and brine, and dried over MgSO₄. After evaporation of the solvent under reduced pressure, the products were separated by the use of silica gel chromatography (CH₂Cl₂/hexane = 1/3–2/5) to give hexakis(icosyloxy)hexadehydrotribenzo[12]annulene (17 mg, 8.2 mol, 22%) as a yellow solid. Further purification was performed by preparative HPLC. mp 76.5–78.0 °C; ¹H NMR (270 MHz, CDCl₃) 6.72 (s, 6H), 3.95 (t, J = 6.8 Hz, 12H), 1.80 (tt, J = 6.8, 6.5 Hz, 12H), 1.50–1.20 (m, 204H), 0.88 (t, J = 6.5 Hz, 18H); ¹³C NMR (67.5 MHz) 149.1, 119.8, 115.9, 91.9, 91.9, 69.2, 32.0, 29.82, 29.76, 29.73, 29.72, 29.50, 29.46, 29.3, 26.1, 22.8, 14.2; IR (KBr) 2919, 2850, 2209, 1512, 1469, 1350, 1229, 720 cm⁻¹; MS (MALD-TOF): m/z 2079 ([M+H]⁺).
3. Typical STM images for DBAs at different concentrations

Figure S1. Typical STM images obtained for different concentrations of DBA-OC12 in TCB. The DBA-OC12 concentration and honeycomb surface coverage are indicated on top of the respective STM images. (A) $V_{bias} = -0.70$ V, $I_{set} = 33$ pA, (B) $V_{bias} = 1.01$ V, $I_{set} = 58$ pA, (C) $V_{bias} = 1.08$ V, $I_{set} = 417$ pA.
Figure S2. Typical STM images obtained for different concentrations of DBA-OC14 in TCB. The DBA-OC14 concentration and honeycomb surface coverage are indicated on top of the respective STM images. (A) $V_{\text{bias}} = -0.63$ V, $I_{\text{set}} = 860$ pA, (B) $V_{\text{bias}} = 1.01$ V, $I_{\text{set}} = 53$ pA, (C) $V_{\text{bias}} = 0.52$ V, $I_{\text{set}} = 620$ pA, (D) $V_{\text{bias}} = 0.80$ V, $I_{\text{set}} = 240$ pA.
Figure S3. Typical STM images obtained for different concentrations of DBA-OC16 in TCB. The DBA-OC16 concentration and honeycomb surface coverage are indicated on top of the respective STM images. (A) $V_{\text{bias}} = 1.01 \text{ V}$, $I_{\text{set}} = 220 \text{ pA}$, (B) $V_{\text{bias}} = 0.60 \text{ V}$, $I_{\text{set}} = 490 \text{ pA}$, (C) $V_{\text{bias}} = 0.80 \text{ V}$, $I_{\text{set}} = 170 \text{ pA}$, (D) $V_{\text{bias}} = -0.58 \text{ V}$, $I_{\text{set}} = 670 \text{ pA}$.
Figure S4. Typical STM images obtained for different concentrations of DBA-OC18 in TCB. The DBA-OC18 concentration and honeycomb surface coverage are indicated on top of the respective STM images. (A) $V_{\text{bias}}=0.81 \text{ V}$, $I_{\text{set}}=53 \text{ pA}$, (B) $V_{\text{bias}}=0.81 \text{ V}$, $I_{\text{set}}=390 \text{ pA}$, (C) $V_{\text{bias}}=0.78 \text{ V}$, $I_{\text{set}}=280 \text{ pA}$, (D) $V_{\text{bias}}=1.02 \text{ V}$, $I_{\text{set}}=170 \text{ pA}$. 

A  $2.6 \times 10^{-5} \text{ mol/L}$  0.7%  
B  $5.2 \times 10^{-5} \text{ mol/L}$  6.3%  
C  $1.7 \times 10^{-6} \text{ mol/L}$  56%  
D  $1.0 \times 10^{-6} \text{ mol/L}$  

20nm  20nm  20nm  20nm
Figure S5. Typical STM images obtained for different concentrations of DBA-OC20 in TCB. The DBA-OC20 concentration is indicated on top of the respective STM images. At $2.4 \times 10^{-6}$ mol/L a honeycomb and close-packed linear pattern are observed to coexist together with featureless domains. These domains have a similar image contrast as the pores in the honeycomb patterns. Therefore, they are believed to be covered by mobile solvent molecules. (A) $V_{\text{bias}} = 1.06 \text{ V}$, $I_{\text{set}} = 77 \text{ pA}$, (B) $V_{\text{bias}} = 0.70 \text{ V}$, $I_{\text{set}} = 110 \text{ pA}$, (C) $V_{\text{bias}} = 0.75 \text{ V}$, $I_{\text{set}} = 36 \text{ pA}$. 
4. Solvent evaporation

Since the STM measurements were conducted with an open sample holder, solvent evaporation is inevitable. The DBA concentration must increase in time. To evaluate the effect of solvent evaporation quantitatively, a control experiment was carried out. A drop of the TCB solvent (about 8 to 9 µL) was deposited on the surface of a piece of freshly cleaved HOPG (the same size as used for STM measurement) at 21°C. The weight of the sample was recorded with a 10 minutes interval (Figure S1). During a typical STM session which lasts 30 to 40 minutes, 15% of the solvent evaporated. Therefore, solvent evaporation leads to a maximum increase in DBA concentration of about 15%. This change has a negligible impact on the data treatment as the concentration intervals are much larger.

![Weight Loss Curve of TCB on HOPG](image)

Figure S6. A weight loss curve of a drop of TCB on a piece of HOPG at 21 °C. The values have been corrected for the weight of the HOPG piece.
5. Concentration calibration

Besides the evaporation of solvent, another factor causing a concentration error is the adsorption of molecules onto the substrate. When the concentration is higher than 1×10^{-4} mol/L, the variation caused by this factor is negligible, but as the concentration becomes lower the error will be significant. To minimize that error we calibrated the free concentration in solution by estimating the amount of molecules adsorbed on the surface, taken into account the relative surface coverage and different density of the two polymorphs. The area of the interface is typically set to 25 mm^2. A comparison of the concentration before and after calibration is listed in table S1.

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<th>5.7×10^{-4}</th>
<th>1.1×10^{-4}</th>
<th>2.9×10^{-5}</th>
<th>5.7×10^{-6}</th>
<th>1.1×10^{-6}</th>
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<tr>
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<td>2.8×10^{-5}</td>
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<td>0.7×10^{-6}</td>
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<td>DBA-OC18 before</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>after</td>
<td>2.5×10^{-5}</td>
<td>4.3×10^{-6}</td>
<td>1.9×10^{-6}</td>
<td>1.1×10^{-6}</td>
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</table>

Table S2. Free DBA concentration (in mol/L) in solution before and after calibration, for DBA-OC16 and DBA-OC18. For DBA-OC12 and DBA-OC14, adsorption leads to a negligible change in DBA concentration.

Figure S7. Plot of $\ln \left( \frac{Y_h}{[DBA]} \right)$ vs $\ln \left( \frac{1-Y_h}{[DBA]} \right)$ for DBA-OC16 and DBA-OC18 before (empty symbol) and after (filled symbol) concentration correction.

<table>
<thead>
<tr>
<th></th>
<th>before</th>
<th>after</th>
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<tbody>
<tr>
<td></td>
<td>$m$</td>
<td>$hkT\ln K$ (meV.nm^2)</td>
</tr>
<tr>
<td>DBA-OC16</td>
<td>2.64±0.24</td>
<td>32±5.9</td>
</tr>
<tr>
<td>DBA-OC18</td>
<td>3.32±0.34</td>
<td>50±6.7</td>
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</table>

Table S3. The influence of the concentration error caused by adsorption on the value of $m$ and $hkT\ln K$. 
6. Qualitative and semi-quantitative evaluation of the interactions in the assembly

The estimation of the energy characteristics of the DBA molecules in the linear and honeycomb patterns (Table 1) is based on parameterization procedures reported previously [2]. Table 1 provides a very rough estimate of the energy characteristics and it should not be considered as a conclusive quantitative treatment. However, in a qualitative and semi-quantitative way it brings insight in the (difference in) energetics of both polymorphs (the honeycomb and close-packed dense-packed linear pattern) from the level of a single molecule to the surface pattern.

A. Parameterization

Interaction of the molecule with the HOPG substrate
Aromatic parts: -65 ± 5 meV/sp² carbon
Alkyl chains: -64.2 meV/CH₂

Interaction between interdigitated alkyl chains
-49.2 meV/CH₂ if flanked at both sides by alkyl chains
-22 meV/CH₂ if only flanked by another alkyl chain at one side.

Oxygen atoms are treated as CH₂ groups to estimate the adsorbate-substrate interaction. Methyl (CH₃) groups are considered as CH₂ groups both in the estimation of adsorbate-substrate and adsorbate-adsorbate interactions.

B. Assumptions/Simplifications

Solvent-molecule and solvent-substrate interactions are not taken into account.
The following aspects are ignored
i) not all alkyl chains are in epitaxy with the graphite substrate
ii) the alkyl chain - alkyl chain interactions are not maximized
a) as far as the extent of alkyl chain interdigitation is concerned and
b) as far as the methylene - methylene interactions of adjacent alkyl chains are concerned, and
iii) the parameterization is based on previous theoretical simulations done in vacuum without taking solvent interactions into account.

However, taking into account both adsorbate-substrate and adsorbate-adsorbate interactions, and the above parameterization and simplifications, the adsorption energy per molecule in the linear pattern was estimated as:

\[ E_{\text{lm}} = 24 \times 65 + 4(n+1) \times 64.2 + 4n \times 49.2 \]

Similarly, the adsorption energy per molecule in the honeycomb pattern could be estimated as:

\[ E_{\text{hm}} = 24 \times 65 + 6(n+1) \times 64.2 + 3n \times 49.2 + 3n \times 22 \]

n is the number of carbon atoms in one alkyl chain.
7. A full version of the thermodynamic model

Suppose one fraction of the surface is covered by the honeycomb pattern and another fraction by the linear pattern. Both physisorbed patterns are in equilibrium with a solution with concentration \([DBA]\). Hence,

\[ \mu_h = \mu_{sol} \quad \text{and} \quad \mu_l = \mu_{sol} \]

where \(\mu_h, \mu_l, \mu_{sol}\) are the chemical potential of a DBA molecule in the honeycomb pattern, the linear pattern and in solution, respectively.

When we convert a unit area of linear patterns into a unit area of honeycomb patterns at equilibrium we must have

\[ l \mu_l = h \mu_h + (l - h) \mu_{sol} \]  

(1)

after dividing by \(l\)

\[ \mu_l = (h/l) \mu_h + [(l - h)/l] \mu_{sol} \]  

(2)

For a dilute solution we can now replace \(\mu_{sol}\) by \(\mu_{sol}^0 + kT \ln[DBA]\)

(3)

where \(\mu_{sol}^0\) corresponds to \(\mu_{sol}\) at standard conditions (ideal molar solution).

In an analogous way we have

\[ \mu_h = \mu_h^0 + kT Y_h \]  

(4)

and \( \mu_l = \mu_l^0 + kT Y_l \)  

(5)

where \(Y_h\) and \(Y_l\) are the fraction of the monolayer area occupied by respectively the honeycomb pattern and the linear pattern.

Combining (2), (3), (4) and (5) yields.

\[ \mu_l^0 + kT Y_l = (h/l)[\mu_h^0 + kT \ln Y_h] + [(l - h)/l][\mu_{sol}^0 + kT \ln[DBA]] \]

or

\[ kT \ln Y_l - (h/l)kT \ln Y_h = (h/l)\mu_h^0 - \mu_l^0 + [(l - h)/l]\mu_{sol}^0 + [(l - h)/l]kT \ln[DBA] \]
\[ \ln Y_h - \left( \frac{h}{l} \right) \ln Y_l = \ln \left( \frac{(h/l)\bar{\mu}^0 - \bar{\mu}_0^0 + \frac{l-h}{l} \bar{\mu}_{\text{sol}}^0}{kT} \right) + \ln [DBA] \]

or

\[ \frac{Y_l}{Y_h^{(h/l)}} = \exp \left[ \frac{(h/l)\bar{\mu}^0 - \bar{\mu}_0^0 + \frac{l-h}{l} \bar{\mu}_{\text{sol}}^0}{kT} \right] [DBA]^{h/l} \]

and

\[ \frac{Y_h}{Y_l^{(h/l)}} = \exp \left[ \frac{-\bar{\mu}_h^0 + \frac{l}{h} \bar{\mu}_l^0 - \frac{l-h}{h} \bar{\mu}_{\text{sol}}^0}{kT} \right] [DBA]^{h/l} \]

With

\[ K = \exp \left[ \frac{-\bar{\mu}_h^0 + \frac{l}{h} \bar{\mu}_l^0 - \frac{l-h}{h} \bar{\mu}_{\text{sol}}^0}{kT} \right] \]

the previous expression becomes

\[ \frac{Y_h}{Y_l^{(h/l)}} = K [DBA]^{h/l} \]

close to complete coverage we have

\[ Y_h + Y_l = 1 \]

Hence

\[ \frac{Y_h}{[1 - Y_h^{(h/l)}]} = K [DBA]^{h/l} \]
with $l/h = m$

$$\frac{Y_h}{[1 - Y_h]^m} = K[DBA]^{-m}$$

or $$\frac{Y_h}{[DBA]} = \left[ \frac{1 - Y_h}{[DBA]} \right]^m K \text{ or } \ln\left( \frac{Y_h}{[DBA]} \right) = m \ln\left( \frac{1 - Y_h}{[DBA]} \right) + \ln K$$

Reference
