

## Role of Pseudopolymorphism on Concentration Dependent Competitive Adsorption at a Liquid/Solid Interface

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### 1. Experimental details

Stock solutions of DBAs with a concentration of 1 mg/g in 1,2,4-trichlorobenzene (TCB) were used to make binary mixtures (normally 1 : 1, in volume) of DBAs with different alkoxy chains. Exact concentrations are mentioned in the figure captions. TCB was chosen because these DBA derivatives are well-soluble in TCB, and more importantly this solvent favors the formation of porous networks. Also important is that the assembling behavior of these molecules has been well investigated at the TCB/graphite interface.<sup>1</sup> For the investigation of the concentration effect on the preferential adsorption, stock solutions of DBA-OC<sub>10</sub> and DBA-OC<sub>16</sub> were mixed at different volume ratios, and diluted subsequently.

For STM measurements a drop of one of the above solutions is applied on a freshly cleaved graphite substrate (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland, USA). STM images were acquired either using a PicoSPM (Agilent) or Nanoscope IIID (Veeco Instruments) operating with constant current mode with the tip immersed in the solution at room temperature (21–22 °C). Pt/Ir (80/20%) tips were prepared by mechanical cutting. The graphite lattice was recorded by lowering the bias right after obtaining images of the assembly. The drift of the image was

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<sup>1</sup> (a) K. Tahara, S. Furukawa, H. Uji-i, T. Uchino, T. Ichikawa, J. Zhang, W. Mamdouh, M. Sonoda, F. C. De Schryver, S. De Feyter, Y. Tobe, *J. Am. Chem. Soc.* 2006, **128**, 16613; (b) S. Furukawa, H. Uji-i, K. Tahara, T. Ichikawa, M. Sonoda, F. C. De Schryver, Y. Tobe, S. De Feyter, *J. Am. Chem. Soc.* 2006, **128**, 3502. (c) S. Lei, K. Tahara, F. C. De Schryver, M. Van der Auweraer, Y. Tobe, S. De Feyter, *Angew. Chem. Int. Ed.* 2008, **47**, 2964.

corrected using the Scanning Probe Image Processor (SPIP) software (Image Metrology ApS) against the graphite lattice.

For the statistical analysis of the surface coverage of different patterns and species identified upon exploring the effect of polymorphism on preferential adsorption, at least 20 large scale images (120 nm × 120 nm) were collected from different surface sites and also for different depositions to correct for site-dependent fluctuations of the concentration. Example images were shown in [Figure S1 to S5](#).

Since the STM measurements were conducted with an open sample holder, solvent evaporation is inevitable. The DBA concentration must increase in time. We have carried out a control experiment to evaluate the effect of solvent evaporation. A drop of the TCB solvent (about 8 μL, the same as used for the STM measurement) 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. 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. On the other hand adsorption of solutes on the surface leads to decrease in concentration, which partially compensate the increase of concentration caused by solvent evaporation.

## **2. Details for the estimation of adsorption energy**

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 [ref. 8]. [Table 1](#) provides a very rough estimation 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 linear pattern) from the level of a single molecule to the surface pattern.

## A. Parameterization<sup>2</sup>

Interaction of the molecule with the HOPG substrate

Aromatic parts:  $-65 \pm 5$  meV/sp<sup>2</sup> carbon

Alkyl chains: -64.2 meV/CH<sub>2</sub>

Interaction between interdigitated alkyl chains

-49.2 meV/CH<sub>2</sub> if flanked at both sides by alkyl chains

-22 meV/CH<sub>2</sub> if only flanked by another alkyl chain at one side.

Oxygen atoms are treated as CH<sub>2</sub> groups to estimate the adsorbate-substrate interaction. Methyl (CH<sub>3</sub>) groups are considered as CH<sub>2</sub> 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:

$$E_{lm} = 24*65 + 4(n+1)*64.2 + 4n*49.2$$

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<sup>2</sup> (a) R. Zacharia, H. Ulbricht, T. Hertel, *Phys. Rev. B* 2004, **69**, 1555406. (b) S. Yin, C. Wang, X. Qiu, C. L. Bai, *Surf. Inter. Analysis*. 2001, **32**, 248. (c) A. J. Gellman, A. R. Paserba, *J. Phys. Chem. B* 2002, **106**, 13231.

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

$$E_{hm} = 24*65+6(n+1)*64.2 + 3n*49.2+3n*22$$

n is the number of carbon atoms in one alkyl chain.

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.

### 3. Series of representative STM images obtained at different concentrations and mole fractions of DBA-OC16 in solution.

Due to big difference in the chain length DBA-OC<sub>10</sub>/DBA-OC<sub>16</sub> form complete phase separated domains at the solid/liquid interface, without mixing even at domain boundaries.

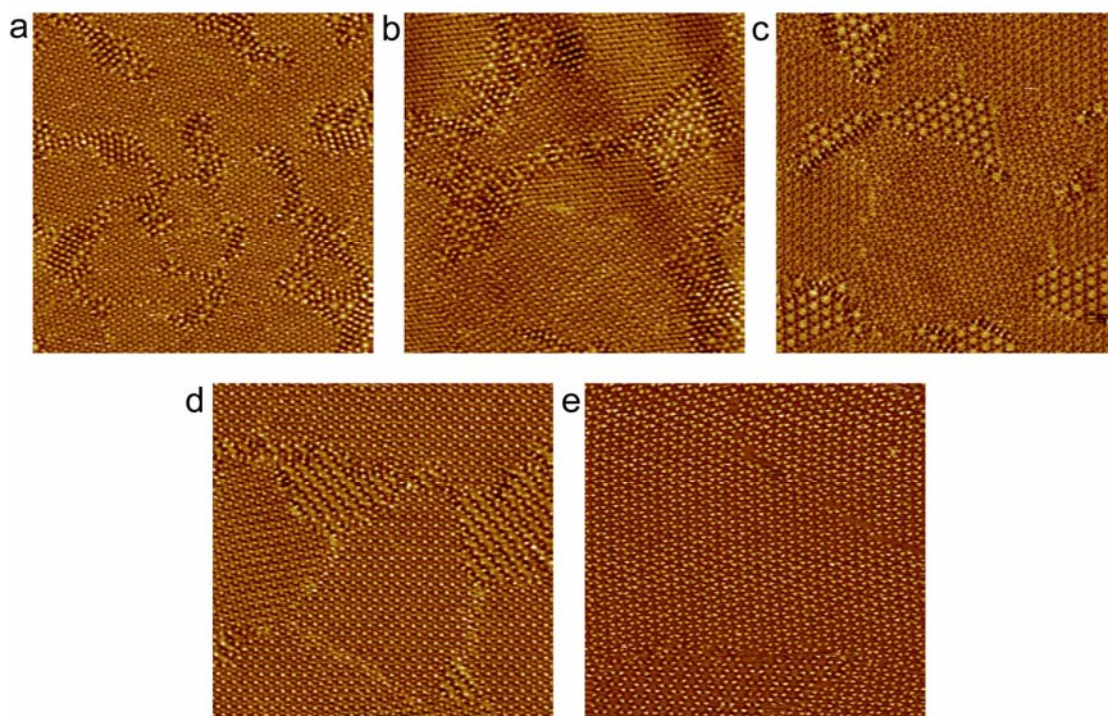


Figure S1. Representative STM images of mixtures of DBA-OC<sub>10</sub>/DBA-OC<sub>16</sub> at the TCB/graphite interface, the DBA-OC<sub>16</sub> mole fraction in solution is 0.12, concentration of DBA-OC<sub>16</sub>: (a)  $4.79 \times 10^{-4}$  M, (b)  $9.58 \times 10^{-5}$  M, (c)  $2.39 \times 10^{-5}$  M, (d)  $4.79 \times 10^{-6}$  M, (e)  $9.58 \times 10^{-7}$  M. **All images are 120 nm × 120 nm.**

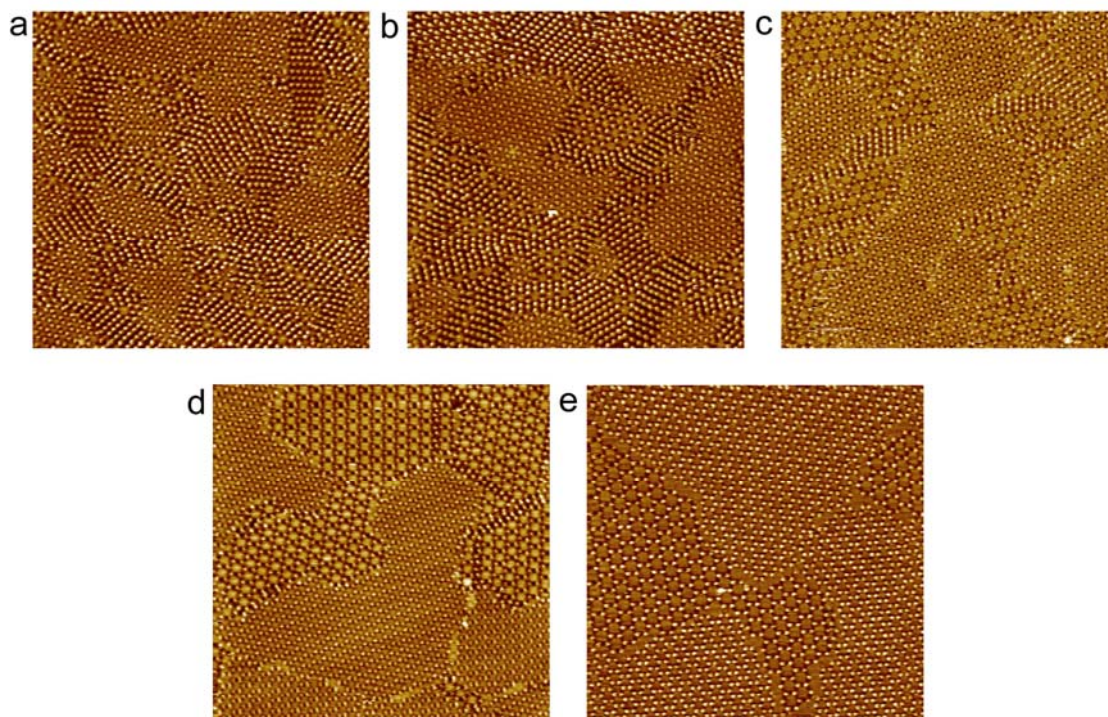


Figure S2. Representative STM images of mixtures of DBA-OC<sub>10</sub>/DBA-OC<sub>16</sub> at the TCB/graphite interface, the DBA-OC<sub>16</sub> mole fraction in solution is 0.26, concentration of DBA-OC<sub>16</sub>: (a)  $3.83 \times 10^{-4}$  M, (b)  $7.67 \times 10^{-5}$  M, (c)  $1.92 \times 10^{-5}$  M, (d)  $3.83 \times 10^{-6}$  M, (e)  $7.67 \times 10^{-7}$  M. All images are 120 nm × 120 nm.

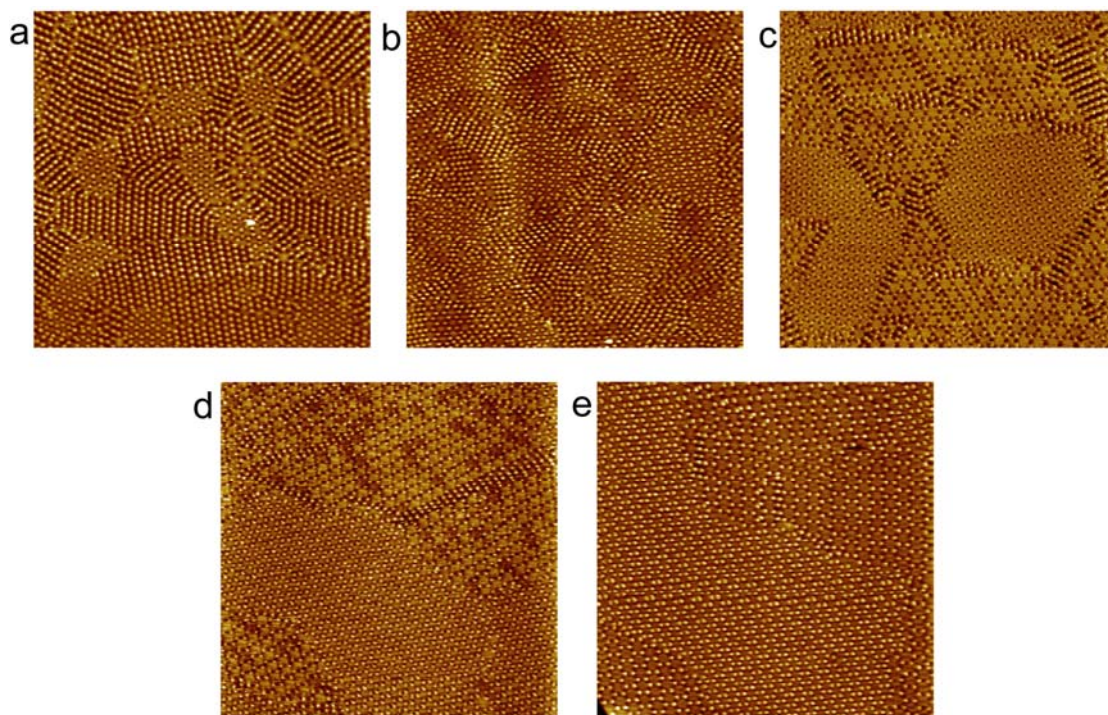


Figure S3. Representative STM images of mixtures of DBA-OC<sub>10</sub>/DBA-OC<sub>16</sub> at the TCB/graphite interface, the DBA-OC<sub>16</sub> mole fraction in solution is 0.42, concentration of DBA-OC<sub>16</sub>: (a)  $2.87 \times 10^{-4}$  M, (b)  $5.75 \times 10^{-5}$  M, (c)  $1.44 \times 10^{-5}$  M, (d)  $2.87 \times 10^{-6}$  M, (e)  $5.75 \times 10^{-7}$  M. All images are 120 nm × 120 nm.

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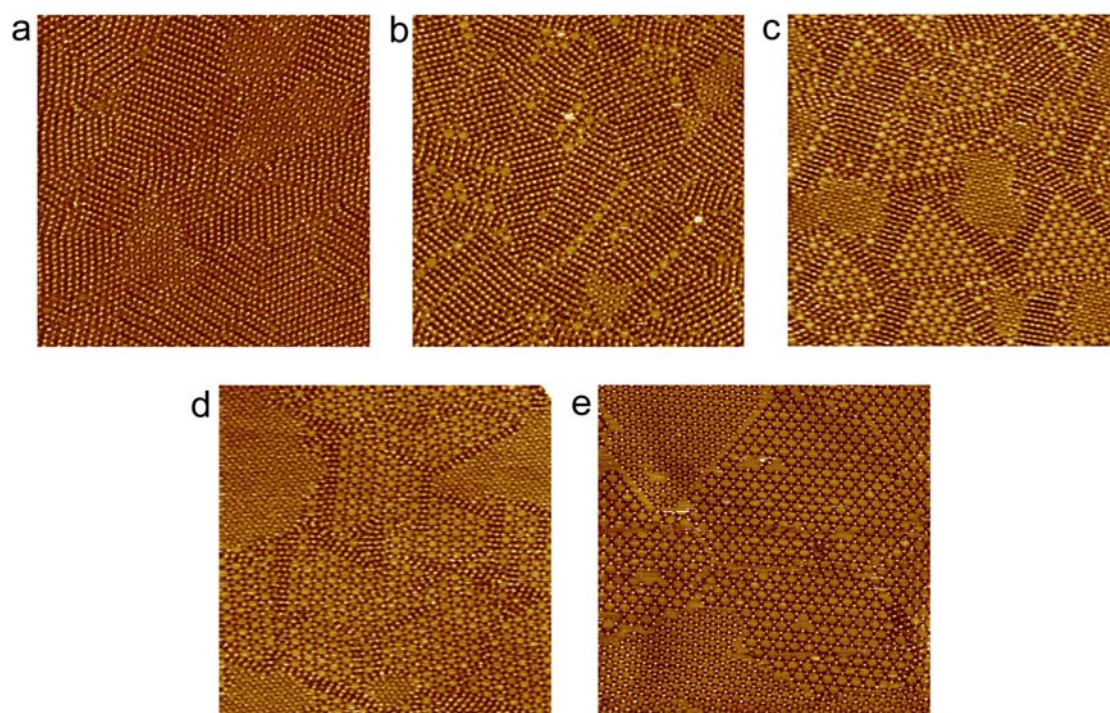


Figure S4. Representative STM images of mixtures of DBA-OC<sub>10</sub>/DBA-OC<sub>16</sub> at the TCB/graphite interface, the DBA-OC<sub>16</sub> mole fraction in solution is 0.59, concentration of DBA-OC<sub>16</sub>: (a)  $1.91 \times 10^{-4}$  M, (b)  $3.83 \times 10^{-5}$  M, (c)  $9.57 \times 10^{-6}$  M, (d)  $1.91 \times 10^{-6}$  M, (e)  $3.83 \times 10^{-7}$  M. All images are 120 nm×120 nm.

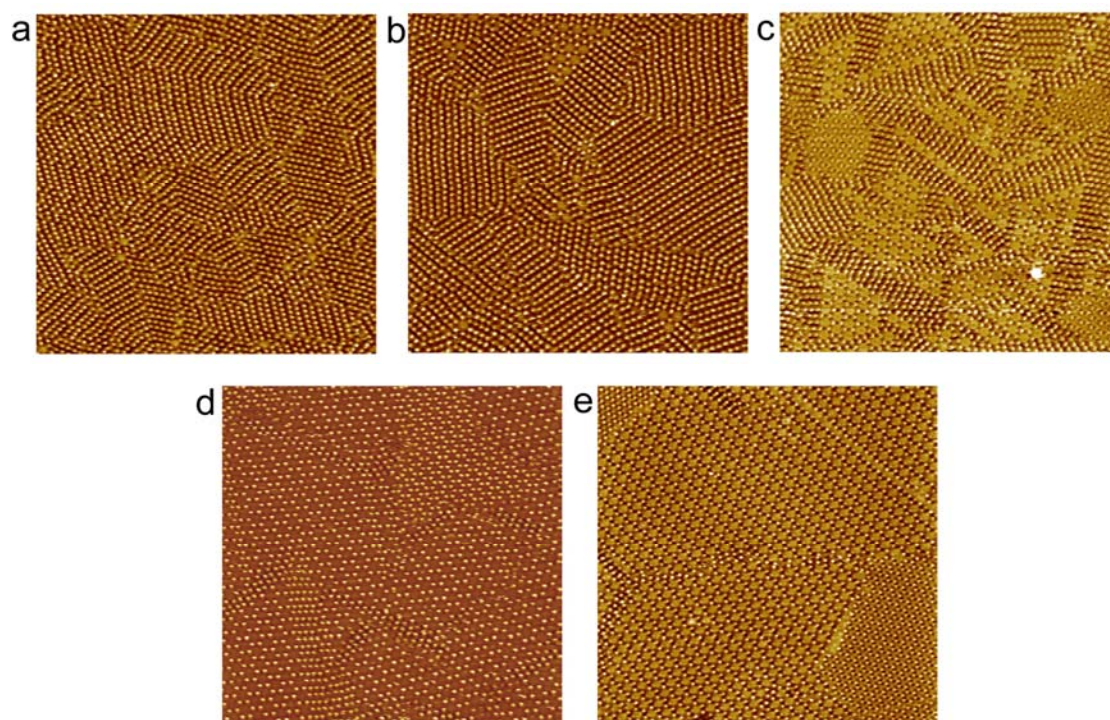


Figure S5. Representative STM images of mixtures of DBA-OC<sub>10</sub>/DBA-OC<sub>16</sub> at the TCB/graphite interface, the DBA-OC<sub>16</sub> mole fraction in solution is 0.78, concentration of DBA-OC<sub>16</sub>: (a)

$9.58 \times 10^{-4} \text{ M}$ , (b)  $1.92 \times 10^{-5} \text{ M}$ , (c)  $4.79 \times 10^{-6} \text{ M}$ , (d)  $9.58 \times 10^{-7} \text{ M}$ , (e)  $1.92 \times 10^{-7} \text{ M}$ . All images are  $120 \text{ nm} \times 120 \text{ nm}$ .

#### 4. Surface fraction of honeycomb pattern (in %) of DBA-OC<sub>16</sub> as a function of concentration

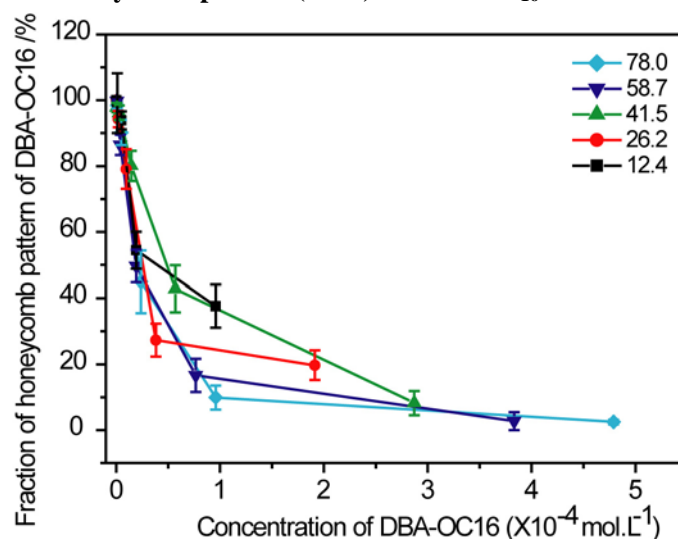


Figure S6. Surface fraction of honeycomb pattern (in %) with respect to the full surface area occupied by DBA-OC<sub>16</sub>, as a function of DBA-OC<sub>16</sub> concentration, for different mole fractions in solution (from 12.4% till 78.0%). The apparent exponential decrease of the fraction of honeycomb pattern as a function of DBA-OC<sub>16</sub> concentration is very similar to the trend observed for the pure DBA-OC<sub>16</sub> system.

#### 5. The effect of adsorption on the composition of solution

To estimate the effect of adsorption on the composition of solutions, we assumed that the volume of solution deposited equals  $8 \mu\text{l}$ , and the wetting area is  $25 \text{ mm}^2$ . Under these assumptions our estimation indicates that only for the lowest concentrations the adsorption induces changes of solution composition with a maximum of  $\sim 12\%$ , while at higher concentration the changes are negligible.

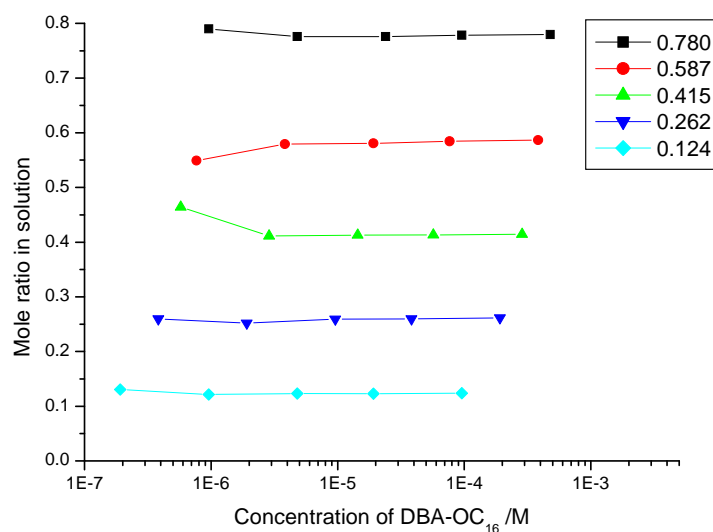


Figure S7. Plot of mole fraction of DBA-OC<sub>16</sub> in solution for different concentrations after correcting the influence of adsorption. Only with the lowest concentrations the adsorption causes apparent changes to the mole ratio in solution. Except when DBA-OC<sub>16</sub> mole ratio equals 0.587, in most cases the adsorption causes an increase in the DBA-OC<sub>16</sub> mole ratio at extremely low concentration, which is consistent with the preferred adsorption of DBA-OC<sub>10</sub> observed. The opposite trend observed for mole ratio 0.587 is attributed to an experimental error, which reflects the limitation of our experimental setup (small solution volume) and lateral concentration fluctuation at the interface.