

Supporting information for

Self-organized lateral patterning of a rare earth complex and stearic acid in Langmuir films

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In the following we discuss optical microscopy results some of which are shown in Fig. 3. For the image, Fig. 3 c, close to the kink that marks the onset of the first order phase transition, a quantitative evaluation (*c.f.* Table 1) in connection with the estimates of the molecular dimensions suggests that *all* SA is organized in the dark core patches while the intervening bright matrix phase consists entirely of a monomolecular layer of Eu(TTA)₃Phen. This may be shown as follows: Let us assume that the two components separate ideally into the dark and bright phase areas – as already suggested by the isotherm, *c.f.* Fig. 6. For the core phase areas, consider the possibility that a well-defined *multilayer* is formed that comprises n individual slabs stacked over each other.[#] One then expects that the molecular areas and the observed fractional distributions of bright and dark phases, x_{matrix} and x_{core} , should obey the relation

$$\frac{A_{hex}^{EuC}}{n} : (k \cdot A^{SA}) = x_{matrix} : x_{core} \quad (1)^*$$

under the condition that

$$\frac{A_{hex}^{EuC}}{n} + k \cdot A^{SA} = A \quad (2)$$

where k is the number of SA molecules per Eu(TTA)₃Phen (for the data shown in Fig. 3, $k = 3$) and A is the average area per Eu(TTA)₃Phen as determined from the isotherm. If our assertion is correct that the system forms well-defined molecular layers, n should be expected to obtain an integer value that reveals the microscopic structure of the systems. These results ought to be consistent for the consecutive sets of data listed in Table 1. At phase transition points, however, we expect this pro-

[#]This is motivated by the facts that (a) the isotherms are well-defined and reproducible although (b) the complex is *not* a conventional amphiphile.

*Molecular-scale areas are generally labeled with the token "A" whereas areas fractions are denoted "x". Thus, molecular dimensions, on the left hand side of Eq. (1) and later equations, are related to mesoscopically visible regions in the molecular surface films, on the right hand side.

cedure to reveal changes of the supramolecular organization of the system. Solving Eq. (1) for n under the assumption, $A^{SA} = 20 \text{ \AA}^2$, with the data in Table 1 that relate to the image, Fig. 3 c, we obtain $n = 1.15$. If we solve Eqns. (1) and (2) simultaneously for n and A^{SA} , $n = 1.04$, $A^{SA} = 22.3 \text{ \AA}^2$ is obtained. Since the highly ordered LS phase^[1] in pure SA monolayers at room temperature is only observed at $\pi > 20 \text{ mN/m}$,^[2] this result is actually more realistic than the one obtained under the *assumption* of $A^{SA} = 20 \text{ \AA}^2$. In fact, areas $A = 22 \dots 24 \text{ \AA}^2$ per molecule have been determined from GIXD for arachidic acid in the (low pressure) L_2 phase.^[3] This result suggests strongly that at the onset of the phase transition the system has segregated into a densely packed, although not crystalline, alkane phase and a monolayer of the Eu complex.

If one tries to guess, in a next step, the molecular organization of the phases that form the meshwork structure at small film areas (*e.g.*, Fig. 3 h), it is immediately realized that the surface film cannot consist of a *monomolecular* layer (of heterogeneous composition): The measured area values in the film, $A \sim 110 \text{ \AA}^2$, are significantly smaller than A_0^{EuC} ($\sim 125 \text{ \AA}^2$, *c.f.* main paper). This shows immediately that the Eu complex is not organized in a monolayer structure. The low compressibility and the general appearance of the isotherm, however, suggest that the compound is organized in a distinct *well-defined* structure, *e.g.* a well-ordered n -layer. As listed in Table 1, the area ratios of the dark patches and the bright interconnecting phase are $\sim 1:1$ in images as the one shown in Fig. 3 h. This is consistent with a molecular organization of the system in which the dark patches consist of SA in a highly ordered, conceivably crystalline, state ($A_0^{SA} \sim 20 \text{ \AA}^2$) while the bright phase is composed of a structure similar to a double layer of tightly packed $\text{Eu}(\text{TTA})_3\text{Phen}$, possibly in the form a hexagonal lattice: $n = 2.13$ is yielded from solving Eqns. (1) and (2).

How does the transition from the well-organized low-pressure structure to the distinct, well-organized high-pressure structure occur? Both fluorescence and scanning force micrographs show remarkable textures that deserve further investigation. From the gray scale distributions in the fluorescence micrographs it is clear that the transition from the initial to the final phase state is nothing less than straight-forward: If our assertion is correct that the film organization at low pressure is that of a demixed monolayer of tightly packed $\text{Eu}(\text{TTA})_3\text{Phen}$ and partially ordered SA, the relative area of the SA core domains should increase upon further compression – since the total film area decreases while the $\text{Eu}(\text{TTA})_3\text{Phen}$ monolayer is transformed into a double-layer structure. As

revealed from Table 1, this is not the case: The area fraction of the core phase *drops* considerably, from 0.34 to below 0.3, after entering the phase transition plateau; it increases again only near the end of the plateau region. We have not succeeded to model the development of the area fractions through the three major distinct regimes of the isotherm – the expanded regime, the plateau regime, and the condensed regime – consistently under the assumption that EuC rings form *around* the SA cores. Rather, an assumption that the brightly luminescent rings form *on top* of the SA monolayer core patches led to a consistent and quantitatively correct description of the observed data.

Let us first summarize the following working hypothesis on the molecular organization of the expanded phase and its successive transformations into the three-phase structure and the 2D mesh-work structure (*c.f.* Fig. 7), as it arises from the quantitative evaluation of the FM images, to be shown in detail below. In the $\text{Eu}(\text{TTA})_3\text{Phen}$ monolayer (expanded regime), each complex is bound to the water surface and to its six nearest neighbors by the interaction of TTA ligands with water or TTA ligands on neighboring complexes in the film. The hydrophobic surface areas of the spherical complexes (gray caps on spheres depicted in Fig. 7), which are dominated by the Phen ligand, are exposed to air. Thus, at the onset of the plateau in the isotherm, the Eu complex forms a tightly packed monolayer, possibly in the form of a hexagonal lattice (Fig. 7, top). As the surface area decreases upon compression, the Eu complexes aggregate – conceivably into tetramers located at the cusps of a trigonal pyramid, as suggested by the putative polar/apolar surface pattern of the complex. All circumstantial evidence – the development of the relative area fractions of the various phases in the monolayer (*vide infra*) as well as the more-than-proportionally increased emission intensity in the ring area – suggests that these oligomers do not associate *laterally* with the SA core patches but rather – at least partially – *on top* of them (center panels of fig. 7). Since the SA molecules are uniaxially oriented across the surface in these core patches, so are their associated dipole moments, and the patches may therefore be considered as dipolar disks.^[4] (Note that only the chain dipoles, and not the inherently larger headgroup dipoles give rise to long-range contributions.^[5, 6]) Since the polarizability of the Eu complex oligomers is large, they are pinned in the electric stray field that emanates at the edge of these dipolar disks, leading to the confinement of the supercomplexes to the observed ring structures. Eventually, as the ring-decorated core patches essentially touch each other upon further compression of the surface film, the dipolar stray field capturing the Eu complex

tetramers is reduced. At this point, capillarity causes the tetramer phase to slip off the core domain boundaries and relocate to the interstitial area that is covered with the $\text{Eu}(\text{TTA})_3\text{Phen}$ monolayer film. As a result, the Eu complex coverage of these areas increases from 1 to 7/3 (Fig. 7, bottom).

The following experimental evidence speaks in favor of this rather complex scenario: (i) The quantitative development of the FM gray level distributions along the isotherm and (ii) the magnitudes of the observed emission intensities in the various phases.

If we parameterize the gray-scale distributions in the images in the spirit of Eqns. (1) and (2) – m is then the (possibly fractional) number of Eu complex layers in the phase formed by Eu oligomers –, three relations have to be satisfied by the model. (i) The $\text{Eu}(\text{TTA})_3\text{Phen}$ complexes are distributed between the matrix phase and the ring phase in the ratio:

$$(1-y)A_{hex}^{EuC} : \left(y \cdot \frac{A_{hex}^{EuC}}{m} \right) = x_{matrix} : x_{ring} \quad (3)$$

where y is the fraction of $\text{Eu}(\text{TTA})_3\text{Phen}$ incorporated in the rings while $(1-y)$ is the fraction of $\text{Eu}(\text{TTA})_3\text{Phen}$ that remains in the interstitial matrix phase. In Eq. (3) we use the fact that the Eu complex is organized in a tightly packed monomolecular layer in the matrix phase. (ii) The relation of the film areas occupied by SA and $\text{Eu}(\text{TTA})_3\text{Phen}$ depends on whether the rings are (a) located adjacent to the SA core domains – thus separating the domains from the Eu complex monolayer film – or (b) located on top of the core domains along their border with the $\text{Eu}(\text{TTA})_3\text{Phen}$ monolayer film. Accordingly, one of two alternate sets of relations have to be fulfilled together with Eq. (3):

$$y \cdot \frac{A_{hex}^{EuC}}{m} : (k \cdot A^{SA}) = x_{ring} : x_{core} \quad (4a)$$

and

$$(1-y)A_{hex}^{EuC} + y \cdot \frac{A_{hex}^{EuC}}{m} + k \cdot A^{SA} = A \quad (5a)$$

or

$$y \cdot \frac{A_{hex}^{EuC}}{m} : \left(k \cdot A^{SA} - y \cdot \frac{A_{hex}^{EuC}}{m} \right) = x_{ring} : x_{core} \quad (4b)$$

and

$$(1-y)A_{hex}^{EuC} + k \cdot A^{SA} = A \quad (5b).$$

The two models, Eqns. (4a, 5a) and (4b, 5b), are obviously extreme cases; any model in between the two – *e.g.*, Eu complex rings that rest partially on the SA core domains and the Eu(TTA)₃Phen monolayer, and cover thus parts of both of these phases – may be realistic.

Solving Eqns. (3–5) for m , y and A^{SA} with the experimental results for the three-phase region tabulated in Table 1 shows that m falls always in the range 1.33 ... 1.44, *independent of the model used*. Thus is strong evidence for the formation of *tetramers*, for which case $m = 4/3$ would be predicted. As expected, y increases monotonically upon compression. The only parameter that depends significantly on the choice of the model is A^{SA} , the value for the area occupied per SA chain in the film, required to satisfy the observed brightness level distribution. For model (a), which implies that the ring phase rests directly on the water surface and occupies thus area within the surface film, A^{SA} is required to be significantly smaller than $A_0^{SA} = 20 \text{ \AA}^2$. We may thus reject this model. On the other hand, for model (b), which implies that the ring phase rests on the hydrophobic top of the surface film and is confined to the rims of the SA core domains, we find from Eqns. (4b, 5b), that A^{SA} falls in the range, 23 ... 28 \AA^2 , and *increases* upon film compression along the isotherm. Intermediate scenarios, *e.g.* sharing the area of the ring phase, which rests on the hydrophobic top of the surface film, between the SA and the Eu(TTA)₃Phen monolayer phases, yields more reasonable agreement of the parameter A^{SA} with the expected value, A_0^{SA} . In all cases – models (a), (b) or their intermediates –, m is found to fall within 1.3 ... 1.5. This is consistent with the conjecture that the ring phase consists of a monolayer of Eu(TTA)₃Phen tetramers, in which 4 Eu complex units occupy the same footprint area as would 3 units in a tightly packed Eu(TTA)₃Phen monolayer film, and thus $m = 4/3$ would be expected.

The conjecture that the ring phase consists of a monolayer of Eu complex tetramers may seem in contradiction with the observed magnitudes of the relative luminescence intensities from the matrix and ring phases, for which a lower limit of ~ 4 has been established (*c.f.* caption to Fig. 3): If the spectral properties of the Eu complex in a monolayer and in the putative tetramer phase were identical, one would expect an increase in emission of only 4/3 over that from the monolayer phase. The excitation spectra in Fig. 1, however, lead to two conclusions: (a) The excitation of the Eu complex *monomers* in the fluorescence microscopy experiment (using glass optics, not quartz!) is quite inefficient: Only the low-energy shoulder at $\lambda > 380 \text{ nm}$ is utilized to excite the complex monomers,

that are presumably forming the monolayer ('matrix') phase. (b) In concentrated solutions, on the other hand, upon aggregation of the complex monomers, an intense band at $\lambda \sim 391$ nm is observed. Consequently, upon the formation of supercomplexes at the air/water interface that form the ring phase, oligomer excitation is expected to be much more efficient, leading to the observed high emission intensity of the ring phase.

In conclusion, *if* the surface structure may be interpreted in terms of homogeneous 2D phases of various compositions with conversions into each other – as suggested by the stability and reproducibility of the π - A isotherms –, then all experimental data are quantitatively accounted for by the assumptions that

- the core phase consists of partially ordered SA molecules
- at the onset of the plateau, the matrix phase consists of a monolayer of (monomeric) Eu complexes
- the ring phase consists of a monolayer of Eu tetramers
- the Eu tetramer monolayer is (at least partially) located on top of the core phase (as opposed to being located adjacent to the core phase)
- at high pressure, the Eu tetramer monolayer is relocated on top of the matrix phase (that consists of Eu complex monomers).

These features are captured in the overall model captured in Fig. 7 as discussed in detail in the main paper.

- [1] A.M. Bibo, C.M. Knobler, I.R. Peterson, *J. Phys. Chem.* **1991**, *95*, 5591-5599.
- [2] E. Teer, C.M. Knobler, C. Lautz, S. Wurlitzer, J. Kildae, T.M. Fischer, *J. Chem. Phys.* **1997**, *106*, 1913-1920.
- [3] K. Kjaer, J. Als-Nielsen, C.A. Helm, P. Tippmann-Krayer, H. Möhwald, *J. Phys. Chem.* **1989**, *93*, 3200-3206.
- [4] H.M. McConnell, *Annu. Rev. Phys. Chem.* **1991**, *42*, 171-195.
- [5] H.M. McConnell, Y.B. Bazaliy, *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 8823-8825.
- [6] P. Krüger, M. Lösche, *Phys. Rev. E* **2000**, *62*, 7031 - 7043.