Floating Mixed Monolayers of Octaalkoxymetallophthalocyanines with Liquid Crystalline Azobenzenes

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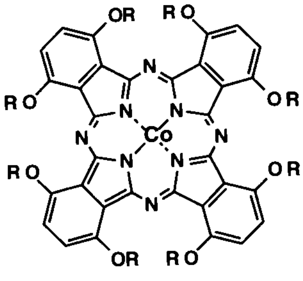
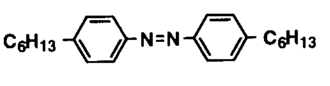
Mixed monolayers consisting of a metallophthalocyanines and a liquid crystalline azobenzene are formed homogeneously on a water surface at temperatures where the azobenzene is in a liquid crystalline state.

Mixed monolayers have been extensively studied to explore ultrathin films with versatile functionality.[1] They are usually fabricated by using amphiphilic component molecules bearing functional moieties or by the stabilization of a functional compound, which form hardly a monolayer by itself, with aid of a fatty acid. We have observed recently that octaalkoxyphthalocyanine metal complexes (CnPcM) form homogeneous mixed monolayers with long-chain normal alkanes on a water surface under controlled conditions including the length of the alkoxyl chains, a subphase temperature and a mixing molar ratio.[2] The macrocyclic rings of CnPcM lie flat on water[3,4] so that a molecular vessel is assembled by the Pc ring as a base and eight long alkoxy chains as a side wall to include non-polar alkane molecules in the cavity. We report here that a nematic liquid crystal (LC) is incorporated in a CnPcM floating monolayer homogeneously under appropriate spreading conditions. This provides a precisely designed model system for the elucidation of an interfacial phenomenon between an LC layer and a substrate surface which plays a key role in the control of LC alignment.[5]



R = $C_{18}H_{37}$: C18PcCo



C6Azo

4,4'-Dihexylazobenzene[6] (C6Azo) melts at 37 ~ 38 °C and shows a transition temperature from isotropic to nematic phase at *ca.* 20 °C and crystallizes immediately during cooling process. The phase transition temperatures are suitable for examining a subphase temperature effect. This monotropic compound was employed here because the orientational direction of guest molecules in monolayers can be evaluated on the basis of the fact that the longitudinal molecular axis is approximately in parallel with π-π* transition moment.

Figure 1 shows surface pressure - area (π-A) isotherms of a mixture of octa(octadecyloxy)phthalocyanine Co complex (C18PcCo) and C6Azo at various mixing molar ratios (*r* = [C6Azo] : [C18PcCo]). Measurements of π-A isotherms were performed on pure water (Milli-Q) filled in a LAUDA FW-1 film balance. A cross-sectional area of the cavity of C18PcCo is estimated to be *ca.* 1.4 nm^2 while that of C6Azo is 0.25 nm^2. This evaluation suggests that five or six C6Azo molecules can be included in the molecular vessel. As shown in Figure 1, the area per C18PcCo increases as the increment of *r* and reaches at a contrast value when the metal complex is mixed with 6 molar amount of C6Azo. The value of an area per C18PcCo estimated from this isotherm, *ca.* 3.0 nm^2, is agreement with an area of Pc ring. It is worthy to note that essentially no alteration of π-A isotherm is caused by adding 12 molar amount or more of C6Azo. It is very likely that excess amount of LC molecules form a multi-layered structure. This makes a marked contrast to mixed monolayers of C18PcCo with normal alkanes which form a homogeneous floating monolayers at an optimum mixing ratio of 1 : 7.[2] The difference in the behavior of mixed monolayers between normal alkanes and the LC arises evidently from whether a long range order exists.

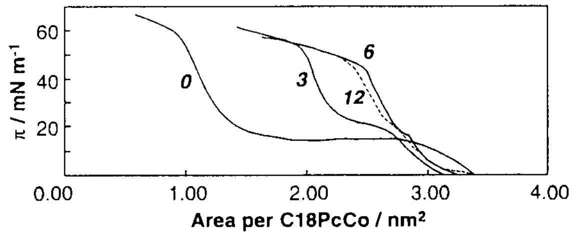


Figure 1. π-A isotherms of monolayers of C18PcCo mixed with C6Az0 at various ***r***. ***r*** = [C6Azo] / [C18PcCo].

π-A isotherms of the mixed monolayers exhibit critical subphase temperature dependence, reflecting the phase transition temperatures of C6Azo. Figure 2 shows the results. At lower subphase temperatures, for example at 5 °C, where C6Azo is crystalline, there are two break points probably ascribable to the transition from flat-laid to tilted orientation of the macrocyclic rings under compression. The first break appears at 15 mN m^{-1}. This value is superimposed with that of a monolayer of C18PcCo alone (Figure 1), implying that two components show a phase separation under these conditions. On the contrary, a π-A isotherm becomes rather smooth at 20 °C and exhibits a steep rise at an occupied area (A_{oc}) of *ca.* 3.0 nm^2, suggesting that a homogeneous host-guest monolayer is formed by entrapping C6Azo molecules in the molecular vessel. When a subphase temperature is set at 30 °C above T_{NI}, A_{oc} decreases considerably. The temperature dependence was visualized clearly by Brewster angle microscopy (BAM) observation (Figure 3). Quite a homogeneous appearance of a monolayer was observed only when a subphase temperature is 20 °C, in a sharp contrast to BAM images at 5 °C and 30 °C, respectively, which display inhomogeneous morphology.

Figure 4 shows absorption spectra of a 1 : 6 mixture of C18PcCo and C6Azo in a toluene solution and in a floating monolayer. It is evident that Pc rings in the monolayer show no

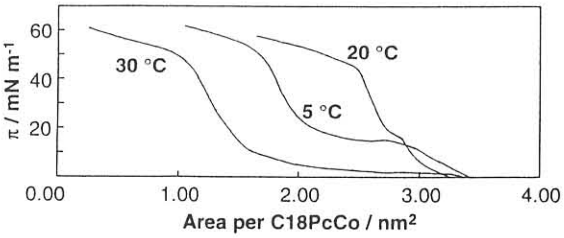


Figure 2. π-A isotherms of a C18PcCo monolayer mixed with C6Azo in *r* = 6 at 5 °C, 20 °C and 30 °C.

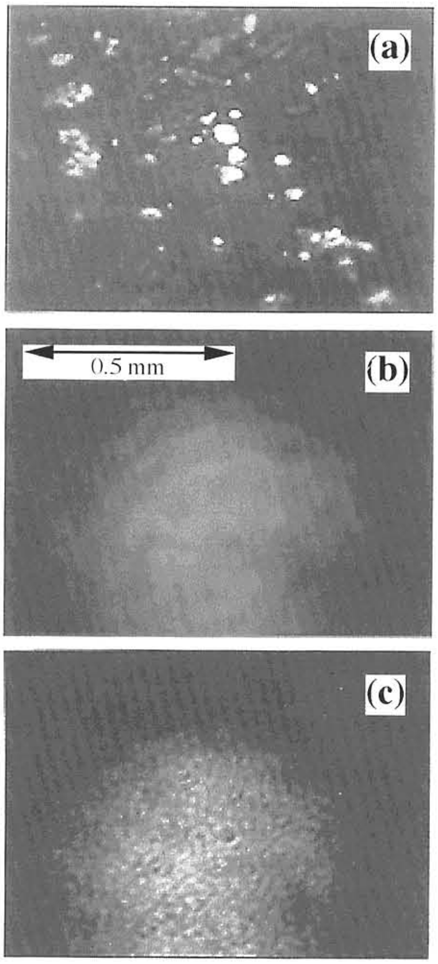


Figure 3. BAM images of mixed monolayers consisting of C18PcCo and C6Azo in a 1 : 6 molar ratio at (a) 5° C, (b) 20 °C and (c) 30 °C, respectively, before and after compression at 20 mN m^{-1}.

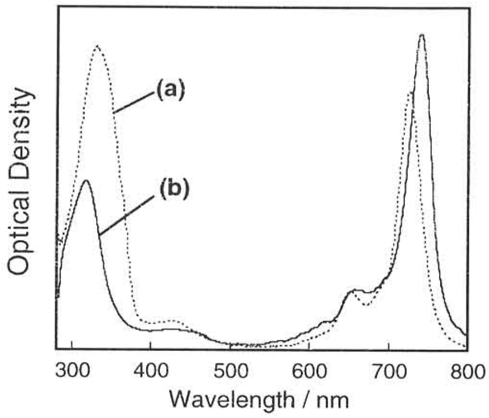


Figure 4. UV-visible absorption spectra of C18PcCo and C6Azo in a 1 : 6 molar ratio (a) in toluene (dotted line) and (b) of a floating monolayer (solid line).

self-aggregation and remain monomeric.[3] An important point to be stressed here is that the absorbance at *ca.* 330 nm predominantly due to the π-π* transition of the azobenzene is prominently reduced in the monolayer. This indicates that the azobenzene exists in a homeotropic alignment on a water surface.

In summary, a novel mixed monolayer system incorporating LC molecules have been developed. One of the prerequisites to assemble homogeneous host-guest monolayers is to operate monomolecular films on a water surface at a subphase temperature below their T_{NI}. It has been confirmed that manifold nematic LC even as mixtures are employed for the fabrication of homogeneous mixed monolayers under the controlled spreading conditions. The present system differs essentially from floating molecular layers of LC reported so far[7,8] since the latter is comprised of LC molecules having a cyano group as a polar site.

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