Supporting Information

Self-assembly of phosphole-lipids in 2D films: The influence of π-interactions and Steric Constraints

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Nomenclature used in the SI figures and tables:

PL1: phosphole-lipid with the core dithienophosphole headgroup

PL2: phosphole-lipid with the extended, benzo-fused dithienophosphole headgroup

C_{12}HB: dodecyl-4-hydroxybenzoate

Table S1. Transfer ratio values measured for LB deposition of **PL1** onto mica from phenol subphases.

Surface pressure ($mN\ m^{-1}$)	**Transfer ratio values**			
	Phenol 1 µM	**Phenol 1 mM**	**Phenol 10 mM**	**Phenol 100 mM**
20	1.2	1.3	1.3	7.6
25	1.9	1.5	1.3	-
30	1.9	1.6	2.1	-
35	1.7	1.6	-	-
40	1.8	1.6	-	-
45	2.1	-	-	-

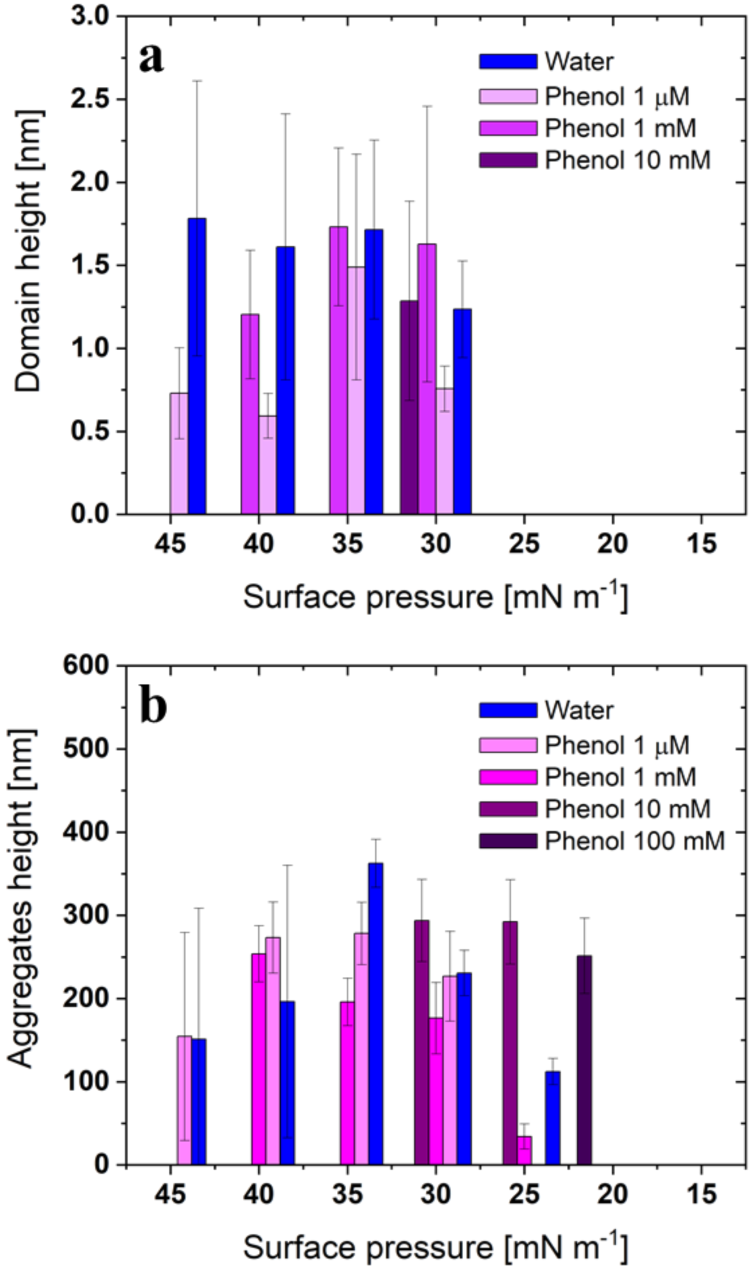

Figure S1. PL1 domain (a) and 3D aggregate (b) heights measured from AFM images as a function of phenol concentration in the subphase. The values and reported errors represent the combined data from at least three locations from each of two independently prepared samples were measured (n>100 domains). The decrease in average aggregate height and increase in error bar for water and 1 µM phenol at high surface pressures reflect the emergence of a second population of aggregates with significantly decreased heights.

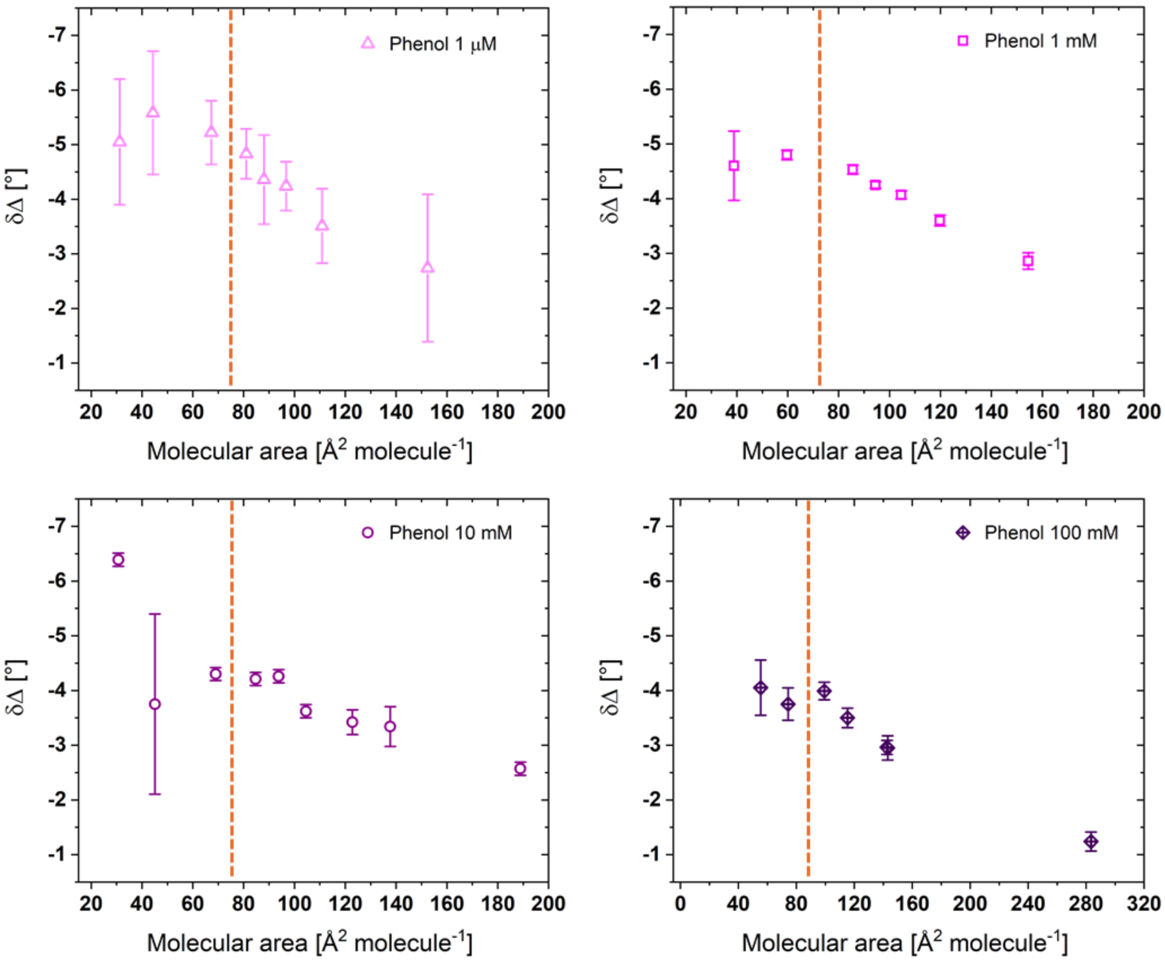

Figure S2. Ellipsometric measurements of **PL1** at air-subphase interface as a function of phenol concentration in the subphase. The dashed line defines the molecular area where the phase transition plateau begins. Each value represents the average of measurements made on three independently formed films. For each independent film, the δΔ is the average of 10 measurements of the same monolayer film at constant surface pressure.

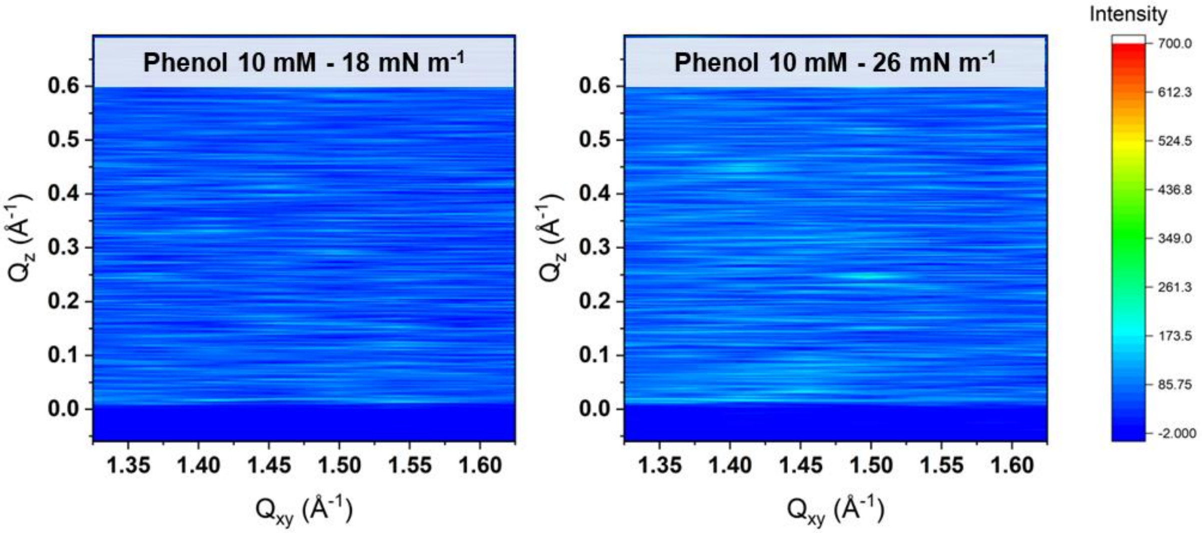

Figure S3. GIXD contour plot of X-ray diffraction intensity as a function of the Q_{xy} (in-plane) and Q_z (out-of-plane) vector components for the **PL1** on 10 mM phenol subphases at two surface pressures below (18 mN m^{-1}) and towards the end of the phase transition plateau (26 mN m^{-1}).

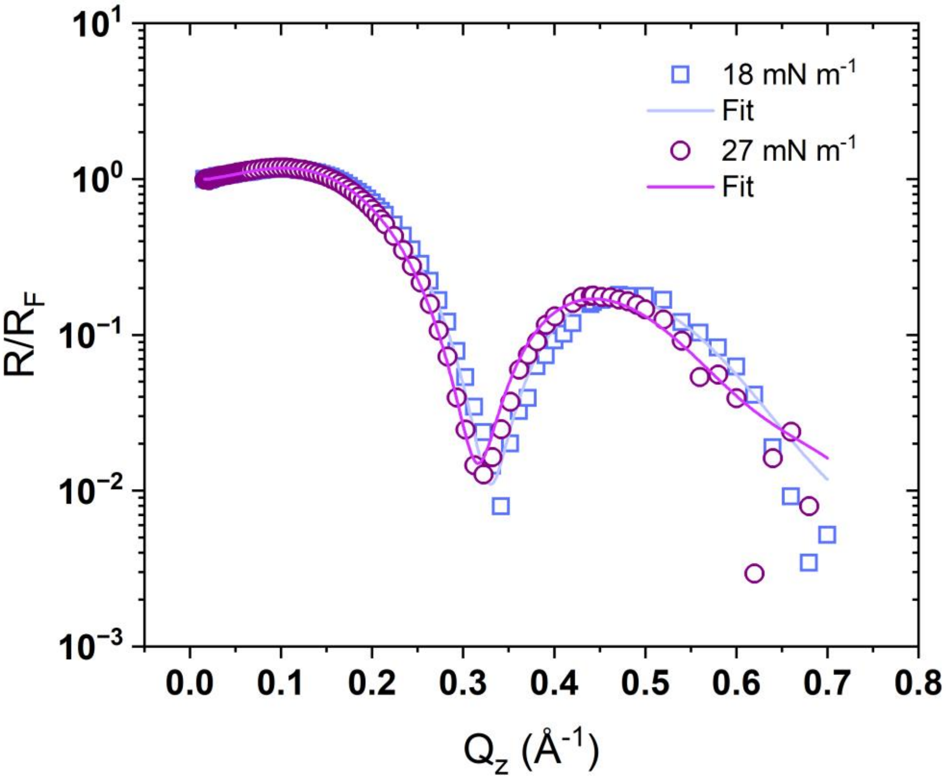

Figure S4. Normalized X-ray reflectivity and their fit model for **PL1** on 10 mM phenol subphase at different surface pressures.

Table S2. Best fit X-ray reflectivity parameters using a two-box model for **PL1** on water and on 10 mM phenol subphase, and **PL1**:**C_{12}HB** lipid mixture on water. Due to the shape of isotherm, experiments at surface pressures above the plateau could not be performed. The values for **PL1** on water were previously reported (ref 31 of main text) and provided here for comparison.

Surface pressure (mN m^{-1})	**Chain region (top box)**		**Headgroup region (bottom box)**	
	Thickness (Å)	**ED (e/$Å^3$)**	**Thickness (Å)**	**ED (e/$Å^3$)**
PL1 on Water				
20	9.8	0.227	8.6	0.415
26	10.1	0.231	9.8	0.422
PL1 on Phenol 10 mM				
18	9.9	0.277	8.8	0.410
27	10.0	0.222	10.3	0.419
PL1:C_{12}HB mixture (1:1 molar ratio) on Water				
17	10.0	0.275	8.5	0.417
25	10.4	0.232	9.9	0.429

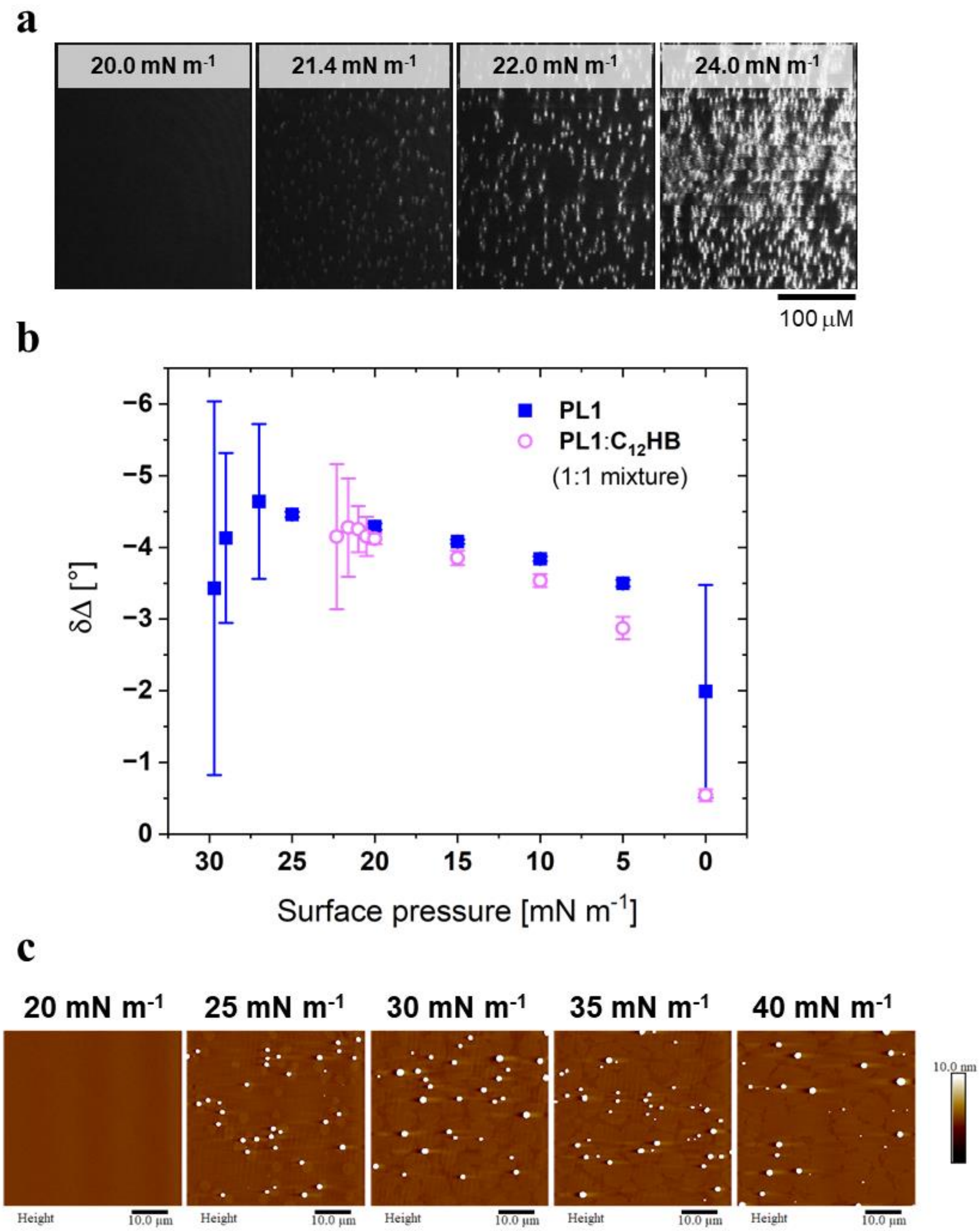

Figure S5. Representative BAM images (a), Ellipsometric measurements (b), and AFM images (c) of a 1:1 mixture of **PL1**: **C12HB** (on ultrapure water subphase). The AFM images are obtained from the LB deposition of mixture film onto mica. For (b), each value represents the average of measurements made on three independently formed films. For each independent film, the δΔ is the average of 10 measurements of the same monolayer film at constant surface pressure.

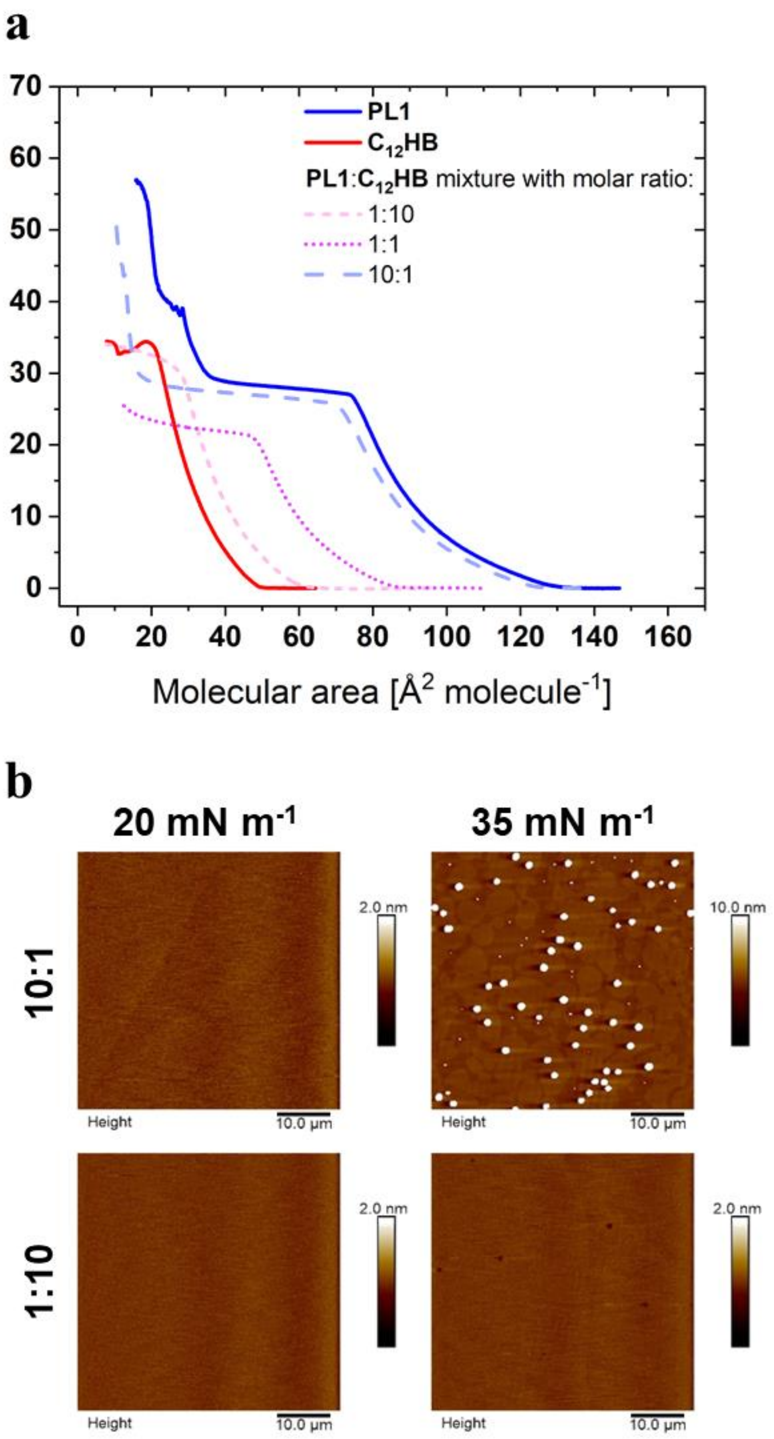

Figure S6. Surface pressure-molecular area of mixture of **PL1**:**C_{12}HB** with molar ratios of 1:10 and 10:1 on water subphase (1:1 mixture isotherm is shown for comparison) (a), and representative AFM images for these two mixtures deposited onto mica by LB at surface pressures of 25 mN m^{-1} (below the plateau) and 35 mN m^{-1} (beyond the plateau).

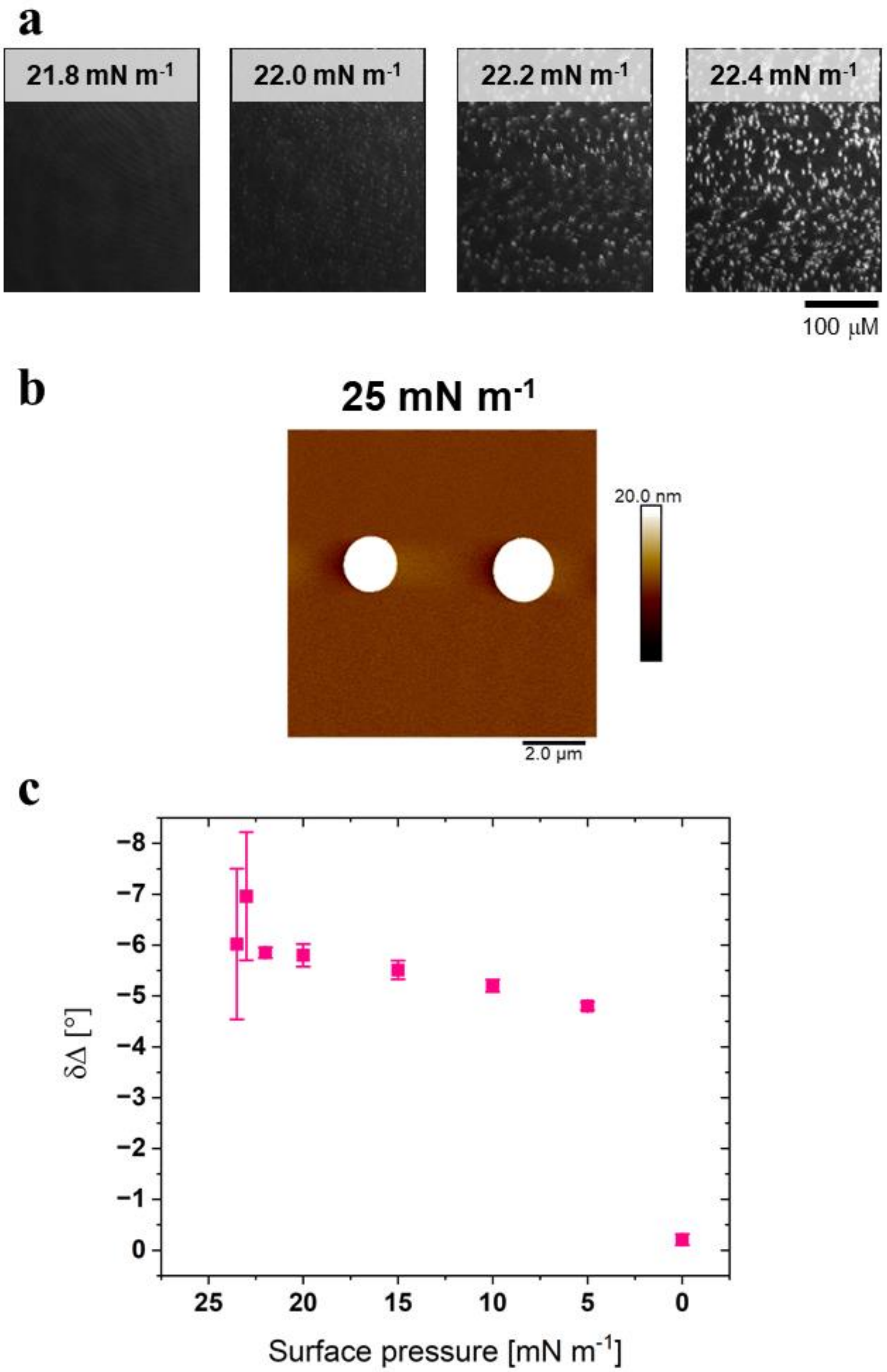

Figure S7. Representative BAM images (a), AFM image (b), and ellipsometric measurements (c) of **PL2** on water subphase. For (c), each value represents the average of measurements made on three independently formed films. For each independent film, the δΔ is the average of 10 measurements of the same monolayer film at constant surface pressure.

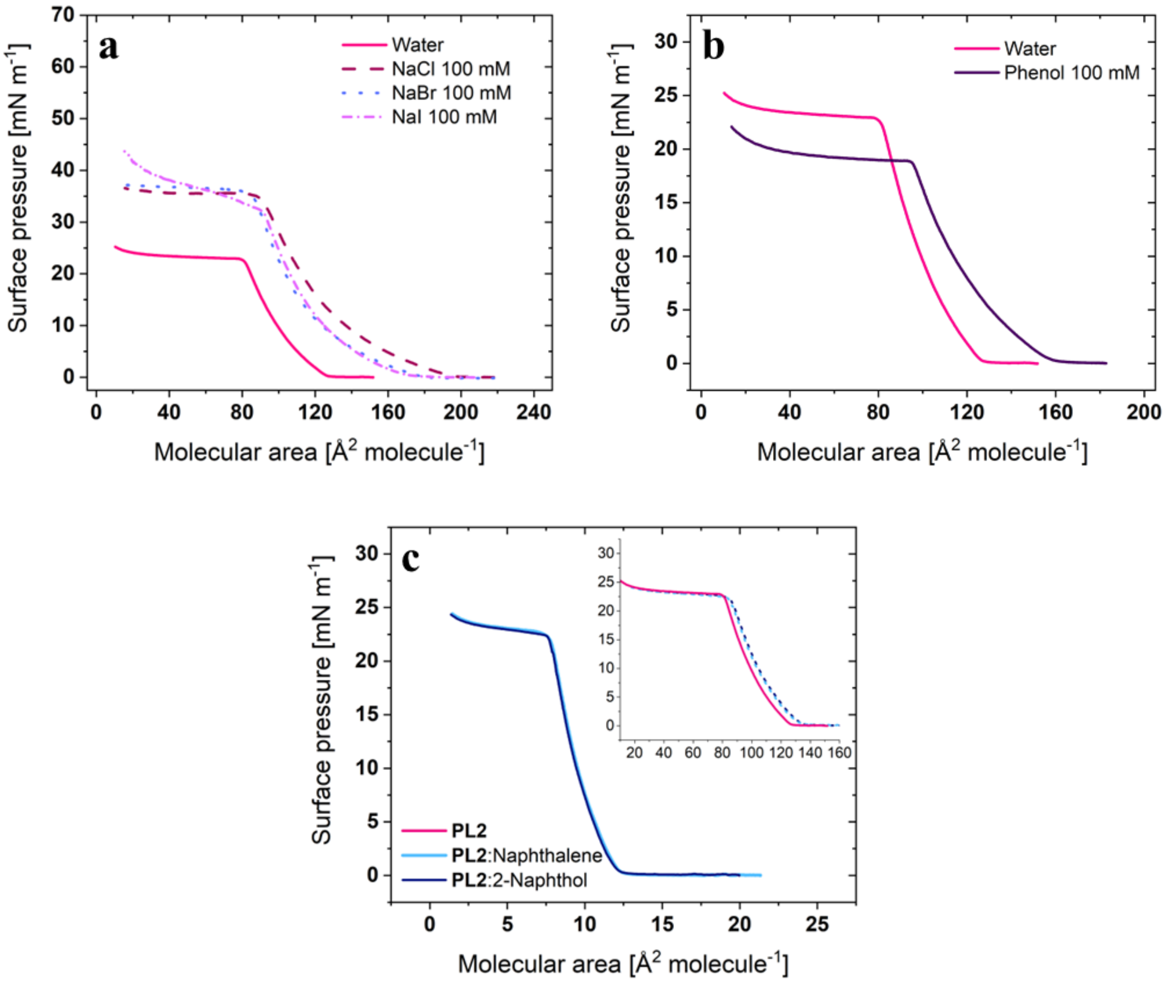

Figure S8. Surface pressure-molecular area isotherms of **PL2** a) with a subphase concentration of 100 mM halide counterions, b) with a subphase concentration of 100 mM phenol and c) co-spread in a 1:10 molar ratio with naphthalene and 2-naphthol (solid lines). For c) the dashed lines in inset represent the same isotherms replotted as a function of pure phosphole-lipid molecular area.