Bilayer porphyrin-graphene templates for self-assembly of metal-organic frameworks

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A new strategy for the formation of bilayer porphyrin-graphene templates to initiate the assembly of various organic or hybrid films including surface metal-organic frameworks on solid substrates is proposed. This strategy involves a one-step assembly of a bilayer at the air-water interface from the organized monolayer of functionalized porphyrin and adsorption layer of graphene oxide (GO). The behavior of monolayers of tetrapyridylporphyrin [1-2] and tetracarboxyphenylporphyrin [2] zinc complexes on the surface of deionized water, aqueous solutions of zinc acetate, GO and GO in the presence of zinc acetate is studied. Using the Langmuir surface balance, in situ fiber optic UV reflection-absorption spectroscopy and fluorescence spectroscopy, the molecular organization of the porphyrin films on surface of pure water is determined and its change under the effect of zinc cations and/or the adsorption layer of the GO is demonstrated. Intensive interactions between the components of the bilayer lead to a substantial shift in the compression isotherms and quenching of fluorescence of the porphyrins. The nature of meso-substituents of porphyrin affects both the structure of the bilayers on the surface of liquid and the morphology of bilayers transferred onto the solid substrate by the Langmuir-Blodgett technique (Figure 1). The proposed approach is interesting in that when the bilayer of firmly bonded porphyrin and GO layers is transferred to a solid substrate, the effect of the latter on the change in the structure of the organic or hybrid films growing on it is screened by the GO layer. At the same time, due to the features of the GO nanosheets, the bilayer is strongly fixed on a solid substrate, which prevents desorption of template when building-up the films by Langmuir-Blodgett technique or layer-by-layer assembly. One of the most important advantages of the proposed strategy is the ability to create templates on solid substrates of any nature without the use of self-assembled monolayers.

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References

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Figure

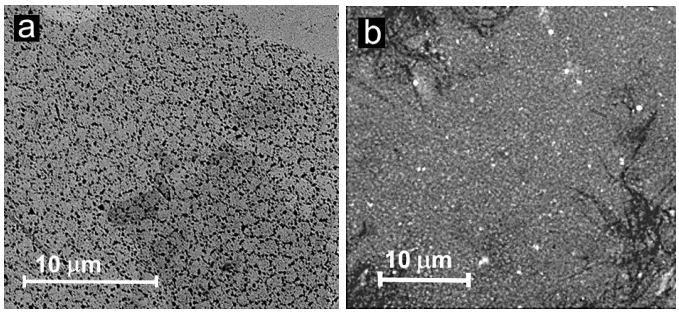

Figure 1: SEM images of the GO/$ZnAc_2$/ZnTPyP (a) and GO/$ZnAc_2$/ZnTCPP (b) bilayers transferred from air-water interface onto silicon support by Langmuir-Blodgett method at 0 mN/m.