Electron-Accepting Phthalocyanine-Pyrene Conjugates: Towards Liquid Phase Exfoliation of Graphite and Photoactive Nanohybrid Formation with Graphene

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Graphene as an outstanding 2D material has attracted great attention due to its multitude of mechanical, optical, and electrical features.¹ In this context, exfoliation of graphite as a top down approach has shown to be a very promising route towards graphene.² Pyrene and its derivatives display a strong affinity towards sp²-nanocarbon networks. For instance, functionalization of phthalocyanines with pyrene addenda has shown to assist in the non-covalent immobilization of chromophores onto carbon nanotubes, in general, and single wall carbon nanotubes, in particular.



Figure 1. Structures of the alkylsulfonyl ZnPc-P conjugate (left) and of the alkylsulfonyl ZnPc (right).

Herein, we describe the synthesis of a zinc(II) alkylsulfonylphthalocyanine-pyrene (ZnPc-P) conjugate, the preparation of a graphene-phthalocyanine nanohybrid, and the investigation of its photophysical properties. In the zinc(II) alkyl-sulfonylphthalocyanine-pyrene conjugate, the presence of pyrene is decisive in terms of non-covalently immobilizing the electron accepting phthalocyanines onto the basal plane of highly exfoliated graphite. It stabilizes single layer graphene during the ultrasonication of graphite by virtue of electronic interactions. By means of full-fledged photophysical investigations, we corroborated that the electronic interactions in the ground and excited state in the nanohybrids are indeed very strong. For example, femtosecond pump probe experiments assist in corroborating an ultrafast charge separation, that is, the generation of the one-electron reduced radical anion of the phthalocyanine and one-electron oxidized graphene after irradiation at 387 nm, followed by slow charge recombination. Alkylsulfonyl-substituted phthalocyanines, which lack the pyrene addenda, were also found to form nanohybrids with exfoliated graphene. This process is, however, less efficient in the latter case than in the earlier.

References

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