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Towards well-structured fullerene–phthalocyanine composites: Co-aggregation of fullerene C_{60} with tetrakis(4-amino-5-phenoxy)phthalocyanine

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ABSTRACT

The paper reports on binary composites prepared from fullerene C_{60} and π-rich cobalt tetrakis(4-amino-5-phenoxy)phthalocyanine (CoPc) being a mixture of four geometrical isomers. Co-aggregation has been conducted under aqueous and non-aqueous conditions by the Langmuir–Blodgett (LB) technique and drop-casting from o-xylene, respectively. The prepared LB composites are badly disordered whereas the cast ones are predominantly structured: depending on the C_{60}/CoPc ratio, the wire-, worm-, or bead-like particles are observed. Optical spectroscopy is used to reveal the aggregation state of fullerene in the composites. The nano-scale heterogeneities resulting from homomolecular aggregation of fullerene are revealed only in the former case. Smooth co-aggregation under non-aqueous conditions is attributed to intermediate formation of the ternary C_{60}–CoPc–xylene solvates. Formation of the well-shaped composite particles seems to be an optional post-aggregation process being favored by the molecular symmetry of the CoPc isomers.

1. Introduction

The fullerene–π-donor systems are of great interest as a material base of organic solar cells [1,2]. Phthalocyanines being organic dyes with extraordinary photophysical properties and photochemical stability are promising π-donor components of such systems. Indeed, fullerene and tetra-*tert*-butyl-phthalocyanine when combined in solution can utilize up to 75% of radiation energy [3].

Two types of the fullerene–phthalocyanine system are known, namely dyads and composites. Dyads are chemically sophisticated and now their prospects seem vague. At any rate, no attempts to apply them in practice are yet reported on [4]. Therefore the present paper deals with a system of the latter type. A merit of the composites is relative inexpensiveness on account of opportunity to use fullerene C_{60} itself. The majority of works is devoted to composites based on the binary system of fullerene C_{60} and unsubstituted zinc phthalocyanine [5–10]. Although these composites had exhibited poor photoconductivity [6], they were widely studied as photovoltaic materials. In particular, the workers [8] managed to prepare the 1:1 composite devoid of the long-range molecular ordering. The photon-to-current conversion efficiency was 1.0–3.4% [9], i.e. by an order of magnitude lower than for silicon. Recently the nanostructural approach was applied to control photophysical processes in the binary composite. As a result, the 1.3% level of conversion efficiency was gained [11]. Presently the fullerene–phthalocyanine system is sooner a model than industrial material [10].

Severe difference in efficiency of the fullerene–phthalocyanine system in the solid state and solution is a general problem. Supposedly it is connected with heterogeneity of the local structure caused by homomolecular aggregation of the components [2,11–13]. In the case of the fullerene–phthalocyanine composites, the aggregation state of intensely colored phthalocyanines is clearly manifested in optical spectra. The spectrum of solid unsubstituted phthalocyanines exhibits a two-band profile [7,14] indicating homoaggregation driven by the intermolecular π–π coupling of high energy. Addition of fullerene C_{60} affects only the relative intensity of two bands [7] and, consequently, results in merely partial disaggregation of phthalocyanine. Moreover, the relative intensity in the roentgen-amorphous sample [8] is practically the same as in the crystalline one [7]. As for the aggregation state of fullerene, the optical spectra presented so far [5–10] shed no light on this vital point. However it seems obvious: if the phthalocyanine component is homoaggregated, the fullerene molecules can hardly avoid homomolecular contacts as well.

Attempts to control the local structure of the fullerene–phthalocyanine composites were undertaken in the works [15,16]. A creative idea was to assemble the wire-like heterostructure or, to be more precise, a kind of supramolecular voltaic pile. The workers [15,16] used organosoluble phthalocyanines, such as tetra-*tert*-butyl- and octakis(octyloxy)-substituted ones. They also used the Langmuir–Blodgett (LB) technique that theoretically allowed preparing the well-ordered fullerene–phthalocyanine films. The LB composite exhibited the

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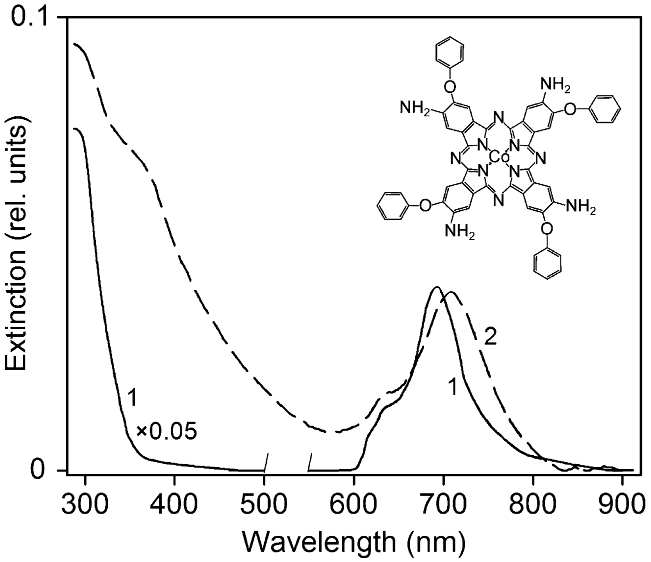

Fig. 1. Optical spectra of phthalocyanine CoPc in solution (xylene–pyridine, 20:1) and in the solid state (the LB sample). The C_{4h}-isomer of CoPc is sketched in.

trivial two-band spectral profile [16]. The wire-like assembly might be observed visually but regretfully no micrographs were presented. Afterwards the same phthalocyanines were used to prepare the fullerene–phthalocyanine assembly with endohedral metallofullerene [17]. Considering the optical spectra [17], one may safely suppose that no fullerene-induced disaggregation of the said phthalocyanines was achieved. Again, no micrographs were presented to confirm self-assembling. High solubility of alkyl-substituted phthalocyanines allows application of casting [18]. However, to our best knowledge, no data on the cast fullerene–phthalocyanine composites were published until now.

Recently the self-assembly concept was applied to prepare the fullerene–porphyrin nanocomposites with unusually high photon-to-current conversion efficiency [19]. As a driving force of the local structure formation, the ground-state charge-transfer interaction [20] was supposed. On this account the nature of the fullerene–phthalocyanine interaction at the molecular level seems also significant. The workers [3,5] were the first who unequivocally stated that only under irradiation the charge transfer from the phthalocyanine molecule to the fullerene occurred. Afterwards a crystalline composite of fullerene C_{60} and octakis(dimethylamino)porphyrazine was prepared [21]. This porphyrazine has eight amino-groups directly connected to the macrocycle and therefore seems more π-basic than any phthalocyanine. The workers [21] studied electrophysical and magnetic properties of the crystals and found no symptoms of the charge transfer. Recently the fullerene–phthalocyanine interaction was studied in solution [22]. The workers [22] used a kind of toluene-soluble unsubstituted zinc phthalocyanine and declared the ground-state charge transfer to exist. They backed up their opinion by theoretical calculations but omitted the counter-data [3,5,21].

The said above may be generalized as follows. The fullerene–phthalocyanine composites were being intensely studied for many years but efficient photovoltaic materials were not designed. The negative results were obtained mainly on the sublimed composites of fullerene C_{60} and unsubstituted phthalocyanines; hence the forced blending of such dissimilar chemical species seems hardly a proper engineering approach. The self-assembly approach to the fullerene–phthalocyanine system was announced a dozen of years ago, but currently the target heterostructures look like mental figures rather than real objects. The results [9,11] are in contrast with impressive achievements in solution-processing of polymeric photovoltaics. Within the last decade, researchers proceeded from nano-scale manipulations [23] with exotic molecules [24,25] to laboratory-scale manufacture [26–29] and field testing [30] of large-area solar cell modules.

To realize the heteromolecular self-assembling in the system under consideration, one should use a phthalocyanine not merely organosoluble but exhibiting molecular affinity for fullerenes. The affinity should be high enough to overcome solid-state homoaggregation of this phthalocyanine. Unfortunately the only fundamental study [22] on the fullerene–phthalocyanine interaction does not answer a key question: Whether this interaction can serve as a structure-forming factor in the solid state? Moreover, no systematic search for fullerene-specific phthalocyanines is noticeable so far. In such an awkward research position, a breakthrough move would be revealing the fullerene–phthalocyanine system whose solid-state structure is determined by the heteromolecular attraction. Therefore the present work was conceived to find out such a system.

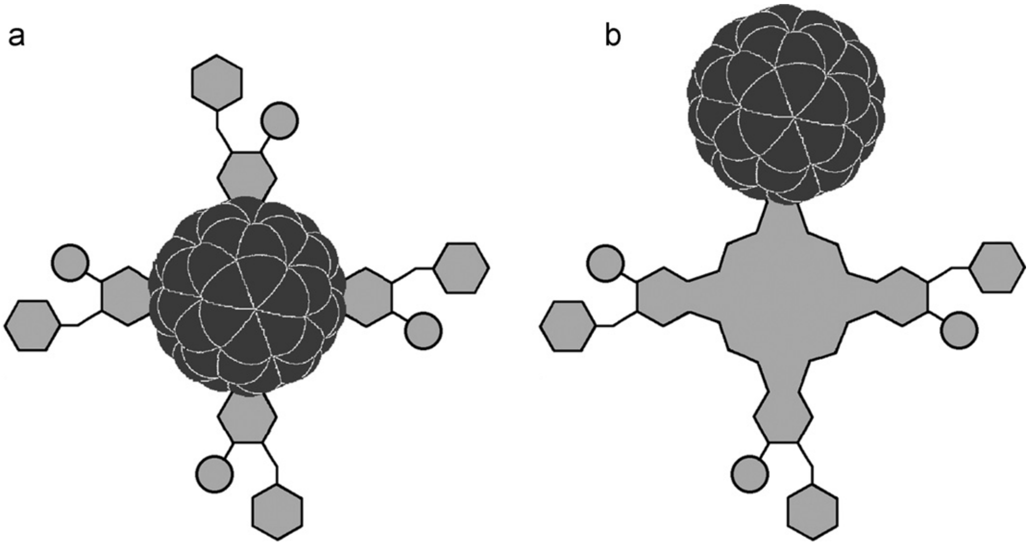

Fig. 2. Two hypothetical modes of the C_{60}–CoPc interaction resulting in 1D (a) and 3D (b) heteromolecular assembling.