

Effect of anion coordination on electron transfer in double-linked zinc phthalocyanine–fullerene dyad

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ABSTRACT

Evidence of the Marcus inverted region behavior for the forward electron transfer reaction in a double-linked zinc phthalocyanine–fullerene dyad was found. The charge separation and recombination processes of the dyad were studied in an ionic environment. The chloride ion coordination to the central zinc of the phthalocyanine macrocycle decreases the energy of the charge separated state and increases the energy of the phthalocyanine first singlet excited state, and thus increases the driving force for the charge separation and decreases it for the recombination. The charge separation is slowed down whereas the charge recombination is accelerated upon the chloride coordination.

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1. Introduction

Among the various chromophores that have been used as molecular components in artificial photosynthetic systems, porphyrins and phthalocyanines are among the preferred and obvious choices due to their intense optical absorption and rich electrochemistry [1]. Both chromophores have distinct redox and photo-physical properties, which render them efficient electron donor units in donor–acceptor (DA) ensembles. Compared to porphyrins, phthalocyanines have more extended aromatic π -electron system and they absorb the light intensively in the red-near infrared region of the spectrum [2].

The development of phthalocyanine-based DA conjugates, such as phthalocyanine–fullerene systems, has attracted a lot of interest and a vast variety of phthalocyanine–fullerene DA compounds has been synthesized and studied during the past decade [3,4]. The phthalocyanine–fullerene dyads have a potential advantage over the porphyrin–fullerene dyads as they may undergo photoinduced electron transfer (ET) even in non-polar media, e.g. in toluene [4]. Similarly to porphyrin–fullerene dyads [5–7], the charge recombination (CR) process has been found to occur in the Marcus inverted region [8–10] for several phthalocyanine–fullerene dyads studied previously [4].

We have previously studied ET dynamics of a zinc porphyrin–fullerene dyad by tuning it with a ligand coordinated to the central zinc of the porphyrin moiety [11,12]. The axial coordination of zinc porphyrin (ZnP) with ligands alters both the electrochemical and spectroscopic properties of the chromophore [13,14]. Among the investigated ligands, the chloride ion was found to be the most effective one, i.e. it resulted in the biggest shift in both the oxida-

tion potential and absorption of ZnP [13]. The effect of ligand coordination to the zinc phthalocyanine (ZnPc) moiety in a DA ensemble was reported to be smaller than that observed in a porphyrin–fullerene dyad [15,16]. However, axial coordination of anions to metallophthalocyanines, let alone to phthalocyanine–fullerene dyads, has not been studied quantitatively.

A double-bridged free-base phthalocyanine–fullerene dyad, **H₂Pc-C₆₀ee** (see Section 2), was earlier found to undergo ET in both polar and non-polar environments. Two conformations resulting in face-to-face and extended orientations were suggested for the dyad, but the examination of the ET energetics suggested that the dyad exists mainly in the extended conformation [17]. In this Letter we use chloride coordination to the ZnPc moiety of a double-linked zinc phthalocyanine–fullerene dyad (**ZnPc-C₆₀ee**, Figure 1) as method to probe dynamics of the photoinduced ET process in the dyad. The experimental results were analyzed in frame of the classical Marcus theory for ET and evidence of the inverted region dependence of the ET rate constant on the free energy of the reaction was found.

2. Materials and methods

The free-base double-linked phthalocyanine–fullerene compound (**H₂Pc-C₆₀ee**) was synthesized and characterized as previously described [17], and metallated to yield **ZnPc-C₆₀ee** in a reaction with Zn(OAc)₂ (see SI section).

The solvents, anhydrous anisole (99%, Aldrich), dimethyl formamide (DMF, 99.8%, LAB-SCAN), anhydrous dichloromethane (CH₂Cl₂, 99.8%, Aldrich), and anhydrous benzonitrile (PhCN, 99%, Aldrich) were used as received. Tetra-*n*-butylammonium chloride (TBACl, Aldrich) was dried over phosphorus pentoxide overnight in vacuum whereas tetra-*n*-butylammonium hexafluorophosphate, (TBAPF₆, 98 %, Aldrich) was dried in a vacuum heater. The

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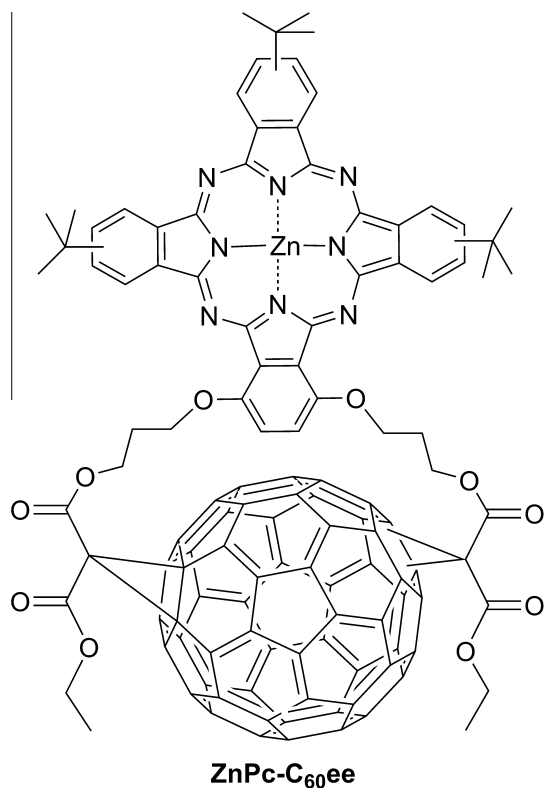


Figure 1. Chemical structure of the studied compound.

concentrations of the salts in the solutions were 0.1 M in both the spectroscopic and the electrochemical measurements.

The absorption spectra were recorded with a Shimadzu UV-3600 spectrophotometer. The fluorescence spectra were measured with a Fluorolog 3 fluorimeter (SPEX Inc.), and corrected using the correction function supplied with the instrument.

The pump-probe method was used to measure the transient absorption spectra in the picosecond and subpicosecond time domains with a time resolution of ~ 200 fs. The excitation wavelength was 390 nm and the transient absorption was monitored in the visible–near infrared region of the spectrum (470–1080 nm). Approximately 70 spectra were measured at variable delay times up to 1 ns. The collected data were fitted globally to obtain decay time constants and spectra associated with the decays as described earlier [18,19].

Differential pulse voltammetry (DPV) was used to measure the oxidation and reduction potentials of the ZnPc and fullerene moieties of the dyad, respectively. The electrochemical electrodes, the supporting electrolytes, the experimental procedure, and the measurement parameters were the same as described previously [11].

3. Results and discussion

The effect of chloride binding on the photoinduced ET reaction of **ZnPc-C₆₀ee** was investigated in four solvents with different polarities ranging from moderately polar anisole to strongly polar DMF.

3.1. Steady state measurements

The absorption spectra of **ZnPc-C₆₀ee** in presence of chloride ions shows clear changes compared to those recorded in the non-ionic environments. The Soret band of **ZnPc-C₆₀ee** in the coordi-

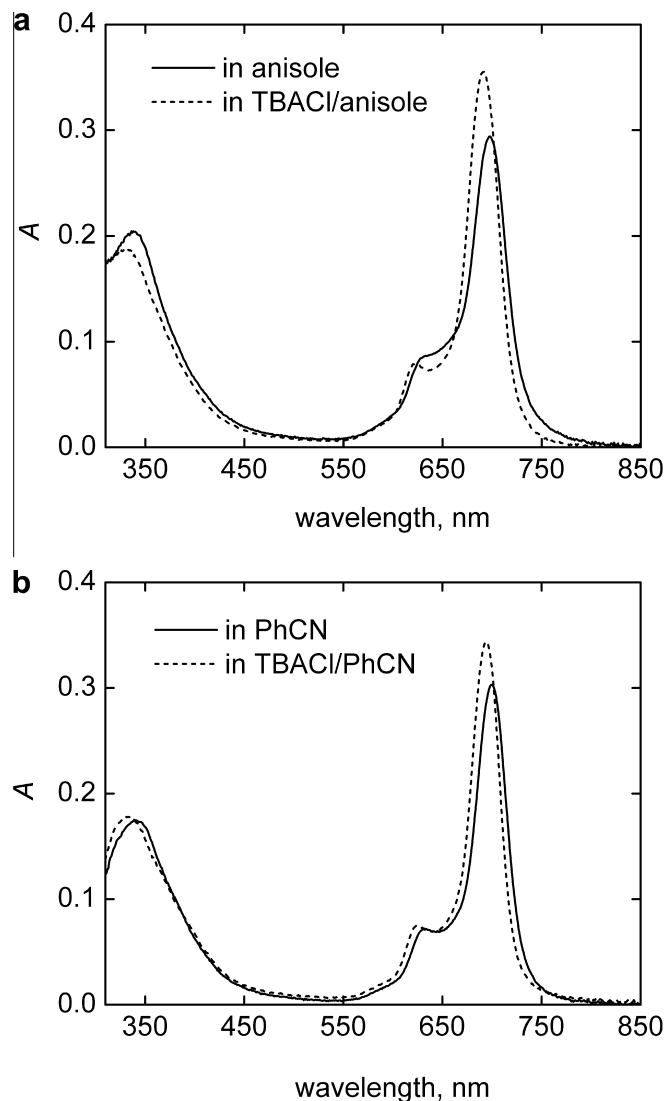


Figure 2. Absorption spectra of $\sim 3 \mu\text{M}$ **ZnPc-C₆₀ee** measured in 1 cm cuvette: (a) in anisole and TBACl/anisole (b) in PhCN and TBACl/PhCN.

nating solution is shifted to the blue by 5–7 nm compared to the corresponding spectra measured in pristine solvents, while the low energy absorption band (Q_1) was shifted to the blue by 5 nm (Figure 2 and Table S1). In addition, the hyperchromic effect was observed for the Q_1 band, i.e. the intensity ratio of the Soret to Q_1 band (Soret/ Q_1) in the coordinated dyad was decreased by 18–25% relative to that of the nonligated one (Figure 2 and Table S1). In accordance with the absorption blue shift, the fluorescence spectrum of the chloride-ligated dyad was also blue shifted compared to that for the nonligated dyad (see SI, Figure S2).

3.2. Electrochemical measurements

The first one-electron oxidation and reduction potentials of the phthalocyanine and fullerene moieties, E_{ox} and E_{red} , respectively, were determined with the DPV measurements of the ligated and nonligated dyads in CH_2Cl_2 . The differential pulse voltammograms of **ZnPc-C₆₀ee** in noncoordinating and chloride-coordinating environments are presented in Figure 3.

The reduction potential of fullerene was found to be the same in both the ligated and nonligated dyads whereas the oxidation potential of the phthalocyanine in the ligated dyad is lower than in

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