



Review

Structures and photoinduced electron transfer of protonated complexes of porphyrins and metallophthalocyanines

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ARTICLE INFO

Article history:

Received 3 December 2011

Received in revised form

17 December 2011

Accepted 24 January 2012

Available online 2 February 2012

Keywords:

Protonated porphyrin

Protonated phthalocyanine

Distortion

Photoinduced electron transfer

Supramolecular complexes

ABSTRACT

Porphyrins and phthalocyanines are planar two-dimensional π -compounds, which are normally difficult to protonate because of the low basicity. When many bulky substituents are introduced to porphyrins and phthalocyanines, however, the macrocyclic π -plane is distorted due to the steric repulsion of the bulky substituents. The π -plane distortion facilitates protonation to afford stable protonated porphyrins and phthalocyanines. Crystal structures of protonated porphyrins and phthalocyanines were determined to clarify the role of hydrogen bonding in the supramolecular assemblies. Protonated porphyrinoids can act as an electron acceptor rather than an electron donor in photoinduced electron-transfer reactions. The rate constants of photoinduced electron-transfer reactions of diprotonated porphyrin with different degrees of distortion were determined and they are evaluated in light of the Marcus theory of electron transfer to determine the reorganization energies of electron transfer, which are affected by the distortion of the π -plane. A distortion of the macrocyclic ligands also affords higher Lewis acidity at a metal center to allow facile axial coordination of ligands, due to poor overlap of the lone pair orbitals with $d_{x^2-y^2}$ or p_x and p_y orbitals of the metal center. Thus, the distortion of the macrocyclic ligands enables one to construct various molecular and supramolecular complexes composed of porphyrins and phthalocyanines. The photodynamics of photoinduced electron-transfer reactions of various supramolecular complexes of distorted porphyrin and phthalocyanines are discussed in relation to structure and photofunction.

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1. Introduction

Porphyrins (Por) and phthalocyanines (Pc) have merited significant interest because they exhibit light-harvesting efficiency for producing charge-separated states as models of the photosynthetic reaction centers [1–14] and photovoltaic cells for energy conversion [15–24]. Porphyrins and phthalocyanines contain extensively conjugated π -systems which enable efficient electron transfer,

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because the uptake or release of electrons usually results in minimal structural change upon electron transfer [25]. In most cases, porphyrins, phthalocyanines and their metal complexes have been employed as electron donors rather than electron acceptors in electron donor–acceptor ensembles [1–14,25], unless strongly electron-withdrawing substituents are introduced to the macrocycles [26]. In addition, cationic porphyrins having high-valent metal ions also act as electron acceptors in electron-transfer reactions [7,27]. In a similar way, a protonated porphyrin (H_4P^{2+}) is expected to gain electron-accepting ability by the electron-withdrawing effect of added protons on the porphyrin ring. The protonation of porphyrin and its analogs such as phthalocyanine is the addition of proton(s) to the aromatic nitrogen atoms involved in the π -conjugated system and thus has the advantage of significant influence on their electronic properties as large as the synthetic modification [28,29]. Main concern in the protonation of porphyrins has been focused on the change of photophysical and structural properties [30], however, the effect of protonation on the redox properties has rarely been examined [31,32]. This is due to the low basicity of planar porphyrins, which require strongly acidic conditions for protonation [30]. On the other hand, non-planar porphyrins, which are derived from the introduction of bulky substituents to the porphyrin core, exhibit higher basicity than planar porphyrins because the lone pairs of the pyrrole nitrogen atoms direct out of the porphyrin mean plane in the non-planar porphyrins [33]. The use of a protonated porphyrinoid as an electron acceptor in porphyrinoid-based electron-transfer systems allows us to expand the variety of donor–acceptor ensembles where a porphyrin moiety normally used as an electron donor.

From a structural standpoint, the construction of porphyrinoid-based donor–acceptor molecular and supramolecular systems using axial coordination and/or noncovalent interactions such as hydrogen bond attracted increasing attention because of its feasibility in preparation, compared to linking them by covalent bonds with energy- and time-consuming synthetic procedures. In this context, many light-harvesting supramolecular assemblies built up by noncovalent interaction have been reported [8–14]. These interactions, however, are usually weakened in coordinating polar solvents that can stabilize the charge-separated states resulting from photoinduced electron transfer. One of the interesting characteristics of protonated porphyrin is the formation of hydrogen bonds between NH protons attached to pyrroles and conjugated bases of Brønsted acids employed for protonation [30]. Thus, the combination of electrostatic interactions (ion pairing) and hydrogen bonding in protonated porphyrin is promising approach to construct discrete and stable supramolecular systems.

This review focuses on structures and electron-transfer properties of protonated porphyrins and phthalocyanines and their molecular and supramolecular assemblies. First, the crystal structures of monoprotonated and diprotonated porphyrins are discussed to clarify the role of hydrogen bonding in the interaction with counter anions. In contrast to the protonation of the porphyrin ring, which occurs only at pyrrole-nitrogen atoms, phthalocyanines can be protonated at two different sites; the isoindole-nitrogen and *meso*-nitrogen atom(s). The crystal structures of both *meso*- and isoindole-protonated phthalocyanines are shown and the spectroscopic and electrochemical properties of these protonated phthalocyanines are discussed in relation with the electron-transfer reactions. Then, the hydrogen bonding and/or strong axial coordination of distorted porphyrinoids utilized to construct molecular and supramolecular electron donor–acceptor complexes composed of protonated porphyrinoids, is discussed. We will also discuss the electron-transfer properties and photoconductivity of a supramolecular architecture constructed by a nonplanar porphyrin called porphyrin nanochannels (PNCs), which

can include a variety of electron-donor molecules in their inner space.

2. Protonation of porphyrins and phthalocyanines

2.1. Structures of mono- and diprotonated porphyrins

Generally, in the case of free-base porphyrins (H_2P) the two protonation steps are almost indistinguishable, yielding the corresponding diprotonated porphyrin (H_4P^{2+}), while the monoprotonated species (H_3P^+) is usually not detected (Scheme 1) [30,34–38]. Many attempts were made to detect and isolate monoprotonated porphyrin by protonation of porphyrins with Brønsted acids [39] or deprotonation of corresponding diprotonated porphyrins [40,41]. The existence of monoprotonated tetraphenylporphyrin was reported based on ion-transfer voltammetry at a polarized water|1,2-dichloroethane interface [42]. Although the crystal structure determination of monoprotonated porphyrin was made on β -substituted octaethylporphyrinium (H_3OEP^+) [43–45], no crystal structure determination was reported on monoprotonated porphyrin having substituents at the *meso* positions.

The effect of counteranion on the acid–base equilibrium [36,37] and the acid-induced J-aggregation of porphyrins [46,47] has been discussed in terms of the formation of hydrogen bonding among NH protons of pyrrole and conjugated base of Brønsted acid. Thus we investigated the protonation of nonplanar and highly basic dodecaphenylporphyrin (H_2DPP) [48–51] and interactions among diprotonated H_2DPP (H_4DPP^{2+}) and counteranions [52].

Absorption spectroscopic titration of saddle-distorted H_2DPP with 2-anthracenesulfonic acid (2-AN- SO_3H) and 2,6-anthracenedisulfonic acid (2,6-AN- $(SO_3H)_2$) in benzonitrile (PhCN) indicates two-step diprotonation, whereas one-step diprotonation could be observed with 2-anthracenecarboxylic acid (2-AN-COOH) (Scheme 1, Fig. 1) [52]. In the case of the reaction of H_2DPP with 2-AN-COOH, the 1H NMR signals due to the 1- and 3-*H* nuclei of 2-ANCOO $^-$ are upfield-shifted even in DMSO- d_6 , however, such shifts are not observed for 2-AN- SO_3H and 2,6-AN- $(SO_3H)_2$ [52]. This indicates that one-step diprotonation is governed by the formation of hydrogen bonding among NH protons of H_4DPP^{2+} and oxygen atoms of the carboxylate. Crystal structures of monoprotonated H_2DPP (H_3DPP^+), $H_3DPP(2-AN-SO_3^-)$, $(H_3DPP)_2(2,6-AN-(SO_3)_2)$, and H_4DPP^{2+} , $H_4DPP(2-AN-COO)_2$, were determined (Fig. 2) [52]. In the crystal structure of H_3DPP^+ , there are hydrogen bonds between the two pyrrole NH and the oxygen atom of the sulfonate group, but there is no interaction with conjugate bases in a polar solvent. In the crystal structure of each protonated species of H_2DPP , the extent of deformation is enlarged as compared with unprotonated H_2DPP , as is usually observed for protonated porphyrin [53–56] with a few exceptions [57,58].

The redox behavior of H_3DPP^+ is irreversible in the cyclic voltammograms (CV) in PhCN and DMSO [52]. In the differential pulse voltammograms (DPV) of H_2DPP , a new reduction peak appeared at -0.70 V (vs SCE) by the addition of one-equivalent of 2-AN- SO_3H in PhCN [52]. The one-electron reduction potential is higher than that of H_2DPP (-1.20 V) and lower than that of H_4DPP^{2+} (-0.45 V). In DMSO, only one reduction peak is observed at -0.85 V upon the addition of 2-AN- SO_3H and at -0.76 V upon addition of 2-AN-COOH. These potentials are anodically shifted as compared to that of H_2DPP in DMSO (-1.26 V). Density functional theory (DFT) calculations were conducted on H_3DPP^+ and the species hydrogen-bonded with 2-ANCOO $^-$ [52]. With the monoprotonated porphyrin, the dihedral angles of pyrroles relative to the H_3DPP^+ mean plane have been estimated as shown in Fig. 3 [52]. The non-protonated

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