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Evidence for the assembly of carboxyphenylethynyl zinc porphyrins on nanocrystalline TiO$_2$ surfaces†

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UV-visible absorption and AFM studies suggest that carboxyphenylethynyl zinc porphyrins aggregate on nanocrystalline TiO$_2$ surfaces in an H-type fashion.

Adsorbing suitable photosensitizers onto high-surface-area nanocrystalline films of semiconductors that have a large band gap, such as titanium dioxide (TiO$_2$), has attracted much research on efficient dye-sensitized solar cells (DSC).[1,2] With efficiencies of conversion of incident photons to electrons (IPCE) near 85% in the visible and near-IR region and overall efficiencies of conversion of photovoltaic cell energy (η) greater than 10%, the N3 dye and the black dye are the most efficient photosensitizers reported.[3,4] Porphyrins and their derivatives have also been considered for this purpose[2a,5–7] primarily owing to their vital roles in photosynthetic reactions. Although many factors must be taken into account in developing an efficient photosensitizer,[2c] widely varied photocurrent efficiencies have been reported for identical sensitizers.[7] Detailed investigation of specially tailored porphyrins indicates that the orientation of the adsorbed photosensitizers has a profound impact on DSC performance.[2a,5–7] With proper design, *i.e.* through a fully conjugated system for efficient charge transfer and with an edgewise adsorption mode for a large coverage of surface area, the best porphyrin-sensitized DSC is reported to attain IPCE$_{\text{Soret}}$ = 85% and η = 5.6%.[5]

Here we report the UV-visible absorption and AFM studies of two carboxyphenylethynyl zinc porphyrins in solutions and on nanocrystalline TiO$_2$ surfaces. Our results indicate that these fully conjugated, edgewise-bound zinc porphyrins adsorbed onto TiO$_2$ surfaces form H-aggregates, *i.e.* the porphyrin moieties assemble perpendicularly with respect to the TiO$_2$ surface. Fig. 1 depicts the molecular structures of these porphyrins: 5-(4-carboxy-phenylethynyl)-10,20-biphenylporphinato zinc(II) and 5-(4-{4-[4-(4-carboxy-phenylethynyl)-phenylethynyl]-phenylethynyl}-phenylethynyl)-10,20-biphenylporphinato zinc(II), denoted ZnCA(PE)$_1$BPP and ZnCA(PE)$_4$BPP, respectively. These porphyrins comprise three major components. First, 10,20-biphenylporphinato zinc(II) (ZnBPP) is chosen as a light-harvesting unit because of its stability against radiation and because the photocurrent efficiency of zinc porphyrins is superior to copper and free-base porphyrins.[2a] Second, one 4-carboxylic group is employed as the anchoring group to ensure effective adsorption onto TiO$_2$ surfaces, to promote electronic coupling with TiO$_2$, and to minimize the porphyrin's adsorption modes.[2a,6,7] Third, the (phenylethynyl)$_x$ (or PE) groups are utilized to control the distance between the porphyrin and the anchoring group because of their rigid, linear structure and their total conjugation.[8] According to structures optimized using a semi-empirical method, the distance between the zinc(II) ion and the carbon of the carboxylic group extends from 11.6 Å for ZnCA(PE)$_1$BPP to 31.5 Å for ZnCA(PE)$_4$BPP. The introduction of PE moieties as spacer groups is well reported for other systems.[9,8b–f]

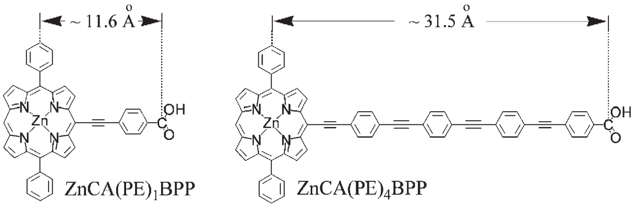

Fig. 1 Structures of carboxyphenylethynyl zinc porphyrins. Distances are measured from zinc(II) ions to the carbon of the carboxylic group of the ZINDO-optimized structures.

The preparation of ZnCA(PE)$_x$BPP involves reacting porphyrin precursors with various carboxyphenylethynyl reagents according to the Sonogashira cross-coupling method.[10] This synthetic strategy has been well developed for preparing porphyrins with a variety of ethyne-linked functional groups.[8] ZnCA(PE)$_1$BPP is synthesized by cross-coupling mono-bromonated ZnBPP with 4-ethynyl-benzoic acid at 80% yield. Cross-coupling 5-[4-(4-iodo-phenylethynyl)-phenylethynyl]-ZnBPP with 4-(4-ethynyl-phenylethynyl)-benzoic acid generates 38% of ZnCA(PE)$_4$BPP. Our attempts to synthesize ZnCA(PE)$_4$BPP *via* other synthetic routes were unsuccessful due to very low reaction yields and the difficulties in recognizing and separating the reaction products. The procedure for synthesizing TiO$_2$ nanoparticles is according to the literature method.[11] Both spin-coating and pasting procedures are employed to generate the TiO$_2$ films used in this report.

Fig. 2 compares the AFM images of the (a) bare, (b) ZnCA(PE)$_1$BPP-, and (c) ZnCA(PE)$_4$BPP-modified TiO$_2$ surfaces (spin-coated samples). For these experiments, the porphyrins are allowed to saturate the TiO$_2$ surfaces. Consistent with our recent SEM observation of TiO$_2$ particle size (~15 nm in diameter),[12] the particle sizes in Fig. 2a range from 15 to 40 nm. Upon ZnCA(PE)$_1$BPP adsorption (Fig. 2b), no significant morphology changes are observed except for the more elongated shapes of the

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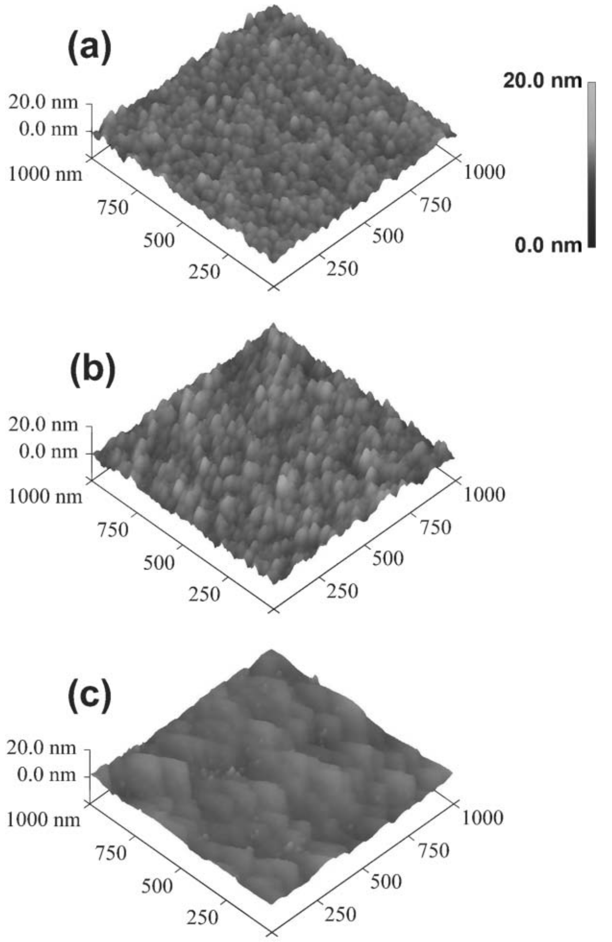

Fig. 2 AFM images of (a) bare TiO_2, (b) $ZnCA(PE)_1BPP/TiO_2$, and (c) $ZnCA(PE)_4BPP/TiO_2$ (spin-coated TiO_2 films). Mean roughness: (a) 12 nm, (b) 13 nm, and (c) 10 nm. Note that the triangular features in (c) are suggested to be TiO_2 aggregates. The small dots in (c) have diameters of 14–40 nm, consistent with the sizes of TiO_2 particles observed in (a).

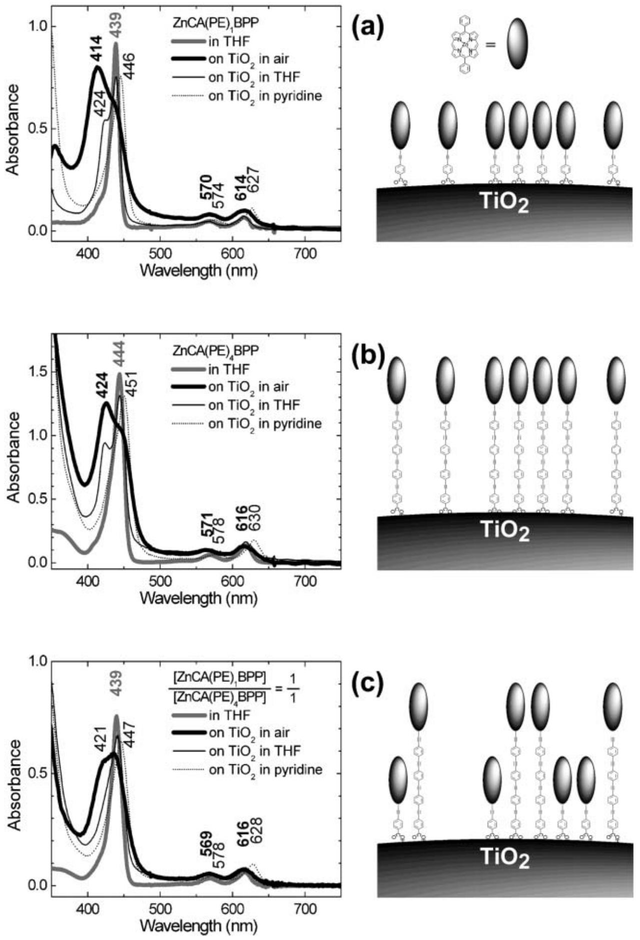

Fig. 3 *Left*, comparison of the absorption spectra of (a) $ZnCA(PE)_1BPP$, (b) $ZnCA(PE)_4BPP$, (c) 1 : 1 $ZnCA(PE)_1BPP$: $ZnCA(PE)_4BPP$ mixture in THF (grey curves), on TiO_2 in air (bold solid curves), on TiO_2 in THF (thin solid curves), on TiO_2 in pyridine (dotted curves). *Right*, schematic presentation of the porphyrin assembly on nanocrystalline TiO_2 surfaces. Note that the lengths of the porphyrins and the diameter of TiO_2 particles are scaled accordingly (~1–3 nm for the porphyrin lengths and ~20 nm for the of TiO_2 particle diameters). Since only very small amounts of the porphyrins are allowed to adsorb onto these TiO_2 films, the right schemes depict part of the spherical surface of an individual TiO_2 particle partially covered by the porphyrins.

particles. This is not surprising since the length of $ZnCA(PE)_1BPP$ is merely ~1 nm and the diameters of TiO_2 particles are 15–40 nm. Interestingly, triangular plate-like features are observed on the surfaces of the $ZnCA(PE)_4BPP$-modified TiO_2 films (Fig. 2c). Upon more extensive investigation, we find similar features on $ZnCA(PE)_1BPP$-modified TiO_2 surfaces (both spin-coated and pasted samples). Furthermore, 2D AFM images of the $ZnCA(PE)_1BPP$-modified TiO_2 pasted films strongly suggest that these "triangular plates" consist of TiO_2 particles (see ESI†). Therefore, these triangular plate-like features should not be caused by the adsorption of $ZnCA(PE)_4BPP$ (~3 nm in length) on TiO_2 surfaces. These features possibly result from the TiO_2 film preparation processes. Nevertheless, the mean roughness values of the bare, $ZnCA(PE)_1BPP$-, and $ZnCA(PE)_4BPP$-modified TiO_2 film surfaces are found to be 12, 13, and 10 nm, respectively. Because of the small changes in the mean roughness, we suggest that the porphyrins are evenly adsorbed on the entire TiO_2 film surfaces. We also performed nanoshaving experiments in order to estimate the thickness of the adsorbed porphyrin layers. However, the experiments were unsuccessful at the time possibly due to the softness of the TiO_2 films, the very thin layer of the adsorbed porphyrins, or the AFM tip being 10 nm in diameter.

Fig. 3 displays the UV-visible spectra of the porphyrins in solutions and on TiO_2 films as well as the schematic illustrations of our suggestions as to the porphyrin adsorption behaviour. Note that only very small amount of the porphyrins are allowed to adsorb on TiO_2 films (*i.e.* the TiO_2 surfaces are partially covered by the porphyrins) in order to present both Soret and Q bands in these spectra. Prolonged adsorption time generates porphyrin-saturated TiO_2 films (used for AFM studies mentioned above) that have over-scaled Soret absorption bands and strong Q bands with nearly identical shapes to those shown in Fig. 3 (bold curves). $ZnCA(PE)_xBPP$ exhibit typical porphyrin UV-visible spectra in solutions as strong Soret bands and weak Q bands (Figs. 3a and b, *left*, grey curves).[13] Upon adsorption on nanocrystalline TiO_2 films, the Q bands shift only slightly and broaden, but new absorption features appear on the blue side of the solution-like Soret bands at 414 and 424 nm for $ZnCA(PE)_1BPP$ and $ZnCA(PE)_4BPP$, respectively. The appearance of the solution-like

Soret bands in the Fig. 3 film spectra reflects a small proportion of monomeric ZnCA(PE)$_x$BPP adsorbed on TiO_2 films. This is consistent with the fact that the TiO_2 surfaces are partially covered by the porphyrins. For the blue-shifted absorptions, the quality of the TiO_2 films (*e.g.*, thickness) seems to have a small effect on the intensities of these blue shoulders. The appearance of these blue shoulders is thus not due to the effects of reflection.[14] The film spectra reveal little interaction between ZnCA(PE)$_x$BPP and TiO_2 nanoparticles, and the appearance of these blue shoulders is attributed to aggregation of ZnCA(PE)$_x$BPP assemblies on the surfaces of the TiO_2 films (Figs. 3a and b, *right*). The stacked, face-to-face porphyrin π-aggregation (or H-aggregation) is known to produce a blue shift of the absorption, whereas the side-by-side porphyrin π-aggregation (or J-aggregation) results in a red shift.[15] We hence suggest that the Soret blue shoulders (Figs. 3a and b, bold curves) are caused by H-aggregation of porphyrins on the TiO_2 surfaces. In contrast to the ZnCA(PE)$_1$BPP/TiO_2 system, red-shifted and much broadened Soret bands are observed for ZnCA(PE)$_1$BPP spin-coated on a glass substrate, indicating the formation of J-type porphyrin aggregates on such a flat glass surface. These phenomena are consistent with literature reports.[16,17]

To extend these spectral observations for ZnCA(PE)$_x$BPP molecules H-aggregated on TiO_2 surfaces and to demonstrate that this aggregation can be well controlled by ligating solvents, we conducted further UV-visible spectral measurements for ZnCA(PE)$_x$BPP/TiO_2 films in air, THF and pyridine. As compared in Figs. 3a–c (*left*, bold solid curves), the Soret blue shoulders of ZnCA(PE)$_x$BPP/TiO_2/air samples are more intense than those of a 1 : 1 mixture of the [ZnCA(PE)$_1$BPP + ZnCA(PE)$_4$BPP]/TiO_2/air system, indicating that the difference in the length of bridge hinders H-aggregation (Fig. 3c, *right*). Furthermore, the blue shoulders of ZnCA(PE)$_x$BPP/TiO_2/air samples become less intense when the films are immersed in THF (thin solid curves) or pyridine (dotted curves). This phenomenon implies ligation of THF or pyridine molecules to the central metal zinc(II) ion of these complexes,[2a,18] which effectively hampers H-type aggregation of ZnCA(PE)$_x$BPP molecues on the TiO_2 surface, and decreases the absorbance in the blue shoulders.[19]

In summary, analysis of UV-visible spectra of ZnCA(PE)$_x$BPP indicates strongly that ZnCA(PE)$_x$BPP are assembled on surfaces of nanocrystalline TiO_2 films in an H-type manner. This finding is consistent with the AFM observation that shows little change in the TiO_2 surface mean roughness upon porphyrin adsorption. Detailed results regarding the synthesis of ZnCA(PE)$_x$BPP (x = 2–3), UV-visible absorption, steady-state and time-resolved fluorescence, and electrochemical properties of ZnCA(PE)$_x$BPP (x = 1–4) will be reported elsewhere.

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