Evidence for the Assembly of Carboxyphenylethynyl Zinc Porphyrins on Nanocrystalline TiO$_2$ Surfaces

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Experimental Section

Materials. Solvents used in the synthesis (ACS Grade) were obtained from Mallinckrodt Baker, Inc. (CH₂Cl₂, CHCl₃ and ethyl acetate; Kentucky, U. S. A.), Haltermann (hexanes; Hamburg, Germany), and Merck (THF; Darmstadt, Germany). These solvents were used as received unless otherwise stated. Tetrahydrofuran (THF) and tetrabutylammonium perchlorate (TBAP) were purified according to the literature methods.¹ Pd(PPh₃)₄ catalyst was purchased from Strem Chemical Inc (MA, U. S. A.). Chromatographic purification was performed with Silica Gel 60 (230-400 mesh, Merck). All other chemicals were ordered from Acros Organics (New Jersey, U. S. A.).

The procedure for synthesis of TiO₂ nanoparticles was according to the literature method.² Both spin-coated and pasted TiO₂ films were used in the experiments, and the UV-visible absorptions of these samples were nearly identical. The adsorption of ZnCA(PE)ₓBPP onto the TiO₂ nanocrystalline films was carried out by immersing the hot glass plates into ZnCA(PE)ₓBPP THF solutions in order to avoid moisture absorption. After vigorously washes with THF several times, the plates were examined by UV-visible absorption and AFM observation to confirm the binding of ZnCA(PE)ₓBPP.

Instrumentation. Absorption spectra were recorded on an Agilent 8453 UV-Visible spectrophotometry system. Fluorescence spectra were measured on a CARY Eclipse Fluorescence spectrophotometer. NMR data were obtained on a Varian Unity Inova 300WB NMR Spectrometer. Elemental analyses were carried out on an Elementar Vario EL III (NSC Instrumentation Center at National Cheng Kung University). Atomic force microscopy (AFM) experiments on the spin-coated samples were performed on a Veeco D3100 Scanning Probe Microscope (tip diameter = 10 nm, Center of Nanoscience and Nanotechnology at National Chung Hsing University). AFM experiments on the pasted samples were performed on a Digital Instrument Scanning Probe Microscope (NS3a controller with a D3100 stage, NSC Instrumentation Center at National Tsing Hua University). For all morphology observations, three locations (edges, centers, and in-betweens) of each sample were studied. An MBraun Uni-lab glove box, a vacuum line and standard Schlenk glassware were employed to process all air-sensitive materials.
General Synthesis Procedure. Sonogashira cross-coupling method was used to carry out most of the reactions in this work. The de-gassed reaction mixtures were stirred under nitrogen at 40°C and monitored with TLC and UV-Visible spectroscopy. Upon completion, the reactions were quenched with NH₄Cl(aq) washes followed by chromatographic separation on silica gel with MeOH/CH₂Cl₂ eluents and crystallization from THF/hexanes.

ZnCA(PE)₁BPP was synthesized by cross-coupling ZnBPPBr and 4-ethynyl-benzoic acid at 80% yield. 4-ethynyl-benzoic acid was obtained from cross-coupling trimethylsilylacetylene with 4-iodobenzoic acid (78%) followed by deprotection reactions in tetrabutylammonium fluoride at 82% yield.

ZnCA(PE)₄BPP was prepared from 5-[4-(4-iodo-phenylethynyl)-phenylethynyl]-ZnBPP and 4-(4-ethynyl-phenylethynyl)-benzoic acid at 38% yield. 5-[4-(4-iodo-phenylethynyl)-phenylethynyl]-ZnBPP was synthesized from cross-coupling 5-(4-ethynyl-phenylethynyl)-ZnBPP with 1,4-diiodo-benzene (39%). 5-(4-ethynyl-phenylethynyl)-ZnBPP was generated by cross-coupling ZnBPPBr with 1,4-diethynyl-benzene at 41% yield. Cross-coupling 1,4-diiodo-benzene with trimethylsilylacetylene yielded nearly 100% of 1,4-bis(trimethylsilyl)benzene. The deprotection reaction in TBAF/THF gave 81% of 1,4-diethynyl-benzene. 4-(4-ethynyl-phenylethynyl)-benzoic acid was generated from cross-coupling 1,4-diethynyl-benzene with 4-iodo-benzoic acid (65%).

Characterization Data.

ZnCA(PE)₁BPP. ¹H-NMR (d₆-DMSO at 2.50 ppm): 10.36 ppm (s, 1H), 9.84 ppm (d, J 5Hz, 2H), 9.46 ppm (d, J 5Hz, 2H), 8.92 ppm (d, J 5Hz, 2H), 8.84 ppm (d, J 5Hz, 2H), 8.25 ppm (m, 8H), 7.86 ppm (m, 6H). Elemental Analysis: C₄₁H₂₄N₄O₂Zn·THF, calculated C 72.83%, H 4.35%, N 7.55%; found C 72.35%, H 4.60%, N 7.27%. UV-Visible absorptions in THF: 439 (log ε = 5.64) nm, 567 (4.21) nm.

ZnCA(PE)₄BPP. ¹H-NMR (d₆-DMSO at 2.50 ppm): 10.34 ppm (s, 1H), 9.83 ppm (d, J 4Hz, 2H), 9.45 ppm (d, J 4Hz, 2H), 8.90 ppm (d, J 4Hz, 2H), 8.82 ppm (d, J 4Hz, 2H), 8.20 ppm (t, J 4Hz, 6H), 7.95 ppm (d, J 8Hz, 2H), 7.86 ppm (overlapped, 8H), 7.66 ppm (overlapped, 10H). Elementa...
C₆₅H₃₆N₄O₂Zn·2H₂O, calculated C 77.57%, H 4.01%, N 5.57%; found C 77.61%, H 4.00%, N 5.36%.

UV-Visible absorptions in THF: 444 (log ε = 5.56) nm, 569 (4.17) nm, 619 (4.53) nm.

Figure 1. AFM images of (a) bare, (b) ZnCA(PE)₁BPP⁻, and (c) ZnCA(PE)₄BPP-modified TiO₂ surfaces (pasted samples). The surfaces of the pasted samples are rougher than those of the spin-coated ones.

Figure 2. AFM images of ZnCA(PE)₁BPP-modified TiO₂ surfaces (the same pasted sample as in Figure 1b). Left: 3D view, right: top-down view. Note that the "triangular plates" are marked in the 3D view image. Importantly, the 2D image suggests that these "triangular plates" in fact consist of nanocrystalline TiO₂ particles.
Figure 3. AFM image of ZnCA(PE)$_2$BPP/TiO$_2$ surfaces (spin-coated samples). This image also shows the "triangular plate" features. The small dots among the "triangular plates" have diameters of ~20-40 nm, consistent with the sizes of the lesser or non-aggregated TiO$_2$ particles.\textsuperscript{2b}

Figure 4. AFM images of ZnCA(PE)$_4$BPP/TiO$_2$ surfaces (spin-coated samples). The small dots among the "triangular plates" have diameters of ~14-40 nm, consistent with the sizes of the lesser or non-aggregated TiO$_2$ particles.\textsuperscript{2b}
Figure 5. Absorption spectra of ZnCA(PE)\textsubscript{1}BPP in THF (grey lines), on TiO\textsubscript{2} films in air (thin solid lines), and pasted on glass (bold solid lines).

References

