

Communications to the Editor

One-Dimensional Polymers of Octasubstituted Phthalocyanines

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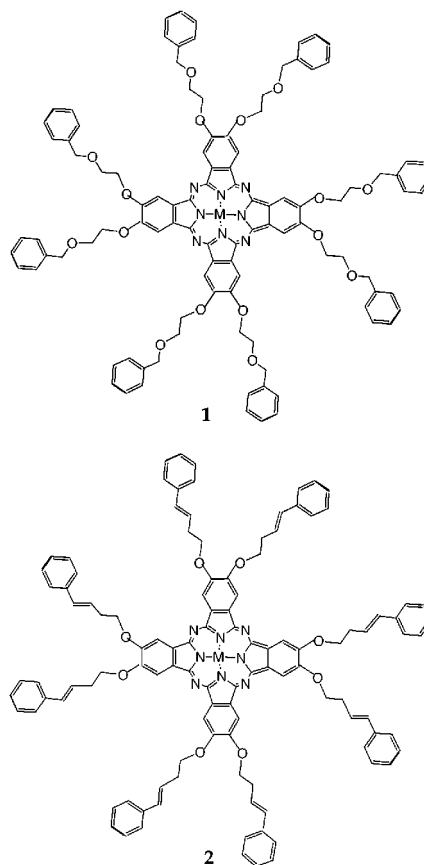
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We recently reported that copper 2,3,9,10,16,17,23,24-octakis-(2-benzyloxyethoxy) phthalocyanine (**1**) exhibits an exceptionally stable discotic mesophase.¹ Moreover, the unusual extent of cofacial self-association of this phthalocyanine (Pc) and the corresponding unmetalated Pc favors the formation of highly ordered rodlike aggregates at the air–water interface which are maintained after transfer to solid supports.² We now report the design of a reactive analogue of Pc **1** that can be used to form one-dimensional polymers of Pc. Wegner and co-workers introduced the concept of 1-D hairy rod polymers, including the rodlike phthalocyaninato-polysiloxanes (PcPS) prepared by condensation of silicon dihydroxyPc.^{3,4} The addition of alkane side chains to these otherwise crystalline materials enhanced their processability as thin films. Here we present a general strategy for the formation of 1-D polymers from disklike monomers which can be easily assembled prior to polymerization.

The key to this strategy is the placement of the reactive site(s) along the side chains of the disklike monomer, rather than at the periphery, because the later approach can result in cross-linking of the discotic columns.⁵ Among the synthetic targets selected to test this concept is Pc **2**, which preserves the freedom to utilize a variety of transition metals, M, at the Pc core. Pc **2** contains eight β -alkyl styryl groups that can react via photostimulated [2 + 2] cycloaddition. The precedence for this strategy comes from the observations of Whitten and co-workers, who demonstrated that photolysis of LB-multilayers of fatty acids and lipids derived from β -substituted styrenes produced dimers via cyclobutane formation.⁶ To prepare **2** a new general Pc synthesis was developed.⁷ *trans*-Styrylethyl alcohol was obtained from DIBAL reduction of the commercially available *trans*-styryl acetic acid. The resulting alcohol was converted to the corresponding tosylate, which was then coupled to the dimethyl ester of bis-4,5-(hydroxy)-phthalic acid. The diester was converted to the bis-4,5-(*trans*-styrylethoxy)phthalonitrile which was used to make the corresponding copper Pc **2** in 54% overall yield following previously reported procedures.⁷ The thin film behavior of **2** at the air–water interface was similar to that reported for **1**.² The pressure versus area isotherm exhibited two phase transitions that are attributed to stable monolayer and bilayer films. Multilayer films (28 monolayers) of **2** were transferred to hydrophobized quartz slides via horizontal transfer methods at the monolayer transition,

as reported previously for **1**,² and used for photochemical and characterization studies.



UV–visible spectra of the resultant films show a strong styryl group absorbance band at 255 nm ($\epsilon = 136\,400$) superimposed on the high-energy tail of the Pc Soret band absorbance, and a nonzero background due to changing optical properties of the thin film. The Pc Q-band is centered at 680 nm. Thin films of **2** were irradiated with 255 nm band-pass-filtered light from a low-pressure mercury at a distance of ~ 2 cm. Ozone production was minimized by placing the sample in a dry nitrogen-flooded environment. The thin film Pc samples were removed from the N₂ flooded environment at timed intervals to measure UV–visible absorption spectra. Figure 1B shows the loss of styryl absorbance obtained by subtracting the spectral background at 255 nm due to the phthalocyanine, 0.35 absorbance units, which was estimated from the absorbance of thin films of **1**. A decrease of the background-corrected styrene absorbance of at least 30% was observed for several samples (Figure 1) suggesting that about one-third of the side chains have reacted. Because of the exponential decay of light penetration into these thin films, the degree of reactivity may be higher near the illuminated surface and lower near the substrate. There was no observed change in the phthalocyanine Q-band intensity during irradiation, indicating that there was little loss of the Pc chromophore during the exposure. In a control experiment a thin film of **1** was found to be photostable when it was illuminated under similar conditions for 1800 min. Only minor changes were observed in the Pc **1** Q-band, similar to those seen during annealing of a multilayer LB film.

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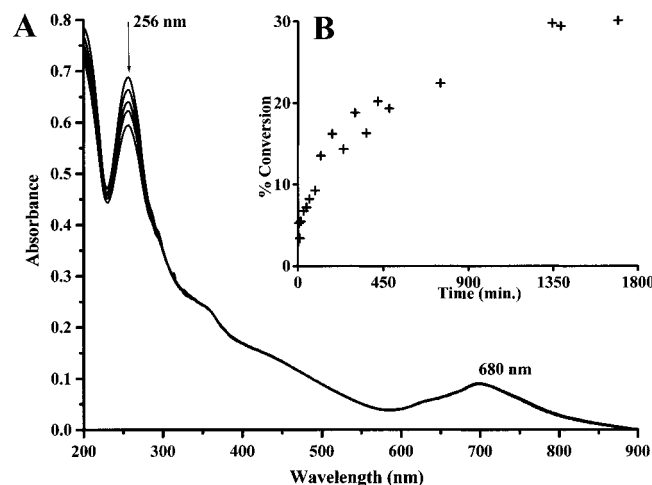


Figure 1. (A) Absorbance spectra of a 28-monolayer LB film of Pc 2 monitored during irradiation with 255 nm filtered light from a low-pressure mercury lamp in a dry nitrogen purged atmosphere. (B) The percent conversion of the styryl band vs time, which was calculated using corrected absorbance values based on an estimated baseline value of 0.35 absorbance units at 255 nm.

The photolyzed **2** was dissolved off of the quartz slide by sonicating in a 1:1 chloroform/benzene solvent mixture for further characterization. Portions of these solutions were cast onto solid supports for MALDI-TOF analysis. In the low-mass region, the MALDI data (obtained on a Bruker Reflex III mass spectrometer) showed a sequence of mass peaks corresponding to monomeric through hexameric **2**. In addition high m/z signals were randomly observed during the MALDI experiment, ranging from ~ 50 500 amu up to at least ~ 204 200 amu (corresponding to a 117 mer). The success of the MALDI analysis is dependent on the ability to desorb and ionize the large rodlike macromolecules from the solid sample matrix. The sizes of the molecular objects revealed in AFM imaging experiments (below) imply that these MALDI data do not probe the highest molecular weight species present, due to incomplete sample ionization. A control experiment performed on the unphotolyzed **2** only shows a major peak at 1745.67 amu (theory 1745.67) with appropriate isotope distribution, and no high mass signals.

The samples for AFM were obtained by casting films on HOPG from very dilute chloroform solutions of the polymer (~ 0.03 μM). AFM images were recorded in tapping mode, using a silicon nitride probe, with a Nanoscope III system. Figure 2A shows a typical image of rodlike structures found in the cast film. Rod lengths were measured within a 500 nm \times 500 nm area that includes the image area of Figure 2A. Only rods with distinct end points were measured and are included in a histogram (Figure 2b) that shows the large variation of rod lengths, with a mean rod length of 72 nm. Both the MALDI and AFM data indicate the presence of macromolecules consistent with Pc rod lengths of 10–40 nm. In addition the AFM data clearly suggests that considerably larger Pc rods are formed during irradiation, with lengths up to 290 nm.

The observed column-to-column distance between adjacent Pc rods was 6.4 ± 0.2 nm, which is approximately twice the expected column diameter for **1**.² The exact molecular rod packing and



Figure 2. (A) Tapping mode AFM image (sample in water) of cast photolyzed material on HOPG. The image is 250 nm \times 250 nm, with a height scale of 2.0 nm. A Fourier domain transformation (inset) of the AFM image indicates the 3-fold symmetry packing of the rodlike structures. (B) A histogram of molecular object length measured within a 500 nm \times 500 nm scan area (not shown, but including Figure 2A). Only complete molecular objects with defined end points were measured with lengths ranging from 5 to 290 nm, with a mean length of 72 nm.

column-to-column distances can only be elucidated after thorough X-ray analysis of **2**. There appears to be precedent, however, for this large spacing between molecular rods from other recent studies of molecular objects cast as thin films on HOPG surfaces.^{8,9} The Pc polymer rods are arranged in domains of 8–10 rods each, aligned along the three principal crystallographic axes of HOPG, suggesting that these rods adopt epitaxial relationships with the HOPG substrate.

The successful strategy employed here for the formation of one-dimensional polymers relies on the expected formation of random dimer bonds between cofacially aligned disklike monomers. The minimum number of such bonds per Pc monomer that is required for polymer formation remains to be determined and will be reported in the future. This molecular design strategy can be extended to other discotic molecules that offer the possibility of synthetic modification of their peripheral chains with reactive groups along their length, rather than at the terminus. In addition to the β -styryl group, it may be possible to utilize cinnamates and chalcones, among others, in the design of discotic monomers for the formation of one-dimensional polymers.

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