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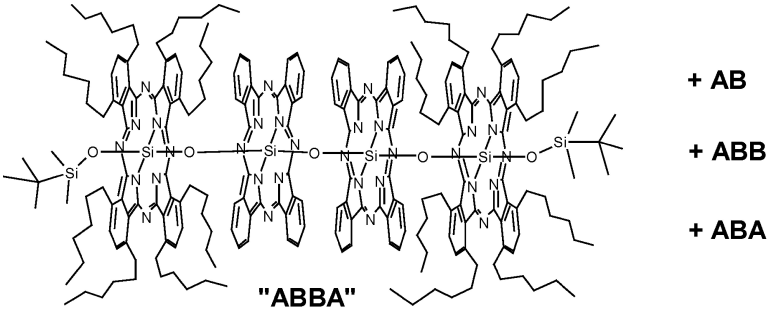

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A Capping Methodology for the Synthesis of Lower μ-Oxo-phthalocyaninato Silicon Oligomers

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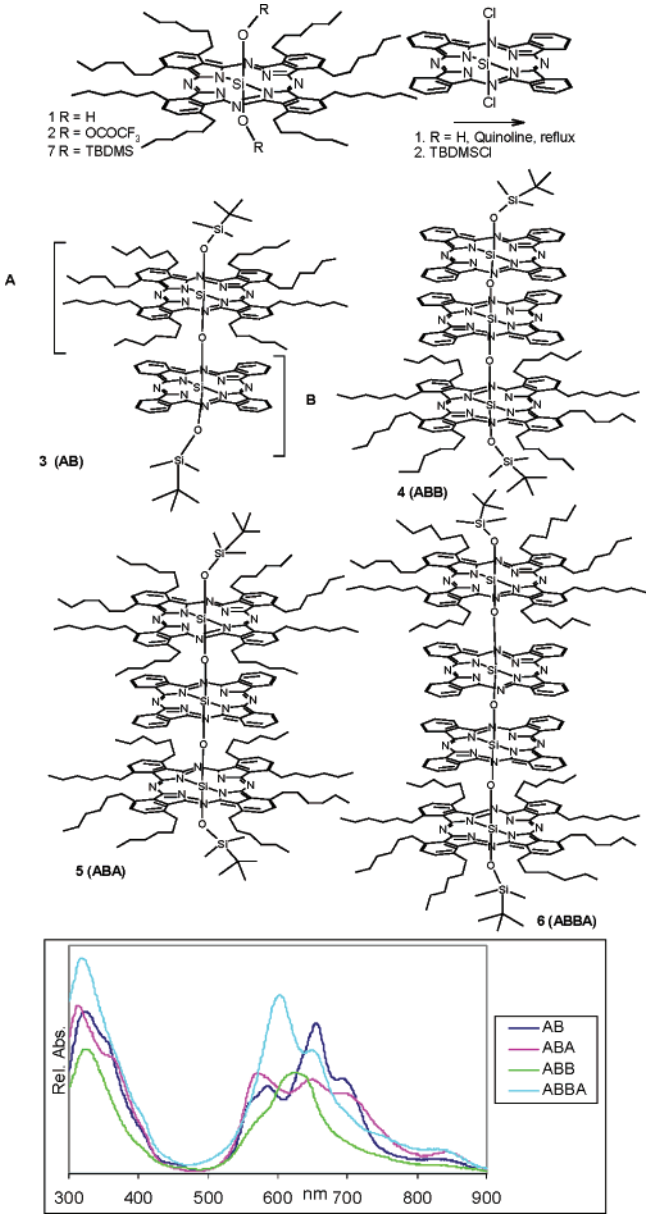
μ-Oxo-bridged silicon phthalocyanine (Pc) oligomers and polymers have attracted much attention for more than four decades.[1] These linearly stacked, chemically stable structures are characterized by a controlled architecture that aligns the component Pc rings cofacially ca. 3.33 Å apart.[2,3] A particularly interesting feature of the polymers is that $\pi-\pi$ interactions provide the basis for one-dimensional conductivity,[4] most notably upon doping with iodine.[5] Oligomers have been identified to have potential in molecular electronic devices and optical switching and optical limiting applications.[6] Research into lower oligomers, in particular, as model compounds for the polymers, has contributed structural information[3] and an understanding of transition energies of the Q-band in the visible region absorption spectrum[3,6−8] and electrochemical properties.[9] Variable temperature ^{1}H NMR spectroscopy has confirmed free rotation of the Pc rings about the Si−O−Si axis.[8]

Polymers and higher oligomers can be obtained by thermal[1] or Lewis acid catalyzed[10] dehydration of dihydroxysilicon phthalocyanine, $PcSi(OH)_2$, but the synthesis of the lower oligomers is more challenging. μ-Oxo-bridged dimers have been prepared by reaction of $PcSi(OH)_2$ with its dichlorosilicon analogue[3] and by thermal condensation of derivatives related to the former.[3,9] Mixed dimers, in which the two Pc rings are substituted differently, have also been obtained after chromatographic separations of the various components of mixed condensations.[8] Routes to the potentially more interesting trimers and tetramers are less well developed, but examples have been isolated as side products during the synthesis of dimers.[10]

We now report a novel approach which, in principle, offers controlled access to lower μ-oxo-bridged oligomers. The strategy suggested itself after failures to polymerize the sterically crowded 1,4,8,11,15,18,22,25-octahexyl $PcSi(OH)_2$, **1**.[11] Thus **1** was recovered intact when heated under conditions that polymerized[12] less sterically demanding 2,3,9,10,16,17,23,24-octaalkoxymethyl derivatives, and only limited amounts of a dimer (Q-band 688 nm, cf. **1** 704 nm) were formed during attempts to polymerize **1** with $FeCl_3$ or $CaCl_2$ catalysis. Attempted separation of the dimer over silica regenerated **1**. Thermolysis of the bistrifluoroacetate ester of **1** (i.e., **2**; 2 h at 200 °C[13]) gave unchanged starting material. Workup of a reaction where **1** was added as a plausible polymerization catalyst gave only **1** itself. We concluded from this series of reactions that the bulky alkyl chains in **1** either restrict formation of a μ-oxo bridge between two molecules of **1** and/or, when such a bridge is formed, it is readily cleaved. This led us to exploit **1** as a capping group to terminate a growing μ-oxo-bridged chain of sterically uncongested monomer units.

Scheme 1. Synthesis of Oligomers **3**−**6** and Their Visible Spectra (toluene)



We tested this "phthalocyanine cap" hypothesis by reacting **1** with dichlorosilicon phthalocyanine (1:1.2) in refluxing quinoline (Scheme 1). TLC monitoring indicated that **1** had been consumed completely after 5.5 h. Removal of quinoline followed by reaction

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with pyridine/aqueous NaOH to convert Si−Cl bonds in residual starting material and products into Si−OH bonds led to isolation of a dark blue residue. Difficulties in chromatographic separation of the components were circumvented by exhaustive silylation of axially ligated OH groups in the mixture using *tert*-butyldimethylsilyl chloride (TBDMSCl). Four bis-silylated products were separated by column chromatography, **3**−**6**, in the sequence of **5**, **6**, **3**, and **4**. Hereafter, **3**−**6** are referred to more conveniently (with yields shown in parentheses) as the AB (35%) dimer, the ABB (13%) and ABA (9%) trimers, and the ABBA (3%) tetramer, respectively, where A refers to the substituted Pc moiety and B to the unsubstituted Pc unit. These products were identified through a combination of MALDI-TOF MS and ^{1}H NMR spectroscopy. Each compound gave a mass spectrum with an isotopic cluster corresponding to M^+ with fragmentation ions corresponding to loss of one (or two) of the silyl protecting groups. The assignment of the sequence of the rings in the oligomers followed from the characteristic sets of ^{1}H NMR signals for the TBDMS groups; two were evident in the spectra of the AB dimer and the ABB trimer, but only one was apparent in those of the ABA trimer and the compound assigned as the ABBA tetramer. With regard to the last of these, we dismissed the alternative BAAB structure, which also fits the data. This followed from the lack of evidence for the formation of stable structures with two adjacent sterically demanding A units either within other products of this experiment or in the earlier attempted self-condensations of **1**. Instead, the results of the present experiment indeed point to the feasibility of using **1** as a capping unit.

With this in mind, we sought to modify the above conditions that led to the AB dimer as the main product in order to favor the formation of the ABA trimer. Thus, a condensation of **1** and dichlorosilicon phthalocyanine in the ratio of 2:1 equiv, followed by exhaustive silylation with TBDMSCl, now afforded a mixture of AB (5%), ABA (19%), and ABB (4%). Also recovered was a significant amount of the bis-TBDMS derivative of unconsumed **1**, viz **7**.

The chemical stability of oligomers **3**−**6** were probed using $BF_3{\cdot}OEt_2$ under conditions reported[14] to cleave silyl protecting groups from a substituted dihydroxysilicon Pc to form the corresponding difluorosilicon Pc. Under these conditions, **3**−**6** all yielded the products of replacement of the terminal TBDMS groups with fluorine; no products arising from cleavage of the μ-oxo bridges were observed. These new derivatives were characterized by ^{1}H and ^{19}F NMR spectroscopy and MALDI-TOF MS. A further indication of lability of the protecting groups was discovered during the preparation of a crystal of the AB dimer for X-ray structure analysis. When methanol was allowed to diffuse slowly into a solution of the compound in chloroform, crystals were obtained of a derivative of AB (**8**) in which the TBDMSO axial ligand attached to ring B is replaced by MeO. Selected bond length and angle data are collected in the Supporting Information. The staggering angle between the rings is ca. 16°, compared to 37° found for the bis-TBDMS-protected homodimer of the unsubstituted compound (the BB dimer using the present terminology).[3]

The lower oligomers of unsubstituted μ-oxo-bridged silicon phthalocyanines exhibit characteristic narrow blue-shifted Q-band absorptions,[15] explicable in terms of an allowed transition to the higher energy exciton level and a disallowed transition to the lower level. However, excitation to the latter is only forbidden at ring staggering angles of 45 and 0°.[6] Kleinwachter and Hanack reported a solvent dependence of the optical spectrum of some alkoxy-substituted dimers; this they assigned to the presence of different conformational isomers.[8] One form exhibits a blue-shifted Q-band, as above, and was assigned a staggering angle of ca. 45°. The other exhibits a multicomponent Q-band with low intensity absorption beyond 750 nm. Calculations showed that this is consistent with a staggering angle of ca. 20°. The spectra of the new oligomers (Scheme 1) show no solvent dependency from toluene, through THF to CH_2Cl_2. Their band shape and band complexity vary significantly. All four compounds show a weak absorption between 800 and 850 nm, indicative of excitation to their low energy exciton levels. This suggests that the small staggering angle between A and B rings observed in the solid state of **8** is maintained in the solutions of **3**−**6**.

In conclusion, we have identified a novel and convenient protocol for the synthesis of mixed lower μ-oxo-silicon phthalocyanine oligomers. The method has the potential to be tuned to favor a particular compound. The oligomers obtained to date are of interest in terms of the complexity of their visible region absorption spectra and should provide useful models for testing theoretical methods for predicting exciton coupling in multichromophore systems.

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Supporting Information Available: Experimental methods and compound characterization data; X-ray crystallographic data in CIF format and diagrammatic representations of the derivative of AB. This material is available free of charge via the Internet at http://pubs.acs.org.

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