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Modular Face-to-Face Assembly of Multichromophore Arrays That Absorb Across the Complete UV−Visible Spectrum and into the Near-IR

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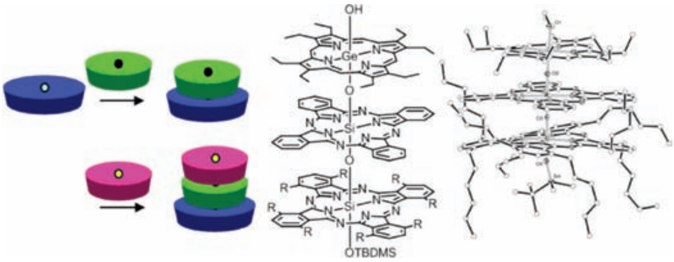
ABSTRACT



Defined face-to-face structures of phthalocyanine and porphyrin chromophores can be prepared using a modular strategy that allows directional, stepwise construction. μ-Oxo linkage between the central group of 14 metalloid atoms Si and Ge ensures π-overlap between the macrocycles, and exciton coupling effects further extend the absorption profile to provide arrays that absorb across the whole UV−visible spectrum and into the near-IR. The strategy is sufficiently versatile to be extended to synthesis of higher defined oligomers and subsequent functionalization or attachment at either or both ends of the stack.

Multichromophore structures with intense complementary absorption characteristics, in particular, those containing the phthalocyanine (Pc) and porphyrin (Pn) macrocyclic ligands, are currently receiving much attention.[1−3] They are of interest for the study of photoinduced energy transfer processes, and particular examples may be suited for applications such as light harvesting.[4] Various approaches have been investigated for linking the individual chromophoric units together to construct a hetero Pc/Pn heteroligand array. These include the use of either conventional conjugating moieties or flexible tethers from the periphery of one macrocycle ring to either the periphery or the central metal of the second,[1,2,4] the use of M(III) metals, especially the lanthanides, to form heteroleptic double or triple decker sandwich complexes,[5] and μ-oxo and μ-nitrido motifs between metal centers such as Fe and Mn at the centers of the participating macrocycles.[6]

μ-Oxo linked face-to-face oligomers[7] of group 14 metalloids containing phthalocyanines and porphyrins are particularly attractive for investigation. The geometry of the systems should promote orbital interactions that offer a

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mechanism for electronic communication[8] along the stack and, in addition, exciton coupling effects[6a] which should dramatically alter and extend the optical absorption profile. However, whereas there has been much work in this direction undertaken on μ-oxo linked SiPc oligomers, it appears that assembly of Pn derivatives containing group 14 elements has not been widely reported.[9] Construction of hetero μ-oxo linked Pc/Pn stacked assemblies therefore provides a significant and interesting synthetic challenge. In this communication, we report a versatile strategy to achieve such arrays.

A key compound to realize this aim is dihydroxysilicon 1,4,8,11,15,18,22,25-octakis(hexyl)phthalocyanine **1** (Figure 1). Unlike unsubstituted dihydroxysilicon phthalocyanine and 2,3,9,10,16,17,23,24-octasubstituted analogues,[3,6a] it does not self-oligomerize.[10] Indeed it does not even form a stable dimer, presumably because of destabilizing steric interactions involving the alkyl chains. However, these are insufficient to inhibit reaction at one of the two axial OH groups with the less sterically demanding unsubstituted dichlorosilicon phthalocyanine, so the group becomes a cap or growth point allowing mixtures of lower oligomers to be isolated and characterized as the bis-TMDMSi derivative, as exemplified by the isolation of the dyad **2**.[9] Interestingly, the synthesis of a hetero-Pc/Pn dyad **3** was achieved by simply reacting **1** with octaethyl dihydroxygermanium porphyrin **4**, establishing that the latter can indeed form a μ-oxo link to another macrocycle but at one face of the Pn core only.[11] In the present work, we introduce compound, **5**, a molecule that is constrained to form a μ-oxo link at just one face, enabling us to complete a strategy to assemble the first heterometallic μ-oxo-linked Pc/Pc′/Pn triads in a controlled modular process (Scheme 1).

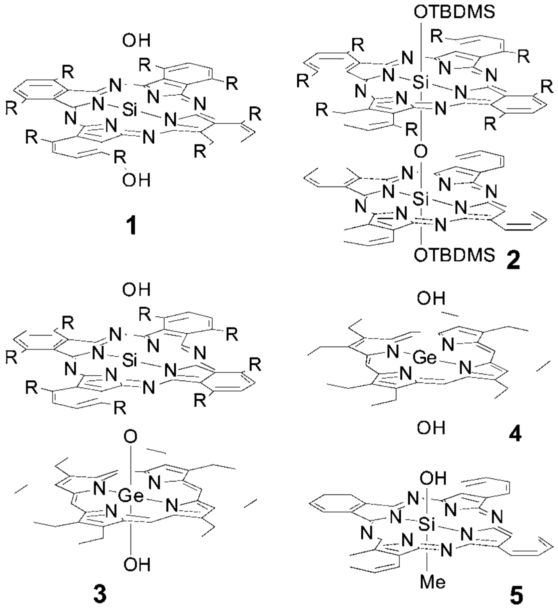

Figure 1. Structures of phthalocyanine and porphyrin derivatives **1**−**5**. R = hexyl.

The first step in Scheme 1 shows the reaction of **1** with **5** to provide a versatile intermediate, the mixed Pc/Pc′ dyad, **6**. To simplify access to the target triad compounds, we developed protocols which avoided the necessity to isolate dyad **6**. The first route to triads from **6**, via dyads **7** and **8** (left-hand side of scheme), is an unambiguous pathway insofar as selective protection/deprotection steps built into the scheme serve to distinguish between the nonequivalent axial sites of the substituted and unsubstituted Pc rings within the structure **8**. This ensures that reaction of **8** with the incoming porphyrin moiety, **4**, that completes the triad must be μ-oxo linked to the unsubstituted Pc ring. Thus, **6** was reacted with TBDMSCl in the presence of pyridine to form intermediate **7** which was taken up in DCM and subjected to light under conditions based on the early findings of Kenney and co-workers for demethylation/hydroxylation of axial methyl-substituted SiPc derivatives.[12] Following workup, the photolysis product **8** was obtained and characterized by MALDI mass spectrometry which showed isotopic clusters corresponding to M^+, $M^+ - OH$, and $M^+ -$ TBDMSO. Further confirmation of the structure of **8** followed from satisfactory assignment of signals in ^{1}H NMR spectra run in both benzene-d_6 and DCM-d_2. The Pc/Pc′ dyad **8** was then reacted with the porphyrin **4** to give the heterometal−heteroligand triad **9**. This gave a MALDI mass spectrum that showed isotopic clusters assigned to M^+, $M^+ - OH$, and $M^+ -$ TBDMSO species. ^{1}H NMR spectra showed signals consistent with the structure, although the OH peak could not be distinguished from other signals.

The second route to triad structures from the Pc/Pc′ dyad **6** (right-hand side of Scheme 1) also employed Kenney's light-induced demethylation/hydroxylation reaction, in this case to generate the dihydroxy Pc/Pc′ compound **10** in 46% yield. This route is more direct and avoids the protection step in the first route and assumes and indeed confirms, see below, that **10** reacts with the germanium porphyrin **4** only at the least sterically hindered axial Si−OH group. The product, the dihydroxy terminated triad **11**, was obtained in 67% yield. Its structure was confirmed from its MALDI mass spectrum and ^{1}H NMR spectral data and further by its

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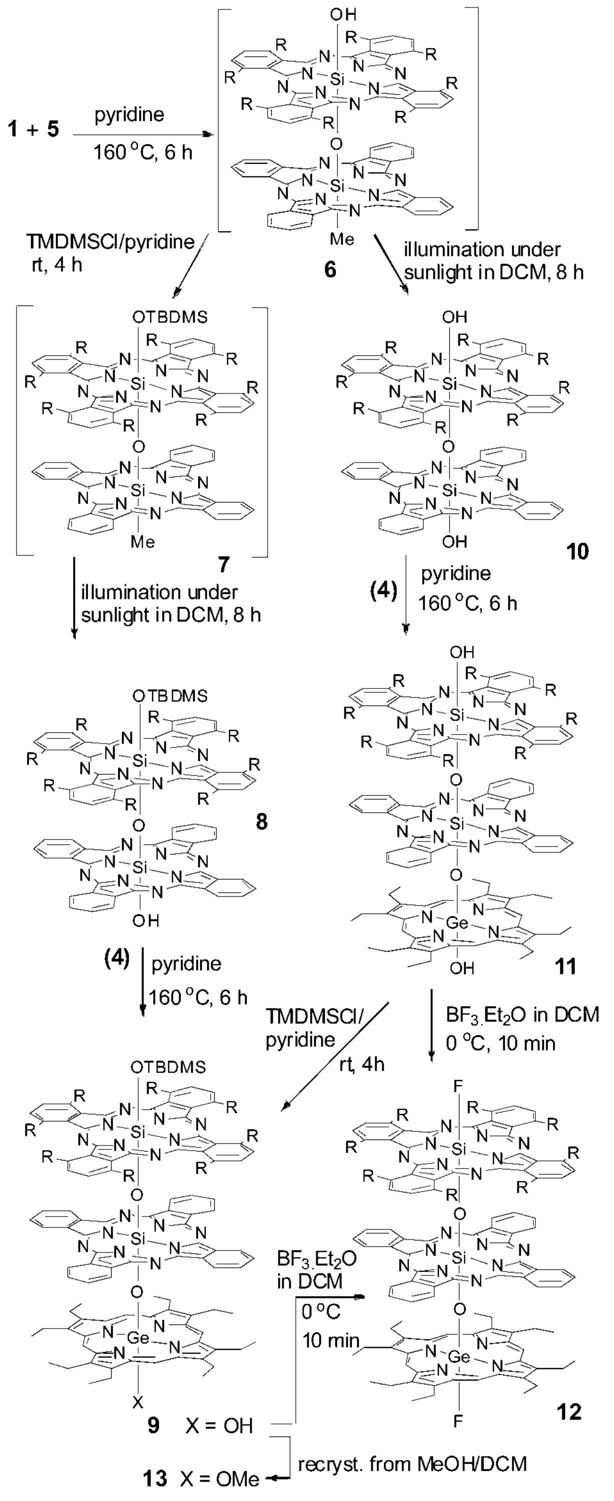
Scheme 1. Synthesis of Compounds[a]



[a] NB. R = hexyl throughout.

conversion into **9** in 93% yield upon reaction with TBDMSCl. The formation of the mono-TBDMS derivative **9** arising from reaction at the silicon is consistent with results we obtained in our earlier work on the heterodyad system derived from **1** and **4**.[10] A preliminary investigation of the stability and reactivity of compounds **9** and **11** was undertaken reacting the compounds with BF_3•etherate. Both were converted in good yields into the bisfluoro triad **12**, and this effectively locks the triad structure and blocks the termini. Triad **12** gave a MALDI mass spectrum showing isotopic clusters at 2430.1 M^+ and 2410.1 $M^+ - F$.

Final confirmation of the formation of triad structures was forthcoming upon recrystallization of **9** from MeOH/DCM. This led to MeO/OH ligand exchange at the Ge atom to afford the new triad derivative **13**, for which results of the single-crystal X-ray structure determination are shown in Figure 2. The central O−Ge−O−Si−O−Si−O chain is essentially linear with the greatest departure from linearity arising in the Ge−O−Si(Pc)- unit where the Ge−O−Si bond angle is 176.88(15)°. The angle between the macrocycles' metalloids Ge•••Si•••Si is 178.36(3)°. Distances between Ge and Si of the central Pc ring and between the latter and the Si of the outer Pc ring are 3.4225(9) and 3.3236(12) Å, respectively. Torsion angles of the outer rings relative to the

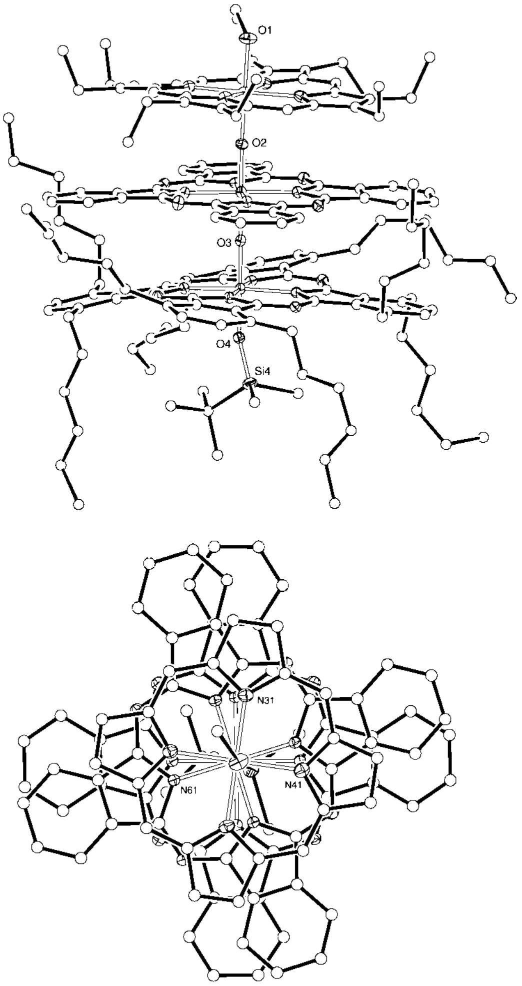


Figure 2. X-ray crystal structure of compound **13** showing, above, a side view of the molecule with the porphyrin ring at the top and, below, a view of the molecule (with alkyl chains removed for clarity) looking along the O−Ge−O−Si−O−Si−O axis showing the relative orientations of the rings to each other.

central SiPc ring are +25° for the GePn ring and +17° for the outer SiPc ring. Details of the structure determination and a molecular packing diagram can be found in the Supporting Information.

The UV−vis spectra of the triad compounds show strong broadband absorption. Figure 3 compares the spectrum of the triad **11** with those exhibited by two of the component ligands. Combination of the complementary chromophores in **11** leads to significant extension of the absorption envelope into the near-infrared and the effective removal of the window of minimal absorption in the visible region spectrum exhibited by the simple combination of the absorption spectra of the component chromophores. This points to complex exciton coupling effects arising from the proximity of the ligands. Interestingly, the strong porphyrin Soret band is essentially retained in the spectrum of **11**. Spectra for the triads **9** and **12** are very similar to that of **11** and indeed overlap fully over wavelengths from 350 to ca. 580 nm. These are shown in the Supporting Information.

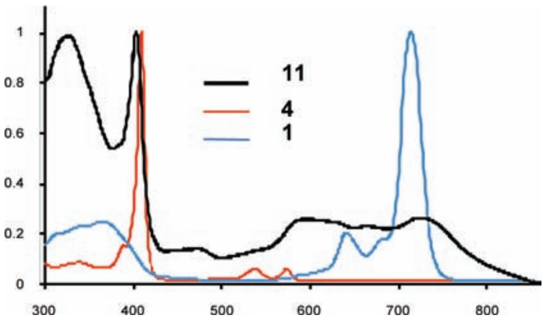


Figure 3. Normalized UV−vis and near-IR spectra of triad **11** and compounds **1** and **4**.

In conclusion, we have developed a strategy for the unambiguous construction of heteroligand, heterometalloid triad structures which contain three different chromophores. The modular approach is versatile and allows controlled, directional assembly. Unwanted self-oligomerization products are precluded, and the assembly path is unambiguous allowing the formation of complex structures with broadband absorption extending from the UV through to near-IR wavelengths. These data may prove of particular interest to those testing theoretical models for predicting exciton coupling effects in complex chromophores.

Acknowledgment. We thank the EPSRC for funding (EP/E028446) and access to the Mass Spectrometry (Swansea) and National Crystallography (Southampton) services.

Supporting Information Available: Experimental methods and compound characterization data. Further UV−vis spectra of triad structures. Details of the X-ray structure characterization with selected data and view of the molecular packing of compound **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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