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Solid-phase synthesis of phthalocyanine and tetraazaporphyrin triangular prisms

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ABSTRACT

A solvent-free, solid-phase one-step reaction between tetra-*tert*-butylated oxotitanium(IV) phthalocyanine and tetraazaporphyrin with 2,3,6,7,10,11-hexahydroxytriphenylene yields novel azaporphyrin cyclic trimers with triangular prismatic orientations. The fluorescence arising from the phthalocyanine and tetraazaporphyrin chromophores is significantly quenched upon trimerization.

There has been considerable interest in the synthesis of porphyrin-based arrays as a pathway for constructing artificial functional systems, since these arrays play a pivotal role in key biological processes such as oxygen transport and electron and/or energy transfer.[1] Despite the many industrial applications for phthalocyanines (Pcs), the synthesis of Pc oligomers is not well developed,[2] with the exception of face-to-face and coplanar Pc systems. Similarly, very little attention has been paid to the synthesis of oligomeric tetraazaporphyrins (porphyrazines) to date. In contrast, there has been rapid progress in oligoporphyrin synthesis. Herein we report the solvent-free, solid-phase synthesis of Pc and tetraazaporphyrin (TAP) cyclic trimers with triangular prismatic structures (**1** and **2**), based on a reaction between oxotitanium (IV) tetra-*tert*-butyl-Pc (**3**) or TAP (**4**) and 2,3,6,7,10,11-hexahydroxytriphenylene (**5**).

Several studies have demonstrated that oxotitanium(IV) Pcs react readily with *ortho*-diol compounds (catechol, oxalic acid, etc.) in organic solvents,[3] despite the fact that M=O groups of early-transition metal (M) porphyrinoid systems are often extremely difficult to cleave. While the solution reaction did not proceed in the case of the present system, we found that the trimerization reaction proceeded effectively in the solid-phase. A mixture of **3** (7.4 mg, 9.3×10^{-3} mmol) and **5** (1.0 mg, 3.1×10^{-3} mmol) was ground at room temperature in a 3:1 molar ratio using an agate mortar. A slight color change from blue to dark green was observed. The IR spectrum of the reaction mixture does not contain the relatively intense Ti=O stretching band of **3** at 971 cm^{-1}.[3] The MALDI-TOF mass spectrum of the reaction mixture contained an intense peak at $m/z = 2671$, which is consistent with the trimeric target complex (**1**). After 15 min of grinding, the reaction mixture was dissolved in a small amount of CH_2Cl_2 and a reasonable yield of pure trimer (3.7 mg, 1.4×10^{-3} mmol, 45%) was obtained after size-exclusion chromatography (Bio-Beads S-X1, CH_2Cl_2).[4] The elution volume of **1** was smaller than that of related Pc dimeric system.[3e] ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$, 300 K) provides further evidence for the formation of a 3:1 complex. A ^{1}H resonance is observed at 3.86 ppm, which can be assigned to the coordinated triphenylene ligand based on the large Pc ring current effect. The change of the chemical shift ($\Delta\delta$) of the trimeric system (−3.87 ppm) is significantly larger than that of catecholate complex (−2.6 ppm[3d]), due to strong shielding at the center of the triangular prism. The chemical shifts corresponding to the Pc aromatic ring and the peripheral *tert*-butyl groups are almost the same as those of the free oxotitanium Pc. This suggests that there is free rotation of the Pc unit in **1** at room temperature.[5]

Figure 1 contains the room temperature UV–visible absorption and magnetic circular dichroism (MCD) spectra of **1** and **3** in toluene. The spectra of the trimeric complexes exhibit broad Q and Soret absorption bands. In contrast to the Faraday *A* term observed for the Q band of **3**, the MCD signal of the Q band of the trimeric system is assigned to a pseudo-Faraday *A* term, which arises from a transition from the nondegenerate ground state to nearly degenerate excited states.[6] The fluorescence intensity associated with the Pc chromophore significantly decreases upon

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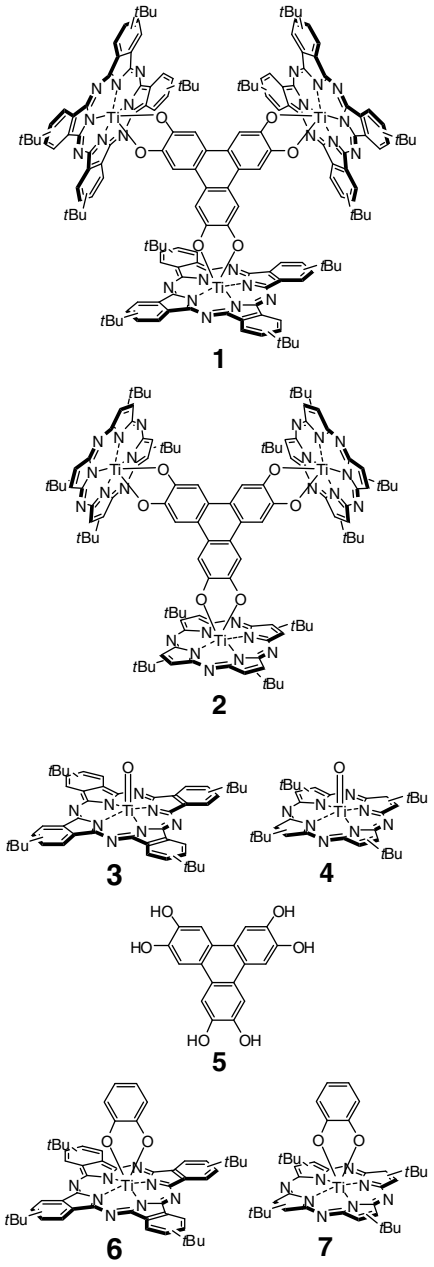

trimerization (Fig. 1b). All these spectral features are essentially identical to those of the catecholate complex (**6**), so we can conclude that the spectral changes are due to a lowering of the effective symmetry of the Pc chromophore upon axial ligation. The interaction between the Pc chromophores is clearly smaller than the interactions between the Pc rings and the axial ligand.

Since oxotitanium(IV) TAPs have not been reported to date, we first had to synthesize oxotitanium(IV) tetra-*tert*-butyl TAP (**4**). Commercially available *tert*-butylated TAP (100 mg, 1.86×10^{-1} mmol) was reacted with $Ti(OBu)_4$ (632 mg, 1.86 mmol) in the presence of urea (230 mg, 2.82 mmol) in refluxing pentanol (1.5 mL) under a nitrogen atmosphere. After 3 days, 25 mL of methanol was added and the solution was refluxed for a further 30 min. After cooling to room temperature, the crude products were extracted from the reaction mixture and were then chromatographed on silica gel using chloroform as the eluent. After evaporation of the solvent, **4** was obtained as a blue-purple powder (58 mg, 9.65×10^{-2} mmol, 58%).[7] Oxotitanium(IV) TAP is a highly fluorescent chromophore as is the case with the phthalocyanine derivatives. TiTAP–catechol complex (**7**) was easily formed by mixing **4** with catechol in solid-phase, as well as in solution.[8]

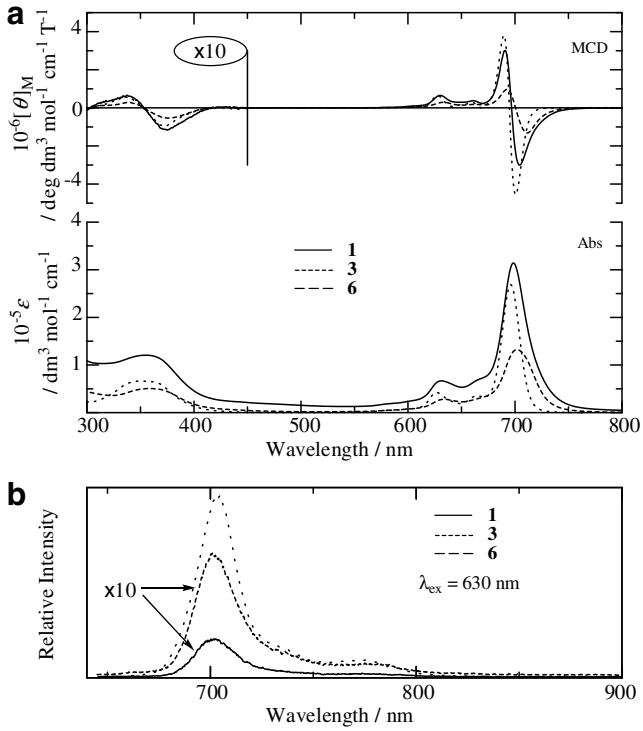

Figure 1. (a) Electronic absorption and MCD spectra of **1**, **3**, and **6** recorded in toluene. (b) Fluorescence emission spectra recorded upon excitation of a toluene solution at 630 nm. The absorbance at 630 nm was 0.10.

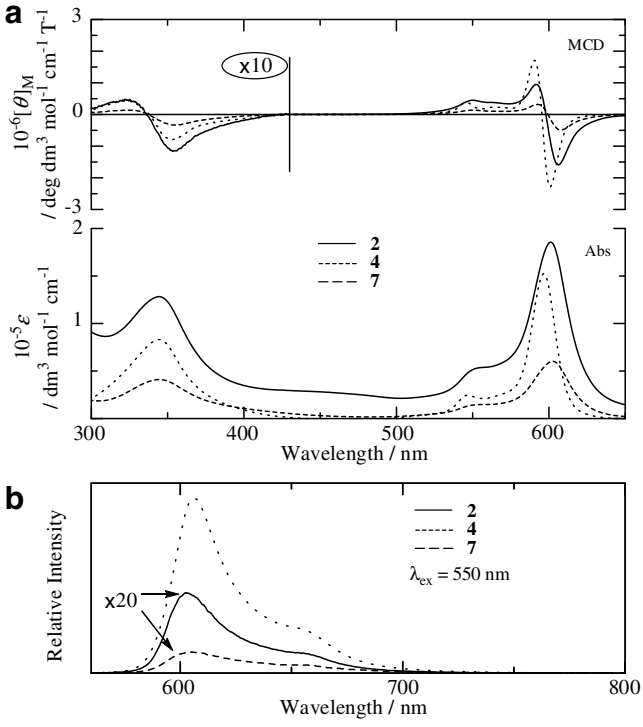

Figure 2. (a) Electronic absorption and MCD spectra of **2**, **4**, and **7** recorded in toluene. (b) Fluorescence emission spectra taken after excitation of a toluene solution at 550 nm. The absorbance at 550 nm was 0.10.

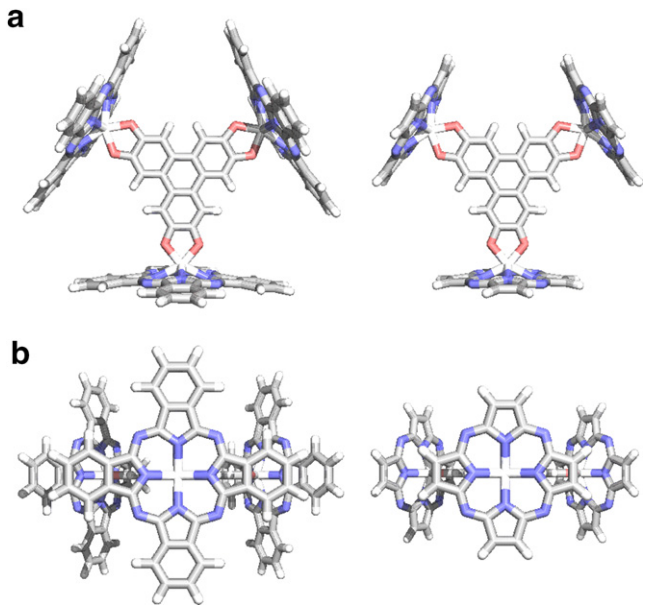

Figure 3. Optimized structures of the Pc trimer (left) and TAP trimer (right) without peripheral substituents (B3LYP/6-31G*). (a) Top view. (b) Side view.

The formation of the TAP trimer (**2**) was accomplished using the reaction conditions that were used for the phthalocyanine system. After the solid-phase reaction, a molecular ion peak (m/z = 2072) was detected for the trimeric complex. The trimer was purified using size-exclusion chromatography (67% yield).[9] The ^{1}H NMR spectrum of the trimer complex is consistent with a 3:1 complex. A large ring current shift is observed for the proton signal of the triphenylene ligand (4.08 ppm). Upon ligation, the spectral changes of the TAP complex appear to be similar to those of the Pc complex (Fig. 2). A broadening of the Q band is observed in the UV–visible spectrum of the trimer (**2**), and the fluorescence intensity decreases significantly relative to that of the starting monomer (**4**).

Figure 3 contains the optimized geometries of the Pc and TAP trimers. The geometry optimizations were carried out at the B3LYP/6-31G* level.[10] Both complexes have prismatic D_{3h} symmetry. There is no significant change in the azaporphyrin structures relative to those of the corresponding monomers. The shortest Ti–Ti distance is approximately 11 Å. The complexes adopt an eclipsed conformation with respect to the pyrrole N atoms and the O atom in the triphenylene unit. This preference has also been predicted in theoretical calculations for the catecholate Pc system (**6**).[3e]

In conclusion, well-defined cyclic Pc and TAP trimers have been successfully formed in the absence of a solvent through a ligand exchange reaction. The high reactivity of the oxotitanium complexes provides a convenient one-step synthetic method for constructing new types of oligo- (or poly-) porphyrinoid systems.

Acknowledgments

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Supplementary data

Supplementary data (^{1}H NMR spectra, size-exclusion chromatography, and UV–vis spectra) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.06.025.

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4. ^{1}H NMR (δ ppm, 400 MHz, $CDCl_3$, 300 K): 9.70–9.22 (br m, 24H), 8.48–8.16 (br m, 12H), 3.86 (br s, 6H), 1.76 (br s, 108H). IR (KBr disc): 1615, 1483, 1395, 1366, 1327, 1281, 1256, 1202, 1152, 1078, 928, 831, 760. UV–vis (toluene) λ_{max} (10^{-5} ε): 699 (3.14), 631 (0.66), 354 (1.21); MCD (toluene) λ_{max} (10^{-5} $[\theta]_M$): 704 (−30.0), 691 (30.1), 661 (3.77), 630 (6.53), 375 (−1.16), 338 (0.66); MS(MALDI-TOF) (m/z): 2671 (M^+).
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7. ^{1}H NMR: (δ ppm, 400 MHz, $CDCl_3$, 300 K): δ 9.21–9.15 (m, 4H), 2.24–2.22 (m, 36H). IR (KBr disc): 1482, 1458, 138, 1362, 1321, 1250, 1202, 1075, 1061, 1026, 1001, 978, 848, 779, 728, 693. UV–vis (toluene) λ_{max} (10^{-5} ε): 597 (1.51), 344 (0.83). MCD (toluene) λ_{max} (10^{-5} $[\theta]_M$): 601 (−22.9), 591 (17.1), 546 (3.82), 352 (−0.80), 323 (0.43). MS(MALDI-TOF) (m/z): 600 (M^+).
8. ^{1}H NMR (δ ppm, 400 MHz, $CDCl_3$, 300 K): δ 9.21–9.08 (m, 4H), 5.68–5.65 (m, 2H), 4.55–4.51 (m, 2H), 2.34–2.04 (m, 36H). UV–vis (toluene) λ_{max} (10^{-5} ε): 603 (0.60), 345 (0.41). MCD (toluene) λ_{max} (10^{-5} $[\theta]_M$): 608 (−4.91), 593 (3.20), 550 (1.38), 356 (−0.34), 325 (0.14); MS(MALDI-TOF) (m/z): 692 (M^+).
9. ^{1}H NMR (δ ppm, 400 MHz, $CDCl_3$, 300 K): δ 9.26–8.88 (m, 12H), 4.08 (s, 6H), 2.34–2.08 (br m, 108H). IR (KBr disc): 1482, 1460, 1441, 1389, 1362, 1275, 1250, 1075, 1059, 1026, 1001, 851, 779. UV–vis (toluene) λ_{max} (10^{-5} ε): 601 (1.86), 344 (1.28). MCD (toluene) λ_{max} (10^{-5} $[\theta]_M$): 606 (-15.9), 591 (9.49), 551 (4.51), 354 (-1.17), 322 (0.48); MS(MALDI-TOF) (m/z): 2072 ($M+H^+$).
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