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Synthesis of Benzene-centered Trinuclear Phthalocyanines by Triple-click Chemistry

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We disclose here the synthesis of novel benzene-centered trifluoroethoxy-coated trinuclear Pc **1** and its nonfluorinated analog **2** with flexible click spacers. UV–vis study reveals that trifluoroethoxy coating can result in the purely nonaggregated, windmill-like molecular structure of **1** without rigid spacers or any external source of help.

The design and construction of multichromophore molecular architectures, such as dyads, triads, and higher order arrays, is an active area of current research in material science. To this end, significant research effort has been devoted to the synthesis of multi-porphyrin molecular arrays.[1] Phthalocyanines (Pcs), porphyrin analogs, have drawn attention as molecular materials that give rise to marvelous electronic and optical properties.[2] These properties arise from their electronic delocalization and are greatly dependent on their aggregation states. In past years, many research groups have concentrated on the preparation of di- and trinuclear Pc derivatives employing different kinds of spacers with a view to explore the application of Pcs.[3] Recently, Torres et al. reported the synthesis of trinuclear Pcs in which three *tert*-butyl-substituted Pc moieties are connected to a central benzene or triazine unit with rigid ethenyl or ethynyl bridges.[4a] They also synthesized a benzene-centered phthalocyanine hexamer.[4b] These compounds have beautiful windmill-like molecular structures and are also interesting from a topological point of view. It is indeed true that rigid spacers are crucial to achieve and control the molecular structures in such multichromophore molecular systems by avoiding intrinsic strong intramolecular aggregation.[5] A couple of years ago, we discovered the unique nonaggregation property of trifluoroethoxy (TFEO)-coated Pcs conjugated with deoxyribonucleosides.[6a] We also synthesized TFEO-coated binuclear Pc wherein two Pcs are covalently linked with a conjugated rigid diyne spacer and noted its prominent avoidance of intermolecular aggregation.[6b] We also recently disclosed the first example of never-closing clamshell Pcs in which the two rings are covalently connected by a flexible linker by "double-click" chemistry.[6d] As part of our ongoing research programs directed to the development of novel functionalized Pcs[6] and the synthesis of fluorine-containing biologically active compounds,[7] we disclose herein a novel benzene-centered TFEO-coated trinuclear Pc **1** in which three Pc rings are covalently connected by a flexible linker using "triple-click" chemistry (Figure 1). Spectroscopic investigation of trinuclear Pc **1** revealed that the windmill-like molecular structure is realized without any help of rigid spacers for the first time (Figure 2). A novel nonfluorinated trinuclear Pc **2** was also synthesized for comparison (Figure 1).

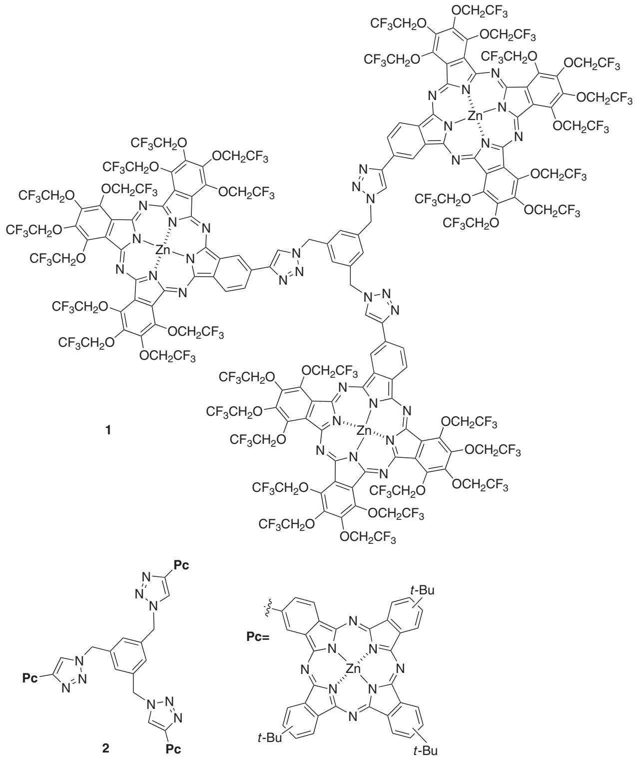

1
2

Figure 1. Structures of newly designed trinuclear Pcs **1** and **2** with click spacers.

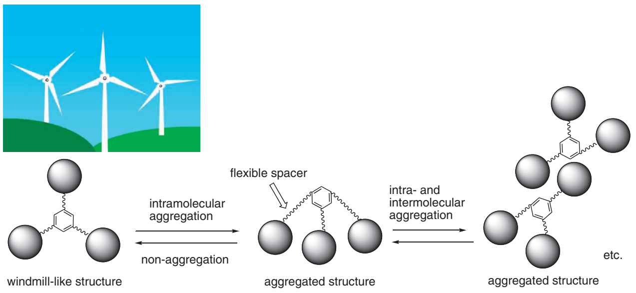
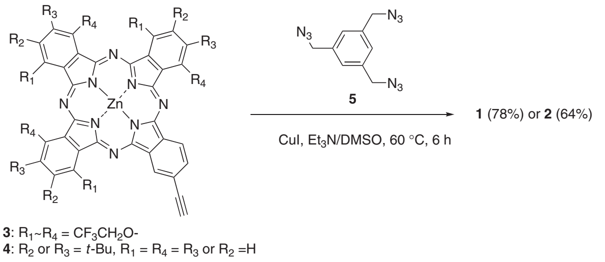


Figure 2. Windmill-like molecular structure vs. aggregated structures of benzene-centered trinuclear Pc with flexible click spacers.

A trifluoroethoxy-coated trinuclear Pc **1** has been synthesized from 23-ethynyl-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate zinc(II) (**3**)[6b] and 1,3,5-tris(azidomethyl)benzene (**5**) by "triple-click" chemistry using CuI, Et_3N, and DMSO in 78% yield. Similarly, **2** has been synthesized from 2(3),9(10),16(17)-tri-*tert*-butyl-23-ethynylphthalocyaninate zinc(II) (**4**)[8] and **5** in 64% yield (Scheme 1).



Scheme 1. Synthesis of trinuclear Pcs **1** and **2**.

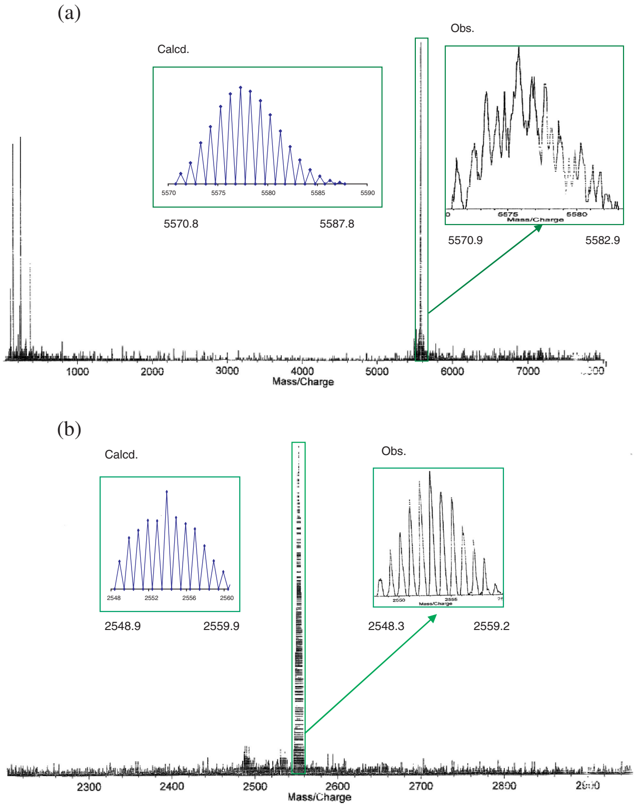


Figure 3. MALDI-TOF MS spectra of (a) Pc **1** and (b) Pc **2**. Inset: Isotopic resolution of the calculated and observed MALDI-TOF main peaks of the trinuclear Pcs.

Target compound **1** is characterized by ^1H and ^{19}F NMR, UV–vis, MALDI-TOF-MS, and FT-IR.

Formation of the trinuclear Pcs **1** and **2** was confirmed by MALDI-TOF mass spectrometry. The Pc **1** shows a prominent peak at m/z 5576 while **2** exhibits one at m/z 2553 (Figures 3a and 3b, respectively). In both cases, the isotopic profiles are compared with the calculated isotopic patterns for the ZnPc-triads, which show a nearly similar match.

The aggregation behavior of **1** and **2** was explored by NMR, UV–vis, and fluorescence spectra. The ^1H and ^{19}F NMR spectra of **1** in *d*-acetone very clearly indicate a nonaggregation behavior, while the nonfluorinated, *tert*-butyl analog of **1** shows broad signals due to aggregation (Figures S3 and S4 in the Supporting Information).[9] In the UV–vis spectra in CH_2Cl_2, **1** exhibits strong absorption at 698 nm of the Q-band, and 357 nm of the B-band, which are indicative of a monomeric state, independent of concentration. Freedom from inter- and intramolecular aggregations was strictly ascertained by the addition of a metal-coordinating molecule, pyridine.[10] Namely, the shape of the spectrum did not change even after the addition of pyridine (Figure 4a). The same phenomenon was observed with other solvents such as $PhCF_3$ and dioxane.[9] On the other hand, the UV–vis spectra of nonfluorinated trinuclear Pc **2** in CH_2Cl_2 shows broadening of the Q-band indicating aggregation, which upon addition of pyridine gives a sharp monomeric peak (Figure 4b). These results clearly demonstrate that only TFEO-coated trinuclear Pc **1** behaves like mono-Pcs, i.e., a windmill-like molecular structure is suggested.

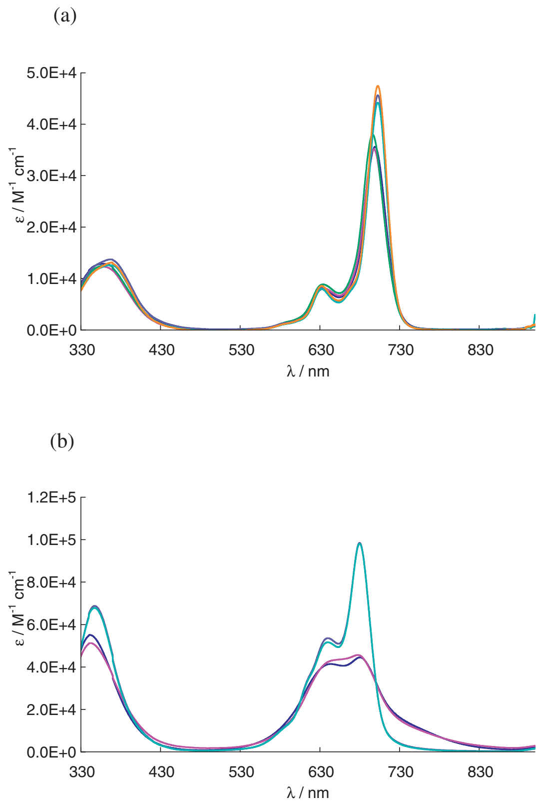


Figure 4. UV–vis spectra of (a) Pc **1** in CH_2Cl_2 (blue, pink, green: ca. 0.5×10^{-4} to 10^{-6} M; ash, cyan, yellow: ca. 0.5×10^{-4} to 10^{-6} M with a drop of pyridine) and (b) Pc **2** in CH_2Cl_2 (blue, pink: ca. 1.0×10^{-4} to 10^{-5} M; ash, cyan: ca. 1.0×10^{-4} to 10^{-5} M with a drop of pyridine).

Steady-state fluorescence spectra of **1** and **2** were next investigated in different solvents as shown in Figure 5 (also see Figure S10 in the Supporting Information).[9] It can be seen that the emission of **2** in $CHCl_3$ is significantly quenched with almost no fluorescence quantum yield (Φ_f) value, which after addition of pyridine or in coordinating solvent like dioxane, gives higher emission intensity at around 685 nm. The observed fluorescence quenching of **2** may be attributed to inter- or intramolecular aggregation. On the contrary, trinuclear Pc **1** shows a single strong emission peak at 762 nm in $CHCl_3$ with a Φ_f value of 0.04. Thus the nonaggregation property of **1**, as revealed by absorption spectra, is further supported by the emission spectra. It should be mentioned here that the previously reported mono-nuclear and dinuclear click-type Pc compounds have shown

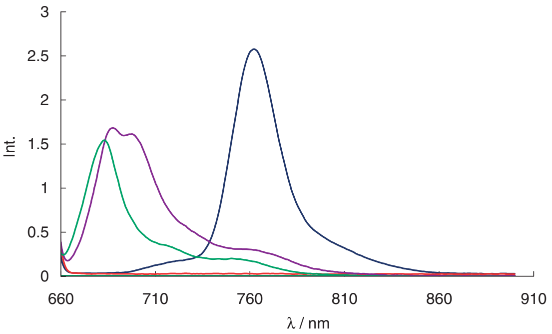


Figure 5. Steady-state fluorescence spectra of **1** (blue: CHCl$_3$) and **2** (red: CHCl$_3$, purple: CHCl$_3$ with a drop of pyridine, green: dioxane) with excitation at 655 nm.

fluorescence at 715 nm with higher Φ_f values of 0.27 and 0.24 respectively in CHCl$_3$[6d] i.e., the Φ_f value of **1** is one order smaller than those of the mononuclear and dinuclear click-type Pcs even in the absence of aggregation phenomenon. The possible reason for the fluorescence quenching in **1** relative to the mononuclear and dinuclear Pcs might be due to the nonradiative recombination processes.[11] Apart from the comparison to the mononuclear and dinuclear Pcs, a couple of general reasons are also conceivable for the low Φ_f value of Pc **1**. i) Electronic interaction is known to occur via a superexchange interaction involving the bonds of the bridge between the two (or more) moieties even if two moieties are ca. 10 Å apart even in the absence of aggregation.[12] Thus, it appears not unusual that the Φ_f value of **1** is about an order smaller than Φ_f of the constituent monomeric species. ii) Low symmetry Pcs generally has lower Φ_f value due to a disruption of the degeneracy in the S1 state.[13]

In summary, we have synthesized a novel windmill-like trifluoroethoxy-coated trinuclear Pc **1** with flexible spacers by triple-click chemistry. The nonfluorinated analog, **2**, comprising *tert*-butyl substituents has also been synthesized for comparison. Spectroscopic investigation reveals that while sterically demanding *tert*-butyl substituents on Pc **2** cannot stop the aggregation, the trifluoroethoxy groups in the trinuclear architecture of **1** can stop it to a great extent without any external source of help such as coordinating solvents. This nonaggregation property of **1** is particularly attractive from the perspective of Pc-based molecular units for the creation of nanomaterials. Preparation of single crystals of **1** is currently underway to ascertain the windmill-like conformational arrangement of **1**.

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