



A dendron of subphthalocyanine trefoil

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ABSTRACT

The synthesis of a dendron composed of tetrameric subphthalocyanine (SubPc) is accomplished by substituting the chlorine groups with phenoxy groups at the axial positions of SubPc with SubPc-triol. The present molecular design of the SubPc-triol introduces three phenol groups at the peripheral positions of the SubPc macrocycle as a tritopic template to construct SubPc dendrons. The self-polycondensation of SubPc-triol as a 'divergent' synthesis only gave a trace amount of the hyperbranched arrays due to poor solubility of the SubPc-triol. In contrast, a 'convergent' synthesis with the terminal SubPc improved the solubility throughout the reaction and a tetrameric SubPc dendron was obtained in moderate isolated yield.

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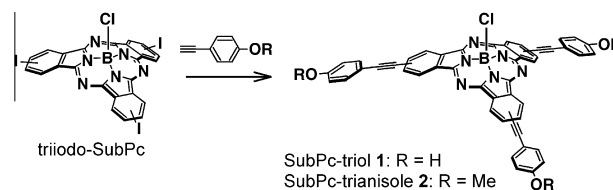
Dendritic or hyperbranched multichromophoric arrays are emerging at the forefront of material chemistry due to their excellent photoelectronic properties.^{1–4} Among them, ligand-to-metal coordination provides a straightforward strategy to construct arborescent structures composed of a metal complex or chromophore.⁴ A non-centrosymmetric dendron of chromophoric unit, on which a highly branched structure converges to the focal core unit through branching π -conjugation or inter-unit electronic interactions, is a promising entity for the development of an energy cascade or a potential gradient aimed at artificial photosynthesis, organic electronics, and nonlinear optics.^{1–6} A three-forked node should be effective at designing a highly branched dendron in order to achieve further enhanced effects of the dendritic arrangement.

The topologically fascinating concave trefoil framework of subphthalocyanine, SubPc, was chosen to triplicate the polymer backbone in a three-dimensional fashion. SubPc is a boron(III) complex of a macrocyclic ligand with a 14π electron system.^{7–10} The labile chlorine atom bound to the central boron atom at the axial position is readily substituted by a nucleophilic phenoxy group.⁸ The new axial substitution is able to deliver functional units into SubPc.⁸ Recently, we have successfully established a template-directed protocol to provide multi-SubPc arrays by employing a multiple phenoxy precursor. Thus, hexakis(4-hydroxyphenyl)benzene as the multiple phenoxy template gave a hexameric SubPc array in moderate isolated yield despite the presence of excessively congested multiple reaction sites.⁹ We now disclose the synthesis of a novel tetrameric SubPc dendron composed of three peripheral SubPc units converging into the focal SubPc bearing tritopic

4-hydroxyphenylethynyl side-arms, SubPc-triol **1**, via radial phenoxy-to-boron(III) bonds.

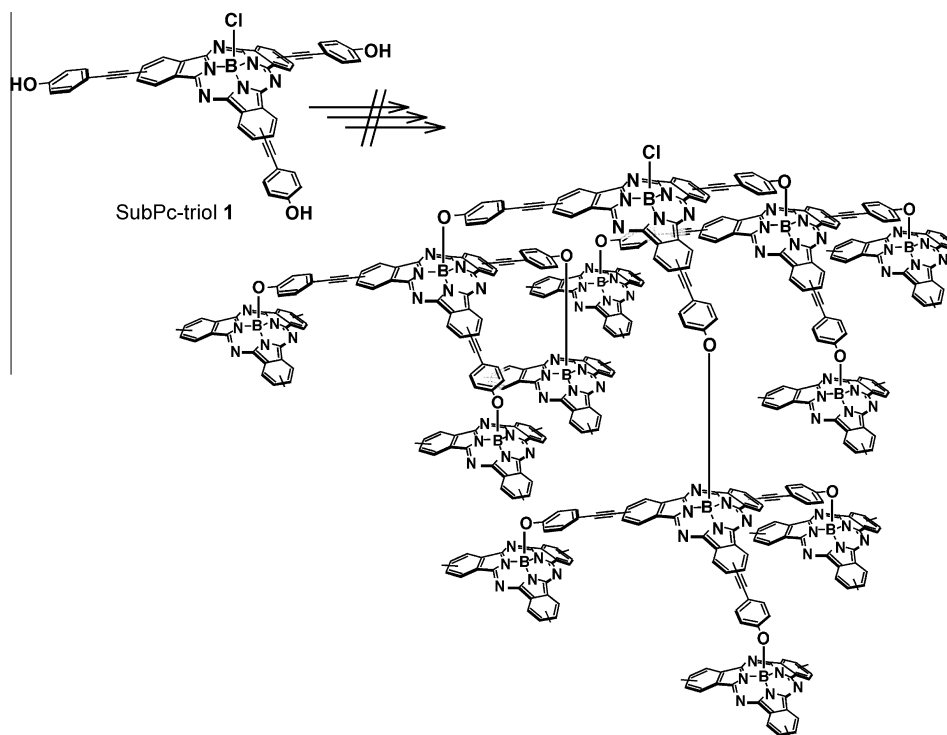
SubPc-triol **1** was derived from triiodo-SubPc and 4-ethynylphenol by the Sonogashira cross-coupling reaction according to literature procedures (Scheme 1).¹⁰ Under the reaction conditions, the undesired axial substitution proceeded in part and gave an insoluble precipitate presumably including polycondensed byproducts. The monomeric SubPc-triol **1** was obtained as a bluish purple powder in a 12% isolated yield.¹¹ In a similar way, SubPc-trianisole **2** was prepared as the reference compound in a 56% isolated yield.¹² The following discussion concerns the synthetic investigations of the dendritic SubPc arrays.

For the first trial, one-pot self-polycondensation of SubPc-triol **1** as a 'divergent' approach was attempted under refluxing conditions using anisole, pyridine, or THF as the solvent (Scheme 2). However, self-polycondensation was restricted presumably by very poor solubility of polycondensed **1** even in such polar solvents. Therefore, no polymeric products higher than the dimeric or trimeric species were obtained (entries 1–6 in Table 1).



Scheme 1. Synthetic scheme of SubPc-triol **1** and SubPc-trianisole **2**. Reagents and conditions: the corresponding ethynylaryl precursor, CuI, Pd(PPh₃)₄, Et₃N, toluene at 35 °C.

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Scheme 2. A 'divergent' approach: one-pot self-polycondensation of SubPc-triol **1** toward the hyperbranched arrays under the reflux conditions of anisole, pyridine, or THF. The results are summarized in entry 1–6 in Table 1.

Table 1
Summary of the reactions of SubPc-triol **1**

Entry	SubPc- <i>t</i> Bu ₃ 3	Conditions	Yield (%)
1	0 equiv	Anisole, rt, 170 h	Trace ^a
2	0 equiv	Anisole, 60 °C, 100 h	Trace ^a
3	0 equiv	Anisole, reflux, 100 h	Trace ^a
4	0 equiv	THF, rt, 170 h	Trace ^a
5	0 equiv	THF, reflux, 100 h	Trace ^a
6	0 equiv	Pyridine, reflux, 100 h	Trace ^a
7	6.5 equiv	Toluene/Et ₃ N, reflux, 22 h ^b	57% ^c

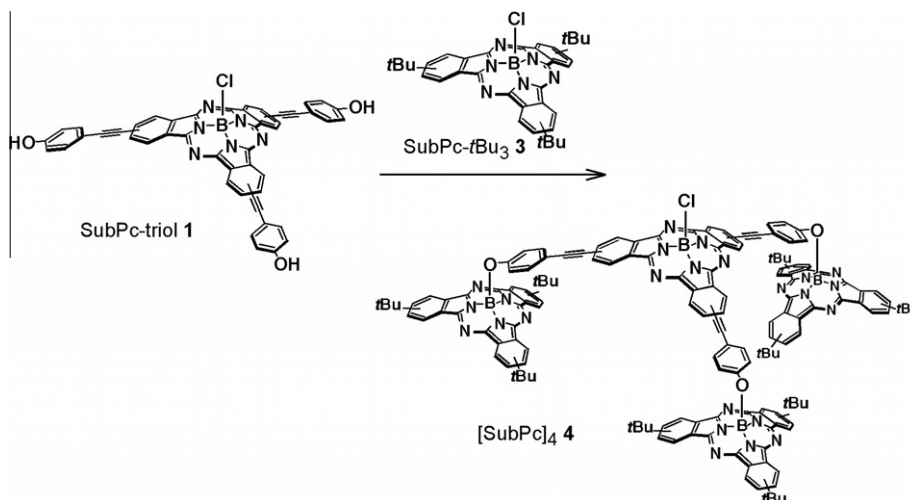
^a No hyperbranched arrays were observed.

^b Compound **1** was soluble in toluene/Et₃N only when **3** was added.

^c Isolated yield based on SubPc-triol **1**.

Additionally, the prolonged reaction times were accompanied by partial ring-expansion to afford phthalocyanine as the byproduct.^{7b} Hyperbranched arrays were only obtained in a trace amount by the self-polycondensation of **1**. However, this limited result suggests that the reactivity of SubPc-triol **1** might be controlled by the solubility of **1** under appropriate conditions. In this case, SubPc-triol **1** would be suitable for the application of a 'convergent' synthesis with SubPc terminal units in the dendritic structure.

In the second stage, a 'convergent' synthesis was examined. To achieve the synthesis of the dendritic SubPc array, a terminal SubPc unit was designed to improve the solubility throughout the reaction. Thus, we introduced SubPc-*t*Bu₃ **3**, which bears the peripheral *tert*-butyl groups, as the terminal unit (Scheme 3). Then,



Scheme 3. A 'convergent' approach: the mixture of SubPc-triol **1** and SubPc-*t*Bu₃ **3** was refluxed in toluene/triethylamine (4/1, v/v) to give the tetrameric dendron [SubPc]₄ **4**. The result is summarized in entry 7 in Table 1.

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