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Asymmetric Phthalocyanine Synthesis by ROMP-Capture-Release

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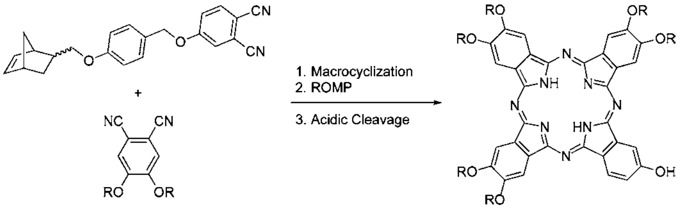
ABSTRACT



Statistical condensation of norbornenyl-tagged phthalonitrile 3 (Pn A) and 4,5-di-4-methoxyphenoxyphthalonitrile 4 (Pn B) followed by ring-opening metathesis polymerization (ROMP) of Pcs AB_3 and B_4 produced asymmetric Pc-appended polymers. Acidic cleavage of the resulting polymers afforded 2,3,9,10,16,17-hexa-(4-methoxyphenoxy)-23-hydroxy Pc 9. A more soluble 2,3,9,10,16,17-hexa-4-pentylphenoxy-23-hydroxy Pc 13 was synthesized by the same strategy and modified with sebacoyl chloride demonstrating that the unmasked hydroxyl site is reactive as a nucleophile.

Phthalocyanines (Pcs) are 18 π-electron tetrapyrrolic macrocycles that have generated interest since their first discovery.[1] A number of exceptional physical and chemical properties arise from their characteristic π-electron delocalization, such as high chemical and thermal stability, intense absorption in infrared/near-IR, semiconductivity, and large optical nonlinearities.[2,3] To explore the utility of Pcs for their applications in materials science, chemical modification of the Pc ring has been extensively investigated. The attachment of various substitutents to the periphery allows fine-tuning of the Pc's self-organization capabilities,[4] as well as suppression of aggregation,[5] useful for applications in optical limiting,[6] photodynamic therapy (PDT),[7] and thin-film photovoltaic devices.[8]

Of particular interest in a number of contexts are asymmetrically substituted Pcs, which can possess improved photodynamic properties[9] and unique second-order nonlinear optical effects.[10] Syntheses of asymmetrically substituted Pcs are relatively scarce. The simplest approach to the preparation of asymmetrically substituted Pcs is the statistical crossover Linstead macrocyclization[11] of two different phthalonitrile (Pn) precursors.[12] However, this method inherently yields a mixture of Pc products, and the isolation of the desired Pcs from the mixture usually requires extensive chromatographic purification. Methods to achieve direct synthesis of asym-

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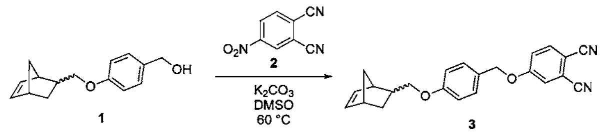
metric Pcs include the linking of two phthalonitrile units prior to macrocyclization,[13] ring expansion of a subphthalocyanine,[14] and the preparation of "half-phthalocyanine" intermediates,[15] although none of these have provided a general approach. Solid-phase techniques were first applied to asymmetric Pc synthesis in 1982,[16] but this method has also not seen widespread application.[17]

Prompted by the recent ROMP-capture-release synthesis of asymmetric porphyrazines by Barrett and Hoffman,[18] we herein describe our development of the ROMP-capture-release strategy to achieve asymmetric Pcs. Our methodology employs solution phase crossover-Linstead cyclization of a norbornenyl-tagged Pn with another Pn, followed by selective capture of asymmetric norbornenyl-tagged Pc under ROMP conditions and acidic cleavage of the target asymmetric Pc from the ROMP polymer. Asymmetric Pcs are obtained directly in relatively high purity, and require only minimal additional purification.

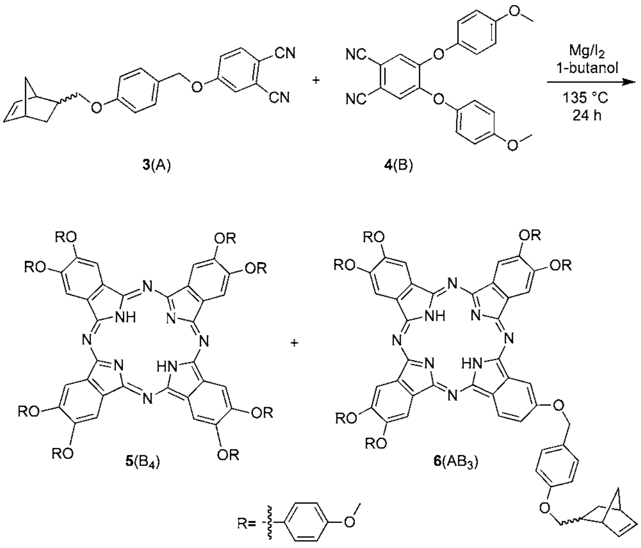
To apply ROMP-capture-release during the synthesis of asymmetric Pcs, our key precursor is norbornenyl-tagged Pn **3** bearing an acid-cleavable benzyl ether linkage (Scheme 1). Pn **3** was prepared by aromatic nucleophilic substitution of commercially available 4-nitrophthalonitrile **2** and previously synthesized benzyl alcohol **1**[18b] in moderate yield.

Scheme 1. Synthesis of Norbornenyl-Tagged Phthalonitrile **3**



A crossover-Linstead cyclization (A + B) was then carried out between norbornenyl tagged Pn **3** (A) and Pn **4**[19] (B) (Scheme 2). To ensure the purity of cleaved products, an appropriate ratio of **3** (A) and **4** (B) must be employed so that the crossover condensation is biased toward the formation of only tag-free and monotagged Pcs **5** (B_4) and **6** (AB_3), respectively. The initial stoichiometric ratio employed was A/B = 1:3, and the resultant crude product mixture was examined by mass spectrometry (MALDI). The mixture contained **5** (B_4) as the most abundant product, followed by **6** (AB_3) and bis-tagged A_2B_2, presumably as a mixture of *cis* and *trans* isomers, as the least abundant product (Figure 1).

Scheme 2. Crossover Condensation of **3** and **4**



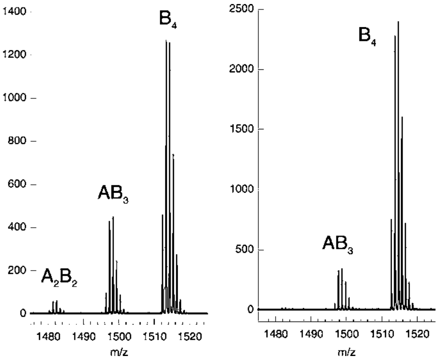


Figure 1. MALDI mass spectrum of the crude mixture from the reaction ratio of (left) A/B = 1:3 and (right) A/B = 1:6.

Based on this product composition, we concluded that a lower A/B ratio was needed to prevent the formation of the A_2B_2 product which, if present, would be incorporated into the ROMP polymer. Thus, additional cyclization reactions were carried out with A/B ratios that varied from 1:4 to 1:7. As expected, MALDI mass spectra of the mixtures obtained from these procedures indicated a decrease in the intensity of the A_2B_2 peak as the A/B ratio decreased. An A/B ratio of 1:6 was determined to be optimum as a mixture of predominantly **5** (B_4) and **6** (AB_3) along with a negligible amount of A_2B_2 was obtained under these conditions (Figure 1).

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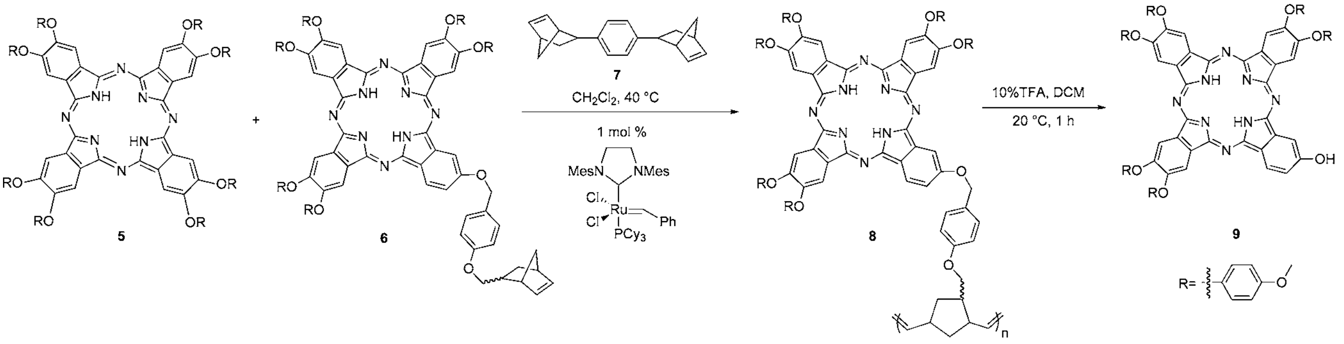
Scheme 3. Preparation of Asymmetric Pc **9** by ROMP-Capture-Release



The crude mixture of **5** (AB_3) and **6** (B_4) was then filtered through silica gel to remove excess magnesium butoxide which has been reported to deactivate Grubbs' catalyst in the next step.[18a] The filtrate was concentrated to give a green residue, which was subjected to typical ROMP conditions in the presence of cross-linker **7** (Scheme 3).[20] Polymerization of this mixture led to the formation of insoluble green polymer **8**, which was then purified by Soxhlet extraction in DCM for 24 h to remove symmetrical Pc **5**. Finally, acidic cleavage was performed using 10% trifluoroacetic acid in CH_2Cl_2 to afford the final product, asymmetric Pc **9**.

The low solubility of Pc **9** in common organic solvents such as CH_2Cl_2, $CHCl_3$, Et_2O, THF, DMSO, benzene, CH_3CN, and pyridine precluded characterization by NMR. However, we obtained mass spectroscopic (MALDI) data identifying the expected molecular ion (Figure 2) and UV−vis spectrophotometric data was consistent with the chromophoric structure of **9** (Figure 3). The UV−vis absorption spectrum exhibited a split Q-band at 701 ($\varepsilon = 1.26 \times 10^5$ M^{-1} cm^{-1}) and 666 nm, vibrational bands at 641 and 608 nm (Figure 2), and B-band at 342 nm, indicating the existence of metal-free, nonaggregated Pc cores.[21]

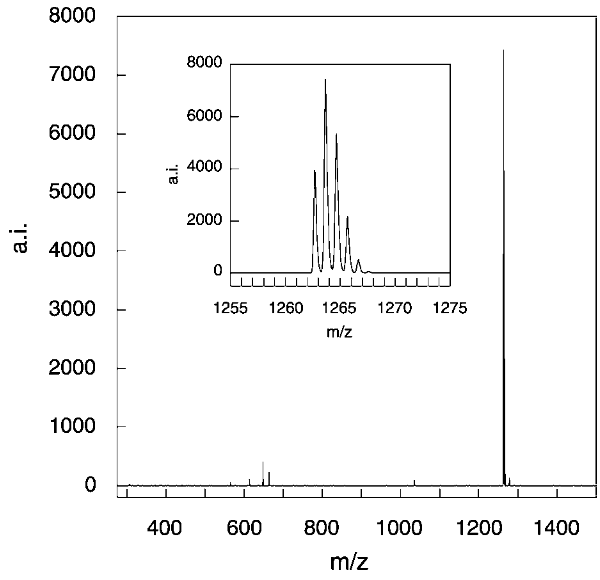


Figure 2. MALDI mass spectrum of cleaved asymmetric Pc **9** showing an $[M + H]^+$ peak at 1263.6238 (calcd 1263.3889).

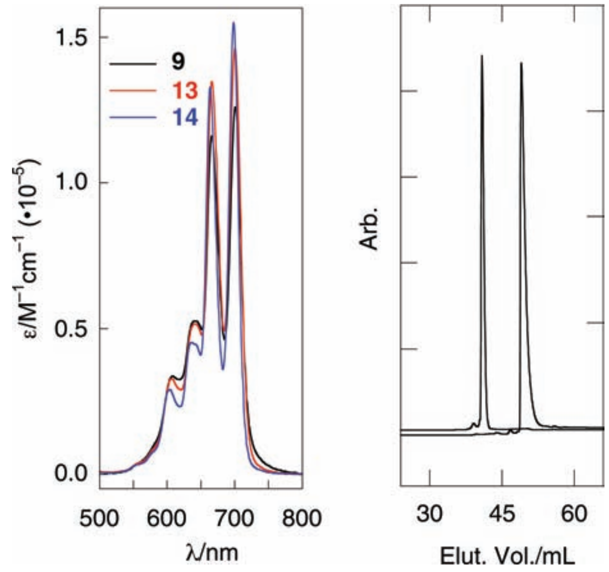


Figure 3. (Left) UV−vis spectrum of asymmetric Pcs **9**, **13**, and **14** in CH_2Cl_2. (Right) GPC of Pcs **13** and **14** in CH_2Cl_2.

A likely rationale for the low solubility of asymmetric Pc **9** stems from the relatively low solubilizing power of the methoxy groups. Therefore, to increase solubility in organic solvents to aid in further manipulation and feasible solution-phase processing, we prepared a more soluble Pc using the ROMP-capture-release strategy derivative by replacing the methoxy groups with pentyl groups.

Similar to the synthesis of Pc **9**, the preparation of soluble asymmetric Pc **13** began with crossover condensation of norbornenyl tagged phthalonitrile **3** and previously synthesized phthalonitrile **12**.[22] The components of the resultant

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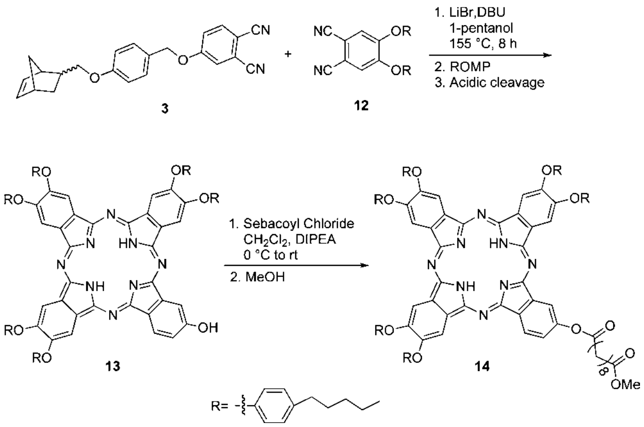
mixture were monitored by MS-MALDI and the ratio of **3** (A)/**12** (B) =1:4 was chosen as the final stoichiometry leading to a product mixture containing only AB_3 and B_4 Pcs. Subsequent ROMP-capture-release and acidic cleavage provided the desired Pc **13** (Scheme 4). Not surprising, Pc **13** exhibited the anticipated enhanced solubility in most organic solvents (e.g., CH_2Cl_2, $CHCl_3$, THF, Et_2O). Thus, unlike Pc **9**, we were able to characterize Pc **13** by NMR and GPC (Figure 3) in addition to MS-MALDI and UV−vis.

Scheme 4. Synthesis of Asymmetric Pc **13** by ROMP-Capture-Release and Transformation to Pc **14** by Acylation



To demonstrate that the hydroxyl group on the unique quadrant of the asymmetric Pcs can be further employed for covalent chemical modification, Pc **13** was acylated using a large excess of sebacoyl chloride to afford asymmetric Pc **14** (Scheme 4). The final methanolysis step not only converted the reactive pendant acyl chloride to an ester, but also helped to minimize the workup and purification. Pc **14** precipitated upon addition of MeOH to the reaction mixture, while other soluble byproduct remained in solution. Filtration followed by column chromatography gave Pc **14** which was successfully characterized by ^1H and ^{13}C NMR, mass spectrometry, combustion analysis, GPC, and UV−vis spectrophotometry (Figure 3).

In summary, we have described the synthesis of asymmetric Pcs via a ROMP-capture-release strategy. In addition to the preparation of asymmetric Pcs **9** and **13** by this method, we also demonstrated a straightforward modification of Pc **13** with an excess of sebacoyl chloride followed by methanolysis to give tethered Pc **14**. This indicates that the hydroxy group on the unique quadrant of the asymmetric Pc is a useful nucleophile and therefore allows the fabrication of potentially complex Pc-containing materials.

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Supporting Information Available: Experimental details and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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