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Frustration of Condensed Phase Aggregation of Naphthalocyanine by Dendritic Site-Isolation

Xiaochun Chen, Nilmi Fernando, and Dominic V. McGrath*

Department of Chemistry and Biochemistry, The University of Arizona, Tucson, Arizona 85721

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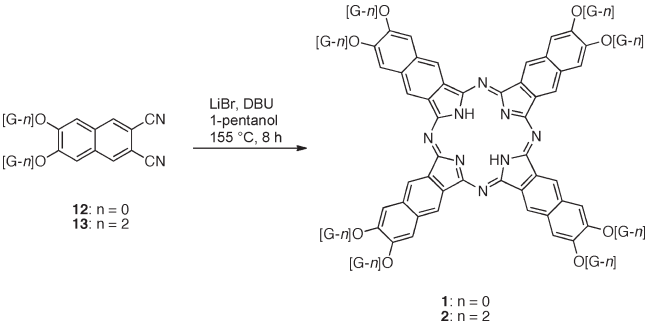
2,3-Naphthalocyanine (Nc) is a tetrapyrrolic macrocycle derived from the linear benzoannulation of phthalocyanine (Pc). Owing to the aromaticity of the extended π system, Nc has high chemical stability and effectively absorbs in near-IR region, which makes this organic semiconductor highly suitable for use in optical based technologies such as optical limiting,[1,2] OLEDs,[3] OFETs,[4] OPVs,[5] and photodynamic therapy (PDT).[6] However, a decisive disadvantage of Nc and corresponding metal complexes is low solubility in organic solvents and high tendency to self-associate into dimers and higher order aggregates, even in dilute solution.[7,8] Much attention has been focused on controlling the solubility and self-association of Nc using peripheral substutituents,[1c,9−11] while little work has been carried out on dendrimer-incorporated Ncs,[12−14] despite an active effort in dendritic phthalocyanine (Pc) materials.[15−19] It is known that the sphere-like dendritic macromolecules can mimic Nature's principle of site isolation by encapsulating and shielding the active core (e.g., photoactive, electroactive, and catalytic moieties) with the bulky dendritic shell.[20] As the active moieties become isolated from one another, detrimental processes arising from intermolecular interactions such as aggregation and self-quenching can be prevented.[21−26] Here, we report the synthesis and aggregation studies of a pair of 3,4,12,13,21,22,30,31-octasubstituted Ncs **1** and **2** (Scheme 1), the first examples of octasubstituted dendritic Ncs. The eight sterically bulky dendrons located on the periphery of the macrocycle effectively eliminate Nc core aggregation in second generation Nc **2** both in solution and the condensed phase.

The synthesis of dendritic Ncs utilized 6,7-disubstituted naphthalonitriles **12** and **13** as precursors (Scheme 1). The synthetic route leading to these naphthalonitriles started from dimethyl 4,5-dihydroxyphthalate **5**,[27] onto which the previously synthesized[28] dendritic alcohols **3** and **4** were introduced via the Mitsunobu protocol (Scheme 2). The obtained diesters **6** and **7** were reduced to the corresponding 1,2-dimethanols (**8** and **9**), and subsequent Swern oxidation provided the disubstituted dendritic phthalaldehydes **10** and **11**.[29] Finally, **10** and **11** were converted to naphthalonitriles **12** and **13** via base-promoted condensation with succinonitrile in DMSO. The metal-free 3,4,12,13,21,22,30,31-octasubstituted dendritic Ncs **1** and **2** were prepared by cyclotetramerization of **12** and **13** using a catalytic amount of LiBr and 1 equiv of DBU in refluxing 1-pentanol.

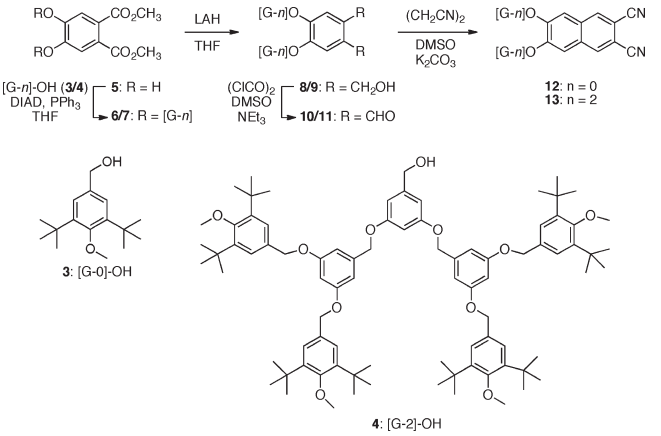
Compounds **1** and **2** were purified by flash column chromatography, although the expected poorer solubility of zeroth generation **1** versus second generation **2** in common aprotic solvents such as THF, chloroform, ether, and CH_2Cl_2 resulted in strong adsorption of **1** to the column material (SiO_2) resulting in low yield (7%) following isolation. Second generation **2** was obtained in moderate yield (40%).

*Corresponding author. E-mail: mcgrath@u.arizona.edu. Telephone: 520-626-4690. Fax: 520-621-8407.

Scheme 1. Synthesis of 0th and 2nd Generation Dendritic Ncs 1 and 2



Scheme 2. Synthesis of Dendritic Naphthalonitriles 12 and 13



Both **1** and **2** were characterized by various spectroscopic methods and elemental analysis. When the ^{1}H NMR spectrum of **1** was obtained in 95:5 $CDCl_3$−DMSO-d_6, a solvent system with which we have success in disrupting molecular aggregation associated with $\pi-\pi$ interactions, we observed well-resolved signals for the substituent groups although signals for the macrocyclic aromatic protons were broadened. In contrast, **2** was readily soluble in $CDCl_3$, and its ^{1}H NMR spectrum showed well-resolved signals for all protons of the substituent dendrons as well as the macrocycle (see Supporting Information).

Initial molecular aggregation studies were performed in solution as a function of increasing volume fraction of EtOH in EtOH−CH_2Cl_2 solutions of **1** and **2**. Upon initial increase in EtOH volume fraction (i.e., 0 → 10 → 20%) aggregation of the Nc core of **1** was indicated by a marked decrease in the absorptivity of the *Q*-band at 783 nm with concomitant increase in aggregate absorbance at 717 nm (Figure 1a). The hypsochromic shift of the *Q*-band from 783 to 717 nm indicates that aggregation of **1** under these solvent conditions was predominantly cofacial H-aggregation. The *B*-bands at 332 and 402 nm exhibited only slight hypochromicity during this change in solvent conditions. Further addition of EtOH (30 → 40 → 50%) caused further decrease of the *Q*-band at 783 nm, but now accompanied by a decrease in absorbance across the entire wavelength range, suggesting exclusion of both **1** and its aggregates from solution due to their low solubility in CH_2Cl_2−EtOH mixtures.

When second generation **2** was assayed under the same conditions, a different response was observed (Figure 1b). Dendrimer **2** exhibited no significant change in its absorption spectrum until

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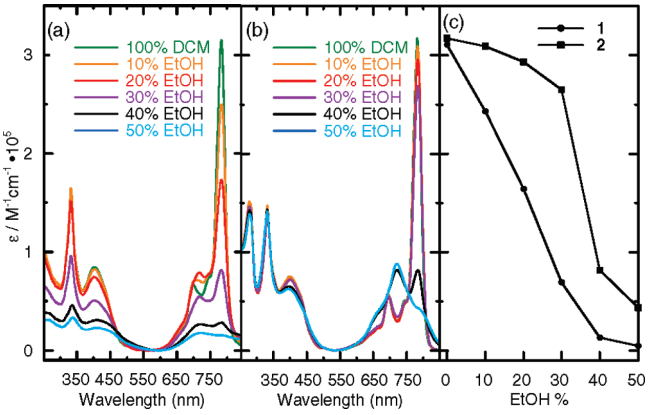

Figure 1. UV−vis spectra for Ncs (a) **1** and (b) **2** in CH_2Cl_2 and CH_2Cl_2-EtOH mixtures; (c) *Q*-band absorptivity at 783 nm.

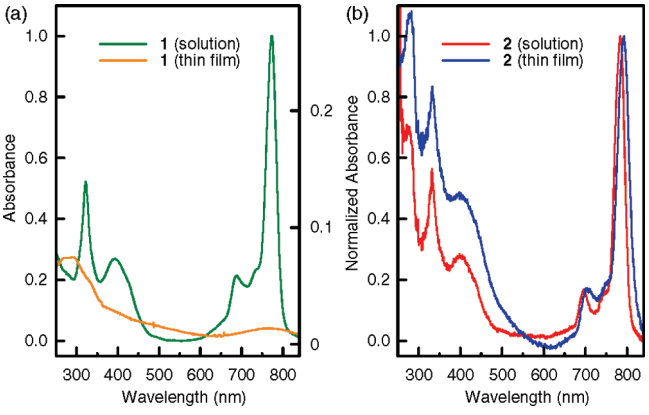

Figure 2. Normalized UV−vis spectra for (a) **1** and (b) **2** in thin film and CH_2Cl_2 solution (1×10^{-5} M).

the fraction of EtOH exceeded 30% in CH_2Cl_2. Higher fractions of EtOH (40→50%) induced a significant hypsochromic shift of the *Q*-band to 722 nm in a hypochromic fashion, indicating predominantly cofacial H-aggregation as seen for **1**. Notably, the *B*-bands of **2** at 332 and 402 nm as well as the benzylaryl ether dendron band at 280 nm essentially remained relatively unchanged over this change in solvent quality, reflecting the increased solubility imparted to **2** by the larger peripheral dendrons.

Second generation dendritic Nc **2** remained monomeric in solution at comparatively higher concentrations of EtOH in CH_2Cl_2 (Figure 1c). However, when compared to previous reports,[27] dendritic Ncs **1** and **2** are both more prone to aggregation in solution under identical conditions than analogous dendrimers with phthalocyanine (Pc) cores. A corresponding second generation dendritic Pc remained monomeric in 1:1 EtOH−CH_2Cl_2.[19] This is reflective of the greater tendency for aggregation of Nc relative to Pc.

Thin films of **1** and **2** were prepared to investigate the nature of the Ncs in the condensed phase. Spin-coated films on quartz substrates were fabricated from chloroform solutions of **1** and **2**. Both compounds formed crack-free solid films, although the appearance of the *Q*-band region in the respective absorption spectra was markedly different (Figure 2). The spectrum of **1** exhibits a broad peak in the *Q*-band region indicating severe aggregation of Nc cores. In contrast, a sharp *Q*-band, slightly shifted bathochromically from the dilute solution spectrum (791 → 783 nm), is observed in the spectrum of second generation **2** indicating a clear lack of aggregation. These contrasting thin-film spectral data indicate that the peripheral substitution of the higher-generation dendritic wedges successfully suppresses cofacial intermolecular interactions and results in steric isolation of the Nc ring in the condensed phase, although the slight bathochromic shift suggests weak edge-to-edge exciton interactions (J-aggregation) occurring in the solid phase.[7,8,30]

Thermal analysis by differential scanning calorimetry (DSC) reveals a glass transition (T_g) for **2** at 80.1 °C as the only transition between 25 and 200 °C (see Supporting Information), while the DSC of **1** indicates no transitions over this same temperature range. This result is consistent with **2** providing an amorphous environment for dendritic site isolation of the naphthalocyanine chromophore, and should allow for melt processing of thin-films of **2**. This glass transition for naphthalocyanine **2** is commensurate with other benzyl aryl ether dendrimers, and represents a decrease in T_g from the smaller compound naphthalonitrile **13** (T_g = 90.5 °C), which in turn possess a higher T_g than the second generation dendron **4** (T_g = 63.8 °C). Deviation from the traditional relationship between T_g and molecular weight for linear polymers when comparing dendrimers of increasing generation has been previously observed.[31]

In summary, we have synthesized two dendritic octasubstituted Ncs that demonstrate the ability of peripheral dendritic substituents of sufficient size to prevent Nc aggregation in solution and the condensed phase. These materials allow for solution processing techniques for nonaggregated thin-films of these ubiquitous organic dyes in applications that rely on site-isolation, such as emissive and optical limiting devices.

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Supporting Information Available: Text giving experimental details and additional characterization data for all new compounds and figures showing NMR spectra, GPC chromatograms, and DSC curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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