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Non-aggregating octasubstituted dendritic phthalocyanines

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Eight poly(aryl) ether dendritic wedges attached to the periphery of a phthalocyanine significantly decreases self-association of these chromophores in solution and the condensed state.

Phthalocyanines (Pcs) are macrocyclic porphyrin-type compounds that are widely used in a large number of materials applications. These materials are known to aggregate, forming stable, non-covalent structures, especially in polar solvents. Aggregation of Pcs leads to excited state quenching and decreased molar absorptivities. Current research has focused on the design of non-aggregating Pcs for specific applications in the fields of optical limiting and photodynamic therapy (PDT).[1,2]

Several approaches have been attempted to reduce Pc self-association using dendritic substituents.[3–6] These have met with ranging degrees of success. McKeown and coworkers[4] have studied the placement of bulky groups along the periphery of Pc chromophores. Four peripheral dendritic substituents, unless coupled with electrostatic repulsion,[3] are ineffective at preventing Pc self-association, even up to third generation dendrimers.[4] Axial dendritic substituents attached to the central atom of a SiPc effectively prevented aggregation.[5] However, this approach limits the range of metals in the Pc. Tuning the properties of Pcs by changing the internal metal is critical to the application of Pcs as sensors, photosensitizers, catalysts, and information storage systems.[7] Attachment of the dendrons to the α-positions on the Pc has been accomplished, but to date, no reports on the aggregation properties of these materials have been made.[8]

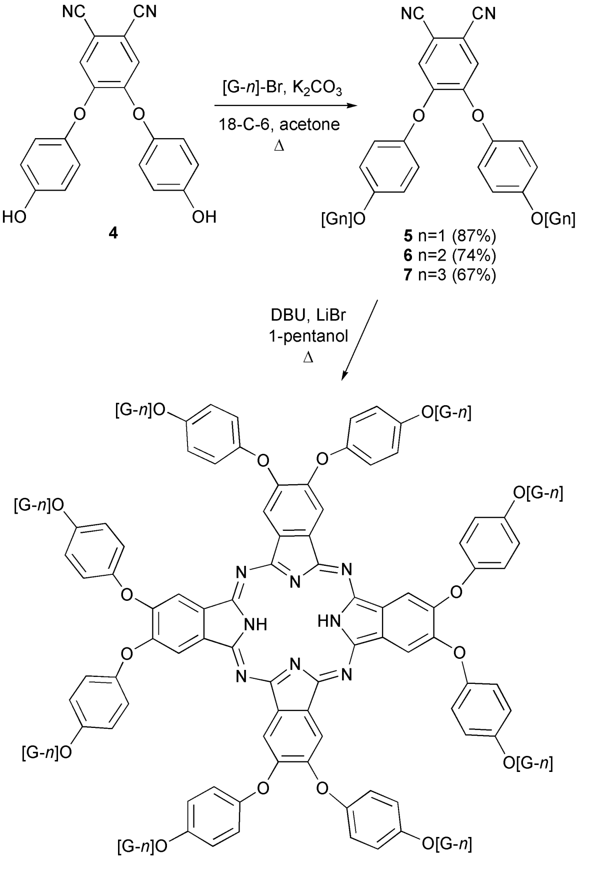
Inspired by recent methodology for the synthesis of octasubstituted Pc chromophores, in this communication we report the synthesis and aggregation studies of 2,3,9,10,16,17,23,24-octasubstituted dendritic Pcs **1–3** (Scheme 1). By placing eight dendritic substituents around the Pc ring, the steric bulk is greatly increased and the ability of these materials to aggregate is effectively decreased. Having the bulky substituents around the periphery of the Pc also maintains the possibility of incorporating a wide variety metals into the macrocycle.

Our strategy for the preparation of metal-free dendritic Pcs **1–3** was the cyclotetramerization of dendritic dialkoxyphthalonitriles. Coupling diphenolic phthalonitrile[9] **4** with dendritic bromides [G-*n*]–Br (*n* = 1,2,3)[10] proceeded in the presence of 18-crown-6, potassium carbonate and acetone at reflux temperatures to provide dendritic phthalonitriles **5–7**.† Compounds **5–7** individually underwent cyclotetramerization in the presence of lithium bromide and DBU in 1-pentanol to yield octasubstituted phthalocyanines **1–3** (Scheme 1).‡

Compounds **1–3** were purified either by flash chromatography on silica gel or by prepatory gel permeation chromatography (GPC). They were found to be extremely soluble in polar aprotic solvents such as THF, acetone, chloroform and methylene chloride and sparingly soluble in methanol and ethanol. UV-Vis absorption spectra obtained of CH_2Cl_2 solutions (1.4×10^{-5} mol dm^{-3}) were consistent with reported spectra of non-aggregated Pcs with a split Q-band at 700 and 665 nm, vibrational bands at 640 and 610 nm, and B-band at 340 nm.[11] The band arising from absorption of the benzylaryl ether dendrons at 280 nm increases appropriately with increasing generation (Fig. 1).

Initial molecular aggregation studies were performed in solution where increasing amounts of ethanol were added to CH_2Cl_2 solutions of **1–3**. The aggregation of the Pcs was indicated by the hypsochromic shift of the Q-band at 700 nm and gradual broadening of the Q-band region in a hypochromic fashion. As the size of the dendron along the periphery increased (*i.e.* **1**→**2**→**3**), the onset of aggregation of the Pc was shifted to higher ethanol concentrations. For **1**, aggregation was seen upon initial volume percent addition of ethanol. Compound **2** remained monomeric with 10% ethanol. Dendrimer **3** exhibited no noticeable aggregation until the concentration of ethanol exceeded 30% in methylene chloride (Fig. 1, inset). Precipitation of **1–3** from solution occurred only when the concentration of ethanol exceeded 50%.

Thin films of **1**, **2** and **3** were prepared to investigate the nature of the Pcs in the condensed state. Spin-coated films on glass substrates were obtained from chloroform solutions of the octasubstituted dendrimers. Compounds **1** and **2** formed crack-



4

5 n=1 (87%)
6 n=2 (74%)
7 n=3 (67%)

1 n=1 (27%)
2 n=2 (22%)
3 n=3 (16%)

Scheme 1

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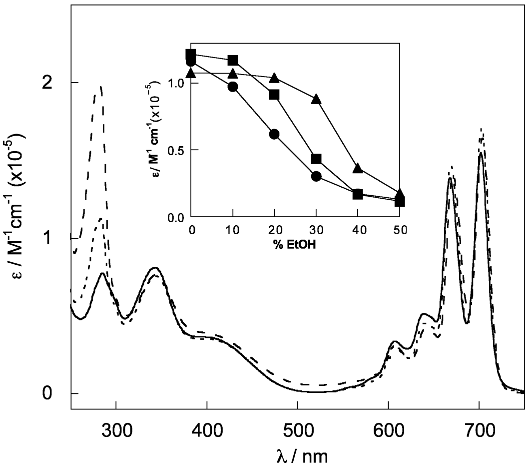

Fig. 1 UV-Vis spectra for **1** (—), **2** (···), and **3** (---) in CH_2Cl_2. Inset: Plot of the effect of increasing ethanol concentration on the absorbance of the Q-band peak ([Pc] = 1.4 × 10^{-5} M): (●) = **1**; (■) = **2**; (▲) = **3**.

free solid films exhibiting a broad peak in the Q-band region indicative of aggregation (Fig. 2). However, the spectrum of **2** suggests less than full aggregation indicating that the increase of peripheral dendron size decreases the ability of the Pc to aggregate. When compared to previous reports, octasubstituted second generation Pc **2** shows less thin film aggregation than a tetrasubstituted third generation Pc prepared by McKeown and coworkers.[4] Compound **3** also formed a crack-free solid film but exhibited a complete lack of aggregation in the solid state as shown by the presence of the split Q-band, a characteristic of non-aggregating, unsubstitiuted Pcs.[11] This complete lack of aggregation in thin film Pcs utilizing unsubstituted poly(aryl) ether dendrons has only previously been reported when the substitution is in the center of the Pc, attached to a silicon atom.[5]

We have synthesized a series of octasubstituted dendritic Pcs. The ability of the Pc to aggregate decreased as dendron size increased from the first to third generation as indicated by solution and thin film studies. Also, eight dendritic substituents around the Pc ring are more effective at preventing aggregation than four dendritic substituents§ of similar structure.[4] The additional bulk around the central core led to better isolation of the Pc despite the relative conformational flexibility of the dendrons used.[12] With the reported synthesis of these compounds, we have found a group of easily tunable Pcs for possible materials applications that remain non-aggregated in relatively dipolar solvents and the condensed state.

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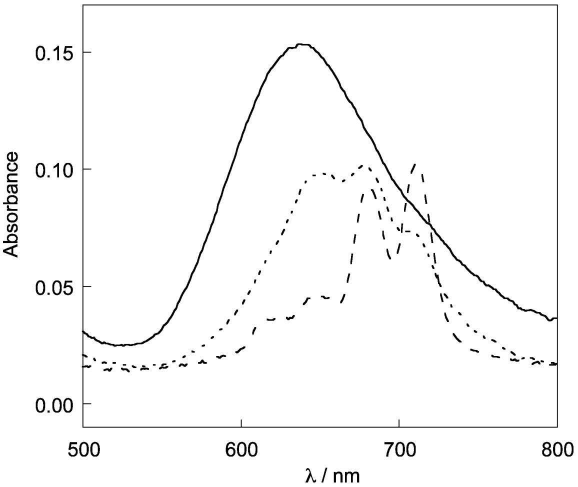

Fig. 2 The UV-Vis spectra of the Q-band region in the thin films derived from **1** (—), **2** (···) and **3** (---).

Notes and references

† No reaction was observed for the alkylation of catechol phthalonitrile with poly(aryl ether) dendritic bromides [G-*n*]-Br (*n* = 1–3).

‡ *General procedure* for cyclotetramerization: a mixture of dinitrile (4 equiv.), LiBr (1 equiv.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (4 equiv.) in 1-pentanol was heated to reflux for 24 h. The mixture was cooled to 0 °C and the solvent decanted. The crude product was precipitated from CH_2Cl_2 by addition of hexanes and purified by flash column chromatography (SiO_2, CH_2Cl_2) giving a dark green solid.

[2,3,9,10,16,17,23,24-Octakis(4-[G1]-phenoxy)phthalocyanine (**1**): dinitrile **6** (0.5 g, 0.53 mmol), DBU (0.08 mL, 0.53 mmol) and LiBr (11 mg, 0.13 mmol) in 1-pentanol (25 mL) yielded **1** (140 mg, 27%): δ_H (500 MHz, $CDCl_3$): 7.42–7.21 (br m, 104 H), 6.98–6.96 (d, *J* 8.5 Hz, 16 H), 6.66 (s, 16 H), 6.52 (s, 8 H), 4.93 (s, 32 H), 4.90 (s, 16 H). MS (MALDI): *m*/*z* 3798.39 (M$^+$).

[2,3,9,10,16,17,23,24-Octakis(4-[G2]-phenoxy)phthalocyanine (**2**): dinitrile **7** (0.35 g, 0.19 mmol), DBU (0.03 mL, 0.19 mmol) and LiBr (4.3 mg, 0.05 mmol) in 1-pentanol (10 mL) produced **2** (77 mg, 22%): δ_H (500 MHz, $CDCl_3$): 7.31–7.18 (m, 168 H), 7.17–7.15 (d, *J* 9 Hz, 16 H), 7.00–6.99 (d, *J* 9 Hz), 6.68–6.65 (m, 16 H), 6.60–6.57 (m, 32 H), 6.52–6.48 (m, 8 H), 6.47–6.44 (m, 16 H), 4.95 (s, 16 H), 4.88 (s, 64 H), 4.86 (s, 32 H). MS (MALDI): *m*/*z* 7194.74 (M$^+$).

[2,3,9,10,16,17,23,24-Octakis(4-[G3]-phenoxy)phthalocyanine (**3**): dinitrile **8** (0.2 g, 0.05 mmol), DBU (0.01 mL, 0.05 mmol) and LiBr (1 mg, 0.01 mmol) in 1-pentanol (5 mL) yielded **3**, which was further purified by preparatory gel permeation chromatography using DCM as the eluent (32 mg, 16%): δ_H (500 MHz, $CDCl_3$):7.40–7.12 (m, 344 H), 6.95–6.93 (d, *J* 9 Hz, 16 H), 6.68–6.62 (m, 24 H), 6.59–6.52 (m, 96 H), 6.44–6.39 (m, 48 H), 4.89 (s, 16 H), 4.82 (s, 128 H), 4.79 (s, 32 H), 4.75 (s, 64 H). MS (MALDI): *m*/*z* 13983.21 (M$^+$).

§ In ref. 4 the dendritic substituents are identical benzylaryl ether dendrons but they lack the benzoquinone spacers present in the dendrimers reported here.

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