Macromolecules **1999,** *32,* 5292−5298

Synthesis and Photophysical Properties of Nonaggregated Phthalocyanines Bearing Dendritic Substituents

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Received March 11, 1999

ABSTRACT: A series of phthalocyanines containing four dendritic substituents with terminal ester or carboxylate functionalities have been synthesized. These compounds having bulky substituents are essentially nonaggregated in organic solvents (for the ester series) or water (for the [G_1] and [G_2] carboxylate series) as demonstrated by the absorption and fluorescence spectroscopy. Photoinduced electron transfer in these compounds has been investigated by a fluorescence quenching method using a series of neutral, anionic, and cationic quenchers. The rates of quenching depend largely on the size of the dendrons. For the carboxylate series with cationic $(TMePyP)^{4+}$ as the electron acceptor, quenching is very efficient, which can be attributed to a static quenching mechanism. Upon excitation of the polyaryl ether dendritic fragments, the ester series show an intramolecular singlet−singlet energy transfer from the dendrons to the phthalocyanine core. The energy transfer quantum yields as determined by steady-state fluorescence spectroscopy are moderate (10.3−13.3%). The singlet oxygen quantum yields of the ester series are comparable with that of unsubstituted ZnPc in DMF, while those of the carboxylate series measured in DMSO are considerably lower.

Introduction

Owing to their high stability and unique physicochemical properties, phthalocyanines and related macrocyclic compounds have found widespread applications in various disciplines.[1] Numerous studies have been carried out to modify these tetrapyrrole derivatives with the goal of tuning their properties and optimizing their performance as advanced materials. For some applications such as photodynamic therapy,[1,2] photoinactivation of viruses in stored blood products,[3] and the photooxidation of mercaptans in petroleum distillates,[4] it is desirable that the macrocycles can be free from molecular aggregation. It has been established that this molecular association, which is actually a very common phenomenon of this family of compounds,[5] will drastically decrease the luminescence quantum yield of the compound, shorten its triplet state lifetime, and reduce its photosensitizing efficiency.[4a,6] The water solubility of these photosensitizers will be an additional advantage despite the fact that the aggregation tendency in such polar medium, in particular, is very high.[7] Hydrophilic and nonaggregated phthalocyanines are therefore important and potentially useful materials, but study of these compounds is still in its infancy.[8]

A substantial number of water-soluble tetra- and octasubstituted phthalocyanines have been reported. The hydrophilic moieties which have been incorporated on the peripheral of phthalocyanine ring include sulfonates,[6c,d,7,9] carboxylates,[10] phosphonates,[10b,11] glucose,[12] polyoxyethylene,[6b,13] and quaternarized amino groups.[14] Another type of water-soluble phthalocyanines contains hydrophilic groups as axial ligands coordinated to the central metal ion such as $Ru(Pc)L_2$ [Pc = phthalocyaninate; L = $PPh_2(3\text{-}C_6H_4SO_3^-)$, 3-pyridinesulfonate].[15] According to spectroscopic studies, most of these compounds are highly aggregated in aqueous media.[6b,7b,9b,c,10b,11b,14b] Photophysical properties of these compounds have only been briefly investigated.[6,13c,16] As part of our continuing program exploring the chemistry and properties of tetrapyrrole derivatives,[17] we report herein the synthesis and photophysical properties of a series of phthalocyanines containing dendritic substituents with terminal ester or carboxylate functionalities. The sterically demanding fragments with a substantial number of hydrophilic moieties in the latter series not only enhance the solubility of these macrocycles in water but also prevent their molecular aggregation, resulting in superior photophysical properties. Both photoinduced intermolecular electron transfer and intramolecular energy transfer in these novel macromolecules are described. Preliminary accounts on phthalocyanine-containing dendrimers have only appeared very recently.[8,18]

Results and Discussion

Synthesis and Characterization. The dendrons [G_n]−OH (n = 1, 2) were prepared from dimethyl 5-hydroxyisophthalate ([G_0]−OH) by the method described by Höger,[19] which involves the Mitsunobu reaction as the key step. Treatment of these phenols with 4-nitrophthalonitrile in the presence of K_2CO_3 gave compounds **1**−**3** in good yields (Scheme 1). Cyclization of these dinitriles under standard conditions[17b,d,20] resulted in the formation of the corresponding zinc(II) phthalocyanines **4**−**6** as mixtures of constitutional isomers. Interestingly, the four methoxycarbonyl groups underwent transesterification in n-pentanol giving the pentoxycarbonyl analogues. Such reaction, however, was not seen by Kimura et al. in the preparation of their phthalocyanine-containing polyether−amide dendrimers.[8] Compounds **4**−**6** were highly soluble in a range of nonpolar to polar organic solvents such as toluene, $CHCl_3$, and acetone and were characterized with elemental analyses, ^1H NMR, IR, and MALDI−TOF mass spectrometry. Intense signals due to the singly charged molecular ions were observed in the MALDI−TOF

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10.1021/ma990367s CCC: $18.00

Scheme 1. Preparation of Dendritic Phthalocyanines

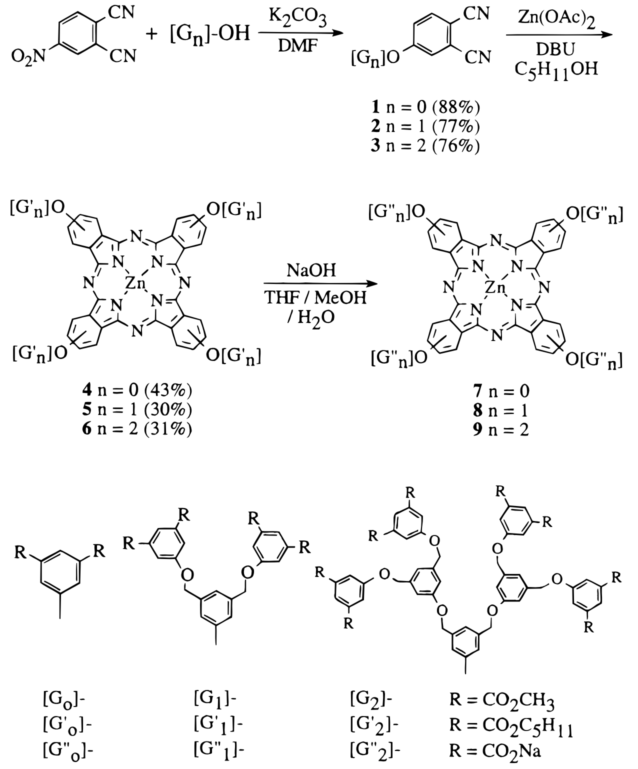

Table 1. UV–Vis Data of Phthalocyanines 4–6 in $CHCl_3$ and 7–9 in Water

	λ_{max} (nm) (log ϵ)		
compound	B-band	vibronic band	Q-band
4	350 (5.35)	610 (5.00)	677 (5.75)
5	352 (5.39)	612 (5.02)	679 (5.80)
6	352 (5.20)	614 (5.06)	680 (5.81)
7	345		638[a]
8	346 (4.33)	615 (3.92)	682 (4.82)
9	350 (4.76)	628 (4.50)	690 (4.88)

[a] Due to aggregated species.

spectra of all these compounds. For the zero and first generation dendrimers **4** and **5**, distinct isotopic distribution could also be resolved which closely resembles the respective simulated spectrum. The UV–vis spectrum of **4** in $CHCl_3$ exhibited a typical B-band at 350 nm and a Q-band at 677 nm together with a weak vibronic band at 610 nm. The absorption maxima and the respective intensities remained virtually unchanged throughout the concentrations ranging from 4.7 × 10^{-7} to 1.5 × 10^{-5} mol dm^{-3}, suggesting that molecular aggregation is not significant for this compound under these conditions. The absorption spectra of **5** and **6** were very similar to that of **4,** and the data are summarized in Table 1.

Upon treatment with NaOH in a mixed solvent system of tetrahydrofuran (THF), MeOH, and water, the terminal ester functional groups in **4**–**6** underwent alkaline hydrolysis yielding compounds **7**–**9**, respectively. With a substantial number of hydrophilic moieties, these compounds possess good solubility in aqueous media, but are insoluble in most organic solvents. The ^1H NMR spectra of **7**–**9** in D_2O showed only the signals due to the aromatic ring protons (at δ 6.8–8.8) and, for **8** and **9**, the methylene protons in the dendritic fragments (at δ 4.8–5.2). Upfield signals due to the pentyl chains in **4**–**6** were not observed, indicating that the hydrolysis was essentially complete. This was corroborated with the IR spectra of **7**–**9** in which the intense carbonyl stretching band at 1721–1724 cm^{-1} assignable to the ester groups in **4**–**6** disappeared, while two intense signals at 1561–1585 and 1371–1383 cm^{-1} emerged which can be assigned to the ν_{asy} and ν_{sym} stretching, respectively, for the carboxylate groups in **7**–**9**.[21]

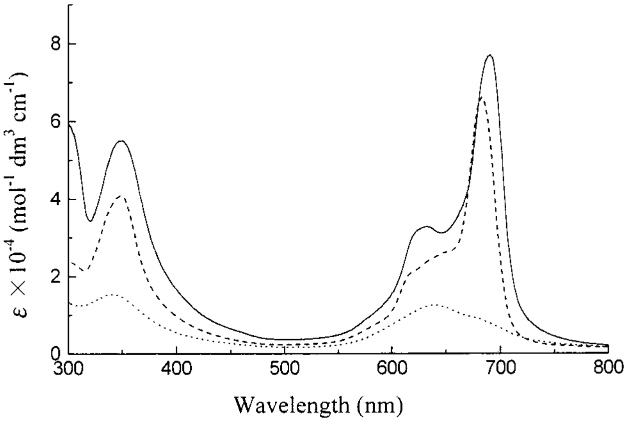

Figure 1. UV–vis spectra of **7** (2.46 × 10^{-6} mol dm^{-3}) (····), **8** (1.14 × 10^{-6} mol dm^{-3}) (- - -), and **9** (1.20 × 10^{-6} mol dm^{-3}) (—) in water.

The absorption spectra of **7**–**9**, recorded in water, are shown in Figure 1, and the data are also compiled in Table 1. The spectrum of **7** shows a broad signal peaking at 638 nm, which can be attributed to a dimeric species.[5b,7b,22] The spectrum did not change significantly within a concentration range of 2.5 × 10^{-7} to 1.0 × 10^{-5} mol dm^{-3} showing that **7** is highly aggregated in water even in such diluted conditions. An aqueous solution of **8** with a concentration of 1.2 × 10^{-4} mol dm^{-3} also gave a broad band at 638 nm in its UV–vis spectrum. But after sonication or being heated to ca. 70 °C, the spectrum changed remarkably, leading to a monomer-like spectrum (Figure 1). The molar absorptivity of the Q-band at 682 nm remained essentially unchanged in 5.0 × 10^{-7} to 1.2 × 10^{-4} mol dm^{-3} solutions indicating that **8** is relatively free from molecular aggregation under these conditions. The spectrum, however, regained its original features when recorded after 24 h had passed. The absorption spectrum of compound **9**, which contains higher generation of dendritic fragments, is typical of spectra due to monomeric phthalocyanines (Figure 1). The Q-band experiences a bathochromic shift by 8 nm when compared with that of **8** and its molar absorptivity remains constant for solutions with concentration up to 4.0 × 10^{-4} mol dm^{-3}. This intense signal, showing that **9** exists mainly as a monomeric species in such a polar medium, is remarkable.

Photophysical Studies. Compounds **4**–**6** showed fluorescence emission at 685–688 nm in $CHCl_3$ upon excitation at 610 nm. The quantum yields were roughly equal to that of ZnPc measured in 1-chloronaphthalene ($\Phi_f = 0.30$).[23] The singlet excited lifetimes (τ_s) were determined by time-resolved experiments in which the fluorescence decay profiles were found to fit to a monoexponential function [$f(t) = A \exp(-t/\tau_s) + B$]. These values as listed in Table 2 are in the same range as those of metallophthalocyanines with a closed-shell metal ion which normally exhibit half-lives shorter than tens of nanoseconds.[23] These results showed that different generations of dendritic substituents do not

Table 2. Photophysical Properties of Dendritic Phthalocyanines 4−9[a]

compound	λ_{em} (nm)[b]	Φ_f[c]	τ_s (ns)	Φ_Δ[d]
4	685	0.30	4.9	0.54[f]
5	686	0.29	4.7	0.52[f]
6	688	0.33	4.7	0.54[f]
7	690	0.01	*e*	0.45[g]
8	691	0.10	2.7	0.34[g]
9	695	0.11	3.5	0.19[h]

[a] For **4**−**6**, $CHCl_3$ was used as the solvent; for **7**−**9**, water was used as solvent unless otherwise stated. [b] Excited at 610 nm. [c] Relative to ZnPc ($\Phi_f = 0.30$ in 1-chloronaphthalene). [d] Relative to ZnPc ($\Phi_\Delta = 0.55$ in DMF). [e] The fluorescence was too weak to determine τ_s. [f] In DMF. [g] In DMSO. [h] In DMSO/water (3:1).

Table 3. Rate Constants for the Quenching of the Fluorescence of 4−6 in $CHCl_3$ and 7−9 in Water

compound	quencher	K_{SV} (mol^{-1} dm^3)[a]	k_q (mol^{-1} dm^3 s^{-1})
4	anthraquinone	4.31×10^3	8.8×10^{11}
5	anthraquinone	1.86×10^3	4.0×10^{11}
6	anthraquinone	7.87×10^2	1.7×10^{11}
7	sodium picrate	1.17×10^3	
8	sodium picrate	3.13×10^2	1.2×10^{11}
9	$(TMePyP)I_4$	2.61×10^5	7.5×10^{13}

[a] Stern−Volmer quenching constants were determined from the steady-state fluorescence measurements.

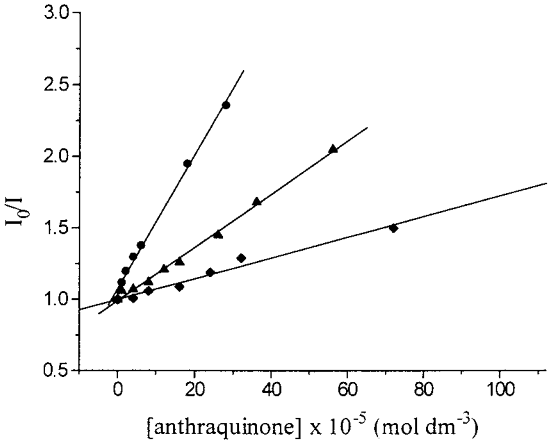

Figure 2. Stern−Volmer plots for the fluorescence quenching of **4** (●), **5** (▲), and **6** (◆) in $CHCl_3$ (1.25×10^{-6} mol dm^{-3}) by anthraquinone.

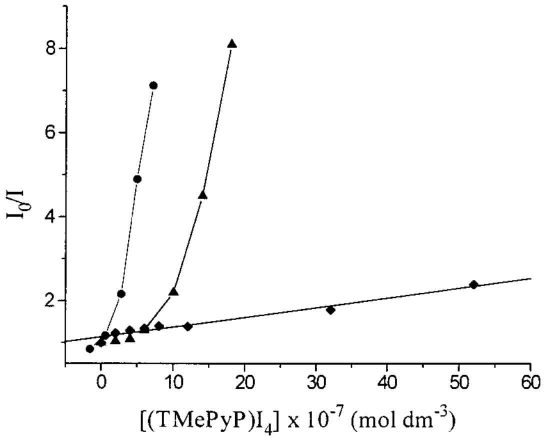

Figure 3. Stern−Volmer plots for the fluorescence quenching of **7** (●), **8** (▲), and **9** (◆) in water (6.0×10^{-6} mol dm^{-3}) by $(TMePyP)I_4$.

induce significant changes of singlet state properties of this series of phthalocyanines. The water-soluble analogues **7**−**9** were also fluorescent in water at a slightly red-shifted position (690−695 nm). The dendritic fragments, however, had pronounced effects on their photophysical properties. Having a larger number of carboxylate terminal groups, compounds **8** and **9** were relatively nonaggregated in water (see above) and showed much stronger emission than **7** (Table 2). It has been found that this intermolecular aggregation provides an efficient nonradiative energy relaxation pathway leading to a short-lived excited−state (e.g., $\tau < 80$ ps for tetrasulfonated ZnPc).[6d] Fluorescence of phthalocyanines is therefore rarely seen in aqueous media.[6d,13c,23] To our knowledge, the intense fluorescence observed for phthalocyanines **8** and **9** in water without the aid of surfactants is virtually unprecedented.[24]

In the presence of anthraquinone, which serves as an electron acceptor, the fluorescence intensities of **4**−**6** measured in $CHCl_3$ solutions were reduced. With increasing concentration of anthraquinone, the quenching of the fluorescence increased. The data could be analyzed using the Stern−Volmer equation (eq 1), where I_o and I are the intensities of fluorescence in the absence and presence of the quencher respectively, [Q] is the concentration of the quencher, and K_{SV} is the Stern−Volmer quenching constant, which is the product of the bimolecular quenching rate constant (k_q) and the lifetime of the fluorescing species in the absence of the quencher (τ_s). Figure 2 shows the Stern−Volmer plots for **4**−**6** from which the values of K_{SV} and k_q (using the τ_s values in Table 2) could be determined (Table 3). It can be seen that the value of K_{SV} is greater for lower generation dendrimer which imposes a less hinder environment for the quencher to reach the vicinity of the phthalocyanine core. As the quenching constant for **6** is still reasonably large, it appears that the four dendritic substituents are not sufficiently bulky to constitute a closed-shell globular structure. The k_q values for these apparent dynamic quenching processes exceed the normal diffusion limit for quenching involving small molecules by about 1 order of magnitude.[25] This may be related to the large encounter distance associated with the dendritic molecules.[26]

$$I_o/I = 1 + K_{SV}[Q] = 1 + k_q\tau_s[Q] \qquad (1)$$

The quenching of the fluorescence intensities of **7**−**9** in water by sodium picrate was also examined. Both of the zero- and first-generation dendrimers **7** and **8** also gave linear Stern−Volmer plots. The corresponding values of K_{SV} and k_q (for **8** only as τ_s for **7** could not be determined) are collected in Table 3. In contrast, the fluorescence intensity of **9** was virtually unchanged upon addition of sodium picrate. This may be attributed to the larger number of negatively charged terminal groups which repel and completely block the approach of the anionic quencher. Similar to observations for the previous series **4**−**6**, fluorescence was more effectively quenched in lower generation dendrimers compared with the higher generation analogues.

These water-soluble phthalocyanines behaved differently in the presence of tetraiodide salt of 5,10,15,20-tetrakis(1-methyl-4-pyridyl)porphyrin [$(TMePyP)I_4$], which acts as a cationic quencher. The fluorescence intensities of **7**−**9** were greatly diminished with an increasing amount of $(TMePyP)I_4$. The very large quenching constant for **9** ($K_{SV} = 2.61 \times 10^5$ mol^{-1} dm^3), estimated from the Stern−Volmer plot (Figure 3), may arise from a static quenching mechanism in which a

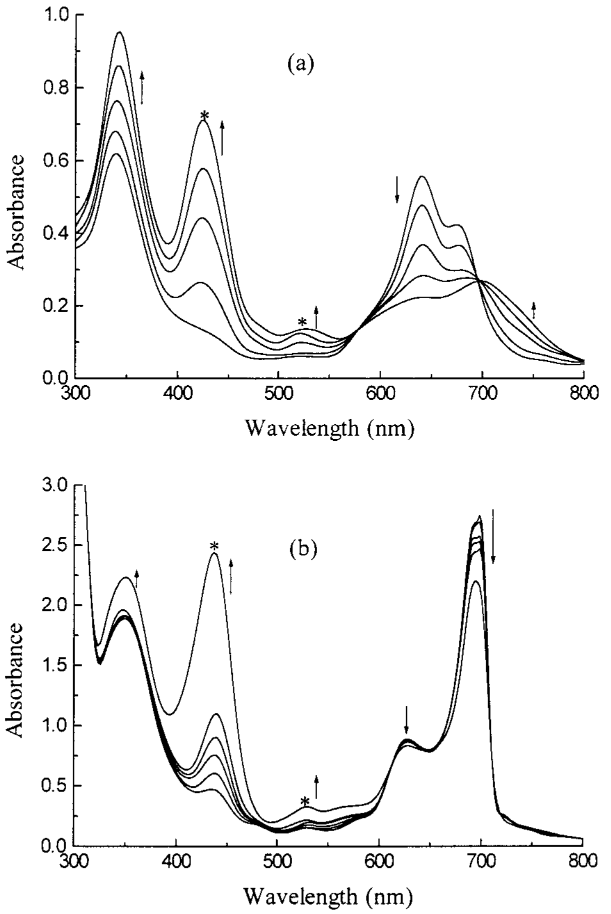

Figure 4. Spectral changes upon titration of (a) **7** (4.5×10^{-5} mol dm^{-3}) and (b) **9** (3.4×10^{-5} mol dm^{-3}) with (TMePyP)I$_4$ in water. [(TMePyP)I$_4$]: 0, 1.1, 2.2, 3.3, and 4.4×10^{-6} mol dm^{-3} for **7**; 0, 1.3, 2.6, 3.9, 5.2, 6.5, and 19.5×10^{-6} mol dm^{-3} for **9**; an asterisk indicates the absorptions due to the quencher.

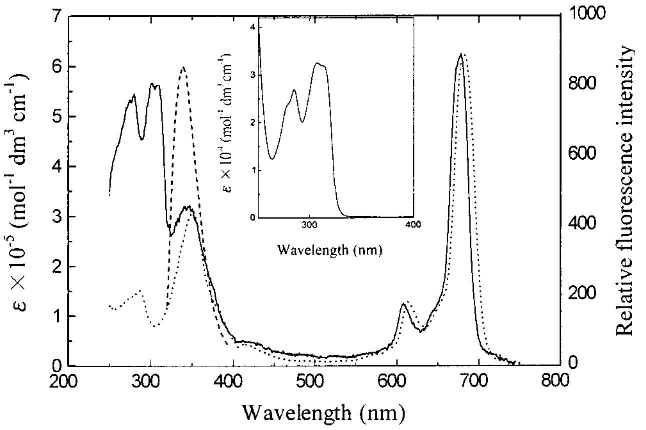

Figure 5. Absorption spectra of [G$_2$]−OH (inset), **6** (—), and **10** (····) in CHCl$_3$ and fluorescence spectrum of [G$_2$]−OH (- - -) when it is excited at 310 nm.

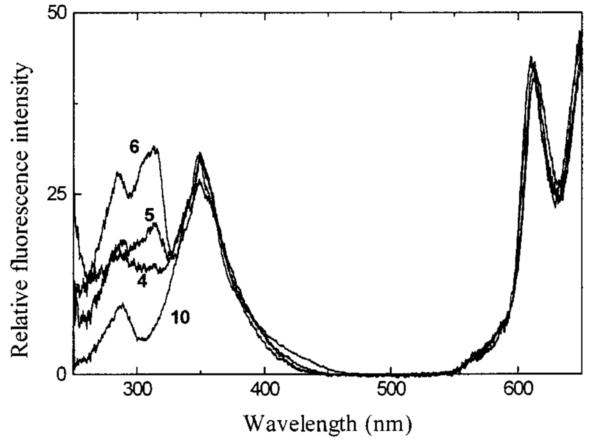

Figure 6. Excitation spectra of **4**−**6** and **10** in CHCl$_3$, monitored at 690 nm. The spectra have been normalized to a constant intensity at 610 nm.

dark complex is formed between the fluorophore and the quencher held by electrostatic forces. The Stern−Volmer plots for **7** and **8** were nonlinear with positive deviation as shown in Figure 3. Static quenching may contribute in addition to dynamic quenching causing the reduced emission in these systems.[26] This is corroborated with the changes in their absorption spectra upon addition of (TMePyP)I$_4$. As shown in Figure 4, the spectrum for **7** is remarkably changed upon titration, while that for **9** remains relatively unperturbed. This may be ascribed to the differences in phthalocyanine−porphyrin separation and the spatial arrangement.

Apart from these photoinduced intermolecular electron-transfer processes, the photoinduced intramolecular energy transfer in **4**−**6** was also examined. This avenue studying excitation energy transfer through dendritic architectures has been of much current interest because of its relevance to biological light-harvesting antennae.[27,28] As shown in Figure 5, the dendron [G$_2$]−OH exhibits two absorption bands peaking at 286 and 308 nm and an emission at 340 nm upon excitation at 310 nm. As this emission band overlaps with the B-band of phthalocyanines, energy transfer from the excited dendrons to the central phthalocyanine may occur in this series of compounds. Figure 5 also gives the UV−vis spectrum of **6** which displays typical B- and Q-bands of phthalocyanine in addition to the UV bands (270−310 nm) due to the dendritic substituents. The molar absorptivities of the latter bands are much higher than those of [G$_2$]−OH reflecting the larger number of chromophores. Upon excitation at 310 nm where the absorption of phthalocyanine is weak, this compound emits strongly at 350 nm due to the dendrons, together with an emission at 690 nm. For comparison, the model compound tetrakis(dodecyloxy)phthalocyaninatozinc(II) (**10**), which does not contain aromatic dendrons, was prepared. This compound exhibited only a very weak emission at 690 nm, which may arise from the weak absorption at 310 nm (Figure 5). The latter emission is clearly due to a singlet−singlet energy transfer, from the excited dendrons to the central phthalocyanine core which acts as an energy trap. The other two phthalocyanines **4** and **5** behaved in a similar manner. Figure 6 shows the excitation spectra of **4**−**6** together with the model compound **10**. The spectra were recorded by monitoring the emission at 690 nm, and were normalized to a constant intensity at 610 nm, where the dendrons do not absorb. It can be seen that as the number and size of the dendrons increase, more photons are collected and transmitted to the phthalocyanine. The light-harvesting efficiency quantified as energy transfer quantum yield (Φ_{ENT}) can be estimated by comparing the normalized (at 610 nm) absorption and excitation spectra by monitoring the emission of the phthalocyanine core at 690 nm.[28,29] As the phthalocyanine B-band is near the bands due to the dendrons, its contribution could be eliminated by subtracting the absorption and excitation spectra of **10** from the respective spectra of the dendritic phthalocyanines. The values of Φ_{ENT} for

4, **5**, and **6** were determined to be 10.3, 10.8, and 13.3%, respectively. Although the energy transfer efficiency is moderate for this series of compounds, this represents a rare example showing that light-harvesting processes occur in the phthalocyanine systems.[30]

By studying a series of porphyrins with different number of five-layered dendron subunits (L5), Jiang and Aida have demonstrated that the energy transduction event is highly sensitive to the morphology of the dendrimer framework that surrounds the energy trap.[28] The Φ_{ENT} values determined for **4**−**6** are comparable with those for monosubstituted P(L5) (10.1%) and disubstituted $\mathrm{P(L5)_2}$ (10.1% for the *anti*- and 19.7% for the *syn*-isomer), but are much smaller than that for tetrasubstituted $\mathrm{P(L5)_4}$ (80.3%) (P = *meso*-porphyrin). If one considers the fact that the energy gap between the dendron's emission and the B-band absorption is smaller for phthalocyanines than porphyrins, a more efficient light-harvesting system may be developed based on phthalocyanines using a higher generation of dendritic substituents.

To evaluate the photosensitizing efficiency of these dendritic phthalocyanines, the singlet oxygen quantum yields (Φ_Δ) of **4**−**9** were also determined using 1,3-diphenylisobenzofuran (DPBF) as the scavenger. As shown in Table 2, the quantum yields for **4**−**6** measured in *N*,*N*-dimethylformamide (DMF) are very close to that of ZnPc, indicating that the dendritic fragments do not have significant effects on the phthalocyanine core in triggering the singlet oxygen formation. As ZnPc also exists mainly in a monomeric form in DMF, it appears that as long as a nonaggregated species is formed the Φ_Δ values of phthalocyanines will not be significantly altered upon substitution on the periphery of the ring.[31]

We also attempted to determine the singlet oxygen quantum yields of **7**−**9** in water using the method reported by Kraljic and El Mohsni.[32] In this method, imidazole was added to induce the bleaching of 4-nitrosodimethylaniline (RNO) as followed spectrophotometrically at 440 nm. However, no significant changes in the concentration of RNO were detected for **7**−**9**. DPBF was then used again as the quencher and measurements were made in dimethyl sulfoxide (DMSO) solutions as these compounds are insoluble in DMF. As compound **9**, being a highly charged species, has limited solubility in DMSO, a small amount of water was also added. As shown in Table 2, these water-soluble phthalocyanines, under visible irradiation, can partially bleach DPBF but the quantum yields are considerably lower than those of **4**−**6**. As mentioned by Wöhrle et al., solvent can be very critical in the Φ_Δ measurements.[31] An account for the difference in Φ_Δ values for these dendritic phthalocyanines and a direct comparison with other photosensitizers cannot be made at this stage which require further investigation.

Conclusion. We have reported the synthesis and photophysical properties of a series of dendritic phthalocyanines which have only been briefly examined previously. These compounds exist mainly in monomeric form in solutions giving an intense fluorescence emission, even in very polar aqueous media. They undergo rapid photoinduced electron transfer with various quenchers and intramolecular energy transfer in which the excited dendrons *funnel* the energy to the central phthalocyanine which acts as an energy trap. The latter remarkable property suggests that a new and efficient light-harvesting system can be developed based on dendritic phthalocyanine systems.

Experimental Section

General Data. Reactions were performed under an atmosphere of nitrogen. THF was distilled from sodium benzophenone ketyl prior to use. DMF was predried over barium oxide and fractionally distilled under vacuum. *n*-Pentanol was distilled from sodium under reduced pressure. Chromatographic purifications were performed on silica gel columns (Macherey-Nagel, 70−230 mesh) with the indicated eluents. Hexanes used in chromatography was distilled from anhydrous calcium chloride. All other reagents and solvents were of reagent grade and used as received. The dendrons $[\mathrm{G}_n]$−OH (n = 1, 2) were prepared by the method described by Höger with minor modification.[19]

Melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer (^{1}H, 300; ^{13}C, 75.4 MHz) in $\mathrm{CDCl_3}$ solutions unless otherwise stated. Chemical shifts were relative to internal $\mathrm{SiMe_4}$ ($\delta = 0$). IR spectra were obtained on a Nicolet Magna 550 FT-IR spectrometer as KBr pellets. Liquid secondary-ion (LSI) mass spectra were measured on a Bruker APEX 47e Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with a 3-nitrobenzyl alcohol matrix. MALDI-TOF spectra were obtained on a Bruker bench TOF mass spectrometer equipped with a standard UV-laser desorption source, using α-cyano-4-hydroxycinnamic acid as matrix. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Photophysical Measurements. UV−vis and steady-state fluorescence spectra were taken on a Hitachi U-3300 spectrophotometer and a Hitachi F-4500 spectrofluorometer, respectively. The quantum yields were determined from the equation $\Phi_{\mathrm{sample}} = (F_{\mathrm{sample}}/F_{\mathrm{ref}})(A_{\mathrm{ref}}/A_{\mathrm{sample}})(n_{\mathrm{sample}}{}^2/n_{\mathrm{ref}}{}^2)\Phi_{\mathrm{ref}}$,[33] where F_{sample} and F_{ref} are the measured fluorescence (area under the fluorescence spectra) of the sample and the reference respectively, A_{sample} and A_{ref} are the absorbances of the sample and the reference, respectively, at the same excitation wavelength, n_{sample} and n_{ref} are the refractive index of the solvent used for the sample and the reference respectively, and Φ_{ref} is the quantum yield of the reference. The fluorescence lifetimes (τ_{s}) were obtained from the decay of transient fluorescence spectra using a picosecond dye laser with an excited wavelength at 610 nm. The details of the experimental setup were described previously.[34] For the determination of singlet oxygen quantum yields (Φ_Δ), the method reported by Wöhrle et al. was employed,[31] except that the absolute light intensity of our system was not determined. All measurements were referenced to ZnPc which has a Φ_Δ value of 0.55.

$\mathrm{C_6H_3([G_0]\text{-}O)(CN)_2}$ (1). To a mixture of 4-nitrophthalonitrile (0.41 g, 2.37 mmol) and dimethyl 5-hydroxyisophthalate ($[\mathrm{G}_0]$−OH) (0.50 g, 2.38 mmol) in DMF (15 mL) was added anhydrous potassium carbonate (0.99 g, 7.16 mmol). The mixture was heated at 60 °C with stirring overnight. The solvent was then evaporated under reduced pressure, and the residue was dissolved in $\mathrm{CHCl_3}$ (50 mL) and water (50 mL). The aqueous layer was separated and extracted with $\mathrm{CHCl_3}$ (3 × 50 mL). The combined organic layers was dried over anhydrous $\mathrm{MgSO_4}$ and rotary evaporated. The residue was subjected to column chromatography using hexanes/$\mathrm{CHCl_3}$ (1:1) as eluent to give the product as a white solid (0.70 g, 88%): mp 141−143 °C; $R_f = 0.35$;^{1}H NMR δ 8.55 (t, J = 1.2 Hz, 1H, Ar−H), 7.93 (d, J = 1.2 Hz, 2H, Ar−H), 7.78 (d, J = 8.7 Hz, 1H, Ar−H), 7.25−7.31 (m, 2H, Ar−H), 3.94 (s, 6H, CH_3); ^{13}C-{^{1}H} NMR δ 164.8, 160.6, 153.9, 135.6, 133.1, 127.9, 125.5, 121.9, 121.8, 117.8, 115.0, 114.6, 109.8, 52.7; IR 1728 s (C=O), 2234 m cm^{-1} (C≡N stretching); HRMS (LSI) m/z calcd for $\mathrm{C_{18}H_{13}N_2O_5}$ ($\mathrm{MH^+}$) 337.0824, found 337.0815. Anal. Calcd for $\mathrm{C_{18}H_{12}N_2O_5}$: C, 64.29; H, 3.60; N, 8.33. Found: C, 64.26; H, 3.58; N, 8.33.

$\mathrm{C_6H_3([G_1]\text{-}O)(CN)_2}$ (2). Anhydrous potassium carbonate (0.25 g, 1.81 mmol) was added to a mixture of 4-nitrophthalonitrile (64 mg, 0.37 mmol) and the dendron $[\mathrm{G}_1]$−OH (0.20 g, 0.37 mmol) in DMF (10 mL). The mixture was stirred at 60

°C for 6 h, and then poured into an ice−water mixture (300 mL). The precipitate formed was filtered off and purified by chromatography using $CHCl_3$/ethyl acetate (4:1) as eluent (0.19 g, 77%): mp 104−105 °C; R_f ($CHCl_3$) = 0.70; ^1H NMR δ 8.31 (t, J = 1.2 Hz, 2H, Ar−*H*), 7.81 (d, J = 1.2 Hz, 4H, Ar−*H*), 7.75 (d, J = 8.7 Hz, 1H, Ar−*H*), 7.45 (s, 1H, Ar−*H*), 7.28−7.31 (m, 2H, Ar−*H*), 7.16 (s, 2H, Ar−*H*), 5.20 (s, 4H, CH_2), 3.95 (s, 12H, CH_3); $^{13}C\{^1H\}$ NMR δ 165.9, 161.3, 158.2, 154.3, 139.9, 135.5, 131.9, 123.6, 123.3, 121.8, 121.6, 120.0, 118.8, 117.8, 115.3, 114.8, 109.3, 69.3, 52.5; IR 1723 s (C=O), 2234 w cm^{-1} (C≡N stretching); HRMS (LSI) *m/z* calcd for $C_{36}H_{29}N_2O_{11}$ (MH^+) 665.1771, found 665.1733. Anal. Calcd for $C_{36}H_{28}N_2O_{11}$: C, 65.06; H, 4.25; N, 4.21. Found: C, 65.05; H, 4.27; N, 4.18.

C_6H_3([G_2]-O)(CN)$_2$ (3). According to the above procedure, 4-nitrophthalonitrile (60 mg, 0.34 mmol) was treated with [G_2]−OH (0.40 g, 0.34 mmol) and anhydrous potassium carbonate (0.23 g, 1.67 mmol) in DMF (8 mL) to give **3** as a white solid (0.34 g, 76%): mp 240−242 °C; R_f ($CHCl_3$) = 0.37; ^1H NMR δ 8.29 (t, J = 1.5 Hz, 4H, Ar−*H*), 7.81 (d, J = 1.5 Hz, 8H, Ar−*H*), 7.69 (d, J = 8.7 Hz, 1H, Ar−*H*), 7.46 (s, 1H, Ar−*H*), 7.21−7.29 (m, 2H, Ar−*H*), 7.143 (s, 2H, Ar−*H*), 7.137 (s, 2H, Ar−*H*), 7.03 (s, 4H, Ar−*H*), 5.15 (s, 4H, CH_2), 5.13 (s, 8H, CH_2), 3.93 (s, 24H, CH_3); $^{13}C\{^1H\}$ NMR δ 166.0, 161.4, 158.9, 158.5, 154.2, 140.4, 138.3, 135.4, 131.9, 123.3, 121.7, 121.5, 120.0, 119.0, 118.7, 117.7, 115.3, 114.8, 113.4, 109.1, 69.9, 69.1, 52.5; IR 1724s (C=O), 2234w cm^{-1} (C≡N stretching); MS (LSI) *m/z* 1321.3 (MH^+). Anal. Calcd for $C_{72}H_{60}N_2O_{23}$: C, 65.45; H, 4.58; N, 2.12. Found: C, 65.01; H, 4.59; N, 2.11.

ZnPc([G'_0]-O)$_4$ (4). A mixture of dinitrile **1** (0.42 g, 1.25 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.10 g, 0.46 mmol) in *n*-pentanol (10 mL) was heated at 90 °C, and then a few drops of DBU was added. The mixture was heated at 140 °C with stirring overnight. The volatiles were then removed under reduced pressure to give a greenish blue solid, which was chromatographed with ethyl acetate/hexanes (10:1) as eluent. The crude product obtained was dissolved in a minimum amount of THF to which MeOH and H_2O were added to induce precipitation. A greenish blue solid was obtained after filtration and drying in vacuo (0.25 g, 43%): R_f = 0.76; ^1H NMR (C_6D_6) δ 8.4−8.9 (m, 4H, Ar−*H*), 7.5−8.0 (m, 8H, Ar−*H*), 6.6−7.3 (m, 12H, Ar−*H*), 4.0−4.4 (m, 16H, CO_2CH_2), 1.2−1.4 (m, 32H, CH_2), 1.0−1.2 (m, 16H, CH_2), 0.7−1.0 (m, 24H, CH_3); IR 1724s cm^{-1} (C=O stretching); MS (MALDI−TOF) an isotopic cluster peaking at *m/z* 1858.12 (M^+). Anal. Calcd for $C_{104}H_{112}N_8O_{20}Zn$: C, 67.18; H, 6.07; N, 6.03. Found: C, 67.58; H, 6.19; N, 5.65.

ZnPc([G'_1]-O)$_4$ (5). By using the above procedure, $Zn(OAc)_2 \cdot 2H_2O$ (12 mg, 0.06 mmol) was treated with dinitrile **2** (0.10 g, 0.15 mmol) and DBU in *n*-pentanol (15 mL) to give **5** as a dark green solid (40 mg, 30%): R_f = 0.85; ^1H NMR (C_6D_6) δ 8.3−8.8 (m, 4H, Ar−*H*), 7.6−8.2 (m, 16H, Ar−*H*), 6.6−7.3 (m, 28H, Ar−*H*), 4.5−5.1 (m, 16H, ArOCH_2), 3.8−4.3 (m, 32H, CO_2CH_2), 1.3−1.6 (m, 64H, CH_2), 1.1−1.2 (m, 32H, CH_2), 0.7−1.0 (m, 48H, CH_3); IR 1721s cm^{-1} (C=O stretching); MS (MALDI−TOF) an isotopic cluster peaking at *m/z* 3623.00 (M^+). Anal. Calcd for $C_{208}H_{240}O_{44}N_8Zn$: C, 68.98; H, 6.68; N, 3.09. Found: C, 68.93; H, 7.12; N, 2.58.

ZnPc([G'_2]-O)$_4$ (6). By employment of the above procedure, $Zn(OAc)_2 \cdot 2H_2O$ (7 mg, 0.032 mmol) was treated with dinitrile **3** (0.12 g, 0.091 mmol) and DBU in *n*-pentanol (15 mL) to give **6** as a dark green solid (50 mg, 31%): R_f = 0.94; ^1H NMR (C_6D_6) δ 8.3−8.8 (m, 8H, Ar−*H*), 7.6−8.1 (m, 28H, Ar−*H*), 6.6−7.3 (m, 60H, Ar−*H*), 4.5−5.1 (m, 48H, ArOCH_2), 3.9−4.3 (m, 64H, CO_2CH_2), 1.4−1.6 (m, 64H, CH_2), 1.3−1.4 (m, 64H, CH_2), 1.0−1.3 (m, 64H, CH_2), 0.7−1.0 (m, 96H, CH_3); IR 1723s cm^{-1} (C=O stretching); MS (MALDI−TOF) a broad signal peaking at *m/z* 7145.5 (M^+). Anal. Calcd for $C_{416}H_{496}O_{92}N_8Zn$: C, 69.92; H, 7.00; N, 1.57. Found: C, 69.62; H, 7.27; N, 1.44.

General Procedure for the Hydrolysis of Compounds 4−6. A solution of compound **4**, **5**, or **6** (100 mg) in THF (5 mL) was added slowly to a mixture of water (10 mL) and MeOH (45 mL) which was previously saturated with NaOH. The mixture was stirred at 40 °C for 4 h, and then the precipitate formed was filtered off and washed with MeOH (50 mL) and $CHCl_3$ (2 × 50 mL). The resulting blue solid contaminated with NaOH was dissolved in water, and several drops of 1 N HCl were added until the pH reached about 7. Ethanol was then added to precipitate the salt, and the mixture was allowed to stand overnight. The product ZnPc([G''_n]−O)$_4$ (n = 0, 1, 2) was collected by filtration and dried in vacuo. The yield of these reactions was almost quantitative.

Acknowledgment. This work was supported by the Research Grants Council of the Hong Kong Special Administrative Region, China (RGC Ref. No. CUHK 4117/98P). We also thank the Sir Edward Youde Memorial Fund Council for a postgraduate fellowship (to A.C.H.N.), Prof. Hezhou Wang and co-workers for the fluorescence lifetime measurements, and Prof. Dominic Chan's group for recording the MALDI−TOF spectra.

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MA990367S