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Metallated Phthalocyanines as the Core of Dendrimers – Synthesis and Spectroscopic Studies

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The complexation of a first-generation dendrimer possessing a metal-free octasubstituted phthalocyanine as its core has been carried out with copper and cobalt chlorides. In the case of the cobalt complex, the synthesis of the dendrimer has been pursued up to the eighth generation. The progressive influence of the branches upon the core has been studied with dendrimers from generation 1 to generation 7, using UV/Vis spectroscopy. These data indicate a progressive isolation of the core.

Introduction

Phthalocyanines[1] possess unique physico-chemical properties, which led to widespread potential applications in various fields such as photodynamic therapy,[2] solar energy conversion,[3] various optoelectronic devices,[4] or catalysed photooxidation of pollutants.[5] The main intrinsic problem when using such compounds is their strong stacking tendency to form dimers and other aggregated species in solution,[6] which induces a significant decrease in the photosensitising efficiency. Thus, much effort has been put into synthesizing nonaggregated phthalocyanines, generally by grafting bulky substituents, which also increase the solubility. One interesting way to achieve this goal consists of grafting dendritic substituents. Several examples have been reported since the first one published in 1997.[7] The phthalocyanine core can be either free,[8] or more generally complexed by a metal (in particular zinc),[7] or connected to a silicon derivative bearing dendritic stoppers.[9] In most cases, these phthalocyanines are tetrasubstituted, and only a few publications have reported the synthesis of octasubstituted dendritic phthalocyanines.[10,11] This is surprising in view of the advantages offered by the octasubstitution over the tetrasubstitution, in particular the absence of regioisomers, and a higher steric hindrance, which should facilitate the isolation of the core (preventing aggregation), even for low-generation dendritic substituents. This observation prompted us to report the synthesis of an octasubstituted metal-free phthalocyanine, which we used as the core for growing phosphorus-containing dendritic branches[12] up to generation 5, including a water-soluble series.[13] Having in hand a series of dendrimers possessing a metal-free phthalocyanine as a core, it appeared interesting to study their complexation ability, and the consequences of the complexation upon their spectroscopic properties. We report here the synthesis and characterization of a series of dendritic phthalocyanine complexes from generation 1 to generation 8, their UV/Vis properties, and the structural information deduced from these data.

Results and Discussion

The complexation could have been carried out with any of the generations from 0 to 5 of the dendrimer having a free phthalocyanine as a core that we have previously synthesized;[12,13] however, from a practical point of view the first generation appears to be the most suitable. Indeed, it is more soluble than generation zero, and it is sufficiently small to ascertain a quantitative complexation. We decided to study the complexation of two metals that were very rarely incorporated into the core of phthalocyanine-containing dendrimers: copper (one example of a first generation only)[14] and cobalt (one example of first and second generations).[15] In both cases the reaction is carried out with the corresponding dichloride derivatives, in the presence of triethylamine as a base in THF (Scheme 1). The complexation reaction is mainly controlled by the disappearance of the band at 3250 cm^{-1} in the infra-red spectra, corresponding to the pyrrolic NH bonds. Indeed, we have previously shown that triethylamine (and even DBU) are unable to deprotonate the phthalocyanine in THF,[12] thus the absence of N–H bonds is exclusively due to the complexation.

We expected that the paramagnetism due to the presence of Cu^{II} could induce an enlargement of the signals detected

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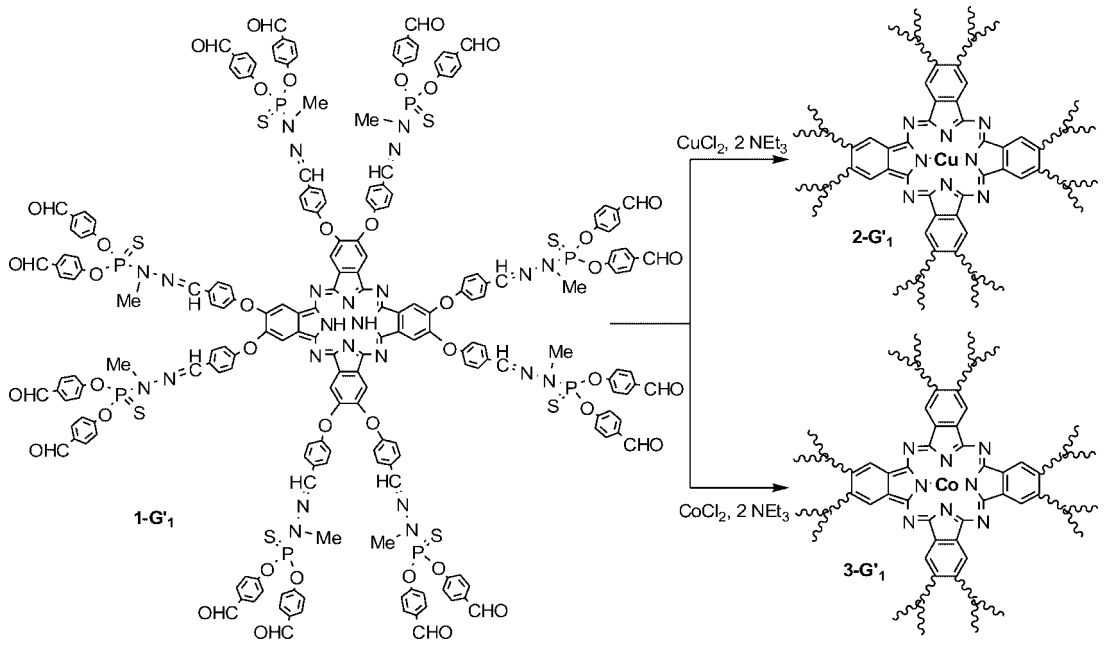


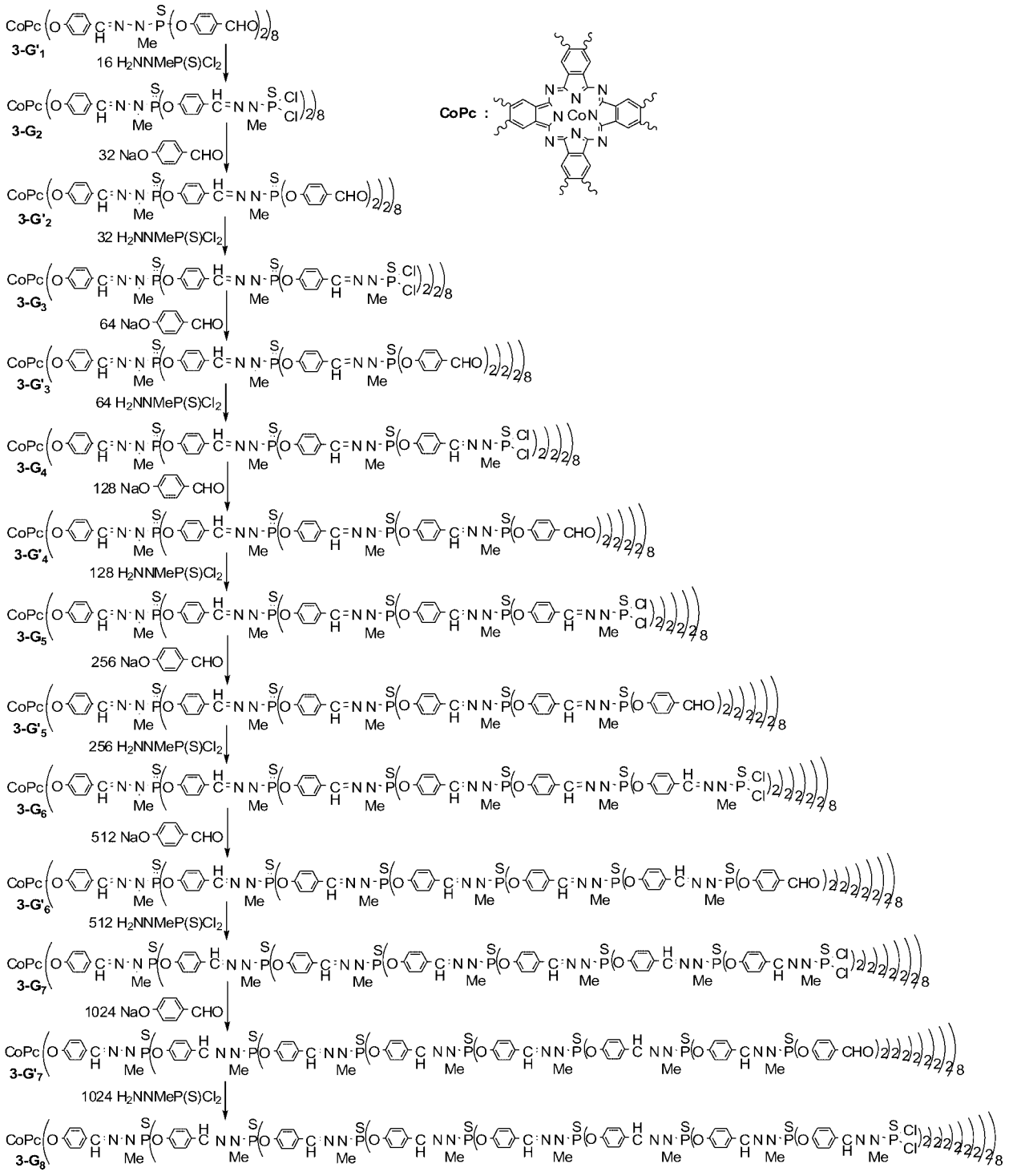
Scheme 1.

by NMR; such a phenomenon is observed and is particularly important for ^{1}H NMR, as mentioned in the single existing example reported so far.[14] On the other hand, Co^{II} in $CoCl_2$ is not paramagnetic, but we observed an enlargement of the NMR signals, indicating that the resulting complex is paramagnetic. No NMR spectroscopic data were reported for the single previous example of a dendritic phthalocyanine cobalt complex,[15] but such paramagnetism is known for cobalt complexes of nondendritic phthalocyanines.[16] The perturbation being less important with the cobalt complex than with the copper one, we decided to grow the dendrimer only from the cobalt complex **3-G′$_1$**, using our classical method of synthesis of phosphorus-containing dendrimers,[12,17] i.e. the repetition of condensation reactions between aldehyde endgroups and the phosphorhydrazide $H_2NNMeP(S)Cl_2$, and substitution reactions of the chlorine atoms by the sodium salt of 4-hydroxybenzaldehyde (Scheme 2). The completion of the condensation reactions is easily shown by ^{1}H NMR, with the disappearance of the singlet corresponding to the aldehyde groups (also detected by ^{13}C NMR and IR). The substitution reaction is monitored by ^{31}P NMR, which firstly displays a signal at ca. 74 ppm, corresponding to the monosubstitution [P(S)-Cl(OC_6H_4CHO)], as well as the signal corresponding to unreacted $P(S)Cl_2$ at δ = 63.3 ppm. Both signals disappear when the reaction has gone to completion, on behalf of the appearance of a signal at δ = 60.5 ppm. The precision of the NMR techniques to ascertain the completion of these reactions is estimated to be 0.5%. These syntheses have been carried out up to the eighth generation **3-G$_8$** [$P(S)Cl_2$ endgroups]. This is not the highest generation obtainable (no particular broadening of signals is observed); however, the series of dendrimers synthesized up to this generation is large enough to study the progressive influence of the branches upon the core, and is the largest series of dendritic phthalocyanines reported in the literature to date, thus we decided to stop at this stage.

The phthalocyanine core is a sensitive probe and sensor, thus it appeared interesting to study the UV/Vis and fluorescence properties of this family of dendritic phthalocyanine complexes. All experiments are carried out with dendrimers with aldehyde endgroups (from **3-G′$_1$** to **3-G′$_7$**), which are more stable than the $P(S)Cl_2$ endgroups. The π-π* transitions of the phthalocyanine ring should afford two types of absorption bands centred at about 300 nm (B-band) and about 670 nm (Q-band) in the UV/Vis spectra.

The B band is not very useful to study the behaviour of the core, since there is a superposition with the absorption band characteristic of the arylhydrazones constituting the branches of the dendrimers. However, this area is interesting to study the dependence of the molar absorption coefficient (ε) on the number of chromophoric units. We have already shown that there is a linear correlation between ε and the number of aryl groups for the dendrimers built from the free phthalocyanine core, at least up to generation four.[12] The question of the linearity remains open for high generations, but plotting the measured values of ε vs. the theoretical number of aryl groups gives a straight line even up to generation seven (Figure 1). Such behaviour both confirms that each arylhydrazone group is electronically independent (no overcrowding on the periphery) and that the expected number of arylhydrazones is indeed present (no large defects, even for high generations), confirming the information deduced from NMR spectroscopic data.

The Q-band of phthalocyanines is in an area where the dendritic skeleton is totally transparent, thus it is able to provide very interesting information concerning the symmetry and the environment of the core. Indeed, free neutral phthalocyanines have a D_{2h} symmetry, inducing a splitting of the Q-band into two components [$Q_y(0,0)$ and $Q_x(0,0)$]



Scheme 2.

giving two main absorptions (ca. 670 and 700 nm). On the other hand, the complexation of a metal induces a D_{4h} symmetry, which should give a single Q-band. The UV/Vis spectrum of the first generation **3-G′$_1$** in the area 650–700 nm displays a single band [λ = 674 nm, Q(0,0)], accompanied as usual by a vibrational band [λ = 610 nm, Q(0,1)] (Figure 2). However, a broad band is also clearly visible between both bands, usually attributed to an aggregation phenomenon. This attribution is confirmed by the fact that it progressively disappears when the number of the generation increases. In the spectrum corresponding to the seventh generation **3-G′$_7$** (see the insert in Figure 2), only the Q(0,0) and Q(0,1) bands are visible, and the intermediate band has totally disappeared; obviously, any aggregation is unlikely for a seventh generation in which the core should be totally protected by the branches.

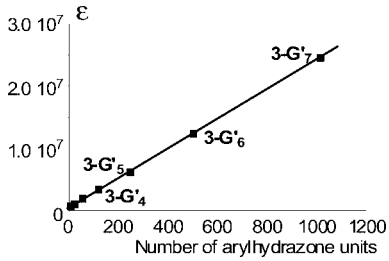


Figure 1. Variation of ε (mol^{-1} L cm^{-1}) at 268 nm with the number of arylhydrazone groups in $CHCl_3$.

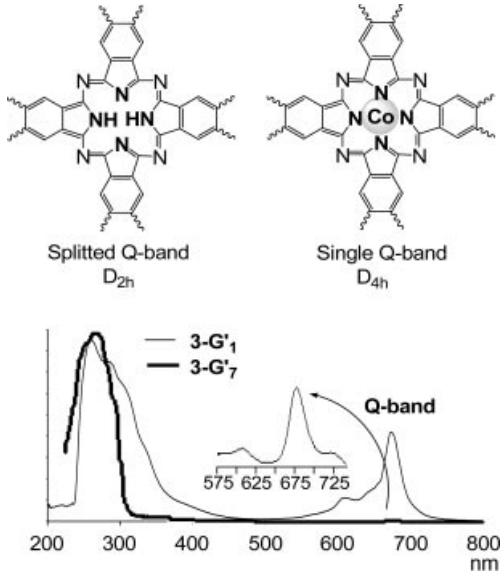


Figure 2. (top) Symmetry of free and complexed phthalocyanine cores, and spectroscopic consequences. (bottom) UV/Vis spectra of the first (**3-G′$_1$**) and seventh (**3-G′$_7$**) generations of the complexed cobalt phthalocyanine; both spectra are normalized to have the same intensity at 268 nm. The insert is an enlargement of the area of the Q-band of **3-G′$_7$** in THF.

The area of the Q-band provides other proofs of the progressive isolation of the core when the generation increases. Indeed, the value of ε_{max} for the Q-band increases linearly from generation 1 to generation 5, and more smoothly from generation 5 to generation 7 (Figure 3). Such behaviour corresponds to a progressive isolation of the core, as shown by an analogous increase of ε already reported for chromophores encapsulated in liposomes.[18] Furthermore, the value of λ_{max} for the Q-band also increases linearly (bathochromic effect) from generation 1 to generation 5, and is practically constant from generation 5 to generation 7. Reichardt has proposed a relationship between solvatochromism and polarity.[19] We may interpret the bathochromic effect observed here as a consequence of the increase of the local polarity induced by the branches (constituted of arylhydrazones) towards the core. We already observed the same phenomenon for dendritic metal-free phthalocyanines up to generation 4.[12] The major (and unprecedented) information obtained here is that this increase is stopped after the fifth generation. We may interpret this phenomenon as a consequence of the steric hindrance around the core: it is already totally encapsulated by the branches of the fifth generation, and the presence of additional branches has no influence on it.

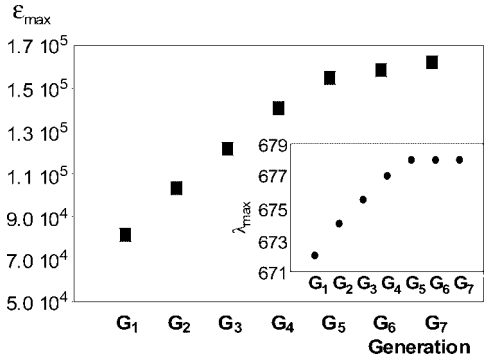


Figure 3. Variation of ε_{max} of the Q-band with the generation. Insert: variation of λ_{max} of the Q-band with the generation for compounds **3-G′$_n$** (n = 1–7), in THF.

Fluorescence also might be particularly suitable to detect the variation of the response of the dendrimer core upon modifications of its local environment. Thus, we tried to study the fluorescence of the series **3-G′$_n$** in THF, via excitation at the beginning of the Q-band at 646 nm and using 3,3′-diethyloxatricarbocyanine iodide (DOTCI) in absolute ethanol as a reference.[20] However, no fluorescence is observed. Such behaviour may seem surprising; indeed, dendritic zinc phthalocyanines in organic solvents have a relatively intense quantum yield (≈ 0.30) even for small generations (0–2),[21] but a complete lack of fluorescence has been observed for some cobalt phthalocyanines.[22] Such behaviour is due to the unfilled d-orbitals of Co^{II} that couple with the π orbital system of the phthalocyanine, providing additional and very efficient channels for π* deactivation.[22] Thus, it is not surprising to observe the absence of fluorescence in our case; indeed, this intrinsic deactivation obviously cannot be prevented by the presence of the dendritic branches, whatever the generation of the dendrimer.

Conclusions

The synthesis of the largest series of dendritic phthalocyanines to date (up to generation 8), and the study of their spectroscopic properties provide interesting insights into the nanoenvironment around the phthalocyanine core and into the role of the dendritic branches. A progressive protection of the core can be deduced from the UV/Vis spectra as expected. The shielding effect of the branches induces an increase of the intensity (ε) of the Q-band specific of phthalocyanines. Furthermore, an increase of the local polarity induced by the arylhydrazone branches constituting the skeleton of the dendrimers is observed, as shown by the bathochromic shift of the Q-band. Both phenomena are observed up to generation 5, but ceased for generations 6 and 7. Such behaviour indicates that the branches of the fifth generation provide a maximum shielding and crowding of the core, and that the influence of additional layers (generations) cannot be detected by the core.

Experimental Section

General: All manipulations were carried out with standard high vacuum and dry-argon techniques. The solvents were freshly dried and distilled (THF and ether over sodium/benzophenone, pentane and CH_2Cl_2 over phosphorus pentoxide). All the vessels were wrapped in aluminum foil to protect the compounds from light. Classical ^1H, ^{13}C, ^{31}P NMR spectra were recorded with Bruker AC 200, AC 250, DPX 300 or AMX 400 spectrometers. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR, $SiMe_4$ for ^1H and ^{13}C NMR spectroscopy. The attribution of ^{13}C NMR signals has been done using J_{mod}, two-dimensional HMBC, and HMQC, Broad Band or CW ^{31}P decoupling experiments when necessary. The numbering used for NMR assignments is depicted in Figure 4. The acquisition of mass spectra (MALDI-TOF) was attempted for the higher generations with a Voyager DE-ST spectrometer (Perseptive Biosystems), but could not afford any data concerning the purity of these compounds, due to rearrangements of the hydrazone linkages, as already observed.[23] UV/Vis spectra were recorded with a Specord 205 spectrophotometer (Analytik Jena).

Dendrimer 2-G′$_1$: 1-G′$_1$ (0.150 g, 0.036 mmol),[12] $CuCl_2$ (0.0049 g, 0.036 mmol) and triethylamine (11.6 μL, 0.083 mmol) in THF (1.5 mL) were heated at 100 °C whilst stirring in a sealed Schlenk tube for 3 h. The mixture was then cooled to room temperature and was filtered through celite. The resulting solution was evaporated to dryness to afford **2-G′$_1$** as a blue powder in 98% yield (0.149 g). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 60.6 (s, P_1) ppm. ^1H NMR ($CDCl_3$): δ = 3.37 (br. s, 24 H, CH_3-N), 7.34 (br. s, 48 H, $C_{0-1}{}^2$-H), 7.79 (br. s, 64 H, $C_{0-1}{}^3$-H, CH=N, CHPc), 9.86 (br. s, 16 H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.8 (d, $^2J_{CP}$ = 12.6 Hz, CH_3-N-P_1), 115.2 (s, C^2), 117.7 (s, $C_0{}^2$, C^1), 122.0 (d, $^3J_{CP}$ = 4.6 Hz, $C_1{}^2$), 128.7 (s, $C_0{}^3$), 129.9 (s, C^3), 131.4 (s, $C_1{}^3$), 131.6 (s, $C_0{}^4$), 133.6 (s, $C_1{}^4$), 139.9 (d, $^3J_{CP}$ = 11.9 Hz, CH=N-N-P_1), 149.8 (s, C^4), 150.0 (s, $C_0{}^1$), 155.1 (d, $^2J_{CP}$ = 7.8 Hz, $C_1{}^1$), 190.8 (br. s, CHO) ppm. IR (KBr): $\tilde{\nu}$ = 1702 cm^{-1} ν_{CHO}. $C_{208}H_{152}CuN_{24}O_{40}P_8S_8$ (4195.5): calcd. C 59.55, H 3.65, N 8.01; found C 59.27, H 3.81, N 7.96.

Dendrimer 3-G′$_1$: 1-G′$_1$ (0.666 g, 0.161 mmol), $CoCl_2$ (0.0209 g, 0.161 mmol) and triethylamine (49.4 μL, 0.354 mmol) in THF (6 mL) were heated at 110 °C whilst stirring in a sealed Schlenk tube for 3 h. The mixture was then cooled to room temperature overnight and was concentrated under reduced pressure. Then dichloromethane (20 mL) was added and the resulting mixture was filtered through celite. The resulting solution was evaporated to dryness to afford **3-G′$_1$** as a dark green powder in 87% yield (0.585 g). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 60.7 (s, P_1) ppm. ^1H NMR ($CDCl_3$): δ = 3.42 (br. s, 24 H, CH_3-N), 7.36 (br. s, 48 H, $C_{0-1}{}^2$-H), 7.76 (br. s, 64 H, $C_{0-1}{}^3$-H, CH=N, CHPc), 9.89 (br. s, 16 H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.9 (br. s, CH_3-N), 118.0 (br. s, $C_0{}^2$), 122.1 (br. s, $C_1{}^2$), 128.6 (br. s, $C_0{}^3$), 131.5 (br. s, $C_1{}^3$), 133.8 (br. s, $C_1{}^4$), 140.0 (br. s, CH=N-N-P_1), 155.2 (br. s, $C_1{}^1$), 190.7 (br. s, CHO) ppm. IR (KBr): $\tilde{\nu}$ = 1702 cm^{-1} ν_{CHO}. $C_{208}H_{152}CoN_{24}O_{40}P_8S_8$ (4190.9): calcd. C 59.61, H 3.66, N 8.02; found C 60.36, H 3.71, N 8.07.

General Procedures for the Synthesis of Dendrimers 3-G$_n$ and 3-G′$_n$

Dendrimers 3-G$_n$: A freshly prepared solution of dichlorothiophosphorhydrazide (0.25 M in $CHCl_3$) was added dropwise to a solution of **3-G′$_{n-1}$** [0.500 g; n = 2 (0.1193 mmol), n = 3 (0.0526 mmol), n = 4 (0.0248 mmol), n = 5 (0.0121 mmol), n = 6 (0.0059 mmol), n = 7 (0.00296 mmol), n = 8 (0.00147 mmol)] in THF (5 to 10 mL). The resulting mixture was stirred overnight then evaporated to dryness. The residue was washed with 20 mL of diethyl ether/pentane (1:1) then dried under vacuum. Dendrimers **3-G$_n$** were obtained as coloured powders from dark green for the lowest generations to light green for the highest generations.

Dendrimers 3-G′$_n$: 4-Hydroxybenzaldehyde sodium salt (5% excess) was added to a solution of **3-G$_n$** [0.600 g; n = 2 (0.0887 mmol), n = 3 (0.0409 mmol), n = 4 (0.0197 mmol), n = 5 (0.0097 mmol), n = 6 (0.0048 mmol), n = 7 (0.00239 mmol)] in THF (10 to 20 mL). The resulting mixture was stirred overnight, and then centrifuged. The solution was concentrated under reduced pressure and the residue was washed with 20 mL of THF/diethyl ether/pentane (1:2:2), then twice with 20 mL of diethyl ether/pentane (1:1). Dendrimers **3-G′$_n$** were obtained as coloured powders (from dark green for the lowest generations to light green for the highest generations) after drying under vacuum.

3-G$_2$: 79% Yield, 0.638 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 62.3 (br. s, P_1), 63.3 (br. s, P_2) ppm. ^1H NMR ($CDCl_3$): δ = 3.36 (m, 72 H, CH_3-N-P_{1-2}), 7.25 (br. s, 48 H, $C_{0-1}{}^2$-H), 7.66 (br. s, 80 H, $C_{0-1}{}^3$-H, CH=N-N-P_{1-2}, CHPc) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.9 (d, $^2J_{CP}$ = 12.3 Hz, CH_3-N-P_2), 33.0 (d, $^2J_{CP}$ = 13.2 Hz, CH_3-N-P_1), 115.5 (s, C^2), 117.6 (br. s, $C_0{}^2$, C^1), 121.9 (br. s, $C_1{}^2$), 128.7 (br. s, $C_0{}^3$, $C_1{}^3$), 129.8 (s, C^3), 131.4 (br. s, $C_0{}^4$, $C_1{}^4$), 139.7 (br. s, CH=N-N-P_1), 140.7 (d, $^3J_{CP}$ = 17.9 Hz, CH=N-N-P_2), 150.3 (br. s, $C_0{}^1$), 151.9 (br. s, $C_1{}^1$) ppm. $C_{224}H_{200}Cl_{32}CoN_{56}O_{24}P_{24}S_{24}$ (6767): calcd. C 39.76, H 2.98, N 11.59; found C 39.89, H 2.93, N 11.71.

3-G′$_2$: 98% Yield, 0.826 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 60.6 (s, P_2), 62.5 (s, P_1) ppm. ^1H NMR ($CDCl_3$): δ = 3.34 (m, 72 H, CH_3-N-P_{1-2}), 7.35 (m, 112 H, $C_{0-2}{}^2$-H), 7.5–8.5 (m, 144 H, $C_{0-2}{}^3$-H, CH=N-N-P_{1-2}, CHPc), 9.90 (br. s, 32 H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.0 (br. s, CH_3-N-P_{1-2}), 118.2 (br. s, $C_0{}^2$, C^1), 121.9 (br. s, $C_{1-2}{}^2$), 128.3 (s, $C_0{}^3$, $C_1{}^3$), 129.2 (s, C^3), 131.5 (s, $C_2{}^3$), 132.1 (br. s, $C_0{}^4$, $C_1{}^4$), 133.7 (br. s, $C_2{}^4$), 139.7–140.1 (m, CH=N-N-P_{1-2}), 151.5 (br. s, $C_0{}^1$, $C_1{}^1$), 155.1 (br. s, $C_2{}^1$), 190.8 (s, CHO) ppm. IR (KBr): $\tilde{\nu}$ = 1702 cm^{-1} ν_{CHO}. $C_{448}H_{360}CoN_{56}O_{88}P_{24}S_{24}$ (9508): calcd. C 56.59, H 3.82, N 8.25; found C 56.31, H 3.91, N 8.23.

3-G$_3$: 81% Yield, 0.624 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 62.2 (br. s, $P_{1,2}$), 63.2 (br. s, P_3) ppm. ^1H NMR ($CDCl_3$): δ = 3.33 (m, 168 H, CH_3-N-P_{1-3}), 7.25 (m, 112 H, $C_1{}^2$-H), 7.4–8.2 (m, 176 H, $C_{1-2}{}^3$-H, CH=N-N-P_{1-3}, CHPc) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.7 (d, $^2J_{CP}$ = 12.9 Hz, CH_3-N-P_3), 32.9 (d, $^2J_{CP}$ = 11.1 Hz, CH_3-N-P_{1-2}), 121.7 (s, $C_{1-2}{}^2$), 128.2 (s, $C_0{}^3$, $C_1{}^3$), 128.5 (s, $C_2{}^3$), 131.3 (s, $C_{1-2}{}^4$), 140.5 (m, CH=N-N-P_{1-3}), 151.6 (s, $C_{1-2}{}^1$) ppm. $C_{480}H_{456}Cl_{64}CoN_{120}O_{56}P_{56}S_{56}$ (14660): calcd. C 39.33, H 3.14, N 11.47; found C 39.98, H 3.19, N 11.48.

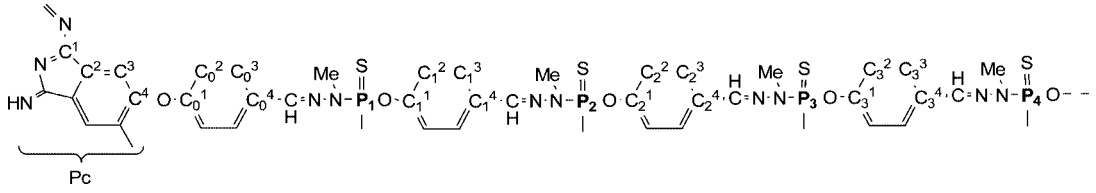


Figure 4. Numbering used for NMR assignments.

3-G′$_3$: 78% Yield, 0.643 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 60.5 (s, P_3), 62.4 (s, P_2), 62.8 (s, P_1) ppm. ^1H NMR ($CDCl_3$): δ = 3.33 (br. s, 168 H, CH_3-N-P_{1-3}), 6.5–7.4 (m, 240 H, $C_{0-3}{}^2$-H), 7.4–8.4 (m, 304 H, $C_{0-3}{}^3$-H, CH=N-N-P_{1-3}, CHPc), 9.93 (br. s, 64 H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.0 (br. s, CH_3-N-P_{1-3}), 121.9 (br. s, $C_{1-3}{}^2$), 128.3 (s, $C_{0-2}{}^3$), 131.5 (s, $C_3{}^3$), 131.8 (s, $C_{1-2}{}^4$), 133.6 (s, $C_3{}^4$), 139.0–140.5 (m, CH=N-N-P_{1-3}), 151.5 (br. s, $C_{1-2}{}^1$), 155.1 (br. s, $C_3{}^1$), 190.8 (s, CHO) ppm. IR (KBr): $\tilde{\nu}$ = 1702 cm^{-1} ν_{CHO}. $C_{928}H_{776}CoN_{120}O_{184}P_{56}S_{56}$ (20142): calcd. C 55.34, H 3.88, N 8.35; found C 55.37, H 3.84, N 8.29.

3-G$_4$: 86% Yield, 0.650 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 62.2 (s, P_3), 62.4 (s, P_2), 62.6 (s, P_1), 63.3 (s, P_4) ppm. ^1H NMR ($CDCl_3$): δ = 3.35 (br. d, $^3J_{HP}$ = 9.4 Hz, 360 H, CH_3-N-P_{1-4}), 7.25 (m, 240 H, $C_{0-3}{}^2$-H), 7.64 (m, 368 H, $C_{0-3}{}^3$-H, CH=N-N-P_{1-4}, CHPc) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.8 (d, $^2J_{CP}$ = 13.8 Hz, CH_3-N-P_4), 33.9 (d, $^2J_{CP}$ = 12.5 Hz, CH_3-N-P_{1-3}), 121.9 (s, $C_{1-3}{}^2$), 128.3 (s, $C_{0-2}{}^3$), 128.7 (s, $C_3{}^3$), 131.5 (s, $C_3{}^4$), 132.1 (s, $C_{1-2}{}^4$), 138.7–139.5 (m, CH=N-N-P_{1-3}), 140.7 (d, $^3J_{CP}$ = 18.6 Hz, CH=N-N-P_4), 151.4 (br. s, $C_{1-2}{}^1$), 151.8 (br. s, $C_3{}^1$) ppm. $C_{992}H_{968}Cl_{128}CoN_{248}O_{120}P_{120}S_{120}$ (30446): calcd. C 39.14, H 3.20, N 11.41; found C 39.21, H 3.17, N 11.58.

3-G′$_4$: 99% Yield, 0.808 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 60.5 (s, P_4), 62.4 (s, P_3), 62.7 (s, P_2), 62.9 (s, P_1) ppm. ^1H NMR ($CDCl_3$): δ = 3.32 (br. s, 360 H, CH_3-N-P_{1-4}), 6.5–7.4 (m, 496 H, $C_{0-4}{}^2$-H), 7.4–8.4 (m, 624 H, $C_{0-4}{}^3$-H, CH=N-N-P_{1-4}, CHPc), 9.89 (br. s, 128 H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.9 (d, $^2J_{CP}$ = 13.1 Hz, CH_3-N-P_4), 33.1 (br. d, $^2J_{CP}$ = 12 Hz, CH_3-N-P_{1-3}), 121.9 (s, $C_{1-4}{}^2$), 128.3 (s, $C_{0-3}{}^3$), 131.5 (s, $C_4{}^3$), 131.8 (s, $C_3{}^4$), 132.1 (br. s, $C_{1-2}{}^4$), 133.6 (s, $C_4{}^4$), 139.0–139.4 (m, CH=N-N-P_{1-3}), 139.6 (d, $^3J_{CP}$ = 17.3 Hz, CH=N-N-P_4), 151.5 (br. s, $C_{1-3}{}^1$), 155.1 (br. d, $^2J_{CP}$ = 7 Hz, $C_4{}^1$), 190.8 (s, CHO) ppm. IR (KBr): $\tilde{\nu}$ = 1702 cm^{-1} ν_{CHO}. $C_{1888}H_{1608}CoN_{248}O_{376}P_{120}S_{120}$ (41410): calcd. C 54.76, H 3.91, N 8.39; found C 54.81, H 3.90, N 8.39.

3-G$_5$: 93% Yield, 0.696 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 62.1 (s, P_4), 62.4 (s, P_3), 62.7 (s, P_{1-2}), 63.2 (s, P_5) ppm. ^1H NMR ($CDCl_3$): δ = 3.33 (br. s, 744 H, CH_3-N-P_{1-5}), 7.22 (br. s, 496 H, $C_{0-4}{}^2$-H), 7.64 (br. s, 752 H, $C_{0-4}{}^3$-H, CH=N-N-P_{1-5}, CHPc) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.9 (d, $^2J_{CP}$ = 12.4 Hz, CH_3-N-P_5), 33.1 (d, $^2J_{CP}$ = 13.0 Hz, CH_3-N-P_{1-4}), 121.9 (s, $C_{1-4}{}^2$), 128.3 (s, $C_{1-3}{}^3$), 128.7 (s, $C_4{}^3$), 131.5 (s, $C_4{}^4$), 132.1 (s, $C_{1-3}{}^4$), 139.1 (m, CH=N-N-P_{1-4}), 140.7 (d, $^3J_{CP}$ = 17.6 Hz, CH=N-N-P_5), 151.4 (br. s, $C_{1-3}{}^1$), 151.8 (br. d, $^2J_{CP}$ = 5 Hz, $C_4{}^1$) ppm. $C_{2016}H_{1992}Cl_{256}CoN_{504}O_{248}P_{248}S_{248}$ (62018): calcd. C 39.04, H 3.24, N 11.38; found C 39.21, H 3.28, N 11.19.

3-G′$_5$: 97% Yield, 0.788 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 60.5 (s, P_5), 62.4 (s, P_4), 62.7 (br. s, P_{1-3}) ppm. ^1H NMR ($CDCl_3$): δ = 3.31 (br. s, 744 H, CH_3-N-P_{1-5}), 6.5–7.4 (m, 1008 H, $C_{0-5}{}^2$-H), 7.4–8.4 (m, 1264 H, $C_{0-5}{}^3$-H, CH=N-N-P_{1-5}, CHPc), 9.89 (br. s, 256 H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.9 (d, $^2J_{CP}$ = 13.1 Hz, CH_3-N-P_5), 33.0 (d, $^2J_{CP}$ = 12 Hz, CH_3-N-P_{1-4}), 121.9 (s, $C_{1-5}{}^2$), 128.3 (s, $C_{1-4}{}^3$), 131.5 (s, $C_5{}^3$), 131.8 (s, $C_4{}^4$), 132.1 (s, $C_{1-3}{}^4$), 133.6 (s, $C_5{}^4$), 138.9–139.2 (m, CH=N-N-P_{1-4}), 139.7 (d, $^3J_{CP}$ = 14.4 Hz, CH=N-N-P_5), 151.4 (m, $C_{1-4}{}^1$), 155.1 (br. d, $^2J_{CP}$ = 7.9 Hz, $C_5{}^1$), 190.8 (s, CHO) ppm. IR (KBr): $\tilde{\nu}$ = 1703 cm^{-1} ν_{CHO}. $C_{3808}H_{3272}CoN_{504}O_{760}P_{248}S_{248}$ (83947): calcd. C 54.48, H 3.93, N 8.41; found C 54.62, H 3.83, N 8.41.

3-G$_6$: 90% Yield, 0.671 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 62.1 (s, P_5), 62.4 (s, P_4), 62.7 (br. s, P_{1-3}), 63.2 (s, P_6) ppm. ^1H NMR ($CDCl_3$): δ = 3.34 (br. s, 1512 H, CH_3-N-P_{1-6}), 7.22 (br. s, 1008 H, $C_{0-5}{}^2$-H), 7.65 (br. s, 1520 H, $C_{0-5}{}^3$-H, CH=N-N-P_{1-6}, CHPc) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.9 (d, $^2J_{CP}$ = 12.6 Hz, CH_3-N-P_6), 33.1 (d, $^2J_{CP}$ = 12.6 Hz, CH_3-N-P_{1-5}), 121.9 (s, $C_{1-5}{}^2$), 128.3 (s, $C_{1-4}{}^3$), 128.7 (s, $C_5{}^3$), 131.5 (s, $C_5{}^4$), 132.1 (s, $C_{1-4}{}^4$), 139.1 (d, $^3J_{CP}$ = 16.7 Hz, CH=N-N-P_{1-5}), 140.7 (d, $^3J_{CP}$ = 18.6 Hz, CH=N-N-P_6), 151.3 (br. s, $C_{1-4}{}^1$), 151.8 (br. s, $C_5{}^1$) ppm. $C_{4064}H_{4040}Cl_{512}CoN_{1016}O_{504}P_{504}S_{504}$ (125162): calcd. C 39.00, H 3.25, N 11.37; found C 39.17, H 3.21, N 11.50.

3-G′$_6$: 91% Yield, 0.737 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 60.5 (s, P_6), 62.3 (s, P_5), 62.7 (br. s, P_{1-4}) ppm. ^1H NMR ($CDCl_3$): δ = 3.32 (br. s, 1512 H, CH_3-N-P_{1-6}), 6.5–7.4 (m, 2032 H, $C_{0-6}{}^2$-H), 7.4–8.5 (m, 2544 H, $C_{0-6}{}^3$-H, CH=N-N-P_{1-6}, CHPc), 9.86 (br. s, 512 H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.9 (d, $^2J_{CP}$ = 12.8 Hz, CH_3-N-P_6), 33.0 (d, $^2J_{CP}$ = 12 Hz, CH_3-N-P_{1-5}), 121.9 (s, $C_{1-6}{}^2$), 128.3 (s, $C_{1-5}{}^3$), 131.5 (s, $C_6{}^3$), 131.8 (s, $C_5{}^4$), 132.1 (s, $C_{1-4}{}^4$), 133.6 (s, $C_6{}^4$), 139.1–139.3 (m, CH=N-N-P_{1-5}), 139.7 (d, $^3J_{CP}$ = 14.1 Hz, CH=N-N-P_6), 151.1–151.8 (m, $C_{1-5}{}^1$), 155.1 (d, $^2J_{CP}$ = 7.0 Hz, $C_6{}^1$), 190.8 (s, CHO) ppm. IR (KBr): $\tilde{\nu}$ = 1702 cm^{-1} ν_{CHO}. $C_{7648}H_{6600}CoN_{1016}O_{1528}P_{504}S_{504}$ (169021): calcd. C 54.35, H 3.94, N 8.42; found C 54.77, H 3.86, N 8.61.

3-G$_7$: 93% Yield, 0.692 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 62.0 (s, P_6), 62.3 (s, P_5), 62.5 (br. s, P_{1-4}), 63.2 (s, P_7) ppm. ^1H NMR ($CDCl_3$): δ = 3.33 (br. s, 3048 H, CH_3-N-P_{1-7}), 7.21 (br. s, 2032 H, $C_{0-6}{}^2$-H), 7.64 (br. s, 3056 H, $C_{0-6}{}^3$-H, CH=N-N-P_{1-7}, CHPc) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.9 (d, $^2J_{CP}$ = 12.6 Hz, CH_3-N-P_7), 33.1 (d, $^2J_{CP}$ = 12.3 Hz, CH_3-N-P_{1-6}), 121.9 (s, $C_{1-6}{}^2$), 128.3 (s, $C_{1-5}{}^3$), 128.7 (s, $C_6{}^3$), 131.4 (s, $C_6{}^4$), 132.1 (s, $C_{1-5}{}^4$), 139.1 (m, CH=N-N-P_{1-6}), 140.7 (d, $^3J_{CP}$ = 18.9 Hz, CH=N-N-P_7), 151.3 (br. s, $C_{1-5}{}^1$), 151.8 (br. d, $^2J_{CP}$ = 6 Hz, $C_6{}^1$) ppm. $C_{8160}H_{8136}Cl_{1024}CoN_{2040}O_{1016}P_{1016}S_{1016}$ (251450): calcd. C 38.98, H 3.26, N 11.36; found C 40.01, H 3.19, N 11.31.

3-G′$_7$: 93% Yield, 0.753 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 60.5 (s, P_7), 62.4 (s, P_6), 62.7 (br. s, P_{1-5}) ppm. ^1H NMR ($CDCl_3$): δ = 3.31 (br. s, 3048 H, CH_3-N-P_{1-7}), 6.5–7.4 (m, 4080 H, $C_{0-7}{}^2$-H), 7.4–8.5 (m, 5104 H, $C_{0-7}{}^3$-H, CH=N-N-P_{1-7}, CHPc), 9.85 (br. s, 1024 H, CHO) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.9 (d, $^2J_{CP}$ = 12.4 Hz, CH_3-N-P_7), 33.0 (d, $^2J_{CP}$ = 12 Hz, CH_3-N-P_{1-6}), 121.9 (s, $C_{1-7}{}^2$), 128.3 (s, $C_{1-6}{}^3$), 131.5 (s, $C_7{}^3$), 131.8 (s, $C_6{}^4$), 132.1 (s, $C_{1-5}{}^4$), 133.6 (s, $C_7{}^4$), 138.8–139.2 (m, CH=N-N-P_{1-6}), 139.7 (d, $^3J_{CP}$ = 15.8 Hz, CH=N-N-P_7), 151.1–151.8 (m, $C_{1-6}{}^1$), 155.1 (br. d, $^2J_{CP}$ = 5 Hz, $C_6{}^1$), 190.8 (s, CHO) ppm. IR (KBr): $\tilde{\nu}$ = 1702 cm^{-1} ν_{CHO}. $C_{15328}H_{13256}CoN_{2040}O_{3064}P_{1016}S_{1016}$ (339167): calcd. C 54.28, H 3.94, N 8.43; found C 54.96, H 4.02, N 8.44.

3-G$_8$: 90% Yield, 0669 g. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 62.1 (s, P_7), 62.4 (s, P_6), 62.6 (br. s, P_{1-5}), 63.2 (s, P_8) ppm. ^1H NMR ($CDCl_3$): δ = 3.32 (br. s, 6120 H, CH_3-N-P_{1-8}), 7.21 (br. s, 4080 H, $C_{0-7}{}^2$-H), 7.63 (br. s, 6128 H, $C_{0-7}{}^3$-H, CH=N-N-P_{1-8}, CHPc) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.9 (d, $^2J_{CP}$ = 12.6 Hz, CH_3-N-P_8), 33.1 (d, $^2J_{CP}$ = 12.6 Hz, CH_3-N-P_{1-7}), 121.9 (s, $C_{1-7}{}^2$), 128.3 (s, $C_{1-6}{}^3$), 128.7 (s, $C_7{}^3$), 131.5 (s, $C_7{}^4$), 132.0 (s, $C_{1-6}{}^4$), 139.1 (br. d, $^3J_{CP}$ = 13.8 Hz, CH=N-N-P_{1-7}), 140.7 (d, $^3J_{CP}$ = 18.4 Hz, CH=N-N-P_8), 151.3 (br. d, $^2J_{CP}$ = 6 Hz, $C_{1-6}{}^1$), 151.8 (d, $^2J_{CP}$ = 6.7 Hz, $C_7{}^1$) ppm. $C_{16352}H_{16328}Cl_{2048}CoN_{4088}O_{2040}P_{2040}S_{2040}$ (504026): calcd. C 38.97, H 3.27, N 11.36; found C 39.99, H 3.12, N 11.21.

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[1] C. C. Leznoff, A. B. P. Lever (Eds.), *Phthalocyanines. Properties and Applications*, VCH Publishers, New York, **1989**, vol. 1; **1993**, vols. 2 and 3; **1996**, vol. 4 .
[2] H. Ali, J. E. van Lier, *Chem. Rev.* **1999**, *99*, 2379–2450.

[3] M. K. Nazeeruddin, R. Humphry-Baker, M. Grätzel, B. A. Murrer, *Chem. Commun.* **1998**, 719–720.
[4] Z. Bao, A. J. Lovinger, J. Brown, *J. Am. Chem. Soc.* **1998**, *120*, 207–208.
[5] B. Meunier, A. Sorokin, *Acc. Chem. Res.* **1997**, *30*, 470–476.
[6] M. T. M. Choi, P. P. S. Li, D. K. P. Ng, *Tetrahedron* **2000**, *56*, 3881–3887.
[7] M. Kimura, K. Nakada, Y. Yamaguchi, K. Hanabusa, H. Shirai, N. Kobayashi, *Chem. Commun.* **1997**, 1215–1216.
[8] M. Brewis, G. J. Clarkson, A. M. Holder, N. B. McKeown, *Chem. Commun.* **1998**, 969–970.
[9] M. Brewis, G. J. Clarkson, V. Goddard, M. Helliwell, A. M. Holder, N. B. McKeown, *Angew. Chem. Int. Ed.* **1998**, *37*, 1092–1094.
[10] M. Kimura, H. Narikawa, K. Ohta, K. Hanabusa, H. Shirai, N. Kobayashi, *Chem. Mater.* **2002**, *14*, 2711–2717.
[11] C. A. Kernag, D. V. McGrath, *Chem. Commun.* **2003**, 1048–1049.
[12] J. Leclaire, R. Dagiral, S. Fery-Forgues, Y. Coppel, B. Donnadieu, A. M. Caminade, J. P. Majoral, *J. Am. Chem. Soc.* **2005**, *127*, 15762–15770.
[13] J. Leclaire, Y. Coppel, A. M. Caminade, J. P. Majoral, *J. Am. Chem. Soc.* **2004**, *126*, 2304–2305.
[14] J. Y. Jaung, *Bull. Korean Chem. Soc.* **2004**, *25*, 1453–1454.
[15] M. Kimura, Y. Sugihara, T. Muto, K. Hanabusa, H. Shirai, N. Kobayashi, *Chem. Eur. J.* **1999**, *5*, 3495–3500.
[16] S. Güner, M. K. Sener, H. Dinçer, Y. Köseoglu, S. Kazan, M. B. Koçak, *J. Magn. Magn. Mater.* **2006**, *300*, e530–e533.
[17] N. Launay, A. M. Caminade, R. Lahana, J. P. Majoral, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1589–1592.
[18] S. Dahli, J. J. Cosa, M. Bishop, D. Phillips, *Langmuir* **1996**, *12*, 293–300.
[19] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319–2358.
[20] A. Georges, G. Patonay, *Talanta* **1997**, *45*, 285–289.
[21] A. C. H. Ng, X. Y. Li, D. K. P. Ng, *Macromolecules* **1999**, *32*, 5292–5298.
[22] A. V. Nikolaitchick, M. A. J. Rodgers, *J. Phys. Chem. A* **1999**, *103*, 7597–7605.
[23] J. C. Blais, C. O. Turrin, A. M. Caminade, J. P. Majoral, *Anal. Chem.* **2000**, *72*, 5097–5105.

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