

# New axially aryloxy substituted gallium phthalocyanines for nonlinear optics

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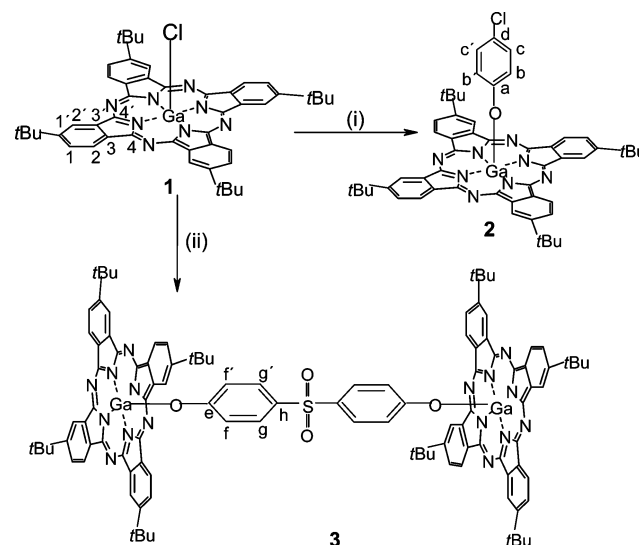
The ability to control reductions in the saturation energy density is important from the point of view of realizing applications where one would require successive layers in the practical limiter to be fabricated from materials of decreasing saturation energy density. In this paper, two new axially aryloxy substituted gallium phthalocyanine compounds: *t*Bu<sub>4</sub>PcGa(*p*-CPO) and [*t*Bu<sub>4</sub>PcGa]<sub>2</sub>·SDPO, have been prepared and structurally characterized. Their nonlinear optical (NLO) properties are described.

It has long been recognized that intense laser beams can easily damage delicate optical instruments, especially the human eye, and consequently the field of optical limiting has invested much effort into the research of materials and processes in an attempt to afford some measure of protection from such beams. An efficient optical limiter will strongly attenuate intense, potentially dangerous optical beams, while exhibiting high transmittance for low-intensity ambient light. Many functional materials such as fullerenes,<sup>1</sup> carbon nanotubes,<sup>2</sup> polymer/nanotube composites,<sup>3</sup> porphyrins,<sup>4</sup> and phthalocyanines (Pc's),<sup>5</sup> which process high dissipative extinction nonlinearity, fast response time, large dynamic range and broadband spectral response, have been widely studied with the view to realization of practical passive optical limiting applications. However, preparation of the required nonlinear optical active materials for practical optical limiters still presents a significant chemical challenge.<sup>5,6</sup>

Among the large number of NLO absorbers that have been identified so far, phthalocyanines are especially attractive because of their great reverse saturable absorption (RSA) properties, and are still being investigated to improve their optical limiting properties and to expand their optical limiting window from the visible to the near IR range.<sup>5–8</sup> Utilizing the chemical reactivity of M–Cl [M = Ga<sup>3+</sup>, In<sup>3+</sup>] and M=O [M = Ti<sup>4+</sup>] bonds, we have successfully synthesized a series of axially substituted or bridged phthalocyanine complexes in attempt to meet the requirements for practical optical limiters by increasing their solubility in organic solvents, decreasing aggregation, and thus maintaining their long excited state lifetimes and good optical limiting properties.<sup>6,7,9</sup> In this communication, we report on the synthesis and nonlinear optical (including optical limiting) properties of new axially aryloxy substituted and bridged gallium phthalocyanines. As a result, axial substitution and dimerization of the gallium phthalocyanine monomer resulted in significant reductions in the saturation energy density of the material displaying clear evidence of the usefulness of structurally modifying the gallium phthalocyanine unit.

*p*-Chlorophenoxygallium(III)2, (3)-tetra(*tert*-butyl)phthalocyanine [*t*Bu<sub>4</sub>PcGa(*p*-CPO)] (**2**) and 4,4'-sulfonyldiphenoxy-axially bridged gallium phthalocyanine dimer {[*t*Bu<sub>4</sub>PcGa]<sub>2</sub>·SDPO} (**3**) were synthesized by the reaction of *t*Bu<sub>4</sub>PcGaCl (**1**)<sup>9a</sup> with *p*-chlorophenol and bis(4-hydroxyphenyl)sulfone, respectively, in anhydrous DMSO at 110 °C in the presence of K<sub>2</sub>CO<sub>3</sub> (see Scheme 1). Confirmation of the structures of compounds **2** and **3** was carried out by UV/Vis, FAB-MS, IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR.†

As expected, the weak absorption band of the Ga–Cl stretching mode<sup>9a</sup> at 351 cm<sup>-1</sup> is absent in the IR spectra of both **2** and **3**. Some new weak absorption peaks associated with the axial aryloxy ligands, for example, 503, 639, 1587, and 1665 cm<sup>-1</sup> for **2**; 634 cm<sup>-1</sup> for **3**, were observed. The molecular peak for **2** (*m/z* = 934.4) was detected in the FAB-MS spectrum. The FAB-MS spectrum of **3** shows a number of fragment peaks. The UV/Vis spectra of **2** and **3** are almost identical. Unlike the axially aryl-substituted gallium phthalocyanine [*t*Bu<sub>4</sub>PcGaX] (e.g. X = *p*-trifluoromethylphenyl),<sup>9a</sup> whose Q and B-bands in the UV/Vis spectra are shifted to the red by a few nanometers relative to *t*Bu<sub>4</sub>PcGaCl (**1**), axial aryloxy substitution at the central gallium atom gives rise to a weak (2–3 nm) blue shift of the Q-band of compounds **2** and **3**. We have reported a similar observation for the μ-oxo-bridged gallium phthalocyanine



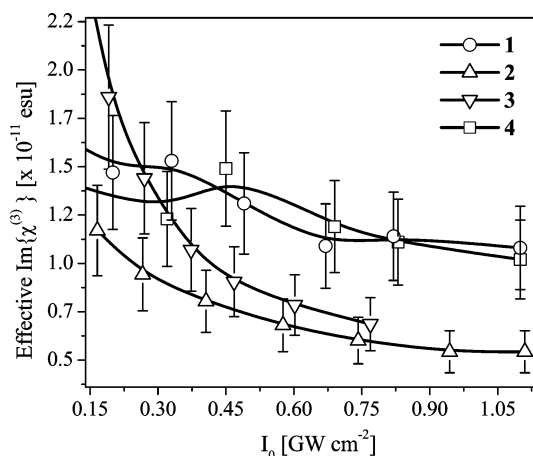
**Scheme 1** Synthesis of compounds **2** and **3**: (i) anhydrous DMSO, *p*-chlorophenol, K<sub>2</sub>CO<sub>3</sub>, 110 °C, 14 h, 87% yield; (ii) anhydrous DMSO, 4,4'-sulfonyldiphenol, K<sub>2</sub>CO<sub>3</sub>, 110 °C, 10 h, 40% yield.

dimer  $[t\text{Bu}_4\text{PcGa}]_2\text{O}$  (**4**) earlier.<sup>9b</sup> These very small blue-shifts suggest that the interactions between the two phthalocyanine rings in **3** and **4**, and between the phthalocyanine ring and the axial ligands in **2** and **3** in the ground state, are very weak.

The <sup>1</sup>H-NMR spectra of **1–3** in CDCl<sub>3</sub> confirm the presence of the expected mixtures of structural isomers of tetrasubstituted phthalocyanines.<sup>6,9</sup> The proton signal of the *tert*-butyl group is split due to the structural isomers. In comparison with the chloro ligand in **1**,<sup>9a</sup>  $\sigma$ -bonded aryloxy groups, *i.e.*, *p*-CPO and SDPO groups, cause a slightly stronger deshielding of the aromatic protons, especially of those closer to the heteroaromatic  $\pi$ -electron system (2,2'-H, see Scheme 1) than does the chloro ligand. In contrast, the signals of the axial ligands are considerably shielded by the influence of the large diamagnetic ring-current of the phthalocyanine rings on the protons of their axial ligands. In **2**, the aromatic signals (2,2'-H), appear at  $\delta = 8.9$ – $9.5$  ppm (multiplet), 1-H appears at  $\delta = 8.2$ – $8.3$  ppm (multiplet) and the *t*Bu protons at 1.9–2.0 ppm. The proton signals of the *p*-CPO ligand are shifted upfield due to the diamagnetic ring-current of the phthalocyanine macrocycle. They appear at  $\delta = 6.8$  ppm (m, H-c,c', 2 H) and 5.3 ppm (m, H-b,b', 2 H), compared to 6.9 (H-c,c') and 7.2 (H-b,b') ppm in the pure *p*-chlorophenol. For **3**, the aromatic 2,2'-H protons give a multiplet between  $\delta = 8.8$ – $9.5$  ppm, 1-H protons appear at  $\delta = 8.3$  ppm (multiplet), and the protons of the *t*Bu group are located at  $\delta = 1.7$ – $1.8$  ppm. The proton signals of the SDPO ligand appear at 6.6 ppm (m, H-f,f'), and 8.1 ppm (m, H-g,g'), whereas pure 4,4'-sulfonyldiphenol gives two aromatic proton signals: 7.0 ppm (H-f,f') and 8.3 ppm (H-g,g').

<sup>13</sup>C NMR results reveal that the chemical shifts of the aromatic carbons on the macrocycles for **2** and **3** are close to the corresponding values for compound **1**.<sup>9a</sup> Only a small deshielding effect is observed for the carbon atoms close to the gallium atom. For example, the signals for the carbon atoms closer to the phthalocyanine core (C-4, 4') are shifted further downfield than the signals for C-3,3'. Carbon atom resonances attributed to the axial *p*-CPO ligand are observed and located at 154.0 ppm (C-a), 116.4 ppm (C-b,b') and 126.6 ppm (C-d), respectively. On the other hand, the locations of the <sup>13</sup>C-NMR signals of the carbons on the axial SDPO ligand in **3** are mainly in the same aromatic region as those of phthalocyanine macrocycles in the <sup>13</sup>C-NMR spectrum.

The open aperture of a Z-scan experiment was used to measure the NLO response in the samples. Compounds **1**, **2**, **3** and the  $\mu$ -oxo-bridged gallium phthalocyanine dimer  $[t\text{Bu}_4\text{PcGa}]_2\text{O}$  (**4**)<sup>9b</sup> were measured in quartz cells with a 1 mm optical path length, and at concentrations of 0.5 g L<sup>-1</sup> ( $\sim 10^{-4}$  M) in toluene. All Z-scans performed exhibited a decrease of transmittance about the focus typical of an induced positive nonlinear absorption of incident light. The theory of Sheik-Bahae *et al.*<sup>10</sup> was fitted (with the waist radius ( $\omega_0$ ) of the beam treated as a free parameter) to the open aperture data and the imaginary third order susceptibilities,  $\text{Im}\{\chi^{(3)}\}$ , and the second molecular hyperpolarizabilities,  $\gamma$ , were calculated from the fits. The size of the waist radius determined from the fitting is given in Table 1. In Fig. 1 the experimentally determined values of  $\text{Im}\{\chi^{(3)}\}$  are plotted as a function of the focal intensity. Each data point on the plot represents an independent open aperture Z-scan of the compound in question and the solid lines are sketched merely as guides to the eye. It can clearly be seen that



**Fig. 1** Plot of effective  $\text{Im}\{\chi^{(3)}\}$  against the on focus beam intensity  $I_0$  for compounds **1–4** at 0.5 g L<sup>-1</sup> in toluene. Each data point represents an independent open aperture Z-scan and the solid lines are intended as guides to the eye.

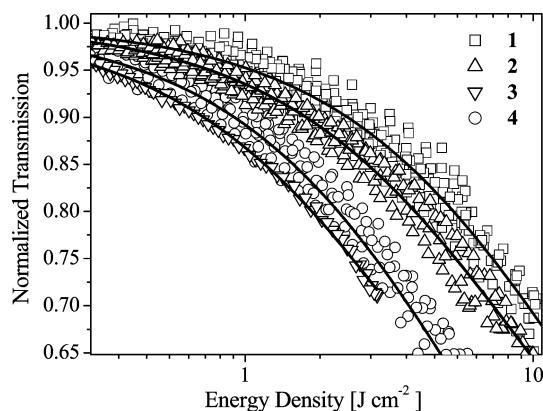
$\text{Im}\{\chi^{(3)}\}$  tends to reduce in magnitude with increasing focal intensity  $I_0$  in the figure. This, coupled with the fact that the closed aperture Z-scans (nonlinear refraction) did not exhibit pure third order effects either, leads to the only conclusion that the absorption effects were a combination of third and higher odd order nonlinear absorptions. Despite this, effective third order nonlinear susceptibilities ( $\text{Im}\{\chi_{\text{eff}}^{(3)}\}$ ) were estimated by suitably interpolating the data in Fig. 1 for all four compounds at on focus intensities of 0.5 GW cm<sup>-2</sup> (arbitrarily chosen). Subsequently  $\text{Im}\{\chi_{\text{eff}}^{(3)}\}$  and molecular second hyperpolarizabilities  $\gamma_{\text{eff}}$  were determined for compounds **1–4** for this sample  $I_0$  value. All calculated coefficients are given in Table 1.

The open aperture spectra were manipulated and replotted with the normalised transmission ( $T_{\text{Norm}}$ ) against the incident energy density per pulse (J cm<sup>-2</sup>) to further investigate the optical limiting. The nonlinear absorption coefficient  $\alpha(F, F_{\text{Sat}}, \kappa)$  where  $\alpha(F, F_{\text{Sat}}, \kappa) = \alpha_0(1 + F/F_{\text{Sat}})^{-1}(1 + \kappa F/F_{\text{Sat}})$  was used to fit the normalised transmission as a function of this energy density to a superposition of all open aperture datasets for each compound.<sup>11</sup> In this expression  $F$  represents the energy density,  $F_{\text{Sat}}$  the saturation energy density,  $\kappa$  the ratio of the excited to ground state absorption cross sections  $\sigma_{\text{ex}}/\sigma_0$ , and  $\alpha_0$  the linear absorption coefficient. The method of least squares regression was employed, where the parameters  $\kappa$  (realistically  $\sigma_{\text{ex}}$  as  $\alpha_0$  was measured) and  $F_{\text{Sat}}$  were treated as free constants in the fitting algorithm. The fitting converged with  $R^2$  values in the region of 0.99 in all cases. The plots of normalized transmission against pulse energy density for compounds **1–4** where the solid lines are theoretical fits to the experimental data are shown in Fig. 2. The  $\alpha_0$ ,  $\kappa$  and  $F_{\text{Sat}}$  values for each compound are given in Table 1.

Compound **1** exhibits the largest excited to ground state absorption cross section ratio  $\kappa \approx (13.5 \pm 0.4)$  and it also possesses the lowest linear absorption coefficient  $\alpha_0 \approx 1.1$  cm<sup>-1</sup> of the series **1–4**. The  $\kappa$  coefficient for compound **3** is the lowest of the series at  $(4.8 \pm 0.6)$  while its linear absorption coefficient,  $\alpha_0 \approx 3.13$  cm<sup>-1</sup>, is the highest of the four compounds by a factor of 2–3 when compared to the linear absorption coefficients of compounds **1**, **2** and **4**. The relatively

**Table 1** Summary of the nonlinear optical properties for gallium phthalocyanine compounds in toluene

Compound	C/g L <sup>-1</sup>	$\alpha_0/\text{cm}^{-1}$	$\text{Im}\{\chi_{\text{eff}}^{(3)}\}/10^{-11}$ esu	$\gamma_{\text{eff}}/10^{-32}$ esu	$\kappa \sigma_{\text{ex}}/\sigma_0$	$F_{\text{Sat}}/\text{J cm}^{-2}$	$\omega_0/\mu\text{m}$
$t\text{Bu}_4\text{PcGaCl}$ ( <b>1</b> )	0.5	1.10	$1.2 \pm 0.2$	$0.84 \pm 0.1$	$13.5 \pm 0.4$	$27.0 \pm 1.0$	23
$t\text{Bu}_4\text{PcGa}(p\text{-CPO})$ ( <b>2</b> )	0.5	1.37	$0.88 \pm 0.2$	$0.69 \pm 0.1$	$9.5 \pm 0.4$	$16.3 \pm 0.9$	25
$[t\text{Bu}_4\text{PcGa}]_2\text{-SDPO}$ ( <b>3</b> )	0.5	3.13	$0.73 \pm 0.1$	$1.13 \pm 0.2$	$4.8 \pm 0.6$	$7.5 \pm 0.8$	31
$[t\text{Bu}_4\text{PcGa}]_2\text{O}$ ( <b>4</b> )	0.5	1.60	$1.30 \pm 0.2$	$1.76 \pm 0.3$	$11.3 \pm 0.1$	$13.5 \pm 1.0$	23



**Fig. 2** Plot of normalized transmission against pulse energy density for compounds **1–4** at  $0.5 \text{ g L}^{-1}$  in toluene where the solid lines are theoretical fits to the experimental data. The fitting parameters are given in Table 1.

large linear absorption coefficient is therefore responsible for the significant reduction in the  $\kappa$  coefficient when the chlorogallium phthalocyanine monomer **1** is substituted with a *p*-CPO group at the axial position. The magnitude of the nonlinear absorption coefficient (directly proportional to  $\text{Im}\{\chi^{(3)}\}$ ) is lowest for compound **3** and largest for compound **4** under  $0.5 \text{ GW cm}^{-2}$  irradiation. Thus, dimerisation of the gallium phthalocyanine monomer resulted in producing compounds with both the largest and smallest nonlinear absorption coefficients in the study.

The  $F_{\text{Sat}}$  values for compounds **1–4** range from  $(7.5 \pm 0.8) \text{ J cm}^{-2}$  for **3** to  $(27.0 \pm 1.0) \text{ cm}^{-2}$  for **1**. Thus, while compound **3** exhibited the lowest nonlinear absorption coefficient it also saturated at the lowest energy density indicating that dimerisation of the gallium phthalocyanine monomer in this way results in a compound that saturates at an energy density 3.6 times lower than compound **1**. The saturation energy density was reduced by a factor  $\approx 1.7$  by the addition of the *p*-CPO at the axial position (compound **2**) and by a factor  $\approx 2$  by dimerisation with a  $\mu$ -oxo-bridge (compound **4**) when compared to the saturation energy density of the chlorogallium monomer (compound **1**). The ability to control reductions in the saturation energy density is important from the point of view of realizing applications where one would require successive layers in the practical limiter to be fabricated from materials of decreasing saturation energy density.

It is worth considering the waist radius of the beam as determined from the fitting of the open aperture spectra. Compound **3** exhibited the largest waist radius ( $\omega_0 \approx 31 \mu\text{m}$ ) of the four compounds with compounds **1**, **2** and **4** exhibiting waist radii  $\omega_0 \approx 23 \mu\text{m}$ ,  $25 \mu\text{m}$  and  $23 \mu\text{m}$  respectively. Dimerisation of compound **1** into compound **3** therefore resulted in larger refraction in the sample enlarging the waist radius of the focused beam by a factor  $\sim 1.3$ . This is a desirable effect in practical optical limiters as it reduces the energy density of the incident pulses.

In summary, the two new axially aryloxy substituted gallium phthalocyanine compounds **2** and **3** have been prepared and structurally characterized. UV/Vis spectral data from compounds **1–3** reveal that the interactions between two phthalocyanine rings in **3**, and between the phthalocyanine ring and axial ligands in **2** and **3** in the ground state are weak. All Z-scans performed exhibit a decrease of transmittance about the focus typical of an induced positive nonlinear absorption of incident light. The nonlinear absorption of these materials (proportional to  $\text{Im}\{\chi^{(3)}\}$ ) was largest for **4** in comparison with **1–3**. Substitution and dimerization of the phthalocyanine monomer resulted in significant reductions in the saturation energy density of the material displaying clear evidence of the usefulness of structurally modifying the gallium phthalocyanine

unit. It was found that compound **3** exhibited by far the largest linear absorption coefficient thereby reducing the ratio of its excited to ground state absorption cross sections to the lowest in the study while exhibiting the lowest saturation energy density of the four compounds. It also defocused the beam to its largest waist radius displaying its competitiveness as a potential optical limiter. Gallium and indium<sup>6,7,9</sup> phthalocyanines are amongst the most promising that have been investigated as limiters of intense light and the current series presents a selection of structural modifications useful for varying their nonlinear optical properties.

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## Notes and references

**†Experimental: General.** The operations for synthesis prior to the termination reaction were carried out under purified argon. Solvents were purified, dried and distilled under dry nitrogen. FT-IR: Perkin-Elmer Spectrum 1000; UV/Vis: Shimadzu UV-365; MS: Varian Mat 711;  $^1\text{H}$ ,  $^{13}\text{C}$  NMR: Bruker AC 250 ( $^1\text{H}$ : 250.131 MHz,  $^{13}\text{C}$ : 62.902 MHz). All Z-scan experiments described in this study were performed using 6 ns pulses from a Q switched Nd : YAG laser. The beam was spatially filtered to remove the higher order modes and tightly focused with a 9 cm focal length lens. The laser was operated at its second harmonic, 532 nm, with a pulse repetition rate of 10 Hz. The samples were prepared at  $0.5 \text{ g L}^{-1}$  in toluene followed by gentle agitation for  $\approx 20$  minutes in a low-power (60 W) sonic bath to ensure complete and uniform dispersal. All subsequent measurements were performed in quartz cells with a 1 mm path length.

***t*Bu<sub>4</sub>PcGa(*p*-CPO) (2).** To a stirred solution of 4-chlorophenol (0.32 g, 2.45 mmol) and *t*Bu<sub>4</sub>PcGaCl (**1**) (0.22 g, 0.26 mmol) in anhydrous DMSO (60 ml) was added slowly K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.53 mmol) under purified argon. After refluxing at 110 °C for 14 h, the reaction mixture was allowed to cool, added to ice water (200 ml) and filtered to afford a dark green solid powder which was recrystallized from a mixture of CH<sub>2</sub>Cl<sub>2</sub>/MeOH (v/v: 4 : 3) by slowly evaporating the more volatile dichloromethane in a rotary evaporator at 40–60 °C under slightly reduced pressure. Yield 87% (214 mg). FAB-MS [*m/z*]: calcd for C<sub>54</sub>H<sub>52</sub>GaN<sub>8</sub>ClO: 934.2; found: 934.4 (M<sup>+</sup>), 809, 805 (*t*Bu<sub>4</sub>PcGa<sup>+</sup>), 789, 773, 749; UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}/\text{nm} = 692, 664(\text{sh}), 624, 356$ ; FTIR (KBr, cm<sup>-1</sup>): 2956(ms), 2862(w), 1725(w), 1613(m), 1585(m), 1483(s), 1394 (m), 1363 (m), 1334 (m), 1281(m), 1256(s), 1200(m), 1156(m), 1087(vs), 1051(m), 1019(vw), 929(s), 894 (w), 828(s), 765(m), 749(s), 694(m), 669(m), 641(w), 601(w), 561(w), 532(m), 503(w), 486(w), 437(w);  $^1\text{H-NMR}$  (CDCl<sub>3</sub>):  $\delta/\text{ppm} = 1.9\text{--}2.0$  (m, 36 H, *t*Bu), 5.3 (m, H-b,b'), 6.8–6.9 (m, H-c,c'), 8.2–8.3 (m, 4 H, H-1), 8.9–9.5 (m, 8 H, H-2, 2');  $^{13}\text{C-NMR}$  (CDCl<sub>3</sub>):  $\delta/\text{ppm} = 32.1$  (*t*BuCH<sub>3</sub>), 36.2 (CMe<sub>3</sub>), 116.4 (C-b,b'), 118.0–119.5 (C-2'), 121.5–123.0 (C-2), 126.6 (C-d), 128.5–128.9 (C-1), 133.6–134.1 (C-3), 135.9–136.2 (C-3'), 151.2–152.2 (C-4,4'), 154.0 (C-a), 154.2–154.5 (C-1').

***t*Bu<sub>4</sub>PcGa<sub>2</sub>-SDPO (3).** A solution of 4,4'-sulfonyldiphenol (37.2 mg, 0.149 mmol) in DMSO (30 ml) was added dropwise into a stirred solution of *t*Bu<sub>4</sub>PcGaCl (0.25 g, 0.297 mmol) and K<sub>2</sub>CO<sub>3</sub> (73.2 mg, 0.53 mmol) in DMSO (40 ml) at 110 °C. After heating for 10 h at the same temperature, the reaction mixture was allowed to cool to the room temperature, quenched with ice water (200 ml), filtered, washed with water to give a blackish green powder which was further purified according to the same method described above. Yield 40% (110.5 mg). FAB-MS [*m/z*]: calcd for C<sub>108</sub>H<sub>104</sub>N<sub>16</sub>Ga<sub>2</sub>SO<sub>4</sub>: 1861.6; found: 1828 (M<sup>+</sup> – H<sub>2</sub>S), 1800 (M<sup>+</sup> – SO<sub>2</sub>), 1763 (M<sup>+</sup> – H<sub>2</sub>SO<sub>4</sub>), 1628 (*t*Bu<sub>4</sub>PcGa<sub>2</sub>O<sup>9b</sup>), 1007, 957, 805 (*t*Bu<sub>4</sub>PcGa<sup>+</sup>); UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}/\text{nm} = 693, 664.5(\text{sh}), 624, 356.5$ ; FTIR (KBr, cm<sup>-1</sup>): 2956(ms), 2917(m), 2857(w), 1725(w), 1613(m), 1507(m), 1483(m), 1464(m), 1407(m), 1394(m), 1364(m), 1334(s), 1281(m), 1257(s), 1200(m), 1158(m), 1148(m), 1087(vs), 1051(m), 1021(w), 968(w), 929(s), 894(m), 861(w), 850(w), 830(ms), 779(w), 765(m), 749(vs), 694(ms), 668(ms), 634(m), 600(m), 564(m), 532(m), 444(w);  $^1\text{H-NMR}$  (CDCl<sub>3</sub>):  $\delta/\text{ppm} = 1.7\text{--}1.8$  (m, 72 H, *t*Bu), 6.6 (m, H-f,f'), 8.1 (m, H-g,g'), 8.3 (m,

8 H, H-1), 8.8–9.5 (m, 16 H, H-2,2');  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 31.9–32.1 (*t*BuCH<sub>3</sub>), 36.0 (CMe<sub>3</sub>), 118.9–119.1 (C-2'), 122.6 (C-2), 128.4–128.5 (C-1), 134.0–134.2 (C-3), 152.2–152.8 (C-4,4'), 153.9–154.1 (C-1').

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