Isolation and Spectroscopic Characterization of Heteroleptic, Anionic and Neutral (Phthalocyaninato)(tetra-4-pyridylporphyrinato)lanthanide(III) Double-Deckers☆

Jianzhuang Jiang[+], **Thomas C. W. Mak**, and **Dennis K. P. Ng***

Department of Chemistry, The Chinese University of Hong Kong,
Shatin, N.T., Hong Kong
Telefax: (internat.) +852/2603-5057
E-mail: dkpn@cuhk.hk

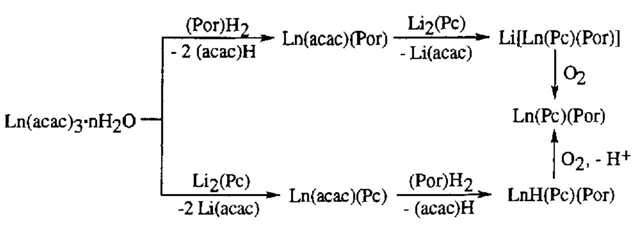
Received January 22, 1996

Key Words: Phthalocyanines / Porphyrins / Lanthanide(III) compounds / Macrocyclic ligands / Double-decker complexes

Treatment of 5,10,15,20-tetra-4-pyridylporphyrin [(TPyP)H_2] with europium(III) or gadolinium(III) acetylacetonate [Ln(acac)$_3$ · $n$$H_2O$] (Ln = Eu, Gd) in 1,2,4-trichlorobenzene produced Ln(acac)(TPyP), which reacted with dilithium phthalocyaninate [Li_2(Pc)] to give Li[Ln(Pc)(TPyP)] in moderate yields. Upon exposure to air, solutions of these compounds converted slowly to the corresponding neutral complexes Ln(Pc)(TPyP). The new compounds were spectroscopically characterized.

Double-decker phthalocyaninato and porphyrinato metal complexes are of much current interest[1]. It has been demonstrated that these sandwich complexes, having two macrocyclic rings located in close proximity, are prospective materials for electronic devices such as semiconductors[2] and visual displays[3] and may serve as structural and spectroscopic models for the dimer of bacteriochlorophyll molecules in bacterial photosynthetic reaction centers[4]. The homoleptic complexes M(Pc)$_2$ and M(Por)$_2$ (Por = general porphyrinato dianion) containing various metal centers have been extensively studied for several decades. The heteroleptic analogs M(Pc)(Por), however, have only been reported recently[1,5]. The syntheses of the latter complexes (for M = Ln^{III}) usually involve the treatment of Li_2(Pc) with Ln(acac)(Por) generated in situ from Ln(acac)$_3$ · $n$$H_2O$ and (Por)H_2 or the reaction of Li_2(Pc) with Ln(acac)$_3$ · $n$$H_2O$ followed by the treatment of (Por)H_2 (Scheme 1). By analogy with the bis(porphyrinato)lanthanide(III) complexes[6], it can be envisaged that for the first reaction pathway the lithiated compounds Li[Ln(Pc)(Por)] may be the primary products, which are subsequently oxidized to the corresponding neutral complexes, while the second route may involve the protonated species LnH(Pc)(Por) as the intermediate. During the course of this study, Weiss et al. prepared a series of lanthanide(III) sandwich compounds Ln(Pc)(TPP) (Ln = La, Pr, Nd, Eu, Gd, Er, Lu, and Y; TPP = dianion of 5,10,15,20-tetraphenylporphyrin) depending on the size of the central metal[7], by one of the above two methods. For Ln = La, they employed the latter route and obtained the protonated compound LaH(Pc)(TPP), which was oxidized to La(Pc)(TPP) with phenoxathiinylium hexachloroantimonate. This led to their proposition that the protonated form LnH(Pc)(TPP) is a common intermediate. For the other metals, the reactions gave the neutral Ln(Pc)(TPP) with no indication of the formation of such intermediate. The isolation of protonated bis(porphyrinato)lanthanide(III) complexes has also been described[8]. However, the proposed lithiated intermediate Li[Ln(Pc)(Por)] has not yet been isolated during the preparation of Ln(Pc)(Por) with the former pathway although the related complexes [Bu_4N][Ln(Pc)(TPP)] and [Bu_4N][Ln(TPP)$_2$] have been prepared independently by reducing the corresponding neutral compounds or treating the protonated species LnH(TPP)$_2$ with NaOEt[5e,6c,7]. This paper describes the isolation and characterization of such lithiated compounds, namely Li[Ln(Pc)(TPyP)] (**1a**, Ln = Eu; **1b**, Ln = Gd), and their conversion into the neutral double-decker complexes Ln(Pc)(TPyP) (**2a**, Ln = Eu; **2b**, Ln = Gd).

Scheme 1



Results and Discussion

Treatment of Ln(acac)$_3$ · $n$$H_2O$ (Ln = Eu, Gd) with (TPyP)H_2 in refluxing 1,2,4-trichlorobenzene gave Ln(acac)(TPyP)[9,10]. The progress of the reactions was

---

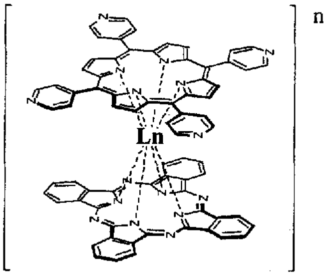
[+] On leave from the Department of Chemistry, Peking University, Beijing 100871, People's Republic of China.

monitored by UV/Vis spectroscopy, and the transformations were essentially completed in ca. 6 h. The UV/Vis spectra of the resulting dark cherry-red solutions showed absorptions at 426, 517, 556, and 593 nm (for Eu) or 426, 516, 557, and 597 nm (for Gd), which are similar to those of other Ln(acac)(Por)[9,10]. The solutions were then refluxed with $Li_2(Pc)$ for a further 12 h to give Li[Ln(Pc)(TPyP)] (**1a**, **b**) (Scheme 2) along with a small amount of the triple-decker complexes $Ln_2(Pc)_2(TPyP)$ as determined by fast-atom bombardment (FAB) mass spectrometry. The mass spectra showed the peaks assignable to the molecular ion of the Eu (*m/z* 1946) or Gd (*m/z* 1956) triple-decker complex. It is worth noting that by using 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin [$(TMPP)H_2$] or $(TPP)H_2$ instead of $(TPyP)H_2$ as the starting material under similar conditions, the triple-decker complexes $Ln_2(Pc)_2(TMPP)$ (Ln = Nd, Eu, Gd)[11] or the double-decker complexes Ln(Pc)(TPP) (Ln = Er, Lu, Y)[7] were isolated, respectively. Presumably, the electron-withdrawing nature of the pyridyl groups leads to a stabilization of the monoanion[12].

Scheme 2

$$Ln(acac)_3{\cdot}nH_2O \xrightarrow[\text{(ii) } Li_2Pc]{\text{(i) } (TPyP)H_2} Li[Ln(Pc)(TPyP)] \xrightarrow{O_2} Ln(Pc)(TPyP)$$

1a Ln = Eu **2a** Ln = Eu
1b Ln = Gd **2b** Ln = Gd



	Ln	n
1a	Eu	-1
1b	Gd	-1
2a	Eu	0
2b	Gd	0

The elemental analyses of **1a** and **1b** suggested the presence of $CHCl_3$ as solvate molecules. The incorporation of MeOH as solvate in the samples did not fit the analytical data. Compounds **1a** and **1b** are moderately soluble in $CHCl_3$ but highly soluble in MeOH. Attempts to grow single crystals for these compounds in $CHCl_3$/MeOH were unsuccessful. Nevertheless, the compounds were well characterized by various spectroscopic methods including NMR (^1H, ^{13}C, ^7Li), UV/Vis, IR, and FAB-MS.

The ^1H-NMR spectrum of **1a** in $CDCl_3$ showed only the signal due to residual $CHCl_3$. However, the spectrum measured in [D_5]pyridine displayed broad bands assignable to each proton in **1a** (Figure 1). It is plausible that, in $CDCl_3$ solution, the lithium ion may attach to the nitrogen atoms in the anion which interferes the NMR spectrum. But in [D_5]pyridine, the lithium ion is solvated by the coordinating solvent and thus separated from the double-decker anion. As shown in Figure 1, the four broad signals at δ = 11.50, 10.51, 9.01, and 6.59 with relative intensity 4:4:4:4 can be assigned to the pyridyl protons. The presence of four distinct signals clearly suggests that there is a restricted rotation about the C(*meso*)–C(pyridine) bond. The two broad signals at δ = 10.73 and 8.60 with relative intensity 8:8 are due to H_α and H_β of the phthalocyanine ring, respectively, whilst the remaining broad signal at δ = 7.75 (8 H) is due to the porphyrin β-pyrrole protons. These results are consistent with a mixed-ring sandwich structure with a paramagnetic metal center. The $^{13}C\{^1H\}$-NMR data were in accord with the proposed structure except that one of the quaternary carbon signals was missing in the spectrum. Probably, the weak signal was obscured by other bands with higher intensity. The $^7Li\{^1H\}$-NMR spectrum of **1a** was also recorded which showed a sharp singlet at δ = 2.56 referenced to 23% aqueous LiBr. This value is very close to those observed for simple lithium salts such as LiBr, LiCl, LiI, and $LiClO_4$, etc. in pyridine[13]. This also supported the hypothesis that **1a** existed in the form of solvent-separated ion pairs in [D_5]pyridine. As expected, the Gd analog **1b** is NMR silent in $CDCl_3$ and [D_5]pyridine due to the strong paramagnetic nature of Gd^{III}.

Figure 2 shows the electronic absorption spectrum of **1a**, which is similar to that of **1b** and agrees well with those of the analogs $[NBu_4][Ln^{III}(Pc)(TPP)]$[5e,7] and Ce^{IV}(Pc)(TPP)[5a,5e]. The spectrum displays strong phthalocyanine and porphyrin Soret bands at 334 and 412 nm, respectively, together with an absorption at 388 nm, which was previously observed for $[Ln^{III}(Pc)_2]^-$ as a weak shoulder but its origin is not clear[14]. The phthalocyanine Q bands appear at 584, 635, and 794 nm while the former two visible bands should also contain a contribution of the porphyrin Q bands. By analogy with $[Ln^{III}(Pc)(TPP)]^-$ and Ce^{IV}(Pc)(TPP), the remaining absorption at 477 nm can be ascribed to a π-π* transition arising from molecular orbitals delocalized over both macrocycles[5e,7].

The high-resolution FAB mass spectra of **1a** and **1b** were measured with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer in the negative-ion mode. The spectra showed an isotopic envelope peaking at *m/z* 1281.21 (Eu) or 1286.13 (Gd), which corresponds to the respective anion $[Ln(Pc)(TPyP)]^-$ (Ln = Eu, Gd). Both clusters appeared as the base peak in the spectra, and their isotopic distribution was in good agreement with the calculated spectra.

The compounds **1a** and **1b** are moderately air-stable in the solid state, but in $CHCl_3$/MeOH solutions the compounds are gradually oxidized in air to the corresponding neutral complexes **2a** and **2b** (Scheme 2). After stirring the solutions of **1a** and **1b** in air for 3 days, about 65% of these starting materials were consumed and converted into **2a** and **2b** almost quantitatively. The neutral products could be separated from the unreacted lithiated compounds by chromatography and recrystallized from a mixture of $CHCl_3$ and MeOH. Compounds **2a** and **2b** gave satisfactory elemental analyses and FAB mass spectra exhibiting the molecular ion peaks with expected isotope pattern.

A sufficiently resolved ^1H-NMR spectrum of **2a** in $CDCl_3$ was obtained. Presumably, the paramagnetic europium ion serves as an internal spin relaxer which suppresses the line-broadening effect of the π radical spin[15].

Figure 1. ^{1}H-NMR spectrum of Li[Eu(Pc)(TPyP)] (**1a**) in [D$_5$]pyridine (δ scale; * indicates solvent)

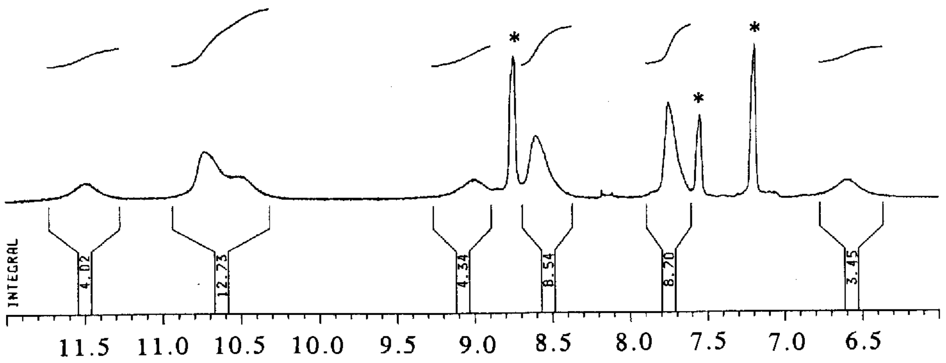
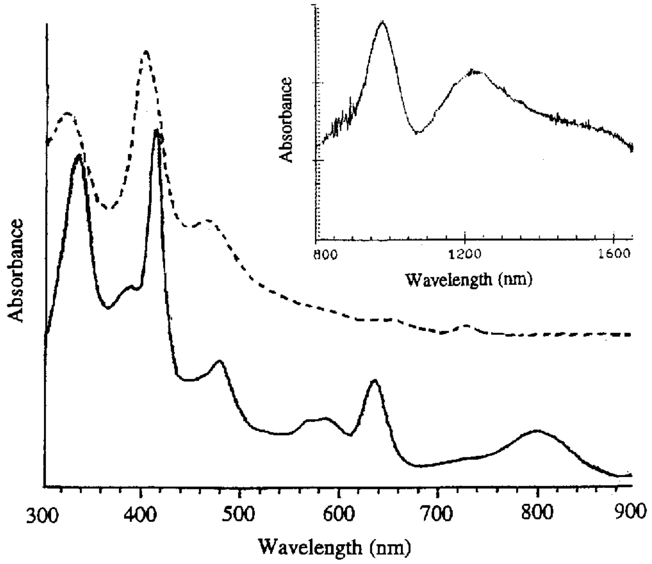


Figure 2. UV/Vis spectra of Li[Eu(Pc)(TPyP)] (**1a**) in MeOH (–) and Eu(Pc)(TPyP) (**2a**) in $CHCl_3$ (---); the inset shows the near-IR spectrum of **2a**



Apart from the four bands at δ = 11.13, 8.60, 7.75, and 7.44 which might be due to the pyridyl protons, the spectrum also displayed three very broad bands at δ = −7.84 (pyrrole), −17.35 (Pc), and −27.46 (Pc) which were tentatively assigned to the macrocyclic ring protons.

The UV/Vis and near-IR spectra of **2a** and **2b** are closely related to those of Ln^{III}(Pc)(TPP) and $[Ce^{IV}(Pc)(TPP)]^{+}$ and thus can be assigned accordingly[5a,5e,7]. As shown in Figure 2, the spectrum of **2a** displays the phthalocyanine Soret band (324 nm), porphyrin Soret band (403 nm), and a strongly attenuated Q band at 729 nm, which indicates the presence of phthalocyanine π radical anion $Pc^{\bullet -}$. The absorptions at 467 and 978 nm, which have counterparts in the spectra of $Ln^{III}(Pc)_2$[16], may be due to a hole in the a_{1u} orbital of phthalocyanine and can be assigned to the $2e_g$ (π) → a_{1u} (π) and $1e_g$ (π) → a_{1u} (π) transitions, respectively. In addition, there is a broad near-IR absorption at 1218 nm which is absent in **1a**. Such near-IR absorption is well-documented for many double-decker complexes containing phthalocyanine or porphyrin π radical anions and may be ascribed to an intramolecular ring-to-ring charge transfer transition[5e,7,16]. Both of the phthalocyanine and porphyrin Soret bands are shifted to the blue by ca. 9–10 nm from **1a** and **1b**, and the visible band at 467 nm and the two near-IR bands are all blue-shifted with respect to those of the TPP analogs Ln(Pc)(TPP) (Ln = Eu, Gd)[7].

The IR spectra of **2a** and **2b** exhibited a strong band at 1311 cm^{-1} which was shown as a diagnostic band for phthalocyanine π radical anion[5c]. The spectra of **1a** and **1b** did not show this band, but a medium band at 1328 cm^{-1} appeared which may be due to a nonoxidized dianionic phthalocyanine[7]. These results together with the electronic absorption data may suggest that the hole in compounds **2a** and **2b** more likely resides on the phthalocyanine macrocycle. The extent of hole delocalization in these complexes, however, is to be investigated as the nature of $TPyP^{\bullet -}$ remains elusive at this stage.

We thank the referees for helpful comments, Dr. *D. Chan* and *R. Lau* for measuring the FAB spectra, and *The Hong Kong Research Grants Council (RGC)* for support in purchasing the Bruker ARX 500 spectrometer through the RGC Central Allocation Scheme 1992. This work was supported by the *RGC* (Earmarked Grant: CUHK 311/94P) and *The Chinese University of Hong Kong* (Incentive Fund 94/95).

Experimental

Chloroform (Merck, GR grade), methanol (BDH, AR grade), and $(TPyP)H_2$ (Aldrich) were used as received. 1,2,4-Trichlorobenzene (Aldrich) was dried with 4-Å molecular sieves and distilled under reduced pressure. Chromatographies were performed on silica gel columns (Merck, 70–230 mesh). The compounds $Ln(acac)_3 \cdot nH_2O$ (Ln = Eu, Gd)[17] and $Li_2(Pc)$[18] were prepared according to the literature procedures. – NMR: Bruker WM 250 (250 MHz for ^{1}H), Bruker ARX 500 (500, 125.8, and 194.4 MHz for ^{1}H, ^{13}C, and ^{7}Li, respectively). For ^{1}H NMR, $CDCl_3$ as solvent, TMS as internal standard, [D$_5$]pyridine as solvent δ_H (the most upfield H) = 7.19; for ^{13}C NMR, [D$_5$]pyridine δ_C (the most upfield C) = 123.5; for ^{7}Li NMR, [D$_5$]pyridine as solvent, 23% aqueous LiBr (δ = 0) as external standard. – UV/Vis: Hitachi U-3300. – Near-IR: Hitachi U-3100. – IR: Nicolet 205. – FAB-MS: Bruker APEX 47e FT-ICR, 3-nitrobenzyl alcohol as matrix. – Elemental analyses: Microanalytical Department, Inorganic Chemistry Laboratory, Oxford or Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Li[Eu(Pc)(TPyP)] (**1a**): A mixture of 210 mg (0.43 mmol) of $Eu(acac)_3 \cdot nH_2O$ and 90 mg (0.15 mmol) of $(TPyP)H_2$ in 10 ml of

1,2,4-trichlorobenzene was refluxed under nitrogen for 6 h. The resulting dark cherry-red solution was cooled to room temp., then 120 mg (0.23 mmol) of $Li_2(Pc)$ was added. The whole mixture was refluxed for a further 12 h, then the volatiles were removed in vacuo, and the residue was chromatographed on a silica gel column with $CHCl_3$ as eluent. A small amount of unreacted $(TPyP)H_2$ and the triple-decker complex $Eu_2(Pc)_2(TPyP)$ were collected as the first fraction. Then the column was eluted with $CHCl_3$/MeOH (6:1) to give a mixture containing **1a** and Eu(acac)(TPyP), which were separated by repeated chromatography with $CHCl_3$/MeOH (20:1) as eluent. The solution containing the product was evaporated to give a dark violet solid which was dried in vacuo. Yield 91 mg (49%). – ^1H NMR ([D_5]pyridine, 250 MHz): δ = 11.50 (br. s, 4H, C_5H_4N), 10.73 (br. s, 8H, H_α), 10.51 (br. s, 4H, C_5H_4N), 9.01 (br. s, 4H, C_5H_4N), 8.60 (br. s, 8H, H_β), 7.75 (br. s, 8H, pyrH), 6.59 (br. s, 4H, C_5H_4N). – $^{13}C\{^1H\}$ NMR ([D_5]pyridine): δ = 180.1, 175.5, 160.0, 148.5, 147.7, 127.5 (C_β), 126.7, 120.7 (C_α), 109.1, 106.2, 93.9 (pyr*C*H). – $^7Li\{^1H\}$ NMR ([D_5]pyridine): δ = 2.56 (s). – IR (KBr): $\tilde{\nu}$ = 1328 cm^{-1} (Pc^{2}). – UV/Vis (MeOH): λ_{max} (lg ε) = 334 nm (4.67), 388 (sh), 412 (4.71), 477 (4.26), 584 (4.00), 635 (4.19), 794 (3.90). – MS (FAB): a cluster peaking at *m/z* 1281.21 (100%) {calcd. for $[^{153}Eu(pc)(TPyP)]^-$ 1281.28}. – $C_{75}H_{43}Cl_9EuLiN_{16}$ (**1a** · 3 $CHCl_3$) (1646.3): calcd. C 54.72, H 2.63, N 13.61; found C 54.66, H 3.03, N 14.39.

Li[Gd(Pc)(TPyP)] (**1b**): According to the method described above, 210 mg (0.43 mmol) of $Gd(acac)_3 \cdot nH_2O$ was treated with 90 mg (0.15 mmol) of $(TPyP)H_2$ and 120 mg (0.23 mmol) of $Li_2(Pc)$ to give **1b** and a trace amount of $Gd_2(Pc)_2(TPyP)$. Yield 87 mg (46%). – IR (KBr): $\tilde{\nu}$ = 1328 cm^{-1} (Pc^{2-}). – UV/Vis (MeOH): λ_{max} (lg ε) = 333 nm (4.81), 390 (sh), 411 (4.86), 476 (4.44), 568 (4.16), 583 (4.17), 637 (4.36), 804 (4.05). – MS (FAB): a cluster peaking at *m/z* 1286.13 (100%) {calcd. for $[^{158}Gd(Pc)(TPyP)]^-$ 1286.29}. – $C_{74.5}H_{42.5}Cl_{7.5}GdLiN_{16}$ (**1b** · 2.5 $CHCl_3$) (1591.9): calcd. C 56.21, H 2.69, N 14.08; found C 56.60, H 2.79, N 14.61.

Eu(Pc)(TPyP) (**2a**): A solution of 30 mg (0.023 mmol) of **1a** in 10 ml of $CHCl_3$ and 5 ml of MeOH was stirred at room temp. in air for 3 d. The color changed gradually from dark blue to dark brown. The volatiles were then removed in vacuo, and the residue was chromatographed with $CHCl_3$/MeOH (30:1) as eluent. A yellowish-brown band was developed which was collected and evaporated to give the product **2a** as a dark purple solid (19 mg, 65%), which could be recrystallized from $CHCl_3$/MeOH. The column was then eluted with $CHCl_3$/MeOH (6:1) to recover unreacted **1a** (10 mg, 35%). – ^1H NMR ($CDCl_3$, 500 MHz): δ = 11.13 (br. s, 4H, C_5H_4N), 8.60 (br. s, 4H, C_5H_4N), 7.75 (br. s, 4H, C_5H_4N), 7.44 (br. s, 4H, C_5H_4N), −7.84 (br. s, 8H, pyrH), −17.35 (br. s, 8H, Pc), −27.46 (br. s, 8H, Pc). – IR (KBr): $\tilde{\nu}$ = 1311 cm^{-1} ($Pc^{\bullet -}$). – UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 324 nm (4.78), 403 (4.90), 467 (4.51), 729 (3.28). – Near-IR ($CHCl_3$): λ_{max} = 978 nm, 1218. – MS (FAB): a cluster peaking at *m/z* 1281.46 (100%) {calcd. for $[^{153}Eu(Pc)(TPyP)]^+$ 1281.28}. – $C_{73}H_{41}Cl_3EuN_{16}$ (**2a** · $CHCl_3$) (1400.6): calcd. C 62.60, H 2.95, N 16.00; found C 61.93, H 2.69, N 16.08.

Gd(Pc)(TPyP) (**2b**): A solution of 30 mg (0.023 mmol) of **1b** in 10 ml of $CHCl_3$ and 5 ml of MeOH was stirred at room temp. in air for 3 d. The reaction, after chromatographic separation described above, gave **2b** (18 mg, 60%) and unreacted **1b** (10 mg, 33%). – IR (KBr): $\tilde{\nu}$ = 1311 cm^{-1} ($Pc^{\bullet -}$). – UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 323 nm (4.76), 402 (4.89), 465 (4.51), 728 (3.32). – Near-IR ($CHCl_3$): λ_{max} = 983 nm, 1210. – MS (FAB): a cluster peaking at *m/z* 1286.52 (100%) {calcd. for $[^{158}Gd(Pc)(TPyP)]^+$ 1286.29}. – $C_{73}H_{41}Cl_3GdN_{16}$ (**2b** · $CHCl_3$) (1405.9): calcd. C 62.37, H 2.94, N 15.94; found C 62.37, H 2.98, N 15.72.

☆ Dedicated to Professor *Shang-Wai Tam* on the occasion of his retirement from The Chinese University of Hong Kong.

[1] R. Guilard, J.-M. Barbe, A. Ibnlfassi, A. Zrineh, V. A. Adamian, K. M. Kadish, *Inorg. Chem.* **1995**, *34*, 1472–1481, and references therein.

[2] J.-J. André, K. Holczer, P. Petit, M.-T. Riou, C. Clarisse, R. Even, M. Fourmigue, J. Simon, *Chem. Phys. Lett.* **1985**, *115*, 463–466; P. Turek, P. Petit, J.-J. André, J. Simon, R. Even, B. Boudjema, G. Guillaud, M. Maitrot, *J. Am. Chem. Soc.* **1987**, *109*, 5119–5122; M. Maitrot, G. Guillaud, B. Boudjema, J.-J. André, H. Strzelecka, J. Simon, R. Even, *Chem. Phys. Lett.* **1987**, *133*, 59–62.

[3] M. M. Nicholson in *Phthalocyanines: Properties and Applications* (Eds.: C. C. Leznoff, A. B. P. Lever), VCH, New York, **1993**, vol. 3, pp. 71–117.

[4] J. W. Buchler, K. Elsässer, M. Kihn-Botulinski, B. Scharbert, *Angew. Chem.* **1986**, *98*, 257–258; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 286–287; J. W. Buchler, *Comm. Inorg. Chem.* **1987**, *6*, 175–191; J. W. Buchler, M. Nawra, *Inorg. Chem.* **1994**, *33*, 2830–2837.

[5] [5a] M. Lachkar, A. De Cian, J. Fischer, R. Weiss, *New J. Chem.* **1988**, *12*, 729–731. – [5b] D. Chabach, M. Lachkar, A. De Cian, J. Fischer, R. Weiss, *New J. Chem.* **1992**, *16*, 431–433. – [5c] K. M. Kadish, G. Moninot, Y. Hu, D. Dubois, A. Ibnlfassi, J.-M. Barbe, R. Guilard, *J. Am. Chem. Soc.* **1993**, *115*, 8153–8166. – [5d] T.-H. Tran-Thi, T. Fournier, A. De Cian, D. Chabach, R. Weiss, D. Houde, C. Pépin, L. Dao, *Chem. Phys. Lett.* **1993**, *213*, 139–144. – [5e] T.-H. Tran-Thi, T. A. Mattioli, D. Chabach, A. De Cian, R. Weiss, *J. Phys. Chem.* **1994**, *98*, 8279–8288.

[6] [6a] J. W. Buchler, J. Hüttermann, J. Löffler, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 71–77. – [6b] J. W. Buchler, A. De Cian, J. Fischer, P. Hammerschmitt, J. Löffler, B. Scharbert, R. Weiss, *Chem. Ber.* **1989**, *122*, 2219–2228. – [6c] J. W. Buchler, P. Hammerschmitt, I. Kaufeld, J. Löffler, *Chem. Ber.* **1991**, *124*, 2151–2159. – [6d] J. Jiang, K. Machida, G. Adachi, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1990–1992.

[7] D. Chabach, M. Tahiri, A. De Cian, J. Fischer, R. Weiss, M. El Malouli Bibout, *J. Am. Chem. Soc.* **1995**, *117*, 8548–8556.

[8] J. W. Buchler, H.-G. Kapellmann, M. Knoff, K.-L. Lay, S. Pfeifer, *Z. Naturforsch., Part B* **1983**, *38*, 1339–1345; J. W. Buchler, M. Kihn-Botulinski, J. Löffler, B. Scharbert, *New J. Chem.* **1992**, *16*, 545–553; G. A. Spyroulias, A. G. Coutsolelos, C. P. Raptopoulou, A. Terzis, *Inorg. Chem.* **1995**, *34*, 2476–2479.

[9] C.-P. Wong, R. F. Venteicher, W. DeW. Horrocks, Jr., *J. Am. Chem. Soc.* **1974**, *96*, 7149–7150; C.-P. Wong, *Inorg. Synth.* **1983**, *22*, 156–162.

[10] J. Jiang, K. Machida, E. Yamamoto, G. Adachi, *Chem. Lett.* **1991**, 2035–2038; G.-F. Liu, Z.-Q. Ma, X.-X. Liu, D.-M. Li, *Acta Chim. Sinica* **1993**, *51*, 791–795.

[11] M. Moussavi, A. De Cian, J. Fischer, R. Weiss, *Inorg. Chem.* **1986**, *25*, 2107–2108.

[12] J. A. Joule, K. Mills, G. F. Smith, *Heterocyclic Chemistry*, Chapman & Hall, London, 3rd ed., **1995**, pp. 3–4.

[13] G. E. Maciel, J. K. Hancock, L. F. Lafferty, P. A. Mueller, W. K. Musker, *Inorg. Chem.* **1966**, *5*, 554–557; Y. M. Cahen, P. R. Handy, E. T. Roach, A. I. Popov, *J. Phys. Chem.* **1975**, *79*, 80–85.

[14] [14a] C. Clarisse, M. T. Riou, *Inorg. Chim. Acta* **1987**, *130*, 139–144. – [14b] H. Konami, M. Hatano, A. Tajiri, *Chem. Phys. Lett.* **1989**, *160*, 163–167. – [14c] A. Germain, T. W. Ebbesen, *Chem. Phys. Lett.* **1992**, *199*, 585–589.

[15] J. W. Buchler, J. Löffler, *Z. Naturforsch., Part B* **1990**, *45*, 531–542.

[16] D. Markovitsi, T.-H. Tran-thi, R. Even, J. Simon, *Chem. Phys. Lett.* **1987**, *137*, 107–112.

[17] J. G. Stites, C. N. McCarty, L. L. Quill, *J. Am. Chem. Soc.* **1948**, *70*, 3142–3143.

[18] P. A. Barrett, D. A. Frye, R. P. Linstead, *J. Chem. Soc.* **1938**, 1157–1163.

[96016]