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Synthesis, spectroscopic characterisation and structure of the first chiral heteroleptic bis(phthalocyaninato) rare earth complexes†

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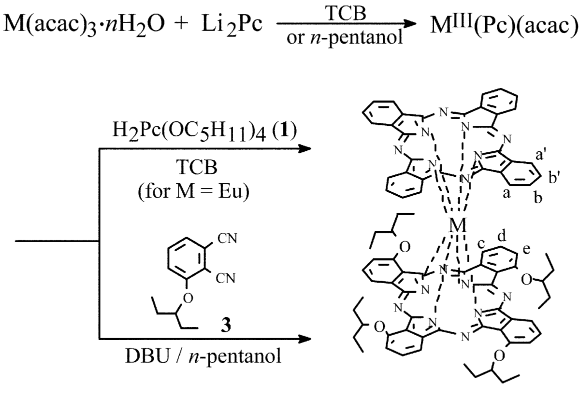
Treatment of $M^{III}(Pc)(acac)$ (M = Sm, Eu, Gd; Pc = phthalocyaninate; acac = acetylacetonate), generated *in situ*, with 3-(3-pentyloxy)phthalonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in *n*-pentanol affords racemic mixtures of the chiral double-deckers $M^{III}(Pc)[Pc(OC_5H_{11})_4]$ [$Pc(OC_5H_{11})_4$ = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninate], which have been spectroscopically and structurally characterised.

Apart from their usage as organic functional dyes, phthalocyanines also serve as versatile macrocyclic tetradentate ligands for a wide range of metals.[1] Complexation with large metal ions such as lanthanides leads to sandwich-type complexes which represent an important and useful class of advanced materials.[2] Their applications range from gas sensors, electrochromic displays and photoconductors to field-effect transistors. Chemical modification of the macrocyclic ligands has been investigated extensively with the goal of enhancing the performance of the materials and facilitating the fabrication process. While most of the studies focus on homoleptic sandwich compounds, heteroleptic analogues with mixed phthalocyaninato ligands remain scarce despite the fact that the use of more than one type of phthalocyaninato ligand can better tune the properties of the sandwich compounds.[3] The rarity is probably due to the shortage of convenient synthetic methods. We have recently reported a number of synthetic routes to heteroleptic phthalocyaninato and porphyrinato rare earth complexes.[4] We describe herein an extension of these methodologies to prepare the mixed double-deckers $M^{III}(Pc)[Pc(OC_5H_{11})_4]$ (M = Sm, Eu, Gd). Due to the C_{4h} symmetry of the $Pc(OC_5H_{11})_4$ ring and the sandwich-like structure, the resulting double-deckers exist as a pair of enantiomers, which co-crystallise in the monoclinic ($P2_1/n$) system. Simon and co-workers have briefly reported the chiral $Lu^{III}(Pc)(Nc^*)$ (Nc* = the C_s isomer of 1,2-naphthalocyaninate), the structure of which has been inferred from ^1H NMR data.[5] This communication reports the first structural characterisation of these novel chiral sandwich compounds.

Treatment of $Eu(acac)_3{\cdot}nH_2O$ with Li_2Pc in 1,2,4-trichlorobenzene (TCB) gave the half-sandwich complex $Eu^{III}(Pc)(acac)$, which further reacted *in situ* with the metal-free 1,8,15,22-tetrakis(3-pentyloxy)phthalocyanine (**1**)[6] to give the mixed double-decker $Eu^{III}(Pc)[Pc(OC_5H_{11})_4]$ (**2b**) in 29% yield (Scheme 1). Alternatively, we found that the precursor 3-(3-pentyloxy)phthalonitrile (**3**) can be used directly instead of the metal-free phthalocyanine **1**. Thus reaction of $Eu^{III}(Pc)(acac)$ with **3** in the presence of DBU in *n*-pentanol also led to the formation of **2b** in 21% yield. By using the same procedure, the samarium and gadolinium analogues **2a** and **2c** were also prepared in comparable yield (Scheme 1).[7] Interestingly, although cyclisation of 3-substituted phthalonitriles usually gives a mixture of four constitutional isomers (with D_{4h}, D_{2h}, C_{2v} and C_s symmetry) of tetra-α-substituted phthalocyanines,[8] only the double-deckers **2a–c**, which have a D_{4h} tetrasubstituted phthalocyaninato ligand could be isolated, while the other constitutional isomers were not detected. It seems that the half-sandwich template [M(Pc)] can have some control on the cyclisation and complexation processes.

Compounds **2a–c** were characterised by elemental analysis and various spectroscopic methods.[9] The MALDI-TOF and liquid secondary ion (LSI) mass spectra of **2a–c** showed an intense isotopic cluster due to the molecular ion, for which the isotopic pattern closely resembled the simulated spectrum. Due to the presence of unpaired electrons in one of the rings and the metal centre, NMR data for these complexes were difficult to obtain. However, upon addition of hydrazine hydrate, the compounds were reduced to the corresponding monoanions, in which both the macrocyclic ligands became diamagnetic.[4d] Well-resolved ^1H NMR spectra could be obtained for the samarium(III) **2a** and europium(III) **2b** analogues. Taking the spectrum of $\{Sm^{III}(Pc)[Pc(OC_5H_{11})_4]\}^-$ (ESI†) as an example, due to the C_4 symmetry of the molecule, the tetra-substituted phthalocyanine ring protons resonate at δ 7.68 (d), 7.52 (t) and 7.13 (d). Interestingly, the α protons of the unsubstituted Pc are no longer equivalent, giving two multiplets at δ 8.23–8.37 and 8.13–8.16. The β protons of the unsubstituted Pc give a multiplet at δ 7.62–7.65. Two well-resolved triplets at δ 1.06 and 0.97 were observed for the methyl protons of the 3-pentyloxy groups as a result of the sandwich-like structure, in which there is restricted rotation of these substituents. The above assignment was confirmed by a two-dimensional ^1H–^1H COSY experiment. Due to the strong paramagnetic character of the Gd^{III} centre, a satisfactory ^1H NMR spectrum of **2c** could not be obtained.

Fig. 1 displays the electronic absorption spectrum of $Gd(Pc)[Pc(OC_5H_{11})_4]$ (**2c**) recorded in $CHCl_3$. The spectrum shows a typical B band at 323 nm with a shoulder at the higher energy side. The slight splitting of this band has been observed previously for unsymmetrical bis(phthalocyaninato) metal com-



2a M = Sm
2b M = Eu
2c M = Gd

Scheme 1

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† Electronic supplementary information (ESI) available: ^1H NMR spectrum of $\{Sm^{III}(Pc)[Pc(OC_5H_{11})_4]\}^-$ in $CDCl_3$/DMSO-d_6 (1 : 1) in the presence of a few drops of hydrazine hydrate. See http://www.rsc.org/suppdata/cc/b3/b301139a/

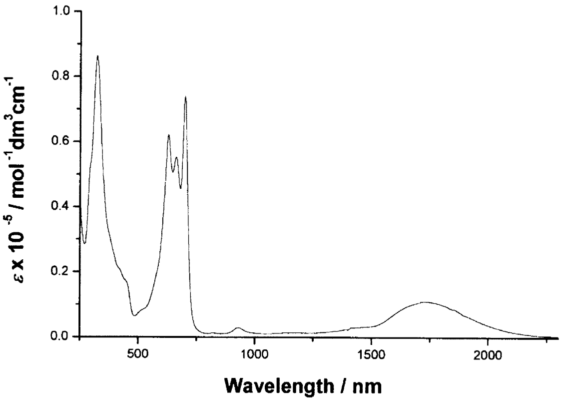

Fig. 1 Electronic absorption spectrum of Gd(Pc)[Pc(OC_5H_{11})$_4$] (**2c**) in $CHCl_3$.

plexes.[4a,c,10] The Q band is also split giving three strong absorptions at 628, 661 and 698 nm, probably due to a lowering of symmetry. The spectrum also shows a weak π-radical anion band at 930 nm together with a characteristic near-IR absorption at 1712 nm, which can be attributed to an intramolecular ring-to-ring charge transfer transition on the assumption that the hole resides mainly on one of the macrocyclic ligands.[2,3]

The molecular structures of the samarium(III) and europium(III) double-deckers **2a–b** were also determined by X-ray diffraction analyses. These represent the first heteroleptic bis(phthalocyaninato) metal complexes which have been structurally characterised. These chiral compounds crystallise in the monoclinic system with two pairs of enantiomeric double-deckers per unit cell.[11] Attempts to resolve the two enantiomers of **2b** by HPLC using a silica gel column coated with cellulose 2,3,6-tris(3,5-dimethylphenylcarbamate)[12] were not successful due to their limited solubility in hexane-containing solvent systems. Fig. 2 shows a perspective view of the structure of **2b**, in which the europium centre is octa-coordinated by the isoindole nitrogen atoms of the two phthalocyaninato ligands, forming a distorted square antiprism. The two N_4 mean planes are virtually parallel (dihedral angle = 1.3°) with a plane-to-plane separation of 2.842 Å. The europium atom lies almost in the centre {1.439 Å [from Pc(OC_5H_{11})$_4$] *vs*. 1.403 Å (from Pc)}. Like the structures of many double-decker complexes,[2,3] the two ligands are not planar and display a saucer shape.

In summary, we have reported the preparation, characterisation and the first structure determination of the novel chiral heteroleptic bis(phthalocyaninato) rare earth complexes M(Pc)[Pc(OC_5H_{11})$_4$] (M = Sm, Eu, Gd).

We thank Prof. Nagao Kobayashi for attempting the optical resolution of **2b**. Financial support from the National Science Foundation of China (Grant No. 20171028), National Ministry of Science and Technology of China (Grant No. 2001CB6105-04), Ministry of Education of China, The Science Foundation of Shandong Province (Grant No. Z99B03) and The Chinese University of Hong Kong is gratefully acknowledged.

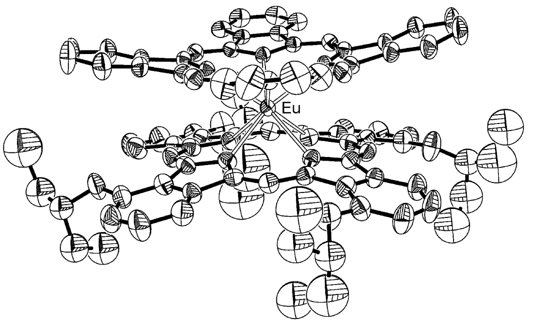

Fig. 2 Molecular structure of Eu(Pc)[Pc(OC_5H_{11})$_4$] (**2b**) showing the 30% probability thermal ellipsoids for all non-hydrogen atoms.

Notes and references

1 *Phthalocyanines – Properties and Applications*, C. C. Leznoff and A. B. P. Lever, eds., VCH, New York, 1989, **vol. 1**; 1993, **vols. 2 and 3**; 1996, **vol. 4**.

2 J. W. Buchler and D. K. P. Ng, in *The Porphyrin Handbook*, K. M. Kadish, K. M. Smith and R. Guilard, eds., Academic Press, San Diego, 2000, **vol. 3**, ch. 20; J. Jiang, K. Kasuga and D. P. Arnold, in *Supramolecular Photo-sensitive and Electro-active Materials*, H. S. Nalwa, ed., Academic Press, New York, 2001, pp. 113–210.

3 D. K. P. Ng and J. Jiang, *Chem. Soc. Rev.*, 1997, **26**, 433.

4 (*a*) J. Jiang, W. Liu, W.-F. Law, J. Lin and D. K. P. Ng, *Inorg. Chim. Acta*, 1998, **268**, 141; (*b*) J. Jiang, M. T. M. Choi, W.-F. Law, J. Chen and D. K. P. Ng, *Polyhedron*, 1998, **17**, 3903; (*c*) J. Jiang, J. Xie, M. T. M. Choi, Y. Yan, S. Sun and D. K. P. Ng, *J. Porphyrins Phthalocyanines*, 1999, **3**, 322; (*d*) J. Jiang, Y. Bian, F. Furuya, W. Liu, M. T. M. Choi, N. Kobayashi, H.-W. Li, Q. Yang, T. C. W. Mak and D. K. P. Ng, *Chem. Eur. J.*, 2001, **7**, 5059.

5 V. M. Negrimovskii, M. Bouvet, E. A. Luk'yanets and J. Simon, *J. Porphyrins Phthalocyanines*, 2001, **5**, 423.

6 K. Kasuga, M. Kawashima, K. Asano, T. Sugimori, K. Abe, T. Kikkawa and T. Fujiwara, *Chem. Lett.*, 1996, 867.

7 In a typical procedure, a mixture of M(acac)$_3$·nH$_2$O (M = Sm, Eu, Gd) (25 mg, 0.05 mmol) and Li_2Pc (30 mg, 0.06 mmol) in *n*-pentanol (4 cm^3) was heated at 120 °C under nitrogen for 8 h. The mixture was cooled to room temperature, then phthalonitrile **3** (50 mg, 0.23 mmol) and DBU (0.03 cm^3, 0.20 mmol) were added. After being refluxed for a further 12 h, the mixture was evaporated under reduced pressure and the residue was chromatographed on a silica gel column using $CHCl_3$ as eluent. Following two green fractions containing a small amount of $H_2Pc(OC_5H_{11})_4$ and M(Pc)$_2$, a blue band with the target heteroleptic double-decker M(Pc)[Pc(OC_5H_{11})$_4$] was developed which was collected and evaporated. The crude product was purified by repeated chromatography followed by recrystallisation from $CHCl_3$/MeOH giving black needles (*ca*. 20% yield).

8 C. Rager, G. Schmid and M. Hanack, *Chem. Eur. J.*, 1999, **5**, 280.

9 *Selected data* for **2a**: ^{1}H NMR ($CDCl_3$/DMSO-d$_6$, 3 drops of hydrazine hydrate) δ 8.23–8.37 (m, 4 H, H_a or $H_{a'}$), 8.13–8.16 (m, 4 H, H_a or $H_{a'}$), 7.68 (d, J = 7.5 Hz, 4 H, H_c), 7.62–7.65 (m, 8 H, H_b and $H_{b'}$), 7.52 (t, J = 7.5 Hz, 4 H, H_d), 7.13 (d, J = 7.5 Hz, 4 H, H_e), 4.48–4.52 (m, 4 H, OCH), 1.72–2.05 (m, 16 H, CH_2), 1.06 (t, J = 7.5 Hz, 12 H, CH_3), 0.97 (t, J = 7.5 Hz, 12 H, CH_3); MS (MALDI-TOF) an isotopic cluster peaking at *m/z* 1523.4 (calc. for MH$^+$ 1523.5); UV-Vis and near-IR ($CHCl_3$) [λ_{max}/nm (log ε)] 322 (5.24), 632 (5.12), 665 (5.07), 703 (5.09), 826 (5.07), 926 (5.21), 1855 (4.80); Anal. calc. for $C_{84}H_{72}N_{16}O_4Sm$: C, 66.38; H, 4.77; N, 14.74. Found: C, 65.82; H, 4.83; N, 13.86%.

For **2b**: ^{1}H NMR ($CDCl_3$/DMSO-d$_6$, 3 drops of hydrazine hydrate) δ 10.40–10.52 (m, 8 H, H_a and $H_{a'}$), 10.16 (d, J = 7.4 Hz, 4 H, H_c), 8.50–8.60 (m, 8 H, H_b and $H_{b'}$), 8.46 (t, J = 7.4 Hz, 4 H, H_d), 8.00 (d, J = 7.4 Hz, H_e), 6.1 (br s, 4 H, OCH), 2.29–2.34 (m, 16 H, CH_2), 1.26 (t, J = 7.4 Hz, 12 H, CH_3), 0.67 (t, J = 7.4 Hz, 12 H, CH_3); MS (LSI) an isotopic cluster peaking at *m/z* 1522.5 (calc. for MH$^+$ 1522.5); UV-Vis and near-IR ($CHCl_3$) [λ_{max}/nm (log ε)] 322 (5.16), 630 (5.01), 663 (4.98), 701 (5.03), 929 (3.62), 1138 (3.59), 1770 (4.20); Anal. calc. for $C_{84}H_{72}EuN_{16}O_4$: C, 66.31; H, 4.77; N, 14.73. Found: C, 65.67; H, 4.61; N, 14.25%.

For **2c**: MS (MALDI-TOF) an isotopic cluster peaking at *m/z* 1527.4 (calc. for MH$^+$ 1527.5); UV-Vis and near-IR ($CHCl_3$) [λ_{max}/nm (log ε)] 323 (4.94), 628 (4.79), 661 (4.74), 698 (4.87), 930 (3.47), 1712 (4.05).

10 A. Pondaven, Y. Cozien and M. L'Her, *New J. Chem.*, 1992, **16**, 711.

11 *Crystal data* for **2a**·$CHCl_3$·$2H_2O$: $C_{85}H_{77}Cl_3N_{16}O_6Sm$, M_w = 1675.33, monoclinic, space group $P2_1/n$ (no. 14), with a = 21.058(7), b = 17.615(6), c = 21.066(7) Å, β = 90.000(5)°, V = 7815.0(5) Å^3, D_c = 1.424 g cm^{-3}, Z = 4. The structure was solved by direct methods and refined by a full-matrix least-squares procedure using 12277 data to a conventional R value of 0.0572 (R_w = 0.1235).

For **2b**·$CHCl_3$: $C_{85}H_{73}Cl_3EuN_{16}O_4$, M_w = 1640.90, monoclinic, space group $P2_1/n$ (no. 14), with a = 21.0430(10), b = 17.4463(8), c = 21.0430(10) Å, β = 90.2620(10)°, V = 7725.3(6) Å^3, D_c = 1.411 g cm^{-3}, Z = 4. The structure was solved by direct methods and refined by a full-matrix least-squares procedure using 18666 data to a conventional R value of 0.0693 (R_w = 0.1777). CCDC reference numbers 202238 and 202446. See http://www.rsc.org/suppdata/cc/b3/b301139a/ for crystallographic data in CIF or other electronic format.

12 N. Kobayashi and T. Nonomura, *Tetrahedron Lett.*, 2002, **43**, 4253.