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New phthalocyanine complexes with rare-earth elements

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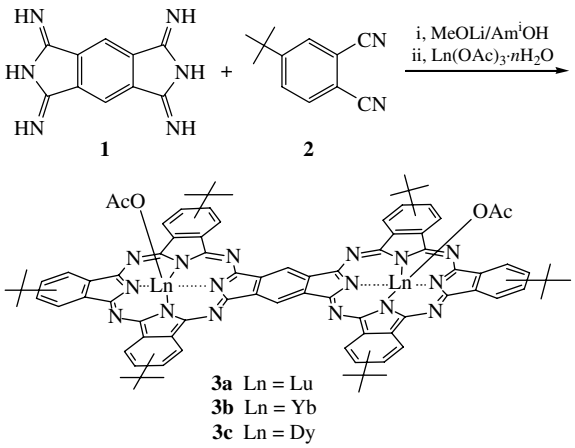
Phthalocyanine complexes involving rare-earth elements and a hexa-*tert*-butyl-substituted binuclear phthalocyanine, in which the macrocycles are linked *via* a common benzene ring, have been synthesised and spectroscopically characterised.

One-, two- and three-decked complexes of rare-earth elements with phthalocyanines are known. The absorption maxima of these compounds are observed at 630–690 nm.[1] It would be of considerable interest to shift this band to the near-IR region in order to create promising laser materials.[2,3] This purpose can be achieved by expanding the phthalocyanine π-system. The annelation of benzene rings with a transition to naphthalocyanine derivatives results in a bathochromic shift by about 100 nm.[4] An even greater shift of the *Q*-band can be achieved by coupling two or more phthalocyanine macrocycles *via* a common benzene ring.[5,6] While solving this problem, we developed a directed synthesis of new Lu, Yb and Dy complexes with a hexa-*tert*-butyl-substituted planar binuclear phthalocyanine of this type. We hope that not only the absorption maximum can be shifted to the near-IR region but also such complexes can be used as building blocks for synthesising supramolecular structures.

The mixed cyclization of bis(diiminoisoindoline) **1** and 4-*tert*-butylphthalodinitrile **2** in the presence of a base and rare earth salts resulted in new complexes **3a–c**.† Unfortunately, the method we developed previously to synthesise similar complexes with zinc and magnesium[5] did not provide even trace amounts of target complexes **3a–c**. In our opinion, the reason is that rare earth metal ions have larger ionic radii than Zn^{2+} and Mg^{2+} and hence are located above the plane of the phthalocyanine rings. As a result, the complexes formed when phthalocyanine macrocycles are assembled undergo almost total destruction under similar conditions; the fact that the corresponding free binuclear ligand can be isolated from the reaction mixture is evidence for this. We optimised our procedure (Scheme 1).†



Scheme 1 *Reagents and conditions*: i, MeOLi, Am^{i}OH, reflux, 2 h; ii, Ln(OAc)$_3$·nH$_2$O, reflux, 0.5 h.

Initially, the mixed cyclization of phthalogens **1** and **2** in the presence of lithium methoxide in isoamyl alcohol was carried out. The reaction was monitored by electronic spectroscopy. The main absorption band intensities in the spectra at 665 and 820 nm (THF) increased in time. Note that the amount of the base primarily affects the reaction depth. By increasing the amount of MeOLi considerably (above 20 equiv. with respect to compound **1**), it becomes possible to reach a maximum efficiency of the band at 820 nm corresponding to the binuclear lithium phthalocyanine complex. After the formation of the phthalocyanine lithium complex was complete, an excess of the corresponding rare earth salt was added to the reaction mixture without isolation of the Li complex. After short boiling, the electronic spectrum of the reaction mixture showed a bathochromic shift (by 10–12 nm) of the characteristic absorption bands observed previously for each rare earth complex. The resulting phthalocyanine products were separated on BioBeads SX-1 cross-linked polymer using THF as an eluent. The first fraction contained phthalocyanine olygomers as by-products, whereas target phthalocyanines **3a–c** were in the second fraction.

The structures of target binuclear phthalocyanines **3a–c** were confirmed by mass spectrometry. The MALDI-TOF mass spectra of binuclear complexes **3a–c** obtained using 2,5-dihydroxy-

† *Synthetic procedure*. MeOLi (445 mg, 11.71 mmol) was added to a solution of compounds **1** (100 mg, 0.47 mmol) and **2** (900 mg, 4.89 mmol) in isoamyl alcohol (30 ml). The mixture was refluxed for 2 h; then, Lu(OAc)$_3$·3H$_2$O (852 mg, 2.63 mmol) was added and refluxing was continued for 30 min. After the reaction was completed, the reaction mixture was cooled and the solvent was evaporated under reduced pressure. The solid residue was washed with aqueous methanol to remove non-phthalocyanine impurities and then separated by chromatography on BioBeads SX-1 (THF) to yield **3a**. Complexes **3b**,**c** were obtained from Yb(OAc)$_3$·4H$_2$O and Dy(OAc)$_3$·4H$_2$O, respectively, in a similar way. Compounds **3a–c** were characterised by electronic spectroscopy in the visible and near-IR regions and by MALDI-TOF mass spectrometry. The structure of diamagnetic complex **3a** was confirmed by ^{1}H NMR spectroscopy.

For **3a**: yield 26%. ^{1}H NMR ([$^2H_8$]THF) δ: 1.75 (s, 54H, Me), 6.45–7.20 (m, 18H, Ar), 9.45 (s, 2H, Ar). UV (THF, λ_{max}/nm): 358, 670, 704, 834. MS, *m/z*: 1940 ([M – 2OAc + 2DHB]$^+$), 3518 (2[M – 2OAc + DHB – Bu^t]$^+$).

For **3b**: yield 21%. UV (THF, λ_{max}/nm): 356, 673, 706, 837. MS, *m/z*: 1938 ([M – 2OAc + 2DHB]$^+$).

For **3c**: yield 23%. UV (THF, λ_{max}/nm): 353, 674, 707, 837. MS, *m/z*: 1917 ([M – 2OAc + 2DHB]$^+$).

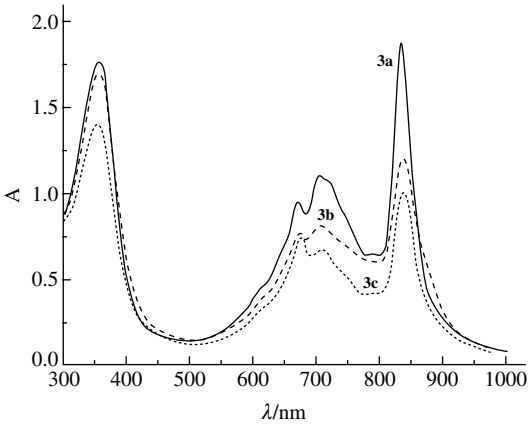


Figure 1 Electronic spectra of binuclear complexes **3a–c** in THF.

benzoic acid (DHB) as a matrix showed $[M - 2OAc + 2DHB]^+$ peaks instead of the molecular ion peaks ($[M^+]$) for all the three complexes. This result additionally confirms the ionic nature of the Ln–OAc bond established previously.[7] However, we failed to obtain the corresponding spectra in the absence of a matrix, presumably due to the low stability of ($[M]^{+\cdot}$) molecular cation radicals. For diamagnetic complex **3a**, the ^{1}H NMR spectrum obtained in addition to the mass spectrum revealed signals from all proton types. It was found that, unlike the corresponding magnesium complex,[5] the signals of aromatic protons in binuclear phthalocyanine **3a** are shifted upfield by about 2 ppm. On the other hand, the signals of *tert*-butyl groups are almost not shifted. Previously unknown complexes **3a–c** were also characterised by electronic spectroscopy (Figure 1); they have intense absorption in the near-IR region. The nature of the lanthanide does almost not affect the electronic spectrum and the position of the *Q*-band, similarly to rare earth monophthalocyanines.[7]

Note that the above type of phthalocyanine rare earth complexes is new, and no information on the syntheses and properties of such compounds is available. Binuclear planar complexes **3a–c** are unique building blocks for supramolecular structures owing to their mobile axial ligands.

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