Novel unsymmetrical monofunctionalized lutetium and dysprosium bisphthalocyanines with seven crown-ether units and one hexyl hexanoate side-group

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The synthesis of novel lutetium and dysprosium bisphthalocyanines bearing seven 15-crown-5 ether units and one hexyl hexanoate side group is described.

Crown-ether substituted monophthalocyanines were first synthesized in 1986.[1–3] Two types of complexes with alkali cations have been shown to occur; the smaller cations occupy the central cavity of the crown-ether whereas the bigger ones require two complexing sites and hence form sandwich-type complexes.[4–7] It has recently been demonstrated that 15-crown-5 ether substituted bisphthalocyanines lead to a nonlinear ion complexation with K^+ and Rb^+.[5]

The linking of phthalocyanine derivatives to the silica surface of the grid of a field effect transistor necessitates the presence of functional groups such as RCO_2H or ROH on the macrocycle. This has been achieved with crown-ether substituted monophthalocyanines.[8,9] The corresponding functionalized lutetium and dysprosium bisphthalocyanines **1a** and **1b** have been synthesized (Fig. 1).

Only a few studies have been devoted to unsymmetrical crown-ether phthalocyanine derivatives.[4,10] Unsymmetrical rare-earth bisphthalocyanines have also been described in a few publications.[11–14] In one case, a lutetium bisphthalocyanine with two different macrocycles has been reported.[15]

The synthesis of 15-crown-5 phthalonitrile **2** is described in the literature.[7,16] The phthalonitrile derivative **3** has been obtained in good yield starting from 2-methoxyphenol.[8,17] The unsymmetrical metal free monophthalocyanine **4** is obtained by reacting 3 moles of **2** with one mole of **3** in refluxing hexanol in the presence of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) and $MgCl_2$.

The crude mixture containing from zero to four hexanoate chains is treated, after evaporation of hexanol, with a mixture of DMF–aqueous HCl (5%) at 60 °C to give the corresponding metal free phthalocyanine derivatives. The DMF is evaporated and the pasty black–green residue is dissolved in chloroform and rinsed with distilled water. The mixture of the different crown-ether phthalocyanines is first purified by column chromatography on Al_2O_3 (CHCl$_3$–MeOH; 95 : 5; v/v) (yield 60%). The monofunctionalized phthalocyanine **4** is isolated *via* preparative thin layer chromatography (Al$_2$O$_3$; CHCl$_3$–MeOH; 97 : 3; v/v). Remaining impurities are removed by Soxhlet extraction with heptane and ethyl acetate. Final purification is achieved by reprecipitation from CH$_2$Cl$_2$–AcOEt mixtures (yield: 20%). It is noteworthy that the ethyl ester has been totally transformed into the corresponding hexyl ester during the synthesis of the phthalocyanine in hexanol. Phthalocyanines with broken crown-ether units have been obtained as side-products. They become the major product if CaCl$_2$ is used instead of MgCl$_2$. A cation assisted ring opening is therefore probable, leading to compound **6**.

Compound **4** is quantitatively transformed into the corresponding dianion using BuLi in DMSO.[18] The addition of
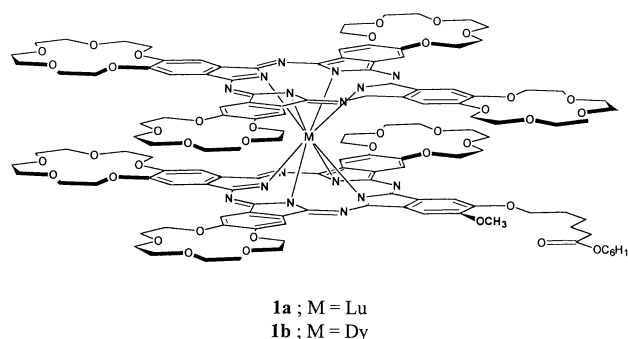

1a ; M = Lu
1b ; M = Dy

Fig. 1 Chemical formula of functionalized crown-ether substituted lutetium and dysprosium bisphthalocyanines. For reasons of clarity, the bisphthalocyanine rings are drawn in an eclipsed geometry whereas a staggered one is the most probable.
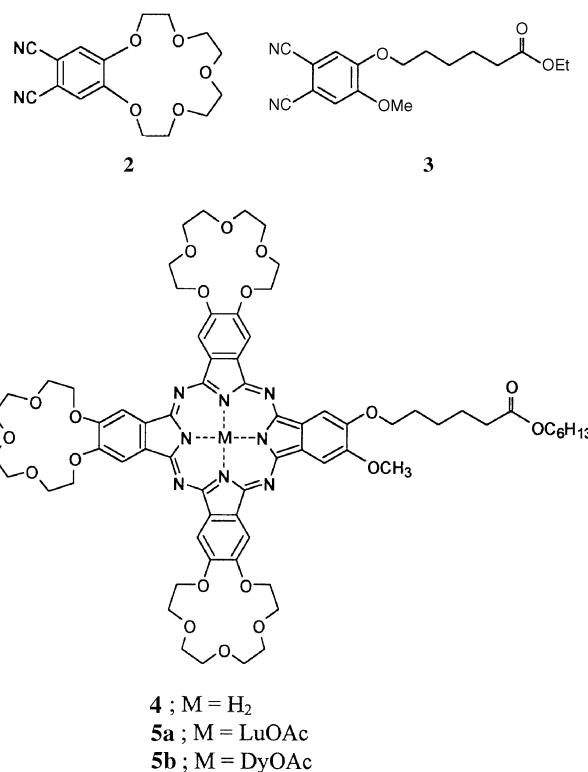

2   **3**

4 ; M = H$_2$
5a ; M = LuOAc
5b ; M = DyOAc

Fig. 2 The various monosubstituted monophthalocyanine derivatives synthesized

Lu(OAc)$_3$ [or Dy(OAc)$_3$] yields the substituted PcLuOAc **5a** and PcDyOAc **5b** after evaporation of DMSO and reprecipitation from Et$_2$O–AcOEt (9 : 1; v/v) mixtures (yield: 90%). **5a** and **5b** are stable in basic and neutral media but they partially give the corresponding bisphthalocyanines whenever the solids are heated over 50 °C.

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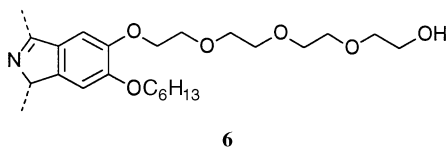
The target unsymmetrical bisphthalocyanines **1a** and **1b** are obtained by heating under reflux **5a** or **5b** with the 15-crown-5 substituted phthalonitrile in hexanol in the presence of DBU. Purification is carried out by (i) filtration on alumina (ii) preparative TLC (CHCl$_3$–MeOH; 97.5:2.5; v/v) (iii) filtration on Bio-Beads SX-3† and (iv) reprecipitation from Et$_2$O–AcOEt–CH$_2$Cl$_2$ (85:10:5; v/v/v) mixtures (yield: 10–20%). Other attempts have been made to synthesize **1a** by coupling two differently substituted phthalocyanines,[19,20] but only very low yields were obtained.

All physical data for **1a**, **1b**, **4** and **5a** are in good agreement with the proposed structures. Compound **5b** has been used as a crude intermediate product in the synthesis of **1b**, without further characterization. The visible absorption properties of **1a** and its reduced and oxidized forms are consistent with those previously described for related compounds.[5]

Work is in progress to study the complexation properties of **1a** towards alkali and alkaline-earth cations to check whether or not nonlinear ion binding processes can take place.

Experimental

Physical data were obtained for compounds **1a**, **1b**, **2** and **3** as follows.

Characterization of **1a**: neutral form: λ_{max}(CHCl$_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 666 (159 000), 603 (30 000), 476 (39 000), 367 (131 000), 291 (102 000); reduced form λ_{max}(CHCl$_3$, 10% hydrazine) 701 (66 000), 627 (164 000), 360 (176 000); oxidized form λ_{max}(CHCl$_3$ + bromine) 703 (54 000), 498 (84 000), 385 (116 000), 336 (79 000), 293 (120 000); ν_{max}(KBr disc)/cm^{-1} 1730 (ester CO); δ_H(300 MHz, CDCl$_3$, ~5.10^{-3} M) 0.8, 1.2, 1.5, 1.8, 1.9, 2.1, 2.4, 3.4–4.3 (broad peaks) (the aromatic protons, OCH$_2$, OCH$_3$ linked to the macrocycle are not seen); MS (MALDI-TOF) (high resolution) Found: m/z 2775 with correct isotopic distribution (calc. 2775.7) (Found: C, 57.37; H, 5.73; N, 7.54; Lu 5.70%. Calc. for C$_{133}$H$_{154}$O$_{39}$N$_{16}$Lu: C, 57.55; H, 5.59; N, 8.07; Lu 6.30%).

Characterization of **1b**: ν_{max}(KBr disc)/cm^{-1} 1725 (ester CO); MS (MALDI-TOF) (1st exp.) Found: m/z 2768.3 (calc. 2763.3) (The difference is due to calibration) (2nd exp.) (MALDI-TOF, high resolution): 2764 (internal calibration) with correct isotopic distribution) (Found: C, 57.10; H, 5.66; N, 7.88; Dy 6.10. Calc. for C$_{133}$H$_{154}$O$_{39}$N$_{16}$Dy: C, 57.81; H, 5.62; N, 8.11; Dy 5.88%).

Characterization of **4**: λ_{max}(CHCl$_3$)/nm (ε/dm^3 mol^{-1} cm^{-1}) 700 (153 000), 662 (124 000), 644 (51 000), 600 (27 000), 422 (36 000), 349 (84 000), 295 (56 000); ν_{max}(KBr disc)/cm^{-1} 3386 (br), 3296 (shp) (NH), 1731 (ester CO); δ_H(300 MHz, CDCl$_3$, ~3.10^{-3} M, 50 °C) −3.4 (br, 2 H), 0.9 (t, 3 H), 1.4 (m, 6 H), 1.8 (m, 2 H), 1.9 (m, 2 H), 2 (m, 2 H), 2.3 (m, 2 H), 2.6 (t, 2 H), 4 (br, 24 H), 4.2 (t, 2 H), 4.3 (br, 12 H), 4.4 (s, 3 H), 4.5–4.6 (br, 14 H), 8.0, 8.1, 8.2 (d, d, s, 8 H); MS (MALDI-TOF) Found: m/z 1333.2 (calc. 1329.5) (calibration: see above). Peaks corresponding to M$_2^+$ (2663.5) and M$_3^+$ (3999.4) are also observed. MS CI

(NH$_3$) 1329 with correct isotopic distribution (Found: C, 61.64; H, 6.37; N, 8.25. Calc. for C$_{69}$H$_{84}$O$_{19}$N$_8$·H$_2$O: C, 61.50; H, 6.43; N, 8.32%).

Characterization of **5a**: neutral form; λ_{max}(CHCl$_3$) 679 (119 000), 614 (23 000), 356 (62 000), 291 (40 000); oxidized form λ_{max}(CHCl$_3$ + bromine) 826 (10 000), 728 (13 000), 537 (19 000), 403 (22 000), 355 (32 000), 284 (47 000); ν_{max}(KBr disc)/cm^{-1} 1724 (br, ester and acetate CO); δ_H(300 MHz, CDCl$_3$–CD$_3$OD, ~5.10^{-3} M) 0.6 (t), 1.1 (br), 1.4 (t), 1.5 (br), 1.7 (t), ~1.9, 2.2 (t), 2.8 (br), 3.2 (s), 3.6 (br), 3.9 (m, br), 4.2 (br), 4.5 (br), 8.5–8.8 (br); MS (MALDI-TOF) Found: m/z 1691 [calc. 1502.4 + 189.17 = 1691.6 for s-PcLuX where X is one molecule coming from the matrix (α-cyano-4-hydroxycinnamic acid)] [Found: C, 52.11; H, 5.52; N, 6.98; Lu, 10.11. Calc. for C$_{71}$H$_{85}$O$_{21}$N$_8$Lu·4H$_2$O (the acetate moieties are included): C, 52.20; H, 5.74; N, 6.86; Lu, 10.71%].

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† Porous styrene–divinylbenzene copolymer with 3% crosslinkage (exclusion limit range = 2000 daltons for beads fully swollen in benzene).