Letter

Ionoelectronics: synthesis and surface grafting of an unsymmetrical lutetium bisphthalocyanine bearing four crown-ether moieties and four hexanoic acid side chains

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The synthesis of an unsymmetrical lutetium bisphthalocyanine for ionoelectronics is reported.

Ionoelectronics[1–4] uses metallic (or molecular) ions to process and store chemical information. It has been demonstrated[1,3] that strong positive cooperative complexation processes (nonlinear effects) are required. However, in order to be addressable, the molecular systems cannot be used in isotropic solutions but must be organized on a two-dimensional substrate. A bisphthalocyanine lutetium derivative unsymmetrically substituted with four crown-ether moieties on one macrocycle and four hexanoic acid side chains on the other have been synthesized (Fig. 1). The target compound **1b** is first grafted on a surface and it then furnishes an anchoring point for the formation of cation-induced pillar-like aggregates.

Only a few papers concern the synthesis of unsymmetrical bisphthalocyanine derivatives.[5–8] Multifunctionalized compounds which enable the grafting of substrates while maintaining the macrocyclic planes approximately parallel to the surface have, as far as we know, never been described. A monofunctionalized lutetium bisphthalocyanine has already been described by our group.[9] The preparation of 4,5-dicyanobenzo-15-crown-5 (**2**) has been previously described.[10–12] The 1-methyl-6-(2-methoxy-4,5-dicyano)phenoxyhexanoate (**9**) has been synthesized in our laboratory[13] but a simpler chemical pathway has been found in which ethyl 6-bromohexanoate was directly reacted with the phthalonitrile derivative (**8**) in the presence of KOH. The previously reported protection (and deprotection) of the phenoxy group[13] has not been found to be necessary.

The phthalocyanine derivative (**3**) abbreviated as $(15C5)_4PcM$ was obtained from 4,5-dicyanobenzo-15-crown-5 (**2**) The magnesium complex thus obtained was demetallated in a DMF–aqueous HCl mixture. After purification over column chromatography, the desired product was precipitated with pentane from a chloroform solution and characterized (**4**) (yield: 22%). The corresponding lutetium acetate monophthalocyanine complex (**5**) was prepared by (i) dissolving the metal-free derivative in DMSO (180 °C), (ii) adding at rt a solution of butyllithium in hexane until the reaction mixture turns into a bluish colour, (iii) finally adding an excess of lutetium acetate. The crude $(15C5)_4PcLuX$ (**5**) (X = OAc) was precipitated from a chloroformic solution with pentane.

The unsymmetrical bisphthalocyanine derivative **1a** was obtained by treating the crude $(15C5)_4PcLuX$ (**5**) with the substituted phthalonitrile (**9**). Several preparative thin-layer chromatographies over neutral alumina afforded a dark powder in 16% yield. Microanalysis, mass spectrometry, infrared and UV/VIS spectra were in agreement with the proposed structure. Hydrolysis of the hexyl ester into the corresponding acid was achieved under reflux in methanol containing an aqueous solution of sodium hydroxide. Precipitation from $CHCl_3$–pentane mixtures gave the tetracarboxylic acid derivative (**1b**) in 65% yield; this compound was characterized by mass spectrometry and UV/VIS spectroscopy.

Trimethoxysilylpropylmethacrylate was then reacted with the surface silanol groups of silica glass.[14] The functionalized surface was in turn photocopolymerized with hydroxyethylmethacrylate to give a *ca.* 1 μm thick membrane (abbreviated polyHEMA) bearing hydroxy groups.

The membrane-coated glass slide was dipped for 2 min into a solution of **1b** (10 mg of **1b** in 2 ml $CHCl_3$–MeOH 9 : 1). The coated glass slide was transferred into a solution of dicyclohexylcarbodiimide (DCC) in toluene. The deposited phthalocyanine layer is not soluble in this medium. However, DDC in solution ensures a covalent linking between the tetracarboxylic acid phthalocyanine derivative and the hydroxy groups of the grafted membrane. The surface density of the grafted phthalocyanine molecules can be roughly estimated

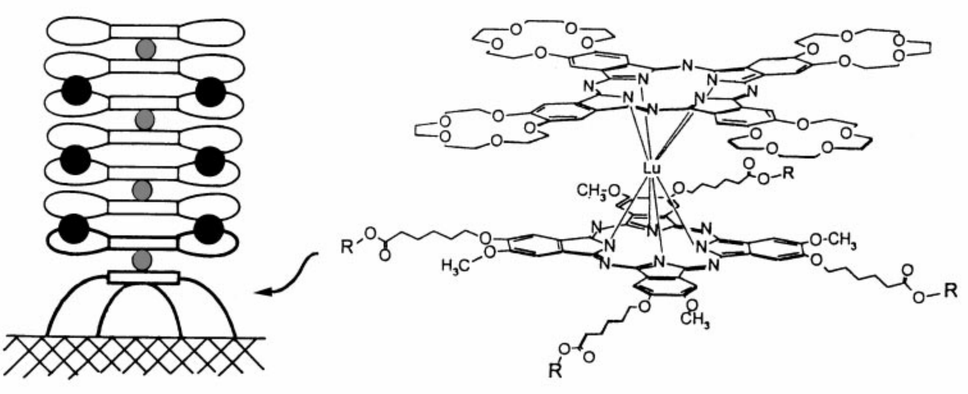

Fig. 1 Schematic representation of the formation of a pillar-like aggregate (see ref. 4) anchored on a surface *via* an unsymmetrically substituted bisphthalocyanine (compound **1a**, R = n-C_6H_{13} ; **1b**, R = H)

from the absorbance spectrum of the layer. A value of 7×10^{13} molecular units per cm^2 is thus found corresponding to 150 $Å^2$ per molecule (assuming a strict two-dimensional binding). This last value is situated between the area corresponding to an unsubstituted phthalocyanine macrocycle (*ca.* 125 $Å^2$) and that determined by X-ray crystallography for $(15C5)_4PcM$ (400 $Å^2$).[15]

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