Iono-electronics: Crown Ether Substituted Lutetium Bisphthalocyanines

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A lutetium bisphthalocyanine substituted with 15-crown 5 moieties is synthesized and thoroughly characterized; large alkali ions induce the formation of aggregates *via* a positive cooperative effect.

The term 'iono-electronics'[1] refers to the treatment and storage of information where the active species is a metallic or molecular ion.

Lutetium bisphthalocyanine (Pc_2Lu) is the first example of an intrinsic molecular semiconductor.[2,3] This unit was already known for its electrochromic properties.[4] The substitution of Pc_2Lu with crown ether moieties allows the material to be intrinsically semiconductive, electrochromic and possess ion binding ability. Our group[5] has already studied thin films of $\{[(15C5)_4Pc]_2Lu\}$ **1** (Fig. 1) by cyclic voltammetry. These studies showed well-defined voltammograms and long-term stability under reduction–oxidation cycling.[5] In this communication, we present a modified synthetic procedure yielding a purer product and a thorough characterization of **1**.

The complexation properties of **1** with alkali ions have also been studied, **1** shows a positive cooperative effect in the ion-binding process. Such a phenomenon has been shown to be the key parameter for making iono-electronics networks.[1]

Lutetium bisphthalocyanine with aza-crown ether substituents has been independently reported.[6]

1 was obtained by refluxing in hexan-1-ol 4,5-dicyanobenzol5C5[7] (3.14 mmol) with $Lu(OAc)_3 \cdot 3H_2O$ (0.392 mmol) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.57 mmol) under argon. Purification was achieved by (*i*) column chromatography over neutral alumina (elution gradient $CHCl_3$: EtOH from 100 : 0–97 : 3 v : v) (*ii*) a preparative TLC (neutral alumina; eluent $CHCl_3$: EtOH 95 : 5 (v : v); $R_f = 0.8$). **1** was finally recrystallized from a mixture CH_2Cl_2: *n* pentane (10 : 3 v : v) to afford a green powder in 19% yield.† Elemental analysis and ^1H NMR (broad peak at δ 1.9) show the presence of approximately four water molecules per molecule of **1**. This indicates that two macrocycles are involved in the complexation of one water molecule. No aggregation is detectable by UV–VIS spectroscopy.

The ion complexation properties of **1** have been determined by UV–VIS spectroscopy in $CHCl_3$. The addition of alkali ion picrates influences the Q-band of the phthalocyanine subunit (666 nm) depending on the nature of the cations (Fig. 2).

The smallest cations (Li^+, Na^+) do not alter the Q-band beyond a 1 : 1 ratio $[M^+]$: [**1**]. ^{13}C NMR spectra however indicate that 8 Na^+ ions are complexed within the molecular unit and that the exchange rate of the cations between occupied and metal-free macrocycles is fast on the NMR time-scale ($v_{ex} >> 570\ s^{-1}$).

The association constants were evaluated by the extraction of aqueous alkali picrates with chloroformic solutions of **1**.[8] By assuming negligible interactions between the eight different binding sites, it is found that $K(Li^+) = 5.8 \times 10^4\ dm^3\ mol^{-1}$ ($-\Delta G_0 = 27.2\ kJ\ mol^{-1}$) and $K(Na^+) = 39.5 \times 10^4\ dm^3\ mol^{-1}$ ($-\Delta G_0 = 31.9\ kJ\ mol^{-1}$).‡

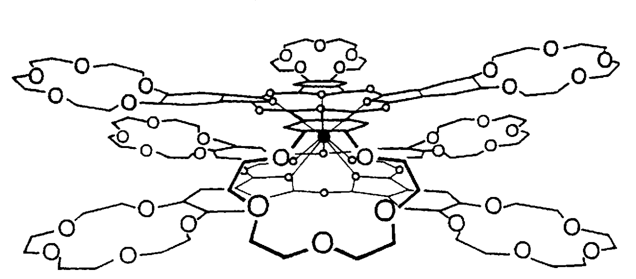

Fig. 1 Chemical representation of lutetium bisphthalocyanine substituted with 15-crown 5 subunits $[(15C5)_4Pc]_2Lu$ (**1**)

The other cations lead to very different results. A larger decrease in the apparent molar extinction coefficient§ of the Q-band is seen for K^+ and Rb^+. Where there is a large excess of ions, the Q-band does not completely vanish as it is the case for $(15C5)_4PcCu$[9,10] where dimeric species are formed. However, solutions and thin films of **1** show no blue shift of the optical absorption spectra contrary to $(15C5)_4PcCu$.

The ratio (4K^+ : **1**) at which a plateau value is obtained when the ion concentration is varied indicates that columnar type aggregates must be formed since intramolecular complexation involving two crown ether subunits is hardly conceivable. The extraction shows a strong complexation of the K^+ ion.‡ However, further calculation of the corresponding association constant cannot be carried out because of the numerous equilibria involved. It may nevertheless be assumed that all added ions are complexed at ratios below the saturation point corresponding to 4K^+ : **1** (Fig. 2). The shape of the titration curve then clearly demonstrates that a positive cooperative ion complexation process must take place. Indeed, two routes are conceivable to form aggregates (Fig. 3).

In the non-cooperative process, mixtures of many different ion complexes are randomly formed. A linear decrease of the free ligand concentration as the concentration of cations increases is therefore not expected. If strong intramolecular ion–ion repulsion occurs, 0.5M^+ : **1** aggregates should first appear and the breakpoint would be observed at this ratio. On the contrary, the discontinuity is obtained at 4K^+ : **1** and the slope is constant up to this point: in consequence, the four complexation sites of the dimer are occupied by metallic ions before further aggregation can occur since the variation of the apparent extinction coefficient reflects the concentration of the monomeric species.

This positive cooperative effect is not unexpected since the local concentration of the crown ether subunit is enhanced within the dimer as compared to the bulk solution.[11] The ratio

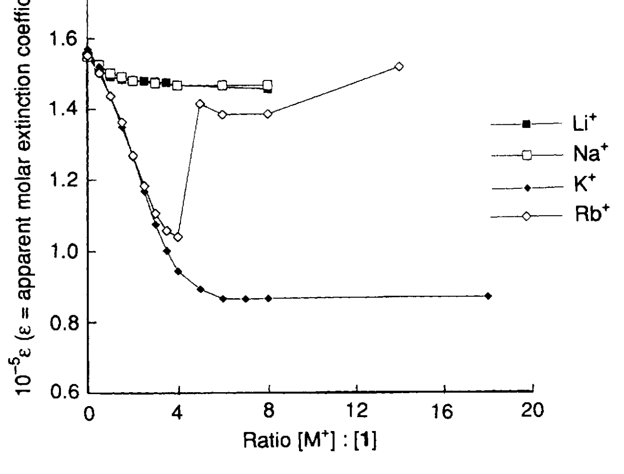

Fig. 2 Apparent molar extinction coefficient of the Q-band of **1** as a function of the ratio $[M^+]/[\mathbf{1}]$. In a $CHCl_3$ solution of **1** ($10^{-5} \times$ mol dm^{-3}) was added the picrate salt (MPic) dissolved in MeOH (2×10^{-3} mol dm^{-3}).

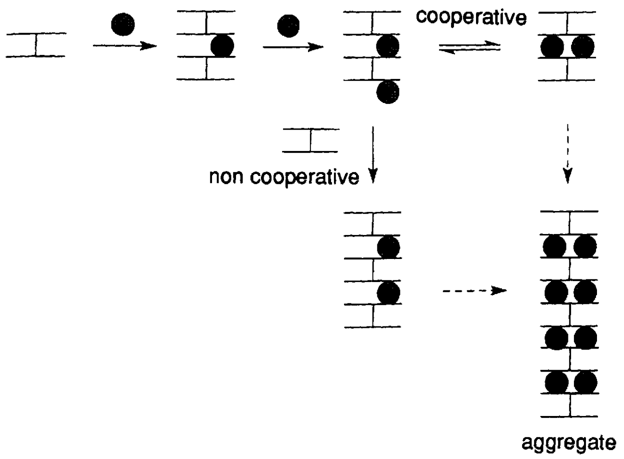

Fig. 3 Schematic representation of the two possible ways for the formation of aggregates. For simplicity reasons, only four out of the eight binding sites have been figured.

of the intramolecular over the intermolecular probability of complexation may be estimated *via* a previously established equation.[11,¶] A value of the order of 100 is found in this way under our conditions.

By using rubidium picrate, the same feature is noted up to a ratio of $4Rb^+ : \mathbf{1}$, but the spectrum of the monomeric species is partly restored by further additions of salts. The formation of complexes of stoichiometries higher than 4 : 1 indeed necessitates the dissociation of the aggregates.

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Footnotes

† **1**: MS (FAB) *m/z*: 2721 (M^+). IR (KBr) 3071, 2860, 1602, 1498, 1450, 1400, 1357, 1323, 1276, 1127, 1102, 1056, 934, 855, 756 cm^{-1}. UV-VIS ($CHCl_3$): ε_{290} 102 000, ε_{367} 132 000, ε_{476} 38 400, ε_{602} 30 200, ε_{666} 165 000; near IR ($CHCl_3$): ε_{910} 6000, ε_{1390} 16 000.

‡ [extracted picrate]/[**1**]: Li^+, 0.065; Na^+, 0.496; K^+, 0.286; Rb^+, 0.094; Cs^+, 0.031, $CHCl_3$ phase [**1**] = 3.8×10^{-4} mol dm^{-3}. Aqueous phase [MPic] = 10^{-2} mol dm^{-3}.

§ The apparent molar extinction coefficient is given by: $(A_0–A)/1C$, $I = 1$ cm (cell length), C = concentration of the dye, A_0 = absorbance of the monomeric species, A = observed absorbance.

¶ $v = k(d_{AB})^{-n}N_{AB}$ v = kinetic of the reaction $A + B \rightarrow C$. d_{AB} = mean distance between A and the closest B reactant. N_{AB} = number of couples A–B per unit of volume. n = dimensionality of the reaction medium.

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