

Substituent and Asymmetry Effects on Lutetium Bisphthalocyanines : from the Calculation of the Electron and Spin Repartitions to the Physicochemical Studies.

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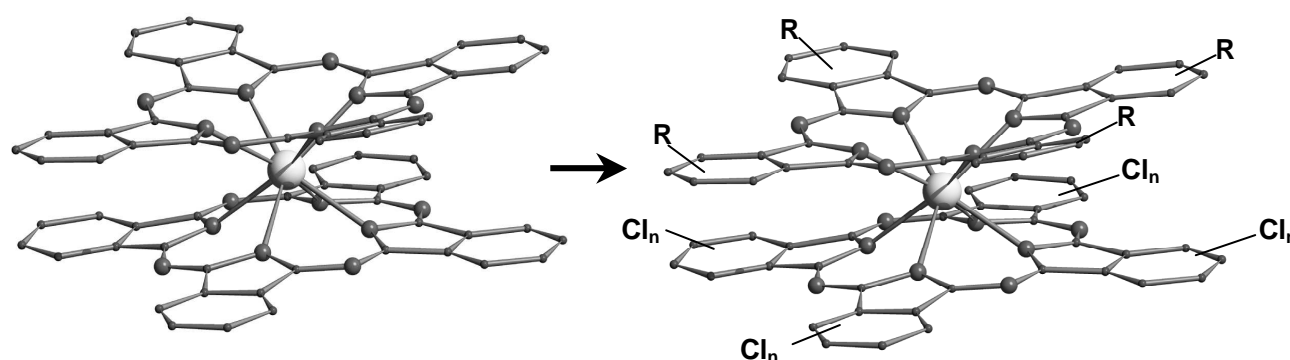


Figure 1 : From the Ln^{3+} bisphthalocyanine to the asymmetrical complexes.

The lanthanide bisphthalocyanines are sandwich complexes of Ln^{3+} with two phthalocyanine ligands, one of the two macrocycles being oxidized to the $\text{Pc}^{\cdot-}$ state: there is one unpaired electron in the molecule, which is a neutral radical. However, this electron is delocalized on both the phthalocyanine rings which cannot be distinguished, when the two macrocyclic units are identical. Our aim has been to create asymmetry in the molecule and to study its influence on the repartition of the electron, by substituting electron withdrawing groups on one of the phthalocyanines and donors on the other. A series of lutetium bisphthalocyanines has been synthesized, with four *t*-butyl groups, or eight -OR substituents, on one macrocycle and four to sixteen -Cl atoms on the other (Figure 1).

The molecular orbital calculation (DFT) reveals that the charge and spin repartitions become unsymmetrical : for the $[(\text{Bu})_4\text{Pc}]\text{Lu}[(\text{Cl})_{16}\text{Pc}]$ derivative, 62% of the charge of the π electrons are on the Cl-substituted phthalocyanine, while the spin of the unpaired electron resides mainly on the other macrocycle (68 %) ; as a consequence, this molecule is highly dipolar ($\mu_{\text{calc}} = 5.35$ D), when the symmetrical complexes have no dipole moment. The real dipole moments are currently under measurement, in order to confirm the theoretical calculations (Figure 2).

Raman and IR spectroscopies, which have been used for the study of heteroleptic complexes of Ln^{3+} with one phthalocyanine and one porphyrin, failed to reveal the asymmetry of the bisphthalocyanines complexes.

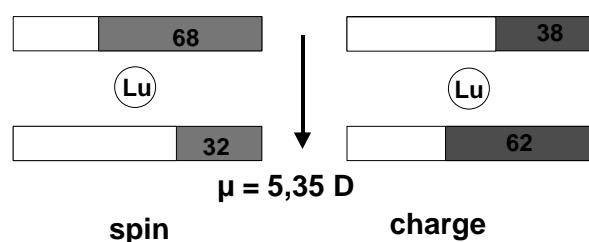


Figure 2 : Repartition of Mulliken charge and spin density for $[(\text{Bu})_4\text{Pc}]\text{Lu}[(\text{Cl})_{16}\text{Pc}]$.

However, the presence of the two different phthalocyanines induces modifications of the complexes, apparent from the evolution of their physicochemical properties as shown by EPR and UV-vis spectroscopies.

The most impressive sign is visible on the voltammograms which prove, not only that a dimer forms in solution at room temperature, but that the one-electron oxidized dimer is fully stable (Figure 3); this compound has been prepared, electrochemically and chemically.

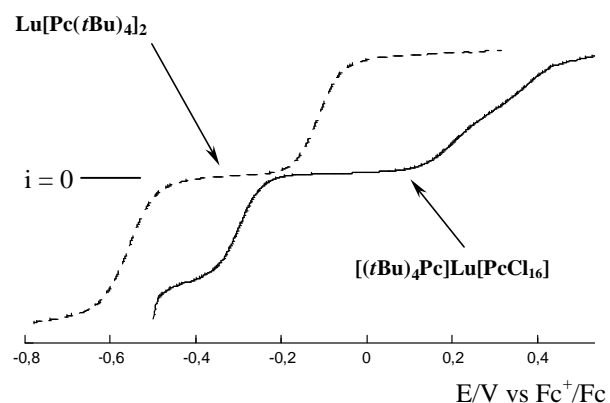


Figure 3 : Voltammetry at a rotating Pt electrode ($N = 500$ rpm, $v = 5$ mV s^{-1}) of solutions in CH_2Cl_2 (Bu_4NPF_6 0.1 M).

The lutetium bisphthalocyanines are mixed valence compounds, the two centers being the π macrocycles having identical redox states in the symmetrical molecules (0.5^+) ; there is a fast electron exchange between the two sites. Asymmetry modifies charge and spin repartitions, which causes a strong dimerization process, probably through dipole interactions.