Charge transfer complexes between carbazole and lutetium bisphthalocyanine

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Received (in Strasbourg, France) 16th February 2001, Accepted 28th May 2001
First published as an Advance Article on the web 1st August 2001

Donor–acceptor complex formation has been shown to occur between carbazole, an electron donor, and lutetium bisphthalocyanine, an acceptor, through π–π interactions. New transitions due to complexation between the two molecules are observed in the near IR, at about 1500 nm, in the solid state (KBr matrix); from the evolution of the absorption bands with the experimental conditions, it appears that more than one charge transfer complex exists. The nature of the molecular orbitals of the donor and acceptor molecules could explain why these interactions are weak.

Organic photoconductors have attracted considerable attention during the past years due to the need for effective and cheap materials for xerography, for the development of photocopiers and laser printers.[1] In a photocopier, the photoconductor is usually sensitive to light in the visible spectral range. For laser printing, the photoconductor must react to 750–850 nm light because the commonly used laser diode emits at 780 nm. For some industrial applications, such as holography, optical commutation or optical valves, it might be useful to obtain photogenerator materials active in the near IR. The first commercial organic photoconductor was based on the association of an electron donor, poly(*N*-vinylcarbazole) (PVCz), and an electron acceptor, 2,4,7-trinitrofluorenone (TNF), which give a charge transfer complex (CTC); this material is active up to 650–700 nm.[2]

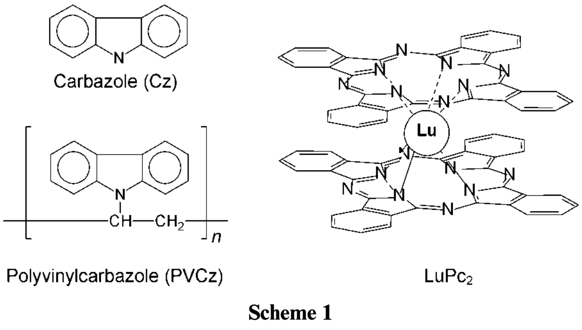
Phthalocyanines have been used as electron acceptors or donors for many applications.[3] However, they are much better electron donors than acceptors because the macrocyclic ring, Pc^{2-}, is more easily oxidized than it is reduced. In contrast, the lanthanide bisphthalocyanines ($LnPc_2$), which are double-decker complexes of trivalent rare earth cations, and also LiPc, the oxidized form of lithium phthalocyanine,[4] are much better acceptors than the other phthalocyanines, because they bear one oxidized macrocycle, $Pc^{\cdot-}$. LiPc is reduced at about 0.2 V whereas the reduction potential of Li_2Pc is about -1.5 V (*vs.* SCE in THF–chloronaphthalene).[5,6] $LuPc_2$ accepts an electron at -0.4 V (*vs.* Fc^+/Fc in CH_2Cl_2).[7,8] These rare earth complexes have another very interesting feature, they strongly absorb light in the visible domain of the spectrum and the near IR.[8] Moreover, various substituents can be grafted on the macrocycle, and this could be used to tune up the power of the acceptor as well as to modify other physico-chemical properties, such as the solubility of the compounds. Lutetium sandwich complexes have already been used in electronic and optoelectronic devices where the easy generation of stable charged species is essential.[4,9] The lanthanide bisphthalocyanines are thus very promising for the photogeneration of charges, for example as electron acceptors associated with PVCz.

Different models have been suggested for the charge photogeneration processes in photoconductors; one, which is frequently used, has been proposed by Melz[10] and relies on Onsager's theoretical work.[11] For the PVCz–TNF pair, Melz has shown that the free charge carriers are produced by the dissociation of an ion pair formed by thermalization of an excited charge transfer complex (CTC*). This intermediate is generated by the irradiation of a complex, formed by the donor (D) and the acceptor (A), in the fundamental state.[10] However, in other photoconducting materials, the excited complex CTC* could result from the meeting of one excited species, D* or A* produced by light absorption, with the other one in its ground state; another way is the excitation of a CTC formed in the ground state. These possibilities must be considered when acceptors other than TNF are associated with PVCz or carbazole.

The aim of the present study was to extend the sensitivity of a photoconductive material based on PVCz above 650 nm, by substituting different lutetium bisphthalocyanines for TNF. More precisely, the goal was to seek out the formation of a charge transfer complex between the carbazole molecule (Cz) and lutetium bisphthalocyanine (Scheme 1), in the ground state. This could help us to understand if carrier generation in photoconducting materials made of polyvinylcarbazole, doped with lutetium sandwich complexes, is induced by the excitation of this ground state CTC, or if other processes must be envisaged.

Experimental

Carbazole (Aldrich) was recrystallized twice in ethanol. Preparation and purification by chromatography of $LuPc_2$ is a well-known procedure.[12] The study of CTC formation between carbazole and $LuPc_2$ has been performed in the solid



Scheme 1

state, in KBr pellets; however, for comparison, a few experiments were performed in Nujol mulls. Two methods have been used to bring in direct contact the two molecular units, the donor Cz and the electron acceptor $LuPc_2$.

Method 1. The contact between $LuPc_2$ and carbazole in the solid state was obtained by evaporation of a solution of the two compounds in dichloromethane. 1 ml of 10^{-4} M $LuPc_2$ in CH_2Cl_2 and 2 ml 5×10^{-5} M carbazole in CH_2Cl_2 were mixed with 250 mg of KBr (10^{-7} mol of each per g of KBr). After evaporation of the solvent, the crude product was crushed in a mortar before making the pellet, in which the $LuPc_2$: Cz ratio r is 1 : 1. Reference pellets with only $LuPc_2$ ($r = 1 : 0$) or carbazole ($r = 0 : 1$) were prepared following the same procedure. The pressure applied to form the pellets ($d = 13$ mm) was about 75×10^6 kg m^{-2}.

Method 2. The acceptor and the donor were brought into contact by thermal diffusion in KBr. $LuPc_2$–Cz pellets ($r = 1 : 1$, $1 : 10$, $1 : 1000$, $1 : 0$, $0 : 1$) were obtained by grinding and mixing $LuPc_2$ and carbazole powders with KBr in a mortar (10^{-4} mol of $LuPc_2$ per g of KBr). The pellets were then heated at 100 °C, under N_2, for several hours. Likely, it is the thermal diffusion of carbazole that allows CTC formation as the sublimation of $LuPc_2$ occurs only at about 450 °C under high vacuum, whereas carbazole sublimes before its fusion point ($F = 245$ °C). The differences between the infrared spectra recorded before and after the thermal treatment have been attributed to CTC formation.

Infrared spectra were recorded on a Bruker IFS 113 V FT-IR spectrometer.

Results and discussion

Nothing attributable to the formation of a CTC, by π–π interactions between the electron donor and the acceptor, is seen in the UV-near IR spectra of solutions of their mixtures (in CH_2Cl_2). When the contact between $LuPc_2$ and carbazole, as solids in KBr, is obtained from solution evaporation (method 1), a band that does not derive from either of the two molecules appears in the near IR spectral range, at about 1560 nm (6400 cm^{-1}), as shown in Fig. 1. The spectrum in Fig. 1 is the difference between the absorption of a pellet obtained following method 1 (see Experimental) and one of a mixture of $LuPc_2$ and carbazole in KBr, pressed after mixing the three dry components. The concentration of the compounds in the two KBr matrices was not exactly the same so that the subtraction does not completely suppress the absorption due to the IVB transition from the $2b_1$ to the $2a_2$ MO levels of $LuPc_2$ at $\lambda_{max} = 1420$ nm (Scheme 2).[13–16] The new absorption band at 1560 nm is more clearly visible from the difference of the logarithms of the two spectra (Fig. 1). This band is attributed to the formation of a complex by close contact between the acceptor and the donor by evaporation of their solution.

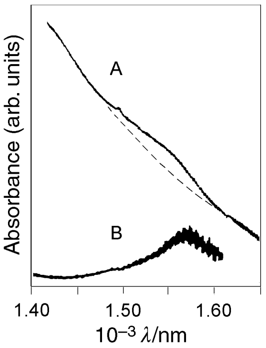
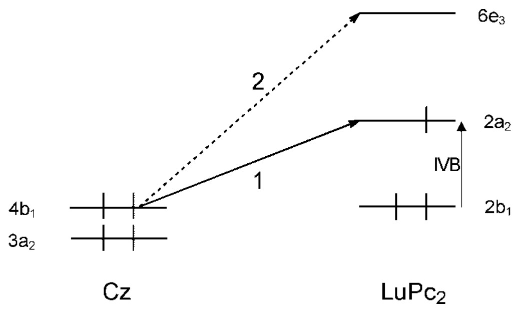


Fig. 1 IR spectroscopy of a carbazole and $LuPc_2$ blend ($r = 1 : 1$) in KBr. The concentration of Cz and $LuPc_2$ is 10^{-7} mol of each for 1 g of KBr. Trace A is the difference between the spectrum after evaporation of the solutions of Cz and $LuPc_2$ on KBr (method 1) and the spectrum of a "dry" mixture; the sloping base line is due to the lower concentration of $LuPc_2$ in the latter pellet. Trace B is the difference between the logarithms of the spectra.



Scheme 2 Sketch of the charge transfer between the carbazole donor and the $LuPc_2$ acceptor. The relative positions of the molecular orbital diagrams for $LuPc_2$[13,14,16] and carbazole[23,24] are not in scale.

As shown in Fig. 2, two bands, at 1290 and 1470 nm appear when the contact between the molecules is obtained by thermal diffusion in the KBr matrix (method 2). These results have been observed after heating the samples ($LuPc_2$: Cz = 1 : 1, 1 : 10, 1 : 1000) at 100 °C, for 5 h; they are different from what is observed when method 1 is followed. Reference samples ($LuPc_2$ or carbazole only, in KBr) reveal no thermal degradation of the compounds, or oxidation by traces of O_2 present in the nitrogen atmosphere, when the pellets are heated. Thus, these two bands can be attributed to the formation of a CTC when carbazole diffuses in KBr and combines with $LuPc_2$. The intensity of the two bands increases with the carbazole concentration, as illustrated in Fig. 3; however, it has to be pointed out that the two bands do not grow similarly. As illustrated in Fig. 4, when one sample ($LuPc_2$: Cz = 1 : 1000) is heated at 100 °C, the intensity of the band at 1470 nm increases all along the heating time (16 h). On the other hand, at 1290 nm, the maximum does not evolve much after 10 h.

As mentioned above, no interaction is detected when the two compounds are present in the same solution, which implies that the complexes do not form appreciably and that the compounds do not react chemically. This is not surprising as carbazole oxidation in acetonitrile, at an electrode surface, occurs at 1.2 V *vs.* SCE,[17] that is to say, at approximately 0.9

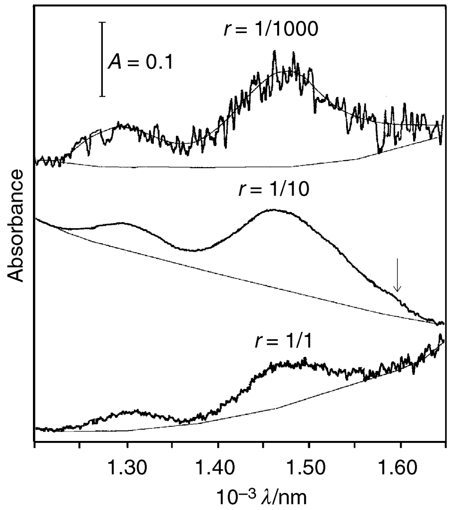


Fig. 2 Evolution of the CTC bands with r, the ratio $LuPc_2$: carbazole. Each trace represents the difference between the spectrum of the mixture in KBr, after heating at 100 °C for 5 h under N_2, and the one of the pellet before heating. For each value of r, the concentration of $LuPc_2$ is 10^{-6} mol per g of KBr. The arrow indicates the wavelength at which a new band appears when the CTC is obtained following method 1.

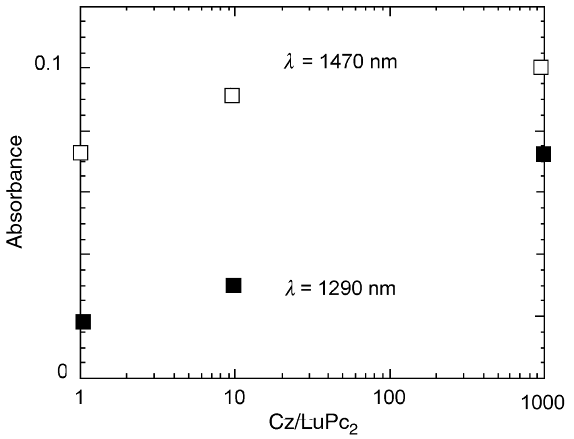


Fig. 3 Evolution of the absorbances at 1290 and 1470 nm with the carbazole : LuPc$_2$ ratio. The bands are those of the spectra in Fig. 2; the conditions are identical for the two experiments.

V *vs.* the formal potential of Fc$^+$/Fc.[18] In dichloromethane, LuPc$_2$ is reduced at about -0.4 V and oxidized at 0.0 V *vs.* $E°$(Fc$^+$/Fc).[7,8] The comparison of carbazole and LuPc$_2$ redox properties, from these potential values, must be done cautiously because the carbazole oxidation at an electrode is irreversible, so that the potential is not a thermodynamic value; moreover, the potentials estimated *vs.* $E°$(Fc$^+$/Fc), from the measurements in different solvents against SCE, include unknown junction potentials. Nevertheless, without any doubt, no redox reaction between carbazole and LuPc$_2$ is possible. None of the two compounds is oxidized or decomposed during heating at 100 °C. Spectra obtained in Nujol mulls are identical, which proves that neither the pressure, nor the KBr matrix, is at origin of the modifications. Consequently, all the new absorption bands observed in the near-IR spectra, for the mixture of the donor and acceptor, must be attributed to the existence of complexes between the electron acceptor and donor.

Both the LuPc$_2$: Cz ratio and the duration of heating at 100 °C influence, but differently, the absorptions at 1470 and 1290 nm (Fig. 3 and 4). This indicates that the bands are not due to two transitions of the same complex, but that they belong more probably to two complexes. Moreover, on the spectrum corresponding to the ratio LuPc$_2$: Cz = 1 : 10 (Fig. 2), a shoulder can be seen at 1550–1600 nm; this is the wavelength at which a transition was observed when the samples were prepared from solutions of Cz and LuPc$_2$ in CH$_2$Cl$_2$ (Fig. 1). As a consequence of these observations, there is no doubt that more than one donor–acceptor complex, probably three different forms, exists between carbazole, the electron donor, and the lutetium bisphthalocyanine. This is not unusual for charge transfer complexes with carbazole; they can differ in their conformation (relative orientation of the donor and the acceptor), but also in their stoichiometry (complexes of higher order D$_n$A). The band at 1290 nm, which continues to grow when *r* increases (Fig. 3), possibly belongs to a complex between one LuPc$_2$ molecule and more than one carbazole. Many studies have illustrated the propensity of carbazole derivatives to form charge transfer complexes characterized by multiple electronic transitions.[19–22] The planar carbazole cycle favors the close approach of the acceptor and so, the π–π molecular interaction essential for CTC formation. Apart from complexes of different stoichiometries, conformers can exist for these CTC; they result from the interaction of the acceptor, through its LUMO, with the two carbazole HOMOs, which have different symmetries.[22] However, from the present study it is not possible to go farther in the discussion about the possible complexes corresponding to the transitions.

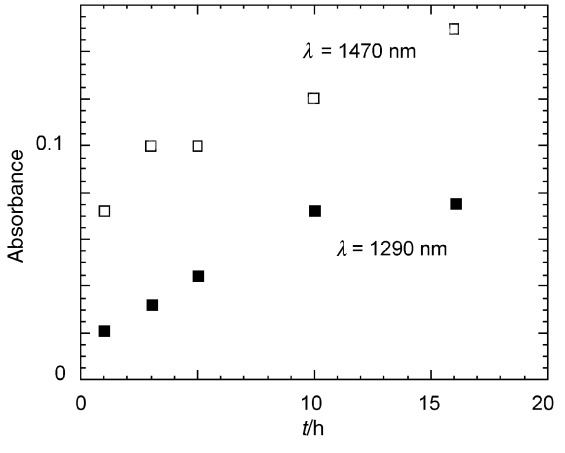


Fig. 4 Evolution of the absorbances at 1290 and 1470 nm with the heating time at 100 °C. The LuPc$_2$: Cz ratio is 1 : 1000.

The charge transfer transitions of the carbazole complexes already described have been observed in the visible spectral range (*e.g.*, 770 nm with TCNQ).[19–22] The new absorption bands, in the present study where the acceptor is LuPc$_2$, appear at higher wavelengths (1200–1600 nm), at much lower energies than usual for charge transfer transitions. The nature of the lutetium bisphthalocyanine, which is a molecular radical, could explain why the transitions require much lower energies. The orbitals of the donor[23,24] and acceptor[13,14,16] have been studied but the calculations for the two molecules are so different that a direct comparison of the energy levels is not possible; the levels are crudely sketched on Scheme 2. The CT transition usually results from the transfer of an electron from the HOMO of the donor to the LUMO of the acceptor (arrow 2, Scheme 2). The lowest energy molecular orbital of LuPc$_2$ that can accept one electron from carbazole is not the LUMO, but the singly-occupied HOMO (SOMO) (arrow 1, Scheme 2). Consequently, the charge transfer between the donor and the acceptor would require a much lower energy, corresponding to a higher wavelength of the associated transition. However, the bands that appear are very close to the so-called IVB band in the bisphthalocyanine spectrum. This is an intervalence band attributed to a transition between the highest filled molecular orbital and the SOMO of the lutetium bisphthalocyanine. This transition corresponds to an intramolecular charge transfer because the two phthalocyanine macrocycles are formally in different redox states.[25] Such a band is also observed in the oxidized actinide and lanthanide double-decker sandwich complexes with porphyrins.[26] Considering the unusually high wavelength at which these new bands appear and the fact that they are very close to the intramolecular charge transfer band of LuPc$_2$, it is difficult to attribute them to a charge transfer transition from carbazole to LuPc$_2$, even if they are undoubtedly associated with the complex formation.

In the present work, intermolecular CTC with carbazole has also been observed for (1,2-Nc)Lu(Pc), the complex in which one of the phthalocyanine units is replaced by a 1,2-naphthalocyanine macrocycle; in this case the absorption transition is observed at 1505 nm. However, all attempts to detect interactions between carbazole and the lutetium bisnaphthalocyanines, (1,2-Nc)$_2$Lu and (2,3-Nc)$_2$Lu, failed. The planarity of the carbazole molecule is particularly favorable to π–π interactions with other conjugated molecules; however, the strength of these interactions depends on many other factors, for example on repulsive forces, which should be particularly important with large molecules such as the lanthanide bisphthalocyanines.[27] The donor–acceptor complexes between LuPc$_2$ and Cz are not the result of a strong association of the two molecules, as shown by the fact that they do not exist in solution. Owing to the existence of multiple complexes and to the weakness of the D–A interaction, it has not been possible to calculate the fraction of the donor and acceptor that interact in a mixture. If the energy gap between the HOMO of the donor and the LUMO of the acceptor is known to be important for CTC formation,[28] the role of orbital symmetry is rarely mentioned. However, it has been demonstrated recently that this factor plays a major role;[29] as seen from Scheme 2, the unfavorable situation could explain the weakness of the complexation.

This study has shown that in solid phases, carbazole, an electron donor, and $Lu(Pc)_2$ or (1,2-Nc)Lu(Pc), an acceptor, form loose ground-state charge transfer complexes. New transitions appear in the near IR spectral range (*ca.* 1400 nm), superimposed on the intramolecular IVB charge transfer transition of the lutetium bisphthalocyanine. This observation is important in the context of designing information for the conception of photoconducting phases based on the association of poly(*N*-vinylcarbazole) with different lutetium bisphthalocyanines, or related molecules. Such photoconductors could be sensitive to near infrared light (*ca.* 1500 nm), exchange energy between the donor and the acceptor through their ground state CTC and generate charged species, D^+ and A^-, by thermalization.

Acknowledgements

The authors thank to J. Y. Moisan and R. Lever (Centre National d'Etudes des Télécommunications of Lannion, France) for the IR spectra. This work was supported by the CNRS, MENRST, and the Région Bretagne through a Ph.D. grant to L. G.

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