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Directed Synthesis of Polyphenyl-substituted Lutetium Bisphthalocyanines

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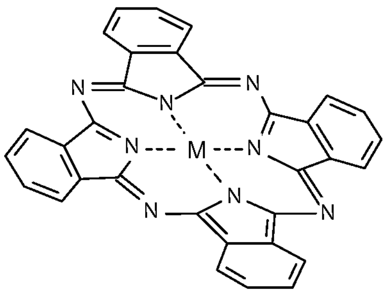
A method of achieving a directed synthesis of polyphenyl-substituted rare earth element bisphthalocyanines has been developed using lutetium bisphthalocyanine as an example.

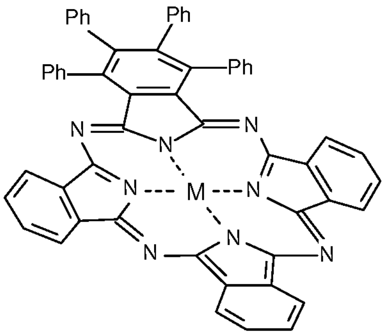
A promising direction for the chemical modification of phthalocyanine molecules is functional substitution in the benzene rings. By changing the substituents present in the phthalocyanine molecules it is possible to synthesize new phthalocyanines with predictable physico-chemical properties.

Previous work has shown that bisphthalocyanines of rare earth elements (REE) possess an unusually intense absorption peak in the near IR region of the spectrum.[1–3] This previous work showed a correlation between the wavelength of the absorption maxima and the REE ionic radii; the bands are shifted bathochromically as the REE ionic radii increase. For example, in the rare earth octa-*tert*-butyl bisphthalocyanine series, the near IR maxima showed a shift from lanthanum octa-*tert*-butyl bisphthalocyanine (2160 nm) to lutetium octa-*tert*-butyl bisphthalocyanine (1390 nm).[3] It is of interest to note that the sandwich-type bisphthalocyanines with [Pc^{2-}Ln^{3+}Pc$^{-\bullet}$]^{0} structure are not the only ones that exhibit absorption in the near IR region; the same properties have been found in the products of one-electron oxidation of bisphthalocyanines of group IV elements, such as hafnium and zirconium [Pc^{2-}M^{4+}Pc$^{-\bullet}$]$^{+}$, see ref. 4.

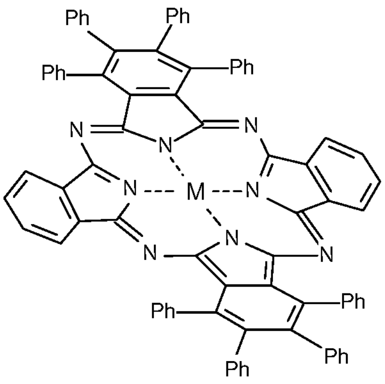
It can be expected that the introduction of different substituents in the macroring will also cause a shift in the electronic absorption spectrum including the peak in the near IR region. In an effort to find new compounds possessing intense absorption in the near IR region of the spectrum, we have tried to synthesize polyphenyl-substituted lutetium bisphthalocyanines using tetraphenylphthalonitrile (TPPN) and lutetium acetate or formate. However, due to the strong overlapping of phenyl rings, TPPN is not susceptible to tetramerization. In order to decrease the steric influence of substituents in TPPN on the formation of phthalocyanine we have studied the tetramerization of TPPN in the presence of unsubstituted phthalonitrile (PN). It has been shown that the formation of a macroring is possible if unsubstituted PN is present in the mixture. The possibility of forming a phthalocyanine, containing only one or two tetraphenylphenylene moieties, is demonstrated by the example of copper



PcM



(Ph$_4$Pc)M



(Ph$_8$Pc)M

Table 1 The composition of polyphenyl-substituted lutetium bisphthalocyanines.

Compound	Composition	Formula	R_f (silufol/benzene)	λ_{max}/nm (CCl_4)
1	$(Ph_8Pc)Lu(PcPh_8)$	$C_{160}H_{96}N_{16}Lu$	0.9	678, 1605
2	$(Ph_8Pc)Lu(PcPh_4)$	$C_{136}H_{80}N_{16}Lu$	0.7	672, 1410, 1555
3	$(Ph_8Pc)LuPc$	$C_{112}H_{64}N_{16}Lu$	0.5	666, 1400, 1525
4	$(Ph_4Pc)Lu(PcPh_4)$	$C_{112}H_{64}N_{16}Lu$	0.3–0.4	662, 1490
5	$(Ph_4Pc)LuPc$	$C_{88}H_{48}N_{16}Lu$	0.2	658, 1380, 1420
6	PcLuPc	$C_{64}H_{32}N_{16}Lu$	0	654, 1370

and cobalt monophthalocyanines.

The compounds obtained in this way can be separated by chromatography. Furthermore, they possess enhanced solubility and a bathochromic shift of the principal absorption bands by 7–10 nm in comparison with their unsubstituted analogues.

In the case of bisphthalocyanines of REE (with Ln^{3+} as counter ion), an increase in the number of possible structures can be expected. In the first step of the bisphthalocyanine synthesis, structures similar to the previously described $(Ph_4Pc)M$ and $(Ph_8Pc)M$ structures of monophthalocyanines of REE (with counter ion at Ln^{3+}) were obtained. A second step allowed us to obtain the following diphthalocyanines: $(Ph_8Pc)_2Lu$, $(Ph_8Pc)Lu(Ph_4Pc)$, $(Ph_8Pc)LuPc$, $(Ph_4Pc)_2Lu$, $(Ph_4Pc)LuPc$, Pc_2Lu.

The synthesis was carried out by fusion of a mixture of tetraphenylphthalonitrile, obtained by the method described in ref. 5, and REE salt in the presence of unsubstituted phthalonitrile (molar ratio 8:1:4). The temperature was gradually raised from 100 to 270–280 °C, holding the reaction mixture at this temperature for 2.5 h. A change in the molar ratio of the reagents allows a variation in the quantitative relation between the phthalocyanines **1**–**6** obtained. The molar ratio stated above was best for the formation of all of the fractions presented in Table 1.

Purification was carried out by chromatography on aluminium oxide using benzene, a mixture of benzene–chloroform and chloroform as solvents. From the TLC results it can be assumed that all the compounds synthesized were homogeneous. Elemental analysis confirmed the proposed composition.

The introduction of the tetraphenyl phthalonitrile moiety in the bisphthalocyanine molecules gave rise to a marked increase in the solubility ($\sim 5 \times 10^{-2}$ M in the case of compound **1**). A bathochromic shift of the absorption spectra of more than 200 nm when compared with the unsubstituted Pc_2Lu (λ_{max} = 1605 nm) was observed. In addition, in the case of unsymmetrical compounds **2**, **3** and **5** a splitting of the spectral band in the near IR region was observed, but at the same time, the visible region of the spectra showed a typical Q band. The absorption spectrum of compound **4** is shown in Fig. 1. The splitting of the band in the near IR region in asymmetrical bisphthalocyanine proves the hypothesis[2] that this absorption band is associated with an intramolecular charge transfer (dianion Pc behaves as an electron donor and ion-radical Pc as an acceptor). The splitting of the band is strong proof of the charge-transfer character of this absorption because the splitting of the band shows experimentally that the transitions are affected by the presence or absence of symmetry between the phthalocyanine rings in the macromolecule.

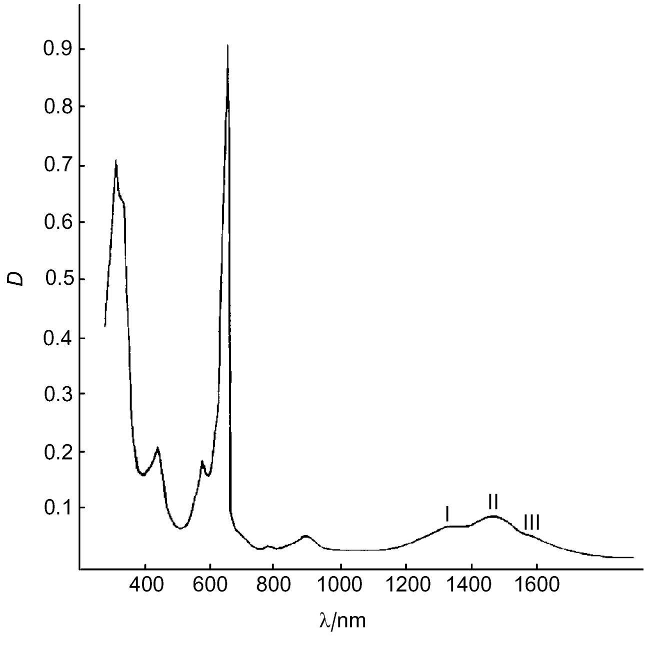


Fig. 1 Absorption spectra of $(Ph_4Pc)Lu(PcPh_4)$ in CCl_4.

Thus, the introduction of a determined number of phenyl parts in the bisphthalocyanine molecule allows not only a shift of the band in the IR spectrum region, but also affects its character. This phenomenon can be expected for all REE series.

The complexes obtained possess all the properties typical of bisphthalocyanines. The electrochromism, the dependence of the electronic absorption spectra on pH, as well as the ability to form Langmuir–Blodgett monolayers, are properties that are now under study.

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