Novel Tribenzhexaazaporphyrins as Unsymmetric Phthalocyanine Analogues

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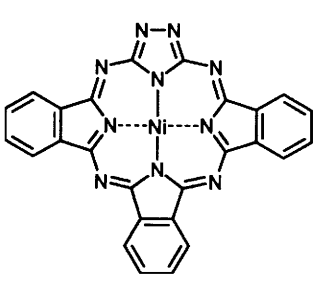
The formal substitution of one isoindole subunit of a phthalocyanine by a 1,2,4-triazole moiety afforded a new family of unsymmetric azaporphyrins—of which compounds **1** and **2** are representative—with potential nonlinear optical properties.

Porphyrins and especially phthalocyanines (Pcs)[1] with their large π-conjugated systems have demonstrated their capability to generate nonlinear optical effects (NLO).[2–4] Moreover, unsymmetric phthalocyanines substituted by both electron-donor and -acceptor groups, have been suggested as promising targets for SHG.[5] Although symmetrical phthalocyanines are well documented, there are few reports on non-centrosymmetric Pc's or Pc analogues due to preparative difficulties.[1] The replacement of the four benzo-fused rings in phthalocyanines by other heteroaromatic fused systems is known,[1] but the formal substitution of only one isoindole subunit in a phthalocyanine by another azole in order to obtain unsymmetrical aromatic systems has received very little attention.[6–8] Thus, the preparation and study of new unsymmetric azaporphyrins could provide important information about aromaticity and charge distribution in these compounds, as well as an important entry into the development of improved materials for NLO applications.

In this communication we report the synthesis and characterization of the nickel complexes **1** and **2**, that belong to a new class of azaporphyrins[9] in which, beside the four *meso* nitrogen atoms, there are two further nitrogen atoms in β-positions. These compounds can be formally designed as tribenzhexaazaporphyrins. To the best of our knowledge, these compounds, to which we have assigned the trivial name triazolephthalocyanines (Tpc), are the first examples of porphyrin or phthalocyanine analogues in which one pyrrole or isoindole subunit has been replaced by a polyazole, such as 1,2,4-triazole. The synthesis of (triazolephthalocyaninato) nickel(II) **1**† was carried out by reaction between 1,3-diiminoisoindoline and 3,5-diamino-1,2,4-triazole (guanazole) in a 3 : 1 molar ratio in the presence of nickel tetrafluoroborate in 65% yield. A minor compound obtained in this reaction was identified as the nickel triazolehemiporphyrazine **3a**[10] (estimated yield ⩽5%). The stoichiometry of the reaction was found to be critical. Thus, a molar ratio 1 : 1 of both reagents afforded compound **3a** as major product.[10] The presence of **3a** can be avoided by using a 5 : 1 molar ratio of the reagents, but in this case NiPc was also obtained. Compound **1**, although rather more soluble than NiPc,[11] is still quite insoluble in common organic solvents and the separation of both is difficult. (Triazolephthalocyaninato)nickel(II) **1** was purified by trituration with hot methanol. The structure of **1** was confirmed by FAB mass spectrometry. The UV–VIS spectrum of the triazolephthalocyanine **1** in TFA (Fig. 1) is consistent with that of nickel triazolehemiporphyrazine in acidic media. Efforts to obtain the free-base form (without metal) by a non-template reaction between guanazol and 1,3-diiminoisoindole have so far proved unsuccessful.

Triazolephthalocyanine **1**, with a C_{2v} symmetry, is a 18 π-electron fully conjugated macrocycle with a core isoelectronic to phthalocyanine. We have reported that the replacement of two opposite isoindole rings in a phthalocyanine by 1,2,4-triazole subunits yields the corresponding nonaromatic triazolehemiporphyrazine instead of the expected 18 π-electron heteroannulene.[12] In agreement with the conclusions given



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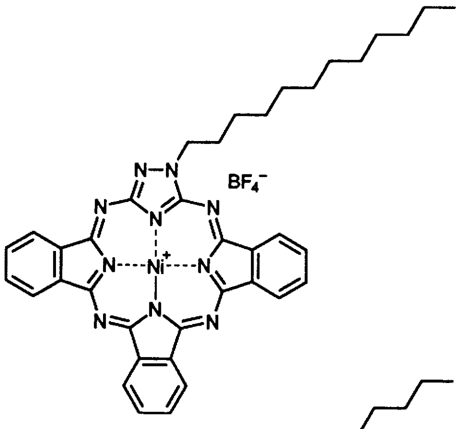

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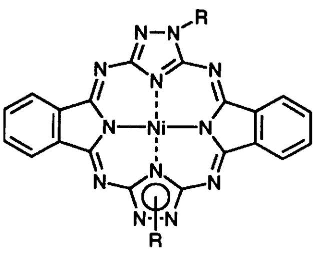
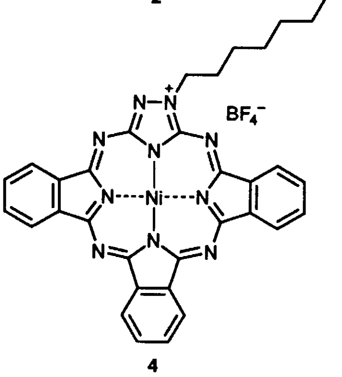


3a R = H
3b R = $C_{12}H_{25}$



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there, the present results point out that in **1** the isoindole unit opposite the 1,2,4-triazole subunit adopts an antiaromatic electron distribution to reach a stable molecule with a 18 π-electron system. The electron acceptor character of the triazole ring should provide an electronic density dissymmetry in compound **1**, giving a net dipolar moment.

The low solubility of **1** prompted us to prepare lipophilic derivatives. To accomplish this, we reacted 3,5-diamino-1-dodecyl-1,2,4-triazole[12] with 1,3-diiminoisoindoline and nickel tetrafluoroborate under the same conditions described above in the preparation of **1**. Thus, the nickel complex **2**,† readily soluble in organic solvents, *e.g.* chloroform, was obtained in a moderate yield (42%). This compound was purified by trituration with hot acetonitrile followed by column chromatography on silica gel using CH_2Cl_2–MeOH (10 : 1) as eluent. In this reaction the hemiporphyrazine **3b**[13] (regioisomer mixture) was also isolated as minor product (yield ≤20%). Compound **2** has FAB-MS and FD-MS spectra according to the proposed structure and shows an intense isotopic cluster corresponding to the cationic part of the compound.

Structure **2**, with three inner tertiary nitrogen groups lacking replaceable hydrogen atoms, represents a non-aromatic, cross-conjugated system. However, it could be formulated as an overall 18 π-electron system **4**. The contribution of this resonance structure to the resonance hybrid (**2**↔**4**) should be low, considering the NMR data.‡ The electronic spectrum of triazolephthalocyanine **2** is shown in Fig. 1. Triazolephthalocyanine **2** shows a high hyperpolarizability value $\gamma^{EFISH} = 10^{-33}$ esu, in $CHCl_3$ at 1.06 μm.

In conclusion, we have synthesized and characterized compounds **1** and **2**, representative of a new family of noncentrosymmetric azaporphyrins related to phthalocyanines. A more detailed investigation on related triazolephthalocyanines with other central metallic ions and electron donor groups on the benzo-fused rings is currently in progress.

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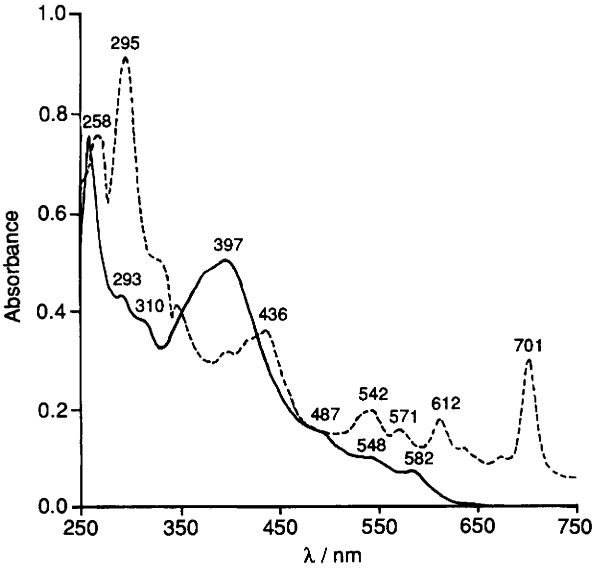

Fig. 1 Electronic spectra of **1** in TFA (continuous line, 2.1 × 10^{-5} mol dm^{-3}) and **2** in $CHCl_3$ (dashed line, 1.4 × 10^{-5} mol dm^{-3})

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Footnotes

† Satisfactory elemental analysis were obtained for compounds **1** and **2**. FAB-MS(*m*-nitrobenzyl alcohol): **1**, *m/z* 523, 525 (M + H^+); **2**, *m/z* 691, 693 (as also found by FD-MS).

‡ The ^1H NMR spectrum of **2** in $CDCl_3$ exhibits a broad signal between δ 7.7 and 8.2, corresponding to the protons of the benzo-fused rings. These chemical shifts are low in comparison with those observed for related type of protons of aromatic nickel phthalocyanine[2,14] (δ *ca.* 9.0) and similar to that of the nonaromatic nickel triazolehemiporphyrazine **3b** (δ 7.7–7.3), thus indicating the lack of aromaticity of the compound. On the other hand, the N–CH_2 group in **2** appears at δ 3.65, lower than the corresponding protons in compound **3b** (δ 3.95).

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