

## Synthesis and Aggregation Properties of Novel Soluble 'Crowned' Metallo-triazolehemiporphyrazines

Fernando Fernández-Lázaro, Angela Sastre and Tomas Torres\*

Departamento de Química Orgánica (C- I), Facultad de Ciencias, Universidad Autónoma de Madrid, 28049-Madrid, Spain

Synthesis and preliminary studies on the aggregation and non-linear optical properties of novel, highly soluble, free and transition metal-complexed triazolehemiporphyrazines **1** containing two 15-crown-5 subunits are reported; aggregation of the 'crowned' metallo-triazolehemiporphyrazines induced by alkali cations is observed for the first time in these kinds of compounds.

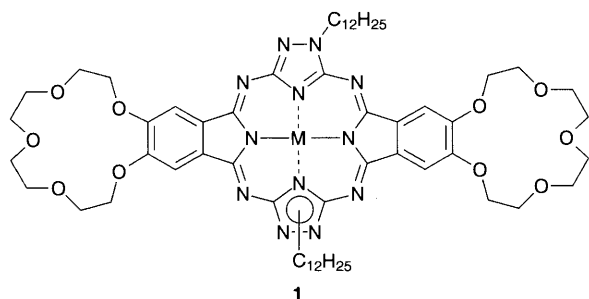
The formal exchange of one or two isoindole rings in phthalocyanine<sup>1</sup> with 1,2,4-triazole affords, respectively, 18  $\pi$ -electron fully conjugated triazolephthalocyanines<sup>2</sup> and the corresponding triazolehemiporphyrazines which display a non-aromatic extended conjugation of 20  $\pi$ -electrons.<sup>3</sup> Both types of compounds show interesting electrical<sup>4</sup> and non-linear optical (NLO) properties<sup>5</sup> that resemble those of metallophthalocyanines,<sup>6,7</sup> and are therefore potential building blocks for the construction of molecular materials for electronic and optoelectronic applications.<sup>8</sup> Nevertheless, the very poor solubility of these metallomacrocycles in organic media often precludes the study of their properties.

The chemical versatility in the preparation of triazolehemiporphyrazines and related compounds<sup>9</sup> provides a unique opportunity of varying the electronic structure through ligand and metal modifications, thus inducing changes in the physical and physico-chemical properties of the molecules, *e.g.* polarity, solubility, redox behaviour, polarizability, *etc.*

Here we report the synthesis and preliminary studies on the aggregation and NLO properties of free and transition metal-complexed triazolehemiporphyrazines **1**, highly soluble in various organic solvents, containing two 15-crown-5 subunits on the isoindole moieties. These kinds of compounds which possess amphiphilic character, are also potentially useful for the construction of ionic channels,<sup>10</sup> through organization by the Langmuir-Blodgett technique.

The synthesis of free triazolehemiporphyrazine **1a**<sup>†‡</sup> was carried out by reaction of 4,5-(3,6,9-trioxadecanediyldioxy)-1,3-diiminoisoindoline and 3,5-diamino-1-dodecyl-1,2,4-triazole in 2-ethoxyethanol at reflux temperature. HPLC analysis (silica column, dichloromethane : methanol = 98 : 2) of compound **1a** indicates the presence of the two possible regioisomers in a 60 : 40 ratio.

The free base **1a** was successfully converted into the corresponding (triazolehemiporphyrazinato)metal(II) complexes **1b-g** (M = Mn, Fe, Co, Ni, Cu or Zn respectively) by reaction with the appropriate metal(II) acetate [iron(II) chloride in the case of **1c**] by the procedure described previously by us for related compounds.<sup>5</sup> Compounds **1b-g** can be purified by column chromatography on silica gel or recrystallization and were characterized by <sup>1</sup>H NMR (**1e, g**), IR, FAB-MS and elemental analysis.<sup>†§</sup>



a, M = H<sub>2</sub>; b, M = Mn; c, M = Fe; d, M = Co; e, M = Ni; f, M = Cu; g, M = Zn

Mössbauer spectral data of the (triazolehemiporphyrazinato)iron(II) **1c** shows that the corresponding  $\mu$ -oxo(triazolehemiporphyrazinato)iron(III) dimer<sup>1,11</sup> was present as an impurity. A more detailed study on this compound is currently under way.

As previously shown,<sup>12</sup> UV-VIS spectroscopy might be a powerful tool to study aggregation phenomena in phthalocyanines in solution. The electronic absorption spectrum of triazolehemiporphyrazine **1a** (in chloroform) is depicted in Fig. 1 (continuous line). The spectrum is dominated by strong absorption bands in the near UV between 330 and 385 nm, together with weak absorptions in the UV-VIS region at 410–590 nm ( $\pi \rightarrow \pi^*$  transitions). The typical Q-band of phthalocyanines and triazolephthalocyanines<sup>13</sup> in the 700 nm region is absent.

The spectrum is slightly modified by introduction of a central metal in compounds **1b-g**.<sup>†</sup> Additional weak bands associated with ligand-to-metal (or *vice versa*) charge-transfer transitions appear in the 400–600 nm region.<sup>14</sup>

The addition of alkali metal ions to a chloroform solution of **1a** gives rise to notable changes in the UV-VIS spectrum. In Fig. 1 the electronic spectra of **1a** at different concentrations of K<sup>+</sup> are depicted (dashed lines). On increasing the concentration of the salt, the absorptions corresponding to the bands in the 330–385 nm region decrease in intensity. Similar qualitative results have been obtained with larger ions (Rb<sup>+</sup>, Cs<sup>+</sup>), but not with smaller ones (Li<sup>+</sup>, Na<sup>+</sup>). Cobalt and nickel complexes (**1d, e**) show the same behaviour in the presence of K<sup>+</sup> and Rb<sup>+</sup>. No changes at all were observed in the UV-VIS spectrum of a model compound<sup>5</sup> similar to **1** but without crown ether subunits,

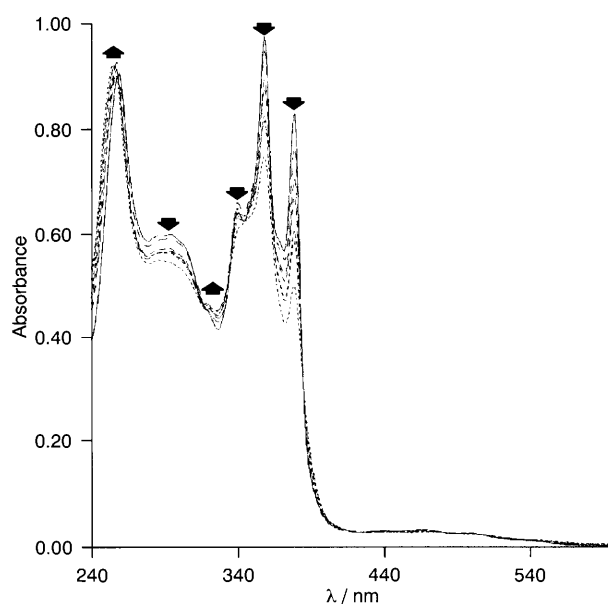


Fig. 1 Electronic spectrum of **1a** (a) in chloroform (continuous line), (b) in chloroform in the presence of increasing concentrations of anhydrous potassium acetate in chloroform containing 1% methanol (dashed lines)

upon addition of increased amounts of  $K^+$ . These facts, observed for the first time in hemiporphyrzine-type compounds, may be rationalized in terms of aggregation of the 'crowned' triazolehemiporphyrzines **1** induced by alkali metal ions, which coordinate the crown ether rings. It is well known that 'crowned' phthalocyanines<sup>15</sup> aggregate in the presence of metal ions. In this case, as in ours, the aggregation is particularly notable when the diameter of the ion exceeds the inner diameter of the crown ether rings. An examination of CPK models of the free triazolehemiporphyrzine **1a** suggests that for  $K^+$  and for  $Rb^+$  a cooperative cofacial interaction between two molecules with two cations, each sandwiched between two crown ether rings, is more favourable.

We have also investigated the aggregation of compound **1a** and the nickel complex **1e** by  $^1H$  NMR spectroscopy. In the first case, the addition of potassium acetate to a solution of **1a** ( $[K^+]:[1a]$  ca. 10:1) monitored by  $^1H$  NMR showed a broadening of the signals corresponding to the crown ethers. The four singlets of the aromatic protons (**1a** is a mixture of two isomers) shift slightly upfield (ca. 0.2 ppm) and become sharper. A similar upfield shift was observed for the two first methylene groups of the lateral chain linked to the triazole. These facts are consistent with cofacial dimer formation which imposes a greater rigidity on the crown ethers and, on the other hand, causes an anisotropic shielding effect between the two hemiporphyrzine rings affecting especially the protons mentioned above. A similar argument has been used to support the cofacial dimer formation of 'crowned' phthalocyanine derivatives.<sup>15a</sup> Nickel complex **1e** behaves similarly on addition of  $K^+$ .

Studies on the supramolecular architecture of ionic channels formed by 'crowned' triazolehemiporphyrzines **1** are under way. Evidence of molecular organization has been observed in Langmuir-Blodgett films of these compounds.<sup>16</sup>

Recently, we have investigated the second-order non-linear hyperpolarizability,  $\gamma$ , of different substituted metallotriazolehemiporphyrzines<sup>5</sup> and phthalocyanines.<sup>7a</sup> The good solubility of metallotriazolehemiporphyrzines **1** in chloroform also allows the determination of their third-order NLO response for obtaining both the real and the imaginary part of  $\gamma$ . A notable enhancement of metal complexation with unfilled d-shell ions has been observed. The values of the hyperpolarizability magnitude  $|\gamma|$  found for these compounds at 1340 nm are in the range of  $0.8 \times 10^{-32}$  to  $0.8 \times 10^{-33}$  esu,<sup>14</sup> i.e. of the same order as those found in phthalocyanine derivatives.<sup>7a</sup>

Received, 24th October 1994; Com. 4/06507G

## Footnotes

† All new compounds gave satisfactory elemental analyses as mono-(**1a**) di-(**1d-f**) and tri-hydrates (**1b, c, g**).

‡ Selected data for **1a** (regioisomeric mixture): Yield 41%; orange-reddish powder, mp 249–254 °C (from DMF).  $\delta_H(CDCl_3)$  14.99, 14.85, 14.72 (each s, 2H, NH), 7.22, 7.17, 7.00, 6.93 (each s, 4H, arom.), 4.1, 3.9 and 3.8 (each br, 36H,  $CH_2O$  and  $CH_2N$ );  $\delta_C(CDCl_3)$  163.1, 162.7, 155.8, 155.5, 155.3, 154.7, 153.9, 153.0, 152.8, 152.2, 128.9, 127.9, 127.2, 105.7, 105.5 (arom.), 71.5, 71.2, 70.2, 70.1, 69.2, 69.0, 68.7, 68.5 ( $CH_2O$ ) and 46.5 ( $CH_2N$ ); FAB-MS (*m*-NBA) *m/z* 1137 ( $M^+$ ); UV-VIS ( $CHCl_3$ )  $\lambda_{max}/nm$  (log  $\epsilon$ ) 259 (4.716), 293 (4.540), 340 (4.575), 358 (4.753) and 379 (4.681);  $\nu_{max}/cm^{-1}$  (KBr) 3300, 1660 and 1495.

§ Selected spectral data for **1b-g** (regioisomeric mixture): **1b**, FAB-MS (*m*-NBA) *m/z* 1189 ( $M^+$ );  $\nu_{max}/cm^{-1}$  (KBr) 1615, 1570 and 1510; **1c**, FAB-MS (*m*-NBA) *m/z* 1191 ( $M + H^+$ );  $\nu_{max}/cm^{-1}$  (KBr) 1620, 1570 and 1510; **1d**, FAB-MS (*m*-NBA) *m/z* 1194 ( $M + H^+$ );  $\nu_{max}/cm^{-1}$  (KBr) 1630, 1580 and 1520; **1e**,  $\delta_H(CDCl_3)$  7.06, 7.03 (each s, 2H, arom.), 6.8 (br, 2H, arom.),

4.0, 3.9 and 3.8 (each br, 36H,  $CH_2O$  and  $CH_2N$ ); FAB-MS (*m*-NBA) *m/z* 1193 ( $M + H^+$ );  $\nu_{max}/cm^{-1}$  (KBr) 1630, 1590 and 1520; **1f**, FAB-MS (*m*-NBA) *m/z* 1198 ( $M + H^+$ );  $\nu_{max}/cm^{-1}$  (KBr) 1610, 1570 and 1510; **1g**,  $\delta_H(CDCl_3)$  7.25, 7.15 (each s, 4H, arom.), 4.15, 3.94 and 3.74 (each br, 36H,  $CH_2O$  and  $CH_2N$ ); FAB-MS (*m*-NBA) *m/z* 1199 ( $M + H^+$ );  $\nu_{max}/cm^{-1}$  (KBr) 1600, 1530 and 1500.

¶ UV-VIS spectrum for **1d** in chloroform (typical for complexes **1b-g**):  $\lambda_{max}/nm$  (log  $\epsilon$ ) 259 (4.733), 295 (4.666), 352 (sh), 364 (4.632), 385 (4.568), 433 (3.814), 479 (3.569) and 513 (3.489).

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