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LETTER

Spectroscopic comparison of tetra-tert-butylated tetraazaporphyrin, phthalocyanine, naphthalocyanine and anthracocyanine cobalt complexes

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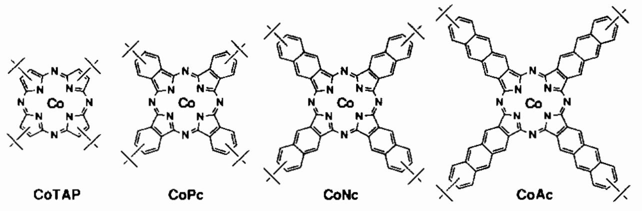
Tetraazaporphyrins (TAPs), phthalocyanines (Pcs) and naphthalocyanines (Ncs) have been studied for their use as dyes and pigments [1a] and for their electrocatalytic activity [1b] and photosensitivity for semiconductor devices [1c, d]. More recently, the interest of chemists has been expanding in many fields such as energy conversion [1e], photosensitizers [1f], gas sensors [1g], low dimensional metals [1h], liquid crystals [1i], non-linear optics [1j] and photodynamic cancer therapy [1k]. However, compared with Pcs and Ncs, much less research has been done on so-called anthracocyanine (Ac) due mainly to the preparative difficulty of the precursors [2]. Elucidation and comparison of the physichochemical properties of such a series of compounds is, on the other hand, of fundamental importance in coordination chemistry containing macrocyclic ligands. In this communication, we report the synthesis, and electronic absorption and magnetic circular dichroism (MCD) properties of a CoTAP, CoPc, CoNc and CoAc. In order to increase the solubility and keep the effect of substituent groups as uniform as possible, all compounds contain four tert-butyl groups at almost similar positions.

CoTAP [3], CoPc, CoNc [4] and CoAc (Scheme 1) were synthesized from *cis*-1,2-dicyano-3,3-dimethyl-1-butene [3], 4-tert-butylphthalonitrile, 6-tert-butyl-2,3-dicyanonaphthalene [5] and 6-tert-butyl-2,3-dicyanoanthracene [6], respectively, according to the literature [7]. After drying *in vacuo* at 100 °C overnight, CoAc showed a metallic deep purplish brown color. *Anal.* CoTAP: Found: C, 64.47; H, 6.81; N, 18.12. Calc. for $C_{32}H_{40}N_8Co$: C, 64.53; H, 6.77; N, 18.81%. CoPc: Found: C, 71.84; H, 6.28; N, 13.32. Calc. for $C_{48}H_{48}N_8Co$: C, 72.44; H, 6.08; N, 14.02%. CoNc: Found: C, 76.72; H, 5.96; N, 11.20. Calc. for $C_{64}H_{56}N_8Co$: C, 77.17; H, 5.67; N, 11.25%. CoAc: Found: C, 79.46; H, 5.70; N, 9.15. Calc. for $C_{80}H_{64}N_8Co$: C, 80.32; H, 5.39; N, 9.37%.



Scheme 1.

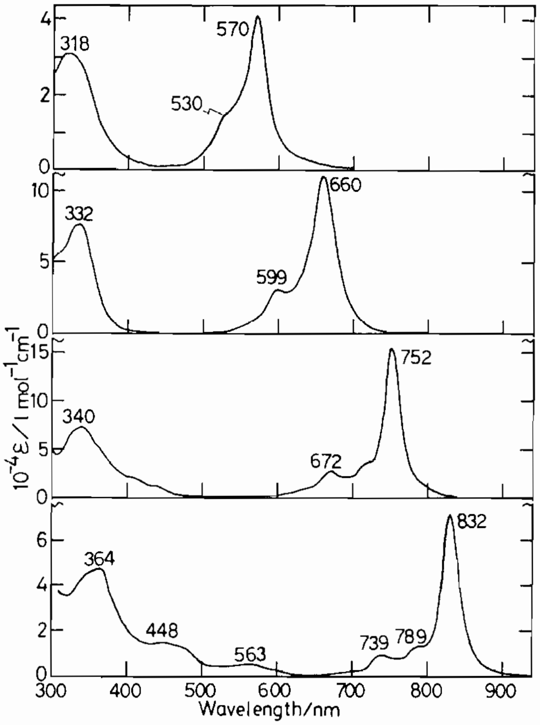


Fig. 1. UV–Vis–near-IR absorption spectra of CoTAP, CoPc, CoNc and CoAc in pyridine.

Figure 1 shows the electronic absorption spectra of the compounds in pyridine. The Q_{0-0} band lies at 570, 660, 752 and 832 nm for CoTAP, CoPc, CoNc and CoAc, respectively, i.e. in order of increasing size of the macrocyclic ligand. The energy differences between the Q bands are 2390 (CoTAP–CoPc), 1850 (CoPc–CoNc) and 1270 (CoNc–CoAc) cm^{-1}. This indicates that, although the Q band shifts to longer wavelength with expansion of the π-conjugated system, the extent of the shift becomes smaller the larger the size of the macrocyclic ligand. From the almost linear decrease of the above energy difference, the Q band

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peak of the tetra-tert-tetracocyanine cobalt complex, if it can be prepared, is conjectured to lie at around 900–910 nm. On the other hand, the change of the absorption coefficient (ϵ) of the Q_{0-0} band does not have a linear dependence on the size of the chromophore. The ϵ values decrease in the order of CoNc > CoPc > CoAc > CoTAP. In order to obtain more quantitative information, the dipole strength (μ) and dipole length of the Q_{0-0} band were estimated [8]. The μ values were 21.9, 49.7, 55.0 and 28.8 D^2 (D; Debye), and the dipole lengths were 0.98, 1.47, 1.55 and 1.12 Å, respectively, in order of increasing molecular size.

The Soret band of TAP derivatives including Pcs and Ncs has been attributed to a transition from the a_{2u} to e_g orbitals under D_{4h} symmetry [9]. As for the case of the Q band, the Soret band shifts to longer wavelengths with annulation (however, in *o*-dichlorobenzene (DCB) the Soret band of CoPc occurs at shorter wavelength than that of CoTAP). The energy differences between the Soret bands in pyridine are 1330, 540 and 2370 cm^{-1} for CoTAP–CoPc, CoPc–CoNc and CoNc–CoAc, respectively.

We have examined our data from the standpoint of molecular orbital (MO) calculations within the framework of the Pariser–Parr–Pople approximation [10] using parameters shown in ref. 11. The calculations were carried out for (pyrrole proton-) deprotonated TAP, Pc, Nc and Ac skeletons. The details will be published in a full paper, but by way of summary we describe here some results which accord to some extent with our data as follows. (i) The calculated Q band shifts to longer wavelengths with annulation, with the extent of shift decreasing with increasing molecular size. The ratio of energy differences between TAP–Pc, Pc–Nc and Nc–Ac was *c.* 2.81:2.10:1.00, respectively, compared with the experimental values of 1.88:1.46:1.00. (ii) The μ value of the Q band increases with molecular size but its rate of increase becomes smaller the larger the molecule (i.e. TAP:Pc:Nc:Ac = 1.00:4.03:5.87:6.77). (iii) As in our experiments in DCB, the Soret band of TAP appears at shorter wavelength than that of Pc, and then shifts to the red on going to Nc and further to Ac.

MCD spectra of the compounds are shown in Fig. 2. Since both the Soret and Q bands are ascribed to a transition to a degenerate excited state, the dispersion curves corresponding to the main Q and Soret absorption bands are contributions of Faraday *A*-terms [9]. Their *A*/*D* values (an MCD parameter) [12] of the Q band are 2.39, 1.69, 1.44 and 0.61 in the order of CoTAP to CoPc, CoNc and further to CoAc, indicating that the orbital angular momentum of the excited state of the ligand diminishes with the increase of ligand size [13].

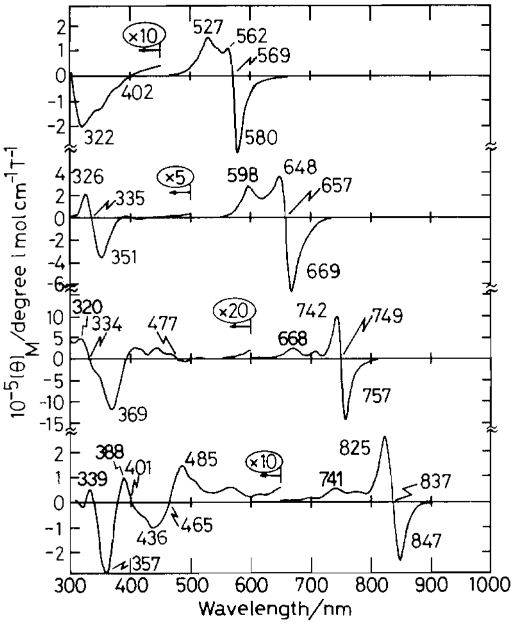

Fig. 2. MCD spectra of CoTAP, CoPc, CoNc and CoAc in pyridine.

In summary, the important results are: (i) ring-expansion produces a bathochromic shift of the Q band but the degree of shift decreases with increasing molecular size; (ii) the ϵ value of the Q band increases with the expansion of the macrocycle but it starts to decrease after reaching a maximum at CoNc, thus ϵ of CoAc is smaller than that of CoNc; (iii) the orbital angular momentum of the excited state of the ligand diminishes with increasing size of the π-system.

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