ChemComm

A tetraazaporphyrin with an intense, broad near-IR band†

Victor N. Nemykin and Nagao Kobayashi*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan.
E-mail: nagaok@mail.cc.tohoku.ac.jp

Received (in Cambridge, UK) 19th September 2000, Accepted 5th December 2000
First published as an Advance Article on the web 4th January 2001

A tetraazaporphyrin (TAP) prepared by condensation of 1-ferrocenyl-1,2,2-tricyanoethylene in the presence of magnesium shows an intense, broad near-IR band in the 700–1300 nm region, which may be ascribed to charge-transfer transitions from the ferrocenyl moiety (substituents) to the TAP ligand.

Ferrocene (Fc)-modified porphyrins,[1] porphyrazines,[2] and phthalocyanines (Pcs)[3] have been reported over the past few decades. Although these compounds show characteristics ascribable to the Fc moiety such as the $Fe^{II/III}$ redox couple, their spectroscopic properties are generally similar to normal porphyrins and Pcs, except for a slight change in the shape or positions seen occasionally. In this regard, the TAP compound which we report here, *i.e.* 2,7,12,17-tetracyano-3,8,13,18-tetraferrocenyl-5,10,15,20-tetraazaporphyrinatomagnesium, **1**, is unusual in showing an intense, broad absorption band in the near-IR region (700–1300 nm), beyond the Q band. TAPs are structurally intermediate compounds between porphyrins and Pcs, and some porphyrins[4] and Pcs[5] are known to show near-IR absorption bands having much weaker intensity than the Q band, which can be assigned to either d–d transitions[6] in the central metal or charge-transfer (CT) transitions from the central metal to the ligands. Our compound **1**, on the other hand, has a broad, intense near-IR band, which may be assigned to charge-transfer from the iron in the substituent group to the TAP ligand, as described below.

Compound **1** was synthesized, in the presence of magnesium, by condensation of 1-ferrocenyl-1,2,2-tricyanoethylene, **2**, which was obtained from chloromercurioferrocene and tetracyanoethylene.[7] Fig. 1 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of **1** and **2**. The starting material **2** showed two absorption peaks at 363 and 628 nm, while the TAP **1** had absorption maxima at 382, 623, and 962 nm. From the shape and intensity of the MCD band, the bands at 382 and 623 nm of **1** are assigned as the Soret and Q bands, respectively. The near-IR band can not be a π–π* transition in the TAP ligand, since the Q band corresponds to the HOMO–LUMO transition in the normal porphyrinic compounds. In addition, the possibility of this being a d–d transition is small because of the large absorption coefficient (ε = 13200 $dm^3\ mol^{-1}\ cm^{-1}$), which is a few orders of magnitude larger than normal d–d transitions ($0 < \varepsilon <$ *ca.* $10^2\ dm^3\ mol^{-1}\ cm^{-1}$; the d–d transition is a forbidden transition by the Laporte selection rule). The only feasible possibility appears to be CT transitions between the Fc moiety and the TAP ligand (the magnesium ion in the center of the TAP skeleton does not participate since it does not contain d electrons). However, since this kind of near-IR band has not been detected in Pcs and porphyrins having only a Fc moiety,[1,3] the presence of electron-withdrawing cyano groups in the close proximity may be of crucial importance. In accordance with this conjecture, the peak wavelength of the near-IR band changed from 962 nm in chloroform to 905 nm in ethanol and further to 888 nm in DMSO.

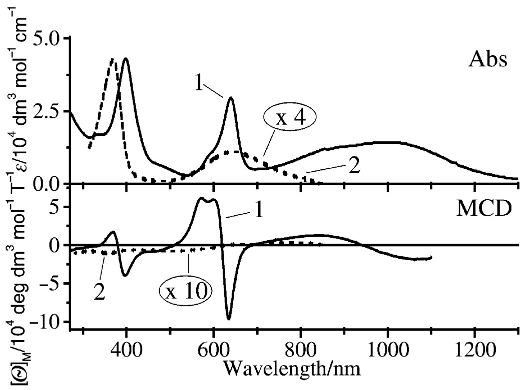

Fig. 1 Electronic absorption and MCD spectra of **1** (solid lines) and **2** (dotted lines) in chloroform.

In order to further gain some insight into the origin of the near-IR band, redox potentials of **1** and **2** were measured in *o*-dichlorobenzene, and the spectra of the electrolysed **1** have been recorded. Compound **2** showed one reversible oxidation peak at 0.38 V *vs.* Fc/Fc^+, which can be assigned to the $Fe^{II/III}$ couple, and one irreversible reduction peak at −1.35 V, which can be tentatively assigned to the formation of the tricyanovinyl-localized anion-radical.[8] The TAP **1** showed two reversible one-electron reduction processes at −0.84 and −1.28 V, and one reversible four-electron oxidation process at 0.06 V and one irreversible quasi one-electron oxidation process at 0.97 V. From the amount of the current and the position, the first oxidation is clearly assigned to the Fc moiety, *i.e.* $Fe^{II/III}$ and other couples are TAP-centered. Of course, an irreversible reduction peak tentatively assigned to the tricyanovinyl moiety in **2** disappeared in **1**, because the two cyano groups of the three cyano groups in **2** were used for the TAP core formation. The potential difference between the 1st oxidation and reduction potential of the TAP ligand (1.81 V) is much smaller than that of general tetraazaporphyrins (*ca.* 2.1–2.2 V)[9] due perhaps to the stabilization of the LUMOs by cyano groups. If the band in the near-IR region of **1** is associated with CT between the Fc moiety and the TAP ligand, the shape of this band should change significantly by electrolysis positive of the first oxidation potential. Accordingly, the solution of **1** was electrolysed at 0.21 V and the concomitant spectroscopic changes were monitored (ESI†). With the progress of electrolysis, the near-IR band faded away, the Soret band lost its intensity by one-third, and the Q band shifted to the red at 663 nm, in accord with the above expectations. From the linear relationship between the absorbance and concentration (Beer's law experiments, ESI†), the possibility of the near IR band being due to the aggregation can also be ruled out.

Furthermore, the molecular orbitals of the starting material **2** were calculated using the time-dependent DFT method, realized in the Gaussian 98W program (B3LYP functional and the SVP basis set).[10] The results of the first 10 lowest transitions are shown in Table 1. Transitions 1–3 and probably 5 correspond to a broad band between *ca.* 500 and 800 nm, and those 7–10 would be related to a strong band at *ca.* 350–400 nm. Taking into account that orbitals 76 (d_{yz}, E = −1.235 eV), 75

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† Electronic supplementary information (ESI) available: absorption spectra and Beer's law experiments. See http://www.rsc.org/suppdata/cc/b0/b007515i/

DOI: 10.1039/b007515i

Table 1 Calculated transition energies, oscillator strength (*f*), and configurations for compound **2**

Transition	Energy/ eV (nm)	f^a	Configurations[b]		
1	1.726 (718)	0.0002	72→74 (75%)	72→76(10%)	
2	1.896 (654)	0.0208	73→74(57%)	73→76(15%)	
3	2.297 (540)	0.0012	71→74(24%) 71→76(11%)	70→74(22%) 70→76(10%)	72→75(14%)
5	2.629 (472)	0.0073	72→75(28%)	73→74(19%) 73→76(14%)	72→76(14%) 71→74(12%)
7	3.223 (385)	0.0170	73→76(27%)	70→74(17%)	
8	3.413 (363)	0.0094	69→74(87%)		
9	3.506 (354)	0.2525	71→74(33%)	70→74(29%)	68→74(16%)
10	3.547 (350)	0.0025	72→76(14%)	73→75(11%) 71→75(10%)	70→75(11%)

[a] *f* greater than 0.0001 are shown. [b] Configurations greater than 10% are shown.

(LUMO+1, d_{xz}, −1.245), 73 (HOMO, d_{xy}, −6.486), 72 ($d_{x2\text{-}y2}$, −6.563), 71 (a_1(π, Fc, 47%) and d_{z2}(53%), −7.305), and 70 (a_1(π, Fc, 51%) and d_{z2}(43%), −7.459) are the iron ion or ferrocene-centered orbitals, while the orbital 74 (LUMO, −3.551) has 76% of its density on the tricyanovinyl fragment, the band to the longest wavelength between *ca.* 500 and 800 nm can be assigned to CT transitions from the filled iron ion orbitals in ferrocene to π* orbitals of the tricyanovinyl group. Unfortunately, similar calculations on **1** could not be performed, because the molecule was too large. However, considering that the Mössbauer parameters of **1** (isomer shift δ = 0.68 mm s^{-1}, quadrupole splitting ΔE_Q = 2.31 mm s^{-1}) and **2** (δ = 0.68, ΔE_Q = 2.06) are similar, and accordingly that the state of the iron ion in the two compounds is similar, the near-IR band of **1** may also be assigned as CT transitions between the Fc moiety and the TAP ligand with electron-withdrawing cyano groups[11] (*i.e.* the above CT transitions in **2** may correspond to the CT transitions from the iron ion in the Fc toward the nitrile groups in the TAP ligand of **1**). Thus, although the CT bands reported so-far on porphyrins and phthalocyanines have always been between the central metal and the ligands,[4,5] compound **1** appears to be the first porphyrin or phthalocyanine which shows a CT band from the metal in the substituent to the parent ligand.

V. N. N. is grateful to JSPS for financial support (grant P98418). This work was partially financed by a Grant-in-Aid for Scientific Research (B) 12020206 from the Ministry of Education, Science, Sports and Culture, Japan to N. K.

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7 Synthesis of compounds **1** and **2** and their representative data. Compound **2**. Following the method reported in E. G. Prevalova, D. A. Lemonovski, V. P. Alekseev, K. I. Grandberg and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, **8**, 1867, to a stirred solution of chloromercurferrocene (2.205 g, 0.01 mol) in 150 ml of acetonitrile, tetracyanoethylene (1.28 g, 0.01 mol) was added in one portion. The mixture was refluxed for 3 h and the solvent evaporated to dryness under reduced pressure. The resulting solid was dissolved in chloroform and chromatographed on an alumina column (Act. II) using chloroform–heptane (1 : 4 v/v) as eluent. The blue band was collected and recrystallized from chloroform–heptane (1 : 19 v/v), to give 1.15 g (40%) of the dark-blue crystals. Anal. Found: C, 63.02; H, 3.28; N, 14.36%. Calcd for $C_{15}H_9N_3Fe$: C, 62.75; H, 3.16; N, 14.64%. MS (EI, 70V) *m/z*: 287 (M$^+$, 100%). mp 132–133 °C. ^{1}H NMR δ ($CDCl_3$, TMS): 4.50 (5H, s, β-Cp), 5.17 (2H, t, α-Cp), 5.27 (2H, t, α-Cp). UV-Vis (λ_{max}, nm (log ε), $CHCl_3$): 300sh, 363 (4.04), 628 (3.43). Compound **1**. 3 ml butyl alcohol solution of **2** (70 mg, 4 mmol) and magnesium butoxide from 12 mg magnesium was refluxed for 4 h under a nitrogen atmosphere. After the solution was cooled to rt, the residue was imposed on a silica-gel column using chloroform as eluent. The green band was collected and further chromatographed on an alumina column (Act. I) using toluene–ethanol (4 : 1 v/v) as eluent. Finally, the green fraction was purified on a gel permeation column (Bio-beads SX-1, Bio-rad) using chloroform as eluent, followed by recrystallization from chloroform–hexane (1 : 19 v/v), to give *ca.* 11 mg (15%) of dark-green **1** as a mixture of several positional isomers. Anal. Found: C, 61.5; H, 3.1; N, 14.3%. Calcd for $C_{60}H_{36}N_{12}Fe_4Mg$: C, 62.22; H, 3.54; N, 13.84%. MS (MALDI-TOF, dithranol) *m/z*: 1172 (M$^+$, 100%) mp > 250 °C. ^{1}H NMR δ ($CDCl_3$, TMS): 4.12 (8H, s, α-Cp), 4.23 (20H, s, β-Cp), 5.19 (8H, s, α-Cp). UV-Vis. (λ_{max}, nm (log ε), $CHCl_3$): 320sh, 382 (4.67), 430sh, 590sh, 623 (4.47), 962 (4.12).

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11 Pcs with directly linked Fc units do not show near-IR bands beyond the Q band.[3a] Accordingly, this suggests that the near-IR band in **1** would not be observed unless cyano groups are not present in the periphery of **1**.