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A highly deformed iron(II) low-spin phthalocyanine which shows two MLCT transitions beyond the Q-band

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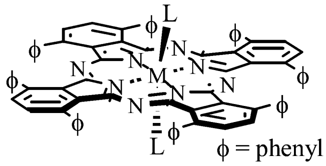
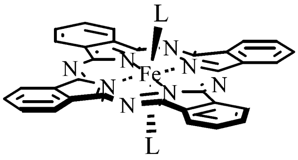
A highly deformed [1,4,8,11,15,18,22,25-octaphenylphthalocyaninato(2-)]iron(II) has been synthesized, and found to show absorption bands which may be assigned to metal-to-ligand charge transfer (MLCT) transitions in the near-IR region beyond the Q-band in pyridine, due to lowering of molecular symmetry to D_{2d} from D_{4h} symmetry of normal metallophthalocyanines.

Phthalocyanines (Pcs) and related macrocyclic compounds such as subphthalocyanines and naphthalocyanines have been developed as the latest dyes and pigments in areas such as photodynamic cancer therapy (PDT), solar cells, nonlinear optics, and catalysts for sulfur-removing processes in the oil industry.[1] In addition, the excited electronic states of expanded Pc derivatives with various π-symmetries have also been examined.[2,3] Although the geometrical symmetry of π-conjugated systems significantly affects excited electronic states,[4] the metal–ligand (M–L) interaction does not appear to be influenced explicitly by molecular symmetry, since the ligand field directly surrounding the central metal is close to D_{4h} symmetry.[4b] Recently, we described Pcs substituted by bulky phenyl groups at the so-called peripheral α-positions (for example, **1**), having notably deformed Pc skeletons.[5] In the present paper, we have found that the deformation of the Pc plane plays an important role in altering the electronic states of Pcs. That is, octa-phenylated iron(II) Pc (**2**) shows a plurality of transitions in the near-IR region (750–1000 nm) beyond the Q-band in pyridine (*i.e.* **3**), which is not observed for unsubstituted, normal planar iron(II) Pc, **4**.



1 : M = H_2 , L = Nil
2 : M = Fe , L = -CN-C_6H_{11}
3 : M = Fe , L = pyridine



4 : L = -CN-C_6H_{11}

In order to obtain **2**, an excess amount of $FeCl_2$ was added to a pyridine solution of metal-free **1**. The mixture was refluxed and cyclohexylisocyanide added without isolation of the iron complex. Further reaction and chromatographic purification gave pure **2** in a moderate yield.† Without axial ligands, the iron complex was very unstable and, therefore, difficult to isolate. Control complex, **4**, was synthesized from commercially available FePc, according to the literature method.[6] Although **2** decomposed immediately when dissolved in chloroform to give a yellowish solution, and gradually in dichloromethane or toluene, it was relatively stable in pyridine, producing pyridine-coordinated **3**. The ^1H NMR spectrum of **2** in pyridine-d_5 (*i.e.* **3**) showed cyclohexyl resonances at 1.11, 1.46, 1.62, and 3.48 ppm which are almost identical to those of free cyclohexyl groups in the same solvent,§ indicating that the axial ligands were replaced with pyridine-d_5. Moreover, the finely resolved resonance structure implies **3** is diamagnetic, *i.e.* the iron exists in a divalent and low spin state (pyridine-coordinated FePcs are generally in a low-spin divalent state).[7] The elemental analysis supports the conclusion that the oxidation state of the iron in **2** with two cyclohexylisocyanide axial ligands is also divalent in the solid state, *i.e.* the result was consistently explained without counter anions. On the other hand, the ^1H NMR of **4** in benzene-d_6 showed cyclohexyl resonances in the region from 0.26 to −1.18 ppm due to a remarkable loop-current effect (this species is also in a low-spin divalent state).[6]

The absorption and magnetic circular dichroism (MCD) spectra of **3** (solid lines) and **4** (dashed lines) in pyridine are shown in Fig. 1. Compound **4** shows a sharp Q-band at 654 nm without noticeable absorption on the longer wavelength side of the Q-band. On the other hand, the Q-band of **3** shifts to the red by *ca.* 860 cm^{-1} (694 nm) and, moreover, broad tails with medium intensity extended into the region of 750–1000 nm. Dispersion type Q MCD curves at 694 and 654 nm for **3** and **4**, respectively, support the view that these bands basically originate from HOMO-LUMO transitions. A band seen at around 430 nm for **4**, which has been assigned as an MLCT ($e_g \rightarrow b_{1u}(\pi)$) characteristic of Fe(II) low-spin Pcs,[8] appeared also for **3** at around 435 nm, supporting the view that the oxidation and spin state of the iron of **3** is also divalent low-spin. The MCD curve corresponding to the absorption tails of **3** consists of a Faraday *A*-term like dispersion at 794 nm and at least one negatively signed *B*-term at around 820–1000 nm, suggesting the presence of at least one degenerate and undegenerate transition in this region.¶ These assignments have been confirmed by band deconvolution analysis overlaid in Fig. 1, which showed one degenerate and one undegenerate transition at 784 and 900 nm, respectively. Since these bands are located on the lower energy side of the Q-band, they are very unlikely to result from π–π* transitions. In addition, large molar extinction coefficients of 13000–18000 L mol^{-1} cm^{-1} precludes the possibility of these bands being *d*–*d* transitions.‖ Furthermore, since the corresponding metal free, Co, Ni, and Zn derivatives show no such near-IR absorption bands,[9] the only feasible possibility appears to be charge transfer (CT) transitions between the Pc and Fe(II).

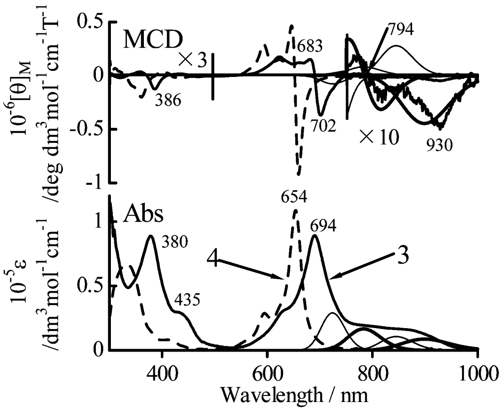


Fig. 1 MCD (top) and absorption (bottom) spectra of **3** (solid lines) and **4** (dashed lines) in pyridine, respectively. Deconvoluted gaussian curves are overlaid in the spectra.

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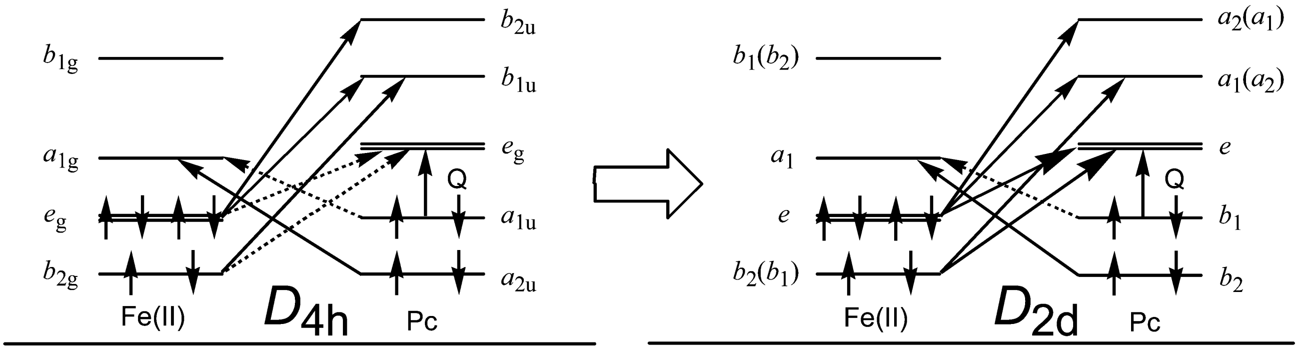

transition	CT	polarization	MCD
$a_{2u} \to a_{1g}$	L→M	Z	B
$a_{1u} \to a_{1g}$	L→M	forbidden	
$b_{2g} \to b_{1u}$	M→L	Z	B
$e_g \to b_{1u}, b_{2u}$	M→L	XY	A
$e_g \to e_g$	M→L	forbidden	
$b_{2g} \to e_g$	M→L	forbidden	

transition	CT	polarization	MCD
$b_2 \to a_1$	L→M	Z	B
$b_1 \to a_1$	L→M	forbidden	
$b_2(b_1) \to a_1(a_2)$	M→L	Z	B
$e \to a_1(a_2), a_2(a_1)$	M→L	XY	A
$e \to e$	M→L	Z	B
$b_2(b_1) \to e$	M→L	XY	A

Scheme 1 Schematic diagrams of the M–L interaction for D_{4h} (left) and D_{2d} (right) symmetry.

As reported recently,[5] octa-phenylated Pc has a highly deformed saddle-shaped skeletal structure, where the maximum deviation from the planarity reaches more than 1 Å at the β-carbon of the pyrroles. This reduces the symmetry of the Pc skeleton to D_{2d} from the D_{4h} of normal metalloPcs.[5] Scheme 1 shows schematic diagrams of the skeletal π and metal d orbitals for D_{4h} (left) and D_{2d} (right) symmetries, respectively. In the case of D_{4h} symmetry, the $e_g \longrightarrow b_{1u}(\pi)$, $e_g \longrightarrow b_{2u}(\pi)$, $b_{2g} \longrightarrow b_{1u}(\pi)$, and $a_{2u}(\pi) \longrightarrow a_{1g}$ transitions are allowed MLCT (first three) and LMCT (last), respectively, while the $e_g \longrightarrow e_g(\pi)$, $b_{2g} \longrightarrow e_g(\pi)$, and $a_{1u}(\pi) \longrightarrow a_{1g}$ transitions are symmetry forbidden. When the molecular symmetry is reduced to D_{2d}, the d orbitals transform as e_g to e, and a_{1g} to a_1, and b_{1g}, b_{2g} to $b_1(b_2)$, $b_2(b_1)$, as depicted in Scheme 1. With D_{2d} symmetry, four CT transitions which are allowed for D_{4h} are still allowed. However, in this case, $e \longrightarrow e(\pi)$ and $b_2(b_1) \longrightarrow e(\pi)$ transitions also become allowed and Faraday *B*- and *A*- terms, respectively, are expected in the MCD spectrum. These considerations, therefore, reasonably support the assignment of the observed near-IR transitions beyond the Q-band as MLCT transitions. The bands deconvoluted at 784 and 900 nm appear, therefore, to be the XY-polarized $b_2(b_1) \longrightarrow e(\pi)$ (Faraday *A*-term) and Z-polarized $e \longrightarrow e(\pi)$ transitions (*B*-term), respectively, which are symmetry forbidden in the case of D_{4h} symmetry.

Compound **4** showed redox couples at +0.22, −1.58, and −1.83 V (*vs.* ferrocenium/ferrocene) in pyridine and +0.08, −0.89, −1.74, and −2.14 V in *o*-dichlorobenzne (*o*-DCB), while those of **2** appeared at −1.33 V in pyridine and +0.37, −0.17, and −1.73 V in *o*-DCB.[10]

In summary, a novel, highly deformed peripherally octa-phenylated iron Pc, **2**, has been synthesized by a metal insertion reaction to the corresponding metal-free derivative in the presence of cyclohexylisocyanide as axial ligands. Compound **2** is unstable if axial ligands are absent and undergoes an axial ligand exchange reaction when dissolved in pyridine to produce **3**. Compound **3** shows broad absorption bands of medium intensity on the lower energy side of the Q-band. From the simultaneous band deconvolution analysis using both absorption and MCD spectra and considerations using group theory, these transitions have been reasonably assigned as MLCT transitions which are forbidden for normal Fe(II)Pcs with D_{4h} symmetry. This is the first example of divalent low-spin Fe(II)Pcs showing absorption bands beyond the Q-band, and therefore provides evidence that the effective symmetry of the saddle-shaped highly deformed Pc is D_{2d} even in the solution phase.

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Notes and references

† **2**: Compound **1** (50 mg, 0.045 mmol) and $FeCl_2$ (100 mg, 0.79 mmol) were heated at 115 °C for 15 min in pyridine (2 mL) under nitrogen. Cyclohexylisocyanide (*ca.* 2 mL) was added and reacted for *ca.* 15 min at 115 °C. The residue was immediately passed through a short alumina column (CH_2Cl_2–pyridine (20:1 v/v)) to remove unreacted metal salt, and the obtained green eluate was evaporated, to give a mixture of **2** and unreacted cyclohexylisocyanide, which was recrystallized from CH_2Cl_2–methanol‡ to give 29 mg (47%) of desired **2**. *Spectral data*: Mass(ESI-TOF): *m/z*: 1394 (M^+); elemental analysis calcd for $C_{94}H_{70}N_{10}Fe$: C, 80.90; H, 5.06, N, 10.04; found: C, 80.72; H, 5.10; N, 10.03.; ^1H NMR (pyridine-d_5, 400 MHz): δ 7.76–7.63 (16H, phenyl), 7.59–7.53 (8H, benzo), 7.31–7.39 (24H, phenyl), 3.48, 1.62, 1.46, and 1.11 (22H, cyclohexyl).; IR(KBr): 2159 cm^{-1} (–NC).

‡ Cyclohexyl isocyanide was chosen because it is liquid and therefore can be readily removed during recrystallization.

§ ^1H NMR for cyclohexylisocyanide (pyridine-d_5): δ 3.50, 1.64, 1.48, and 1.13 ppm.

¶ Compound **2** with two cyclohexylisocyaninde axial ligands in toluene also shows similar absorption and MCD spectra to those of **3** before decomposition.

‖ The extinction coefficient for a typical *d–d* transition is between $0 < \varepsilon < 10^2$ L mol^{-1} cm^{-1}.

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