Modulation of iron spin in ethane-bridged diiron(III) porphyrin dimer: anion dependent spin state switching

FIROZ SHAH TUGLAK KHAN, ANJANI KUMAR PANDEY and SANKAR PRASAD RATH*

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh 208 016, India

E-mail: sprath@iitk.ac.in

MS received 26 March 2018; revised 15 April 2018; accepted 17 April 2018; published online 5 July 2018

Abstract. The multiheme cytochrome *c* involves extensive interaction among the heme centers to enable them to perform a wide variety of enzymatic activities. In an attempt to exploit such heme–heme interactions in the synthetic diheme, an ethane-bridged diiron(III) porphyrin dimer has been utilized that can switch easily between *syn* and *anti* conformations due to highly flexible nature of the bridge. Upon protonation using 5% aqueous Brønsted acid, the dichloromethane solution of diiron(III)- μ -oxo porphyrin dimer immediately changes its color from green to red leading to the formation of a series of μ -hydroxo complexes. However, long exposure of the Brønsted acid converts the μ -hydroxo complex to five-coordinate diiron(III) porphyrin dimer in which the counter anion switches its position to act as an axial ligand. In the present study, the investigation has been extended further using Brønsted acids containing strongly coordinating anions such as HN_3 , HNCS and L-(+)-Lactic acid (HLA) in which the anions eventually coordinate to iron centers directly as axial ligands. A comprehensive account of the anion-mediated spin state change in the ethane-bridged diiron(III) porphyrin dimer has also been presented here.

Keywords. Diiron(III) porphyrin dimer; spin state; axial ligand; counter anion; structure elucidation.

1. Introduction

Multiheme cytochrome *c* constitutes one of the extensive classes of proteins that play crucial roles in long-range electron transfers as well as enzymatic catalysis.^{1–4} The family follows high structural conservations in terms of spatial arrangements of the heme units.^{3,4} Understanding the importance of heme structural arrangements is crucial for wide variations of their functional properties. However, due to a large number of heme centers in the proteins as well as the efficient coupling among the individual heme units, their spectroscopic analysis is often complicated.^{1–4}

The diheme cytochrome *c* (DHC2) from *Geobacter sulfurreducens* is the simplest member of such multiheme family in which two heme moieties are linked covalently through a single polypeptide chain.^{3a} Two heme units in DHC2 differ from each other in terms of their macrocyclic deformations as well as axial ligand orientations and such discrepancies are proposed to be originating through heme–heme interactions.^{3a} Our group has been actively engaged in unmasking the

effects of such interactions using ethane-bridged porphyrin dimer as a synthetic model of the diheme centers in DHC2.^{5–9} The large structural and functional discrepancies in dihememes, relative to their monoheme analogs, confirm the essential role played by such heme–heme interactions in the diheme complexes.⁵ Moreover, a reasonable choice of the linker allows precise regulation of the macrocyclic spatial arrangement for such inter-ring interactions and possible electronic communications.^{5–13}

In an attempt to exploit such interactions in the synthetic diheme, our group has recently reported a series of μ -hydroxo ethane-bridged diiron(III) porphyrin dimers.⁹ The molecules are synthesized through simple protonation of the corresponding oxo-bridged complex using Brønsted acids containing weakly coordinating counter anions. In these μ -hydroxo complexes, two iron(III) centers are found mostly inequivalent and thereby stabilizing two different spin states of iron in a single molecular framework despite both the cores having identical molecular structure.⁹ Spin states are also found to be counter anion specific.⁹ Such fascinating change in the spin state mediated through counter anions has been very unique as the anions are far

*For correspondence

from the metal centers but still control the spin state without changing the overall topology of the complexes. It has been found that along with the nature of the counter anions, intermacrocyclic interactions are indeed responsible for stabilizing two inequivalent iron centers.^{5b,c} In the present study, we extend the investigation further using Brønsted acids containing strongly coordinating anions such as HN_3 , HNCS and $\text{L-(+)-Lactic acid (HLA)}$ in which the anions eventually coordinate to iron centers directly as axial ligands. We also provide here a brief comprehensive account of the anion mediated spin state variations in the ethane-bridged diiron(III) porphyrin dimer.

2. Experimental

2.1 Materials

μ -oxo[*syn*-1,2-bis{iron(III) 5-(2,3,7,8,12,13,17,18-octaethylporphyrinyl)}ethane] ($(\text{ETA})\text{Fe}_2\text{O}$) was prepared by literature methods.^{8a} Reagents and solvents were purchased from commercial sources and purified by standard procedures.

2.1a $(\text{ETA})\text{Fe}_2(\text{N}_3)_2$: ($\text{ETA})\text{Fe}_2\text{O}$ (100 mg, 0.082 mmol) was dissolved in 40 mL dichloromethane. 700 mg NaN_3 was dissolved in 15 mL distilled water and the solution was acidified with concentrated H_2SO_4 . The dichloromethane solution was stirred together with the aqueous solution for 1 h. The organic layer was separated and then dried over anhydrous Na_2SO_4 . The solution was then filtered and evaporated to dryness. The solid product was dissolved in minimum volume of chloroform and carefully layer with *n*-hexane. Upon standing for 6–8 days, the dark red crystalline solid was formed which was collected by filtration, washed well with *n*-hexane and dried in vacuum. Yield: 85 mg, 80%. UV-Vis (dichloromethane) [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)]: 380 (2.2×10^5), 417 (2.1×10^5), 511 (2.0×10^4), 550 (1.8×10^4), 642 (5.4×10^3). ^1H NMR (CDCl_3 , 295 K): meso-*H*: -42.0 , -56.7 ; CH_3 : 6.5(2), 6.7(5); CH_2 : 34.4, 36.6, 37.3, 38.9(2), 40.9, 42.3, 47.5; $\text{CH}_2(\text{b})$: 68.0 ppm. IR, $\nu(\text{N}_3)$: 2058 cm^{-1} .

2.1b $(\text{ETA})\text{Fe}_2(\text{NCS})_2$: ($\text{ETA})\text{Fe}_2\text{O}$ (100 mg, 0.082 mmol) was dissolved in 40 mL dichloromethane. 1.05 g KNCS was dissolved in 15 mL distilled water and the solution was acidified with concentrated H_2SO_4 . The dichloromethane solution was stirred together with the aqueous solution for 1 h. The organic layer was separated and then dried over anhydrous Na_2SO_4 . The solution was then filtered and evaporated to dryness. The product was then dissolved in minimum volume of chloroform and carefully layer with *n*-hexane. Upon standing for 6–8 days, the dark red crystalline solid was formed which was collected by filtration, washed well with *n*-hexane and dried in vacuum. Yield: 91 mg, 84%. UV-Vis (dichloromethane) [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)]: 384 (2.1×10^5), 410 (2.0×10^5), 508 (1.9×10^4), 549 (1.8×10^4), 654 (5.7

$\times 10^3$). ^1H NMR (CDCl_3 , 295 K): meso-*H*: -46.6 , -64.1 ; CH_3 : 6.8(2), 7.0(2); CH_2 : 36.6, 38.1, 41.4, 42.1, 47.8, 48.5(2), 56.2; $\text{CH}_2(\text{b})$: 66.5 ppm. IR, $\nu(\text{NCS})$: 2027 cm^{-1} .

2.1c $(\text{ETA})\text{Fe}_2(\text{LA})_2$: ($\text{ETA})\text{Fe}_2\text{O}$ (100 mg, 0.082 mmol) was dissolved in dichloromethane (40 mL), 10% $\text{L-(+)-Lactic acid (HLA)}$ aqueous solution (10 mL) was added, and the mixture was stirred for 15 min. The organic layer was separated, dried with Na_2SO_4 , concentrated to dryness and the solid thus obtained was redissolved in a minimum quantity of dichloromethane and the solution was then carefully layered with cyclohexane in the air. After standing for 6–8 days at room temperature in air, a dark red crystalline solid was obtained, which was collected by filtration, washed well with the mother liquor, and dried in vacuum. Yield: 97 mg, 86%. UV-Vis (dichloromethane) [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)]: 396 (2.0×10^5), 420 (1.9×10^5), 520 (2.1×10^4), 550 (1.9×10^4), 649 (5.6×10^3). ^1H NMR (CDCl_3 , 295 K): meso-*H*: -40.3 , -57.4 ; CH_3 : 6.6(2), 6.9(2); CH_2 : 34.9, 37.4, 38.0, 39.5, 40.4, 43.5, 45.1, 45.6; $\text{CH}_2(\text{b})$: 63.5 ppm.

2.2 Instrumentation

UV-Vis spectra were recorded on a PerkinElmer UV/Vis spectrometer. Infrared spectra were recorded on a Vertex 70 Bruker spectrophotometer. ^1H NMR spectra were recorded on a JEOL 500 MHz instrument. The spectra for paramagnetic molecules were recorded over a 100-kHz bandwidth with 64 K data points and a 5-ms 90° pulse. For a typical spectrum between 2000 and 3000 transients were accumulated with a 50- μs delay time. The residual ^1H resonances of the solvents were used as a secondary reference.

2.3 X-ray structure solution and refinement

Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer equipped with CRYO Industries low-temperature apparatus and intensity data were collected using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data integration and reduction were processed with SAINT software.¹⁴ An absorption correction was applied.¹⁵ The structure was solved by the direct method using SHELXS-97 and was refined on F^2 by a full-matrix least-squares technique using the SHELXL-2014 program package.¹⁶ Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions. In the refinement, hydrogens were treated as riding atoms using SHELXL default parameters.

3. Results and Discussion

Ethane-bridged diiron(III)- μ -oxo porphyrin dimer ($(\text{ETA})\text{Fe}_2\text{O}$) (Scheme 1) was synthesized following a reported procedure.^{8a} Upon protonation using 5% aqueous solution of Brønsted acid (HX) containing weakly

Scheme 1. Synthetic outline of the complexes.

Figure 1. UV-Visible spectra in dichloromethane of (ETA)Fe₂O (green line), (ETA)Fe₂OH·ClO₄ (red line) and (ETA)Fe₂(N₃)₂ (blue line) at 295 K.

coordinating counter anions, the dichloromethane solution of (ETA)Fe₂O immediately changes its color from green to red leading to the formation of a series of μ -hydroxo complexes (ETA)Fe₂OH·X (Scheme 1).⁹ Such drastic color change in μ -hydroxo complexes is reflected in the UV-Visible spectra which displays blue shift in the Soret band as compared to the μ -oxo complex. Such a blue-shift in the Soret band (Figure 1) reflects the extreme closeness of two porphyrin macrocycles in the μ -hydroxo complex.¹⁷ Brønsted acids used were HI, HBF₄, HPF₆, HSbF₆ and HClO₄ and HTNP (2,4,6-trinitrophenol) which eventually produced the corresponding μ -hydroxo species. Upon large exposure of the Brønsted acids, μ -hydroxo complex (ETA)Fe₂OH·X converts to the corresponding five coordinate diiron(III) porphyrin dimer (ETA)Fe₂X₂ in which the counter anion switches its position to act as an axial ligand (Scheme 1).⁹ In the present work, we have

used Brønsted acid (HX) containing strongly coordinating anions such as HN₃, HNCS and L-(+)-Lactic acid (HLA). Addition of such acids to the dichloromethane solution of (ETA)Fe₂O immediately changes the color from green to red due to the formation of five-coordinate complex (ETA)Fe₂X₂ in which the anion X coordinates to the metal as an axial ligand. The molecules are also isolated in the solid state and structurally characterized.

The highly flexible ethane linker facilitates an easy switching between *syn* and *anti* conformations of the porphyrin dimer. UV-Visible spectroscopy is a powerful tool to determine the conformation of such porphyrin dimers in solution. A split Soret band is observed only for the *anti*-conformation due to two well-resolved transitions associated with the exciton coupled B_⊥ and B_{||} electronic transitions^{5a} and agrees well with Kasha's exciton coupling theory.¹⁸ A single Soret band observed for μ -oxo as well as a μ -hydroxo dimer at 407 and 372 nm, respectively, highlights the *syn* conformation.^{8a} However, a split Soret band (at 380 and 417 nm) is observed for (ETA)Fe₂(N₃)₂ as well as for other axially ligated five-coordinate ethane-bridged diiron(III) porphyrin dimers (ETA)Fe₂X₂ (X: NCS and LA) conferring the stabilization of *anti*-conformation in solution (Figure 1).

3.1 Crystallographic characterizations

Dark red crystals of (ETA)Fe₂(N₃)₂, (ETA)Fe₂(NCS)₂ and (ETA)Fe₂(LA)₂ were obtained *via* slow diffusion of either n-hexane or cyclohexane into the chloroform solutions of the respective complexes in the air at room temperature. All the complexes crystallize in the triclinic crystal system with *P*-1 space group. Perspective views of the complexes are shown in Figures 2–4 along with their packing diagram. Crystal data and data collection parameters are listed in Table 1. Five-coordinate heme centers are in *anti* positions with respect to each other in all the three complexes. Here, while N₃ ion binds to the iron center in an angular fashion ($\angle$ Fe–N–N, 129.2(3)°), NCS ion binds almost in a linear fashion with an angle of 163.3(4)° with iron.

The Fe–N (N₃) and Fe–N_{por} distances are 1.956(3) Å and 2.070(3) Å, respectively, in (ETA)Fe₂(N₃)₂ while the iron atom is displaced by 0.52 Å in the complex from the least-square plane of C₂₀N₄ porphyrinato core (Δ_{24}^{Fe}). For (ETA)Fe₂(NCS)₂, the Fe–N(NCS) distance is 1.972(5) Å while Fe–N_{por} and Δ_{24}^{Fe} distances are 2.046(3) Å and 0.58 Å, respectively. In complex (ETA)Fe₂(LA)₂, however, the Fe–O(LA) and the Fe–N_{por} distances are 1.882(4) and 2.062(5) Å, respectively, while Δ_{24}^{Fe} is 0.53 Å. For all the three complexes reported here, the Fe–N_{por}

Figure 2. (A) A perspective view of $(\text{ETA})\text{Fe}_2(\text{N}_3)_2$ showing 50% thermal contours for all non-hydrogen atoms at 100 K, and (B) diagram illustrating the molecular packing of $(\text{ETA})\text{Fe}_2(\text{N}_3)_2$. H-atoms have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Fe1–N1, 2.059(3); Fe1–N2, 2.078(3); Fe1–N3, 2.074(3); Fe1–N4, 2.069(3); Fe1–N5, 1.956(3); N5–Fe1–N1, 101.96(12); N5–Fe1–N2, 103.27(13); N5–Fe1–N3, 102.38(12); N5–Fe1–N4, 101.02(12); N6–N5–Fe1, 129.2(3).

and Δ_{24}^{Fe} distances are very characteristic of high-spin ($S=5/2$) iron(III) porphyrins.^{5,19–21} As can be seen, Fe–L distance follows an order: Fe–N (N_3) < Fe–N (NCS) < Fe–O (LA) which is, however, the order of their axial ligand strength also. Porphyrin rings are distorted in all three complexes reported here, however, the ring is most distorted in $(\text{ETA})\text{Fe}_2(\text{NCS})_2$. The *meso* carbons that are connected through the ethane linker are displaced the most which is presumably to minimize the non-bonded contact between the two porphyrin rings.

Table 2 compares the selected structural and geometrical parameters of diiron(III) porphyrin dimers reported here along with similar five-coordinate diiron(III) analogs reported earlier. Fe–N (N_3) distance is shorter as compared to Fe–N (NCS) which suggest N_3^- binds stronger to iron(III) than NCS^- . As can be seen in Table 2, the average Fe– N_{por} bond distances are more or less similar in the complexes. The only exception being the cases of $(\text{ETA})\text{Fe}_2(\text{SO}_3\text{CF}_3)_2$ and $(\text{ETA})\text{Fe}_2(\text{TNP})_2$, where Fe– N_{por} distances are significantly smaller which, in turn, stabilize intermediate-spin ($S=3/2$) state of iron in the complexes. In general, the Fe–N (L) distances are shortest followed by Fe–O (L) and Fe–S (L) distances

Figure 3. (A) A perspective view of $(\text{ETA})\text{Fe}_2(\text{NCS})_2$ showing 50% thermal contours for all non-hydrogen atoms at 100 K, and (B) diagram illustrating the molecular packing of $(\text{ETA})\text{Fe}_2(\text{NCS})_2$. H-atoms have been omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Fe1–N1, 2.047(4); Fe1–N2, 2.042(4); Fe1–N3, 2.046(4); Fe1–N4, 2.048(4); Fe1–N1L, 1.973(5); Fe2–N1A, 2.039(4); Fe2–N2A, 2.051(4); Fe2–N3A, 2.046(4); Fe2–N4A, 2.047(4); Fe2–N2L, 1.971(5); N1L–Fe1–N1, 100.39(18); N1L–Fe1–N2, 104.24(18); N1L–Fe1–N3, 106.59(18); N1L–Fe1–N4, 104.34(18); C1L–N1L–Fe1, 166.9(4); N2L–Fe2–N1A, 100.07(18); N2L–Fe2–N2A, 107.47(17); N2L–Fe2–N3A, 106.20(18); N2L–Fe2–N4A, 100.12(17); C2L–N2L–Fe2, 163.3(4).

which also reflect the strength of axial binding for the respective ligand with iron(III) porphyrin dimers.

Five-coordinate iron(III) porphyrins are known to stabilize a variety of spin states of iron such as high-spin ($S=5/2$), intermediate-spin ($S=3/2$), and admixed spin with various proportions of $S=3/2$ and $S=5/2$ states.^{19–21} The nature of the axial ligand decisively affects the spin states of iron. Even H-bonding interaction with the axial ligand which, thereby, controls the axial ligand strength can also change the iron spin state.^{20a} Deformations of the porphyrin ring are also known to affect the electronic structure of iron.^{20,21}

Porphyrin ring deformation is known to stabilize intermediate-spin of iron ($S=3/2$) over the high-spin state ($S=5/2$) in iron(III) porphyrins.^{19–21} As seen from Figure 5, the porphyrin is less distorted in $(\text{ETA})\text{Fe}_2(\text{N}_3)_2$ while it is much more distorted

Figure 4. (A) A perspective view of $(\text{ETA})\text{Fe}_2(\text{LA})_2$ showing 50% thermal contours for all non-hydrogen atoms at 100 K, and (B) diagram illustrating the molecular packing of $(\text{ETA})\text{Fe}_2(\text{LA})_2$. H-atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–N1, 2.061(4); Fe1–N2, 2.061(5); Fe1–N3, 2.076(4); Fe1–N4, 2.049(5); Fe1–O1L, 1.882(4); O1L–Fe1–N1, 105.20(18); O1L–Fe1–N2, 102.6(2); O1L–Fe1–N3, 98.98(18); O1L–Fe1–N4, 103.52(19); C1L–O1L–Fe1, 142.1(5).

in $(\text{ETA})\text{Fe}_2(\text{TNP})_2$ which accounts for the stabilization of intermediate-spin of iron in the latter complex. However, both the cores are unequally distorted in $(\text{ETA})\text{Fe}_2\text{OH}\cdot\text{I}_3$ (trace C, Figure 5); core-II is more distorted than that of core-I. Structural features are very characteristic of a nearly high-spin ($S = 5/2$) state of iron in core-I and admixed intermediate ($S = 3/2$ with a minor contribution from $S = 5/2$) in core-II in $(\text{ETA})\text{Fe}_2\text{OH}\cdot\text{I}_3$.^{9f} Therefore, unequal ring deformations mediate two inequivalent iron centers within the same molecule in $(\text{ETA})\text{Fe}_2\text{OH}\cdot\text{I}_3$!

3.2 ^1H NMR

The solution structure and properties of the iron(III) porphyrins can be obtained through their ^1H NMR spectra. Spectral assignments were made based on their relative intensities, line width and also, by comparing with the spectra of similar complexes. The spectra of $(\text{ETA})\text{Fe}_2(\text{NCS})_2$ and $(\text{ETA})\text{Fe}_2(\text{N}_3)_2$ are recorded for pure crystalline samples of the complexes and are compared with $(\text{ETA})\text{Fe}_2(\text{TNP})_2$ and $(\text{ETA})\text{Fe}_2(\text{ClO}_4)_2$ in Figure 6. In complex $(\text{ETA})\text{Fe}_2(\text{NCS})_2$, there are

eight methylene resonances between 36.6 and 56.2 ppm, bridging CH_2 protons at $\delta = 66.5$ ppm while the two *meso* signals appear at $\delta = -46.6$ and -64.1 in 2:1 intensity ratio (trace A, Figure 6). Similar proton resonance patterns are observed for $(\text{ETA})\text{Fe}_2(\text{N}_3)_2$ where the eight methylene signals appear between 34.4 and 47.5 ppm, bridging CH_2 protons at $\delta = 68.0$ ppm along with the two *meso* signals at $\delta = -42.0$ and -56.7 (trace B, Figure 6).

The ^1H NMR chemical shifts of the methylene and *meso* protons are highly sensitive towards the spin states of iron.^{20,21} The five-coordinate high-spin ethane-bridged diiron(III) porphyrin dimers display the $-\text{CH}_2$ signals to the downfield regions at around +40 ppm and the *meso* protons appear at the far upfield at around -40 ppm.²¹ The complexes $(\text{ETA})\text{Fe}_2(\text{NCS})_2$, $(\text{ETA})\text{Fe}_2(\text{N}_3)_2$ as well as $(\text{ETA})\text{Fe}_2(\text{LA})_2$ show similar pattern of proton resonances (Figure 6) and therefore are assigned to have high-spin state of iron in solution which are also observed in the solid state X-ray structure of the complexes. However, in case of $(\text{ETA})\text{Fe}_2(\text{TNP})_2$, the eight methylene signals (trace C, Figure 6) appear within a narrow region (16.1 to 20.4 ppm; average: 17.5 ppm) and two sharp *meso* resonances at -5.1 and -15.6 ppm which is assigned to have an intermediate-spin state of iron in solution.^{7b} This stabilization of intermediate-spin of iron(III) is attributed to more ruffled porphyrin macrocycle as observed in its solid state. Trace D (Figure 6) shows the ^1H NMR spectrum of $(\text{ETA})\text{Fe}_2(\text{ClO}_4)_2$ where the pattern, as well as positions of methylene and *meso* resonances, have been ascribed to the high-spin state of iron in the complex.^{8a} Therefore, the proton NMR spectra clearly demonstrates the role played by the axially ligated anions in modulating the spin states in five-coordinate iron(III) porphyrins.

The counter anion has been shown to perturb the spin state ordering in diiron(III) porphyrin dimers through multiple phenomena such as hydrogen-bonding interactions, switching positions between counter anion and axial ligand, ion-pair interactions, charge polarization, etc.^{5c,d} A beautiful example of the spin state switching is shown in Figure 7. ^1H NMR spectrum of $(\text{ETA})\text{Fe}_2\text{O}$ (trace A) is broad and the signals appear within the diamagnetic region due to strong antiferromagnetic coupling between the unpaired spins of iron through the oxo bridge.^{8a} However, protonation of the oxo group by HClO_4 reduces the antiferromagnetic coupling significantly and produces remarkable changes in the ^1H NMR spectra due to the formation of $(\text{ETA})\text{Fe}_2\text{OH}\cdot\text{ClO}_4$ in which eight methylene signals (within $\delta = 16.1$ to 21.6 ppm), bridging methylene protons at 33.6 ppm and two *meso* signals at -3.8 and -15.6 ppm in 2:1 intensity ratio (trace B, Figure 7) are observed.^{9e} The spectral

Table 1. Crystal data and data collection parameters of (ETA)Fe₂(N₃)₂, (ETA)Fe₂(NCS)₂ and (ETA)Fe₂(LA)₂.

	(ETA)Fe ₂ (N ₃) ₂	(ETA)Fe ₂ (NCS) ₂	(ETA)Fe ₂ (LA) ₂
Formula	C ₇₆ H ₉₂ Cl ₆ Fe ₂ N ₁₄	C ₇₇ H ₉₁ Cl ₃ Fe ₂ N ₁₀ S ₂	C ₈₀ H ₁₀₀ Fe ₂ N ₈ O ₆
<i>T</i> , K	100(2)	100(2)	100(2)
Formula weight	1526.03	1438.77	1381.37
Color	Dark red	Dark red	Dark red
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> , Å	10.208(5)	11.4620(17)	10.316(3)
<i>b</i> , Å	13.014(5)	14.933(2)	12.668(4)
<i>c</i> , Å	14.665(5)	22.960(4)	14.646(4)
α , deg	100.369(5)	80.712(3)	95.124(5)
β , deg	98.134(5)	87.651(3)	101.031(5)
γ , deg	99.440(5)	67.536(3)	100.656(6)
<i>V</i> , Å ³	1860.8(13)	3583.0(9)	1830.7(9)
Radiation (λ , Å)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)
<i>Z</i>	1	2	1
<i>d</i> _{calcd} , g.cm ⁻³	1.362	1.334	1.253
<i>F</i> (000)	800	1516	736
Crystal size (mm ³)	0.20 x 0.18 x 0.12	0.22 x 0.16 x 0.12	0.18 x 0.14 x 0.10
μ , mm ⁻¹	0.659	0.626	0.454
No. of unique data	6793	12936	6637
No. of restraints	0	0	0
No. of parameters refined	450	863	442
GOF on <i>F</i> ²	1.046	1.010	1.035
<i>R</i> ^{1a} [<i>I</i> > 2 σ (<i>I</i>)]	0.0602	0.0716	0.0838
<i>R</i> ^{1a} (all data)	0.0779	0.1223	0.1328
<i>wR</i> ^{2b} (all data)	0.1655	0.2183	0.2466
Largest diff. peak and hole	1.124 and -0.799 e.Å ⁻³	0.863 and -0.795 e.Å ⁻³	1.380 and -0.616 e.Å ⁻³

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; ^b wR2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}}$$

Table 2. Selected structural parameters for five coordinate ethane-bridged diiron(III) porphyrin dimers (ETA)Fe₂X₂.

Complex		Fe-N _{por} ^a	Fe-N/O/S ^b (L)	Δ_{24}^{Fe} ^c	Δ_{24}^d	Spin state (<i>S</i>)	Ref.
(ETA)Fe ₂ (ClO ₄) ₂	Core I	2.062(9)	1.873(9)	0.44	0.11	5/2	8a
	Core II	2.057(9)	1.940(7)	0.42	0.11	5/2	
(ETA)Fe ₂ (SO ₃ CF ₃) ₂		1.978(3)	2.066(3)	0.26	0.21	3/2	7c
(ETA)Fe ₂ (OPh) ₂		2.057(3)	1.916(2)	0.51	0.12	5/2	7b
(ETA)Fe ₂ (OAr) ₂ (Ar: 2,4,6-tribromophenol)		2.077(3)	1.864(3)	0.52	0.08	5/2	7b
(ETA)Fe ₂ (OAr) ₂ (Ar: 2,6-diisopropylphenol)	Core I	2.066(5)	1.807(4)	0.55	0.20	5/2	7b
	Core II	2.075(5)	1.813(4)	0.56	0.13	5/2	
(ETA)Fe ₂ (TNP) ₂		1.972(3)	2.000(2)	0.23	0.26	3/2	7b
(ETA)Fe ₂ (SPh) ₂		2.059(2)	2.2829(11)	0.61	0.20	5/2	7a
(ETA)Fe ₂ (SAr) ₂ (Ar: 2,4,6-trimethylthiophenol)		2.052(4)	2.2842(19)	0.58	0.19	5/2	7a
(ETA)Fe ₂ (SAr) ₂ (Ar: 2,6-dichlorothiophenol)		2.058(2)	2.3136(10)	0.41	0.16	5/2	7a
(ETA)Fe ₂ (SAr) ₂ (Ar: 2,3,4,5,6-pentafluorothiophenol)		2.053(6)	2.316(2)	0.55	0.19	5/2	7a
(ETA)Fe ₂ (N ₃) ₂		2.070(3)	1.956(3)	0.52	0.10	5/2	tw
(ETA)Fe ₂ (NCS) ₂	Core I	2.046(4)	1.973(5)	0.58	0.28	5/2	tw
	Core II	2.046(4)	1.971(5)	0.58	0.27	5/2	
(ETA)Fe ₂ (LA) ₂		2.062(5)	1.882(4)	0.53	0.10	5/2	tw

^aAverage value in Å. ^bDistance (in Å) of axial ligand. ^cAverage displacement of atoms in Å from the least-squares plane of the C₂₀N₄ porphyrinato core. ^dDisplacement of Iron in Å from the least-squares plane of the C₂₀N₄ porphyrinato core.

Figure 5. Out-of-plane displacements (in units of $0.01 \text{ \AA}$) of the porphyrin core atoms of (A) $(\text{ETA})\text{Fe}_2(\text{N}_3)_2$, (B) $(\text{ETA})\text{Fe}_2(\text{TNP})_2$ and (C) $(\text{ETA})\text{Fe}_2\text{OH}\cdot\text{I}_3$ from the mean plane of the C_{20}N_4 porphyrinato core. The horizontal axis shows the bond connectivity between atoms.

pattern is characteristic of the intermediate-spin state of iron. Trace C, however, shows the ^1H NMR signal of $(\text{ETA})\text{Fe}_2(\text{ClO}_4)_2$ which contains ClO_4^- in axial coordination. The molecule shows eight methylene signals observed within $\delta = 34.0$ to 58.9 ppm along with two *meso* signals (at -35.2 and -52.4 ppm in 1:2 intensity ratio) and one bridging methylene signal (at 64.5 ppm) which are characteristic features for the high-spin state of iron.^{8a} Therefore, the ClO_4^- anion controls the metal spin state by changing its role from axial coordination to counter anion in the μ -hydroxo complex.

Similarly, a comparison has also been made in Figure 8 to highlight such distinct changes in proton signals along with the spin state of iron just by switching the role of the anions from counter anion to axial coordination. The complex $(\text{ETA})\text{Fe}_2\text{OH}\cdot\text{I}_3$ shows two separate sets of resonances in two well distinct regions for its *meso*, methylene and bridging protons.^{9f} Such set of signals arise because of two inequivalent iron porphyrin cores in the same molecule: one core stabilizes iron having a nearly high-spin state while the other core stabilizes admixed intermediate-spin state.^{9f} However, axial coordination of the iodo anion in $(\text{ETA})\text{Fe}_2\text{I}_2$ renders both the iron centers equivalent in high-spin state which is inferred from the presence of only one set of eight

Figure 6. ^1H NMR spectra (in CDCl_3 at 295 K) of (A) $(\text{ETA})\text{Fe}_2(\text{NCS})_2$, (B) $(\text{ETA})\text{Fe}_2(\text{N}_3)_2$, (C) $(\text{ETA})\text{Fe}_2(\text{TNP})_2$ and (D) $(\text{ETA})\text{Fe}_2(\text{ClO}_4)_2$. *m* and *m'* are *meso* protons of the porphyrin ring as shown in Scheme 1.

Figure 7. ^1H NMR spectra (in CDCl_3 at 295 K) of (A) $(\text{ETA})\text{Fe}_2\text{O}$, (B) $(\text{ETA})\text{Fe}_2\text{OH}\cdot\text{ClO}_4$ and (C) $(\text{ETA})\text{Fe}_2(\text{ClO}_4)_2$.

Figure 8. ^1H NMR spectra (in CDCl_3 at 295 K) of (A) $(\text{ETA})\text{Fe}_2\text{OH}\cdot\text{I}_3$ and (B) $(\text{ETA})\text{Fe}_2\text{I}_2$.

diastereotopic methylene signals from $\delta = 37.1$ to 60.7 , bridging methylene protons at 77.1 ppm and two *meso* signals at -44.4 and -59.3 ppm (trace B, Figure 8).^{8a}

Modulation of iron spins by counter anions as well as stabilization of two different spin states of iron in the same molecule as observed in the μ -hydroxo complex $(\text{ETA})\text{Fe}_2\text{OH}\cdot\text{X}$ require some discussion here. An extensive computational study on the μ -hydroxo

complex has revealed that subtle environmental perturbation can indeed change the spin state ordering as observed in the experiment.^{9a-c} A tightly associated counter anion imposes a significant steric effect on one of the two porphyrin rings (Scheme 2) as a result of its close proximity which thereby deforms the ring more compared to the other one.^{5c,d,9a} This has resulted in the formation of two inequivalent iron centers that

Scheme 2. Proposed role of counter anion X in the μ -hydroxo complex (ETA)Fe₂OH·X.

stabilize two different spin states in the same molecule.^{9a} In contrast, ClO₄[−] counter ion, however, forms an H-bonding with the μ -OH group and thus interacts equally with both the rings which makes the iron centers equivalent (Scheme 2). Moreover, larger interheme separation (by moving from an ethane to a larger diethylpyrrole bridge or by changing μ -OH to μ -F) results in only a weaker/negligible inter-ring interaction and, as a result, iron centers become equivalent.¹⁰

4. Conclusions

Upon protonation using Brønsted acid (HX) containing strongly coordinating anions such as HN₃, HNCS and L-(+)-Lactic acid (HLA), the dichloromethane solution of (ETA)Fe₂O produces a series of five-coordinate diiron(III) porphyrin dimer complex (ETA)Fe₂X₂ (X: N₃, NCS, LA). The structural and geometrical parameters obtained from the molecular structures of (ETA)Fe₂(N₃)₂, (ETA)Fe₂(NCS)₂ and (ETA)Fe₂(LA)₂ are very characteristic of high-spin ($S=5/2$) states of iron. However, in the case of (ETA)Fe₂(TNP)₂, an intermediate-spin state of iron is stabilized which is attributed to more ruffled porphyrin macrocycle coming out of stronger intramacrocyclic interaction in the complex. The solid-state structure of (ETA)Fe₂X₂ is also preserved in solution as confirmed by the ¹H NMR spectroscopy.

A brief comprehensive account of the anion-mediated spin state change in the ethane-bridged diiron(III) porphyrin dimer has also been presented here. The anion affects the spin state ordering in diiron(III) porphyrin dimers by switching its roles between axial-ligand and counter anion. When ClO₄ acts as a counter anion, it stabilizes the intermediate-spin of iron in the μ -hydroxo complex, however, upon axial coordination in five-coordinate diiron(III) porphyrin dimers, it generates high-spin iron center. Such effect of counter anion is even more profound in case of the μ -hydroxo complex (ETA)Fe₂OH·I₃ where two inequivalent iron centers are

stabilized in the complex in which one core stabilizes the high-spin state of iron while the other one stabilizes admixed intermediate-spin state. However, axial coordination of the iodide anion in (ETA)Fe₂I₂ renders both the iron centers equivalent in high-spin state. As can be seen, anion switches its position from counter anion (in the μ -hydroxo complex) to axial ligand in (ETA)Fe₂X₂ and thereby changing the structure and properties of the respective complex.

Supplementary Information (SI)

CCDC-1831623, 1831624 and 1831625 contain the X-ray crystallographic details in CIF format for (ETA)Fe₂(LA)₂, (ETA)Fe₂(N₃)₂ and (ETA)Fe₂(NCS)₂, respectively. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or [from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

We are thankful to the Department of Science and Technology, Government of India and Council of Scientific and Industrial Research (CSIR), New Delhi for financial support. F.S.T.K. thanks University Grants Commission (UGC), India and A.K.P. thanks CSIR, India for their fellowships.

References

- (a) Liu J, Chakraborty S, Hosseinzadeh P, Yu Y, Tian S, Petrik I, Bhagi A and Lu Y 2014 Metalloproteins Containing Cytochrome, Iron–Sulfur, or Copper Redox Centers *Chem. Rev.* **114** 4366; (b) Paquette C M and Louro R O 2014 Unveiling the Details of Electron Transfer in Multicenter Redox Proteins *Acc. Chem. Res.* **47** 56; (c) Bewley K D, Ellis K E, Firer-Sherwood M A and Elliott S J 2013 Multi-heme proteins: nature's electronic multi-purpose tool *Biochim. Biophys. Acta* **1827** 938; (d) Akutsu H and Takayama Y 2007 Functional Roles of the Heme Architecture and Its Environment in Tetraheme Cytochrome *c* *Acc. Chem. Res.* **40** 171; (e) Pereira I A and Xavier A V 2005 In *Encyclopedia of Inorganic Chemistry* R B King (Ed.) (New York: John Wiley & Sons) **5** p. 3360; (f) Stevens J M, Daltrop O, Allen J W A and Ferguson S J 2004 C-type Cytochrome Formation: Chemical and Biological Enigmas *Acc. Chem. Res.* **37** 999
- (a) Watanabe H C, Yamashita Y and Ishikita H 2017 Electron transfer pathways in a multiheme cytochrome MtrF *Proc. Natl. Acad. Sci. U S A* **114** 2916; (b) Santos T C, Silva M A, Morgado L, Dantas J M and Salgueiro C A 2015 Diving into the redox properties of Geobacter sulfurreducens cytochromes: a model for extracellular electron transfer *Dalton Trans.* **44** 9335; (c) Breuer M, Rosso K M and Blumberger J 2014 Electron flow in multiheme bacterial cytochromes is a balancing act between

- heme electronic interaction and redox potentials *Proc. Natl. Acad. Sci. U S A* **111** 611; (d) Zhang Y, Liu C, Balaeff A, Skourtis S S, and Beratan D N 2014 Biological charge transfer via flickering resonance *Proc. Natl. Acad. Sci. U S A* **111** 10049; (e) Soares C M and Baptista A M 2012 Simulation of multihaem cytochromes *FEBS Letters* **586** 510; (f) Burggraf F and Koslowski T 2014 Charge transfer through a cytochrome multiheme chain: Theory and simulation *Biochim. Biophys. Acta* **1837** 186; (g) Fonseca B M, Paquete C M, Salgueiro C A and Louro R O 2012 The role of intramolecular interactions in the functional control of multiheme cytochromes *c* *FEBS Letters* **586** 504
3. (a) Heitmann D and Einsle O 2005 Structural and Biochemical Characterization of DHC2, a Novel Diheme Cytochrome *c* from *Geobacter sulfurreducens* *Biochemistry* **44** 12411; (b) Abreu I A, Lourenço A I, Xavier A V, LeGall J, Coelho A V, Matias P M, Pinto D M, Carrondo M A, Teixeira M and Saraiva L M 2003 A novel iron centre in the split-Soret cytochrome *c* from *Desulfovibrio desulfuricans* ATCC 27774 *J. Biol. Inorg. Chem.* **8** 360; (c) Brige A, Leys D, Meyer T E, Cusanovich M A and Van Beeumen J J 2002 The 1.25 Å Resolution Structure of the Diheme NapB Subunit of Soluble Nitrate Reductase Reveals a Novel Cytochrome *c* Fold with a Stacked Heme Arrangement *Biochemistry* **41** 4827; (d) Gibson H R, Mowat C G, Miles C S, Li B -R, Leys D, Reid G A and Chapman S K 2006 Structural and Functional Studies on DHC, the Diheme Cytochrome *c* from *Rhodobacter sphaeroides*, and Its Interaction with SHP, the *sphaeroides* Heme Protein *Biochemistry* **45** 6363
 4. (a) Sharma S, Cavallaro G and Rosato A 2010 A systematic investigation of multiheme *c*-type cytochromes in prokaryotes *J. Biol. Inorg. Chem.* **15** 559; (b) Hartshorne R S, Jepson B N, Clarke T A, Field S J, Fredrickson J, Zachara J, Shi L, Butt J N and Richardson D J 2007 Characterization of *Shewanella oneidensis* MtrC: a cell-surface decaheme cytochrome involved in respiratory electron transport to extracellular electron acceptors *J. Biol. Inorg. Chem.* **12** 1083; (c) Pattarkine M V, Tanner J J, Bottoms C A, Lee Y -H and Wall J D 2006 *Desulfovibrio desulfuricans* G20 tetraheme cytochrome structure at 1.5 Å and cytochrome interaction with metal complexes *J. Mol. Biol.* **358** 1314
 5. (a) Lai D, Khan F S T and Rath S P 2018 Multiheme Proteins: Effect of Heme-Heme Interactions *Dalton Trans.* **47** 0000; <https://doi.org/10.1039/C8DT00518D> (b) Sil D and Rath S P 2015 An ethane-bridged porphyrin dimer as model of di-heme proteins: inorganic and bioinorganic perspectives and consequences of heme-heme interactions *Dalton Trans.* **44** 16195; (c) Guchhait T, Sasmal S, Khan F S T and Rath S P 2017 Oxo- and hydroxo-bridged diiron(III) porphyrin dimers: inorganic and bio-inorganic perspectives and effects of intermacrocyclic interactions *Coord. Chem. Rev.* **337** 112; (d) Khan F S T, Guchhait T, Sasmal S and Rath S P 2017 Hydroxo-bridged diiron(III) and dimanganese(III) bisporphyrins: modulation of metal spins by counter anions *Dalton Trans.* **46** 1012
 6. (a) Singh A K, Khan F S T and Rath S P 2017 Silver(III) · · silver(III) interactions that stabilize the *syn*-form in a porphyrin dimer upon oxidation *Angew. Chem., Int. Ed.* **56** 8849; (b) Dey S and Rath S P 2014 *Syn-anti* conformational switching in an ethane-bridged Co(II)bisporphyrin induced by external stimuli: effects of inter-macrocyclic interactions, axial ligation and chemical and electrochemical oxidations *Dalton Trans.* **43** 2301; (c) Brahma S, Ikbal S A and Rath S P 2011 *Syn-anti* Conformational Switching: Synthesis and X-ray Structures of *Tweezer* and *Anti* Form in a Zinc Porphyrin Dimer Induced by Axial Ligands *Inorg. Chim. Acta* **372** 62
 7. (a) Sil D, Khan F S T and Rath S P 2014 Axial thiophenolate coordination on diiron(III)bisporphyrin: influence of heme-heme interactions on structure, function and electrochemical properties of the individual heme center *Inorg. Chem.* **53** 11925; (b) Bhowmik S, Dey S, Sahoo D and Rath S P 2013 Unusual stabilization of an intermediate spin of iron upon axial phenoxide coordination on a diiron(III)bisporphyrin: effect of heme-heme interactions *Chem. Eur. J.* **19** 13732; (c) Bhowmik S, Ghosh S K and Rath S P 2011 Control of spins by ring deformation in a diiron(III)bisporphyrin: reversal of ClO₄⁻ and CF₃SO₃⁻ ligand field strength on the magnetochemical series *Chem. Commun.* **47** 4790; (d) Bhowmik S, Sil D, Patra R and Rath S P 2011 Axial Phenoxide Coordination on Di-Iron(III)bisporphyrin: Insights from Experimental and DFT Studies *J. Chem. Sci.* **123** 827
 8. (a) Ghosh S K, Patra R and Rath S P 2010 Synthesis and characterization of *anti*-bisFe(III) porphyrins, *syn*-bisFe(III)-μ-oxo porphyrin and *syn*-bisFe(III)-μ-oxo porphyrin cation radical *Inorg. Chem.* **49** 3449; (b) Ghosh S K, Patra R and Rath S P 2010 Synthesis, structure and photocatalytic activity of a remarkably bent, cofacial ethene-linked diiron(III) μ-oxobisporphyrin *Inorg. Chim. Acta* **363** 2791; (c) Ghosh S K, Patra R and Rath S P 2008 Remarkably bent, ethane-linked, diiron(III) μ-oxobisporphyrin: synthesis, structure, conformational switching, and photocatalytic oxidation *Inorg. Chem.* **47** 10196
 9. (a) Khan F S T, Pandey A K and Rath S P 2016 Remarkable anion dependent spin state switching in diiron(III)-μ-hydroxo bisporphyrins: what role do counter ions play? *Chem. Eur. J.* **22** 16124; (b) Sil D, Bhowmik S, Khan F S T and Rath S P 2016 Experimental and theoretical investigation on a series of novel dimanganese(III)-μ-hydroxo bisporphyrins: magneto-structural correlation and effect of metal spin on porphyrin core deformation *Inorg. Chem.* **55** 3239; (c) Sainna M A, Sil D, Sahoo D, Martin B, Rath S P, Comba P and de Visser S P 2015 Spin state ordering in hydroxo bridged diiron(III)bisporphyrin complexes *Inorg. Chem.* **54** 1919; (d) Ghosh S K, Bhowmik S, Sil D and Rath S P 2013 Effect of heme-heme interactions and modulation of metal spins by counter anions in a series of diiron(III)-μ-hydroxo bisporphyrins: unusual stabilization of two different spins in a single molecular framework *Chem. Eur. J.* **19** 17846; (e) Bhowmik S, Ghosh S K, Layek S, Verma H C and Rath S P 2012 Protonation of an oxo-bridged diiron unit makes two iron centers different: a new class of diiron(III)-μ-hydroxo bisporphyrin and control of spins by counter anions *Chem. Eur. J.* **18** 13025; (f) Ghosh S

- K and Rath S P 2010 A remarkably bent diiron(III)- μ -hydroxo bisporphyrin: unusual stabilization of two spin states of iron in a single molecular framework *J. Am. Chem. Soc.* **132** 17983
10. (a) Sil D, Khan F S T and Rath S P 2016 Effect of interporphyrin distance on spin-state in diiron(III) μ -hydroxo bisporphyrins *Chem. Eur. J.* **22** 14585; (b) Sil D, Kumar A and Rath S P 2016 Diiron(III)- μ -fluoro bisporphyrins: effect of bridging ligand on the metal spin state *Chem. Eur. J.* **22** 11214
 11. (a) Guchhait T, Sarkar S, Pandit Y A and Rath S P 2017 Probing bis-Fe^{IV} MauG: isolation of highly reactive radical intermediates *Chem. Eur. J.* **23** 10270; (b) Pandit Y A, Sanfui S and Rath S P 2017 Intermacrocyclic Interaction Triggers Facile One-pot Synthesis of a Chlorin-Porphyrin Heterodimer *Chem. Eur. J.* **23** 13415; (c) Sil D, Dey S, Kumar A, Bhowmik S and Rath S P 2016 Oxidation triggers extensive conjugation and unusual stabilization of two di-heme dication diradical intermediates: role of bridging group for electronic communication *Chem. Sci.* **7** 1212; (d) Dey S, Sil D and Rath S P 2016 A highly oxidized cobalt porphyrin dimer: spin coupling and stabilization of the four-electron oxidation product *Angew. Chem., Int. Ed.* **55** 996; (e) Pandit Y A, Sanfui S and Rath S P 2017 Intermacrocyclic interaction triggers facile one-pot synthesis of a chlorin-porphyrin heterodimer *Chem. Eur. J.* **23** 13415; (f) Dey S, Sil D, Pandit Y A and Rath S P 2016 Effect of two interacting rings in metalloporphyrin dimers upon stepwise oxidation *Inorg. Chem.* **55** 3229
 12. (a) Mondal P, Sarkar S and Rath S P 2017 Cyclic Bisporphyrin Based Flexible Molecular Containers: Controlling Guest Arrangements and Supramolecular Catalysis by Tuning Cavity Size *Chem. Eur. J.* **23** 7093; (b) Mondal P and Rath S P 2017 A Tunable Cyclic Container: Guest-Induced Conformational Switching, Efficient Guest Exchange and Selective Isolation of C₇₀ from Fullerene Mixture *Chem. Asian. J.* **12** 1824; (c) Mondal P and Rath S P 2016 Cyclic Zn(II) bisporphyrin Based Molecular Switch: Supramolecular Control of Complexation Mediated Conformational Switching and Photoinduced Electron Transfer *Chem. Eur. J.* **22** 5607; (d) Chaudhary A and Rath S P 2012 Encapsulation of TCNQ and acridinium ion within bisporphyrin cavity: synthesis, structure, photophysical and HOMO-LUMO gap mediated electron transfer properties *Chem. Eur. J.* **18** 7404; (e) Chaudhary A and Rath S P 2011 Efficient complexation of pyrrole-bridged di-zinc(II) bisporphyrin with fluorescent probe pyrene: synthesis, structure, and photoinduced singlet-singlet energy transfer *Chem. Eur. J.* **17** 11478; (f) Mondal P, Chaudhary A and Rath S P 2013 Supramolecular BODIPY-Zn(II)-Bisporphyrin Dyad and Trinitrofluorenone Encapsulated Triad as Models of Antenna-reaction Center: Synthesis, Structure and Photophysical Properties *Dalton Trans.* **42** 12381
 13. (a) Valderrey V, Aragay G and Ballester P 2014 Porphyrin tweezer receptors: Binding studies, conformational properties and applications *Coord. Chem. Rev.* **258** 137; (b) Harvey P D, Stern C, Gros C P and Guillard R 2007 The photophysics and photochemistry of cofacial free base and metallated bisporphyrins held together by covalent architectures *Coord. Chem. Rev.* **251** 401; (c) Rosenthal J, Bachman J, Dempsey J L, Esswein A J, Gray T G, Hodgkiss J M, Manke D R, Luckett T D, Pistorio B J, Veige A S and Nocera D G 2005 Oxygen and hydrogen photocatalysis by two-electron mixed-valence coordination compounds *Coord. Chem. Rev.* **249** 1316
 14. SAINT+, 6.02 ed. 1999 (Madison, WI : Bruker AXS)
 15. Sheldrick G M 2000 SADABS 2.0.
 16. Sheldrick G M 2014 SHELXL-2014: Program for Crystal Structure Refinement (Göttingen, Germany : University of Göttingen)
 17. Scheidt W R, Cheng B, Safo M K, Cukiernik F, Marchon J C and Debrunner P G 1992 New class of bridged diiron(III) complexes with a single hydroxo bridge. The preparation and structure of (μ -hydroxo)bis((octaethylporphinato)iron(III)) perchlorate *J. Am. Chem. Soc.* **114** 4420
 18. Kasha M, Rawls H R and Bayoumi M A E 1965 The exciton model in molecular spectroscopy *Pure Appl. Chem.* **11** 371
 19. Weiss R, Gold A, Turner J 2006 Cytochromes *c'*: Biological models for the $S = 3/2, 5/2$ spin state admixture? *Chem. Rev.* **106** 2550
 20. (a) Sahoo D, Quesne M G, de Visser S P and Rath S P 2015 Hydrogen bonding interactions trigger a spin-flip in iron(III)-porphyrin complexes *Angew. Chem., Int. Ed.* **54** 4796; (b) Sahoo D and Rath S P 2015 Controlled generation of highly saddled (porphyrinato) iron(III) iodide, tri-iodide and one-electron oxidized complex *Chem. Commun.* **51** 16790; (c) Sahoo D, Guchhait T and Rath S P 2016 Spin modulation in highly distorted Fe(III) porphyrinates using axial coordination and their π -cation radicals *Eur. J. Inorg. Chem.* 3441; (d) Chaudhary A, Patra R and Rath S P 2010 Binding of Catechols to Iron(III) Octaethyl Porphyrin: An Experimental and DFT Investigation *Eur. J. Inorg. Chem.* 5211; (e) Patra R and Rath S P 2009 Cyanide binding to Iron in a Highly Distorted Porphyrin Macrocycle: Synthesis and Structure of Low-Spin Fe(II) Dicyano Porphyrin *Inorg. Chem. Commun.* 515; (f) Patra R, Chaudhary A, Ghosh S K and Rath S P 2008 Modulation of Metal Displacements in a Saddle Distorted Macrocycle: Synthesis, Structure, and Properties of High-Spin Fe(III) Porphyrins and Implications for the Hemoproteins *Inorg. Chem.* **47** 8324
 21. Nakamura M, Ohgo Y and Ikezaki A 2010 In *Handbook of Porphyrin Science* K M Kadish, K M Smith and R Guillard (Eds.) (Singapore: World Scientific) **7** Ch. 32 p. 1