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Synthesis and characterization of monomer and dimer complexes of porphyrin iron(III) with bridging phenylcyanamide ligands

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ABSTRACT

Several new mono and dinuclear complexes of $[(P)Fe^{III}(L)]$, in which P is the dianion of tetraphenylporphyrin(TPP) and tetramesitylporphyrin(TMP) and L is the monoanion of 4-azo(phenylcyanamido)benzene (apc) (1) and (2) or dianion 1,4-di cyanamidobenzene (dicyd) (3), (4), (7), (8) and 4,4'-azo-diphenylcyanamide (adpc) (5), (6), (9), (10) have been prepared by the reaction of $[(P)Fe^{III}CI]$ with appropriate thallium salts of phenylcyanamide derivatives. Each of the complexes has been characterized by FT-IR, UV–Vis, ¹H NMR, MALDI-TOF and EPR spectroscopic data. In non-coordinating solvents (such as toluene or chloroform) these complexes exhibit ¹H NMR spectra that are characteristic of highspin (S = 5/2) species. The cyanamide group (NCN) of the bridging ligand is coordinated to Fe(III) ions through the nitrile-nitrogen. The iron(III) phenylcyanamide complexes are not reactive toward dioxygen, they convert into [TPPFe^{III}CI] when treated with HCI. EPR and NMR have shown that in dinuclear complexes weak magnetic interactions take place between two iron(III) paramagnetic centers.

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1. Introduction

Expansion of the π -electronic system of component molecules is one of the most important and promising approaches, not only to achieve high conductivity, but also for attracting strong effective magnetic coupling [1–3]. Furthermore, molecular materials with special properties, such as one or two dimensional electronics based on planar π -conjugated molecules, are a very active field today, due to their potential applications in a new generation of electronic, magnetic, and/or photonic devices [4–9]. Porphyrin arrays have attracted considerable interest as synthetic targets due to the potential for exploitation as photochemical devices. These porphyrins become self-assembled together due to the axial ligand or periphery. These compounds have electronic, magnetic and photonic properties and application in semiconductors, transistors, solar cells and electroluminescents [10–14].

The discovery of the *N*,*N*'-dicyanodiimines derived from benzoquinones (DCNQIs), naphthoquinones (DCNNIs), and anthraquinones (DCNAIs) family of strong electron acceptor molecules by Hünig and Aumüller in 1984 [15] has led to the development of a large variety of highly conducting materials [16]. In this regard, [TPPMn][tetracyanoethylene] · 2PhMe has shown to act as a molecule-based magnet [17–21] and (2,5-dimethyl-*N*,*N*'-dicyanoquinone diimine)₂Cu (DCNQI) has shown to exhibit extremely high conductivity of 500000 S cm⁻¹ at 3.5 K [22]. Crutchley et al. [23,24] have largely investigated DCNQI and phenylcyanamide (ligands as analogue of DCNQIs) in both neutral and anionic forms with $Mn^{\rm II}$ and other metals.

1,4-Dicayanamidobenzene (dicyd) and 4,4'-azo-diphenylcyanamide (adpc) ligands are well-suited for intramolecular electro- and magneto- communications via a hole-transfer mechanism [23,25,26]. Work on dinuclear systems derived from cyanamide or dicyanamide anions acting as bridging ligands is a fast-growing research field due to the large variety of topologies, dimensionalities, and magnetic properties that can be obtained [27].

Therefore, due to large π -conjugated systems in porphyrins and phenylcyanamides and magnetic properties of Fe(III), which is usually high-spin in porphyrin complexes [28–30], we have previously reported porphyrin iron(III) with phenylcyanamide derivatives as the axial ligand. So, here we wish to report the synthesis and characterization of 10 porphyrin iron(III) with extended azodiphenylcyanamide and phenyldicyanamides in monomer or dimer forms. These complexes are thoroughly characterized and magnetic interaction in dimers is discussed.

2. Experimental

2.1. Reagents and materials

Dichloromethane, *N*,*N*-dimethylformamide, methanol, *p*-chloranil, toluene, I₂, *n*-hexane, benzophenone, Na and iron (III) chloride were reagent grade and purchased from Merck and pyrrole, benzaldehyde and 2,4,6-trimethylbenzaldehyde were from Fluka. Prior to use, dichloromethane and methanol were pre-dried and distilled over P_2O_5 and Mg + I₂, respectively. Toluene was



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n P-Fe-Cl + Tl-X	solvent	P-Fe-X	+	n TlCl
		(1-10)		ł

(1)	$X : NCN-C_6H_4-N=N-Ph (apc)$	P : tetraphenyl Porphyrin(TPP)	n = 1
(2)	$X : NCN-C_6H_4-N=N-Ph - (apc)$	P : tetramesityl Porphyrin(TMP)	n = 1
(3)	$X: NCN-C_6H_4-N=C=N^{-}Tl^{+} (dicyd-Tl)$	P : TPP	n = 1
(4)	$X: NCN-C_6H_4-N=C=N^{-}Tl^{+} (dicyd-Tl)$	P : TMP	n = 1
(5)	$X: NCN-C_6H_4-N=N-C_6H_4-N=C=N^{-}Tl^{+} (adpc-Tl)$	P : TPP	n = 1
(6)	$X: NCN-C_6H_4-N=N-C_6H_4-N=C=N^{-}Tl^{+} (adpc-Tl)$	P : TMP	n = 1
(7)	$X : NCN-C_6H_4-N=C=N-Fe-P$ (dicyd-FeP)	P : TPP	n = 2
(8)	X : NCN-C ₆ H ₄ -N=C=N-Fe-P (dicyd-FeP)	P : TMP	n = 2
(9)	$X: \ \text{NCN-C}_6\text{H}_4\text{-}\text{N}=\text{N-C}_6\text{H}_4\text{-}\text{N}=\text{C}=\text{N-Fe-P} \ (adpc\text{-}\text{FeP})$	P : TPP	n = 2
(10)	X : NCN-C ₆ H ₄ -N=N-C ₆ H ₄ -N=C=N-Fe-P (adpc-FeP)	P : TMP	n = 2

Scheme 1. Metathesis reaction and abbreviation for synthesis of iron Porphyrin phenylcyanamide derivatives.

pre-dried and distilled over Na and benzophenone. All manipulations involving phenylcyanamide coordination to iron(III)porphyrin were carried out under nitrogen using standard Schlenk technique. Tetraphenylporphyrin (TPPH₂) and tetramesithylporphyrin(TMPH₂) were synthesized by Lindsey's [31] and Hoffmann's methods [32], respectively and TPPFeCl and TMPFeCl by Adler's method [33]. Extra care to exclude any trace of impurity of μ -oxo dimer and pre-treatment of TPPFeCl with HCl was necessary. Preparation of the thallium salts of phenylcyanamide derivatives ligands has been previously reported [34].

Caution: Thallium is toxic.

2.2. Physical measurements

2.2.1. Spectroscopy

UV-Vis spectra were recorded on a Shimadzu 2100 spectrometer using a 1 cm path length cell in toluene at room temperature. The FT-IR spectra (4000–400 cm⁻¹) of solid samples were recorded on a Bomem MB-series spectrophotometer, in the solid state (KBr). ¹H NMR spectra for paramagnetic complexes were acquired on a Bruker AC-300 MHz spectrometer at ambient temperature in C₆D₆. The ¹Hnmr spectra were collected over a 50-kHz bandwidth with 16 K data points and a 5-µs 45° pulse. For a typical spectrum, between 1000 and 5000 transients were accumulated with a 50-ms delay time. The signal-to-noise ratio was improved by apodization of the free inducting decay. For MALDI-TOF-MS measurement the reaction products were collected in a capillary Pyrex tube, which was immersed in liquid nitrogen. Elemental analysis was performed using a Heraeus CHN-O rapid analyzer. The collected products were analyzed using Kratos Kompakt MALDI-TOF-MS in reflectron mode. Dithranol and lithium bromide were used as matrix and cationization agent, respectively. The matrix has resonance absorption at laser energy (λ = 337 nm) and thus absorbs the laser energy, causing rapid heating of the matrix. This rapid heating results in expulsion and soft ionization of the sample molecules without fragmentation [35]. X-band electron paramagnetic resonance were recorded on toluene at liquid nitrogen temperatures on a Joel RE2x electron spin resonance spectrometer by using DPPH (g = 2.0036) as a standard. All abbreviations for complexes 1–10 and for phenycyanamide derivatives are presented in scheme 1.

2.3. Preparation of complexes 1-10

2.3.1. Preparation of monomer PFe-NCN- C_6H_4 -NN- Ph (1) and (2)

Fifty milligrams of tetraphenylporphyrin iron chloride, TPPFeCl powder (0.071 mmol) and 100 mg (0.235 mmol) of thallium salt of apc⁻Tl⁺ were placed together in a two-neck round-bottom flask.

After 30 min of vacuum and then under nitrogen atmosphere (Schlenk technique), 50 ml dry toluene was transferred to the reaction flask and stirred for 24 h. The mixture was filtered and the volume of filtrate was reduced to 10 ml and then 50 ml of dried *n*-hexane was added in portion while the solution was stirring. Precipitate was removed by filtration and dried in air. Compound **2** was prepared by the same procedure except that TPP was replaced by TMP. FT-IR, UV–Vis data and yields of products are summarized in Table 1. *Anal.* Calc. for $C_{57}H_{37}FeN_8$ (891.847) (**1**): C, 76.7; H, 4.2; N, 12.6. Found: C, 75.9; H, 3.9; N, 12.2%. *Anal.* Calc. for $C_{69}H_{61}FeN_8$ (1060.171) (**2**): C, 78.1; H, 5.8; N, 10.6. Found: C, 77.9; H, 5.7; N, 10.2%.

2.3.2. Preparation of monomers PFeNCN- C_6H_4 -NCN-Tl(3) and (4)-(6)

Eighty milligrams (0.142 mmol) of thallium salt of dicydTl₂ was placed in a two-neck round-bottom flask, and 50 ml dry methanol was transferred to the flask. After 20 min under vacuum, the flask was placed under N₂ atmosphere (Schlenk technique). Then 100 mg (0.142 mmol) of TPPFeCl dissolved in 50 ml dried and distilled toluene was added to the reaction flask by dropping funnel during 4 h. The mixture reaction stirred for 30 h under dried nitrogen atmosphere at room temperature. After 30 h, the mixture reaction was filtered and the volume of the filtrate was reduced to approximately 10 ml and then 50 ml of dried *n*-hexane was added in portion while the solution was stirring. Precipitate was removed by filtration and dried in air. Compound **4** was prepared by the

Table 1

UV–Vis electron absorption^a and FT-IR data^b for P–Fe–L complexes **1–10** and thallium salts of phenylcyanamide.

Complex	UV-Vis ^c		v(NCN) ^{d,e}		Yield
	Soret band	Q bands	Thallium salt	Complex	(%)
TPPFe(apc) (1)	418	505, 570	2059	2069	78
TMPFe(apc) (2)	417.5	507, 571	2059	2085	81
TPPFe(dicyd)Tl (3)	418	504, 572	2045	2073, 2122	64
TMPFe(dicyd)Tl (4)	417	510, 571	2045	2030, 2066	66
TPPFe(adpc)Tl (5)	418	506, 571	2040	2042, 2084	77
TMPFe(adpc)Tl (6)	417.5	507, 573	2040	2050, 2102	79
TPPFe(dicyd)FeTPP (7)	419	505, 574	2045	2120	61
TMPFe(dicyd)FeTMP (8)	419.5	512, 578	2045	2110	69
TPPFe(adpc)FeTPP (9)	419	511, 579	2040	2085	68
TMPFe(adpc)FeTMP (10)	419	508, 577	2040	2110	76

^a In nm.

^b In cm⁻¹.

^c In toluene.

^d KBr disk.

e Strong.

same procedure except that TPP was replaced by TMP and the compound **5** was prepared by the same procedure except that dicydTl₂ was replaced by adpcTl₂. Compound **6** was also prepared by the same procedure except that TPP and dicydTl₂ were replaced by TMP and adpcTl₂. FT-IR, UV–Vis data and yields of products are summarized in Table 1.

2.3.3. Preparation of dimers PFeNCN- C_6H_4 -NCN-FeP (**7**) and (**8**)–(**10**)

Seventy-three milligrams (0.071 mmol) of complex **3** was placed in a two-neck round-bottom flask, and 50 ml of dry methanol was transferred to the flask. After 20 min under vacuum, the flask was placed under N₂ atmosphere (Schlenk technique). Then 50 mg (0.071 mmol) of TPPFeCl dissolved in 50 ml of dried and distilled toluene was added to reaction flask by dropping funnel during 4 h. The mixture reaction stirred for 24 h at room temperature. After 24 h, it was filtered and the volume of the filtrate was reduced to approximately 10 ml. precipitate was removed by filtration and dried in air. Compound **8** was prepared by the same procedure except that TPP was replaced by TMP and compound **9**

was prepared by the same procedure except that dicydTl₂ was replaced by apcdTl₂. Compound **10** was prepared by the same procedure except that TPP and dicydTl₂ were replaced by TMP and apcdTl₂. FT-IR, UV–Vis data and yields of products are summarized in Table 1. *Anal.* Calc. for $C_{96}H_{60}Fe_2N_{12}$ (1493.22) (**7**): C, 77.2; H, 4.0; N, 11.2. Found: C, 76.5; H, 3.9; N, 11.4%. *Anal.* Calc. for $C_{120}H_{108}Fe_2N_{12}$ (1829.84) (**8**): C, 78.7; H, 5.9; N, 9.2. Found: C, 76.6; H, 5.7; N, 8.8%.

3. Results and discussion

The most studied synthetic iron porphyrins are those with anionic axial ligands [36]. To the best of our knowledge, no studies of dimer complexes of bridging ligands for example, phenylcyanamide derivatives to iron were reported in the literature until the present work, where we describe the first synthesis and spectroscopic of dimer iron (III) porphyrin with dicyd and adpc axial ligands. The Fe^{III}porphyrin complexes of 1,4-dicyanamidobenzene(dicyd) and 4,4'-azo-diphenyl cyanamide(adpc) were



Fig. 1. (a) MALDI-TOF mass spectra of a TPPFe(dicyd) FeTPP (7) and (b) MALDI-TOF mass spectra of a TMPFe(dipcyd)FeTMP (8).

synthesized in generally good yields to the following metathesis reaction in refluxing dry toluene. Scheme 1 shows the reaction equation and abbreviation used.

During preparation period, this reaction is very sensitive to moisture and to a less extent to O₂. The presence of water results in the formation of µ-oxo dimer, PFe–O–FeP. The µ-oxo dimer impurity is hard to remove, since chromatography on silica gel or aluminum oxide may lead to its additional formation. The reaction vields for compounds 1-10 were quantitative, although during the process of precipitation and isolation 20-30% of the products were lost, isolated yields are reported in Table 1. These products are less sensitive to moisture or oxygen after formation. So, no effort was made to exclude air or moisture for spectroscopic studies. All compounds are fairly soluble in non-coordinating solvent except for saturated hydrocarbons. Phenylcyanamide derivative complexes readily react with HCl and result in the formation of starting PFeCl. Attempt to make suitable crystals for the dimer complexes were failed. However, MALDI-TOF of compound 7 shows the mother peak at 1492.84 (expected for $C_{96}H_{60}Fe_2N_{12}$ at 1493.22) and for compound 8 the mother peak at 1829.84 (expected for C₁₂₀H₁₀₈Fe₂N₁₂ at 1829.84), Fig. 1.

4. Spectroscopic characterization

4.1. IR and UV-Vis studies

Cyanamide group is a three atom π -system, which is a poorer π -acceptor but better donor analogous of nitrile ligands [37]. The IR spectra of the neutral ligands (dicydH₂ and adpcH₂) show a strong band around 2225–2250 cm⁻¹ that is assigned to ν (C=N) of the cyanamide groups [23] and coordinated nitrile in Fe^{III}–CN complexes was reported at 2129 cm⁻¹ [38]. The IR spectrum of the thallium salt of the anion ligands of dicydTl₂, adpcTl₂ and apcTl shows a very strong band at 2045, 2040 cm⁻¹ and 2059 cm⁻¹, respectively for ν (N=C=N) stretch.

Coordination of neutral and anionic dicyanamidobenzene ligands to metal cations can occur via amine or nitrile nitrogens and there are examples in the literature of both types of coordination [23]. Transition metal complexes appear to prefer coordination to the nitrile nitrogen. This may be due to the π -back-bonding and donor properties of the nitrile groups and the steric hindrance that would be experienced upon coordination to the amine of N-alkyl- or N-phenyl-substituted cyanamides. The neutral cyanamide ligands have π -donor properties that are due to the delocalization of the amine electron lone pair into a nitrile π -bond of the correct symmetry [23,39,40]. The anionic cyanamide ligand is expected to be a strong π -donor ligand because two lone pairs can delocalize into the nitrile π system. It is suggested that the resonance structure B (scheme 2) will dominate when the anion ligand is coordinated to Fe (III) [41].

The IR spectra of the monomer complexes (**1** and **2**) exhibit strong absorption bands for v(N=C=N) at 2069 and 2085 cm⁻¹, respectively. The IR spectra of the complexes **3–6** shows two strong absorption bands at arounds 2030–2070 cm⁻¹ due to coordination of NCN to thallium and 2075–2125 cm⁻¹ due to coordination of cyanamide to the iron. Two cyanamides are inequivalent in compounds **3–6** due to their coordination to iron and thallium. Com-



Scheme 2. Three modes of coordination of dicyanamides ligands.



Fig. 2. UV–Vis spectra of TPPFeCI (–), TPPFe-dicyd-Tl (---) (**3**) and TPPFe-dicyd-FeTPP (…) (**7**), 10^{-6} M in toluene.

parison with thallium salts and iron dimers in **7–10** clearly demonstrate that lower frequency is for coordination to thallium and higher frequency for coordination to iron. The presence of only one sharp and intense absorption band at around 2070–2095 cm⁻¹ for the cyanamide stretching frequency in the dinuclear complexes **7–10**, provides evidence that both cyanamide moieties on the phenyl ring of the bridging ligands, dicyd and adpc, are equivalent in the solid state. When the cyanamide moieties are inequivalent (**3–6**), multiple v(N=C=N) bands are observed [24]. However, in these complexes, v(N=C=N) consistently frequency shifted around 10–80 cm⁻¹ higher in contrast with the thallium salts. The same trend was observed for monomer complexes of tetraphenylporphyrin manganase(III) and tetraphenylporphyrin iron(III) of phenylcyanamides [42,43]. The v(N=C=N) frequencies for thallium salts and compounds **1–10** are listed in Table 1.

Fig. 2 shows UV–Vis spectra of compounds **3** and **7** in toluene in comparison with TPPFeCl. These spectra and the results for other compounds in Table 1 indicate the similarity of the electronic spectra of prepared compounds.

The UV–Vis spectra of iron(III) porphyrin are sensitive to oxidation and spin state of iron(III). Differentiation of the nature of axial ligands of iron(III) porphyrin when accompanied by spin change, is often possible by UV–Vis spectra [44].

The λ_{max} values of the phenylcyanamide-ligated species are in the same range to those of the Cl⁻, N_3^- and NCS⁻ iron porphyrin species in the soret region. This confirms the existence of high-spin iron(III) oxidation states. Fig. 2 also indicates higher absorption coefficient of **7** and **3** due to the coordination of a longer π -conjugated axial ligand.

4.2. ¹H NMR studies

¹H NMR spectroscopy has been shown to be a uniquely definitive method for detecting and characterizing iron porphyrins. The hyperfine shift patterns are sensitive to the iron oxidation, spin and ligation state. Pyrrole protons in particular provide a direct probe of the porphyrins macrocycle [37]. Magneto chemical series proposed by Reed et al. are based on the position of the ptrrole protons in TPPFe-X ranging from –62 ppm to +80 ppm for different Xligands [45,46].

The ¹H NMR spectra of mono and dinuclear phenylcyanamide complexes are shown in Figs. 3 and 4, respectively, and full assignment of signals for compounds **1–10** are presented in Table 2. Resonance assignments have been made on the basis of relative intensity, line width, previous assignments of P–Fe–L moiety in high-spin Fe(III)complexes [43,44] and direct comparison of signals in compounds **1–10**.



Fig. 3. ¹H NMR spectra of iron(III)porphyrin complexes: TPPFedicyd-Tl (3), TPPFe(dicyd) FeTPP (7) and TMPFe(dicyd)FeTMP (8) in C₆D₆ at 300 K. ^{*} impurity of TPPFeCl and compound (7).



Fig. 4. ¹H NMR spectra of iron(III)porphyrin complexes with azo-phenylcyanamides: TPPFe(apc) (1) and TPPFe(adpc)FeTPP (9) in C₆D₆ at 300 K.

 Table 2

 ¹H NMR spectral data of P-Fe-L complexes.^a

Complex	pyrr-H	m-H	H_2	H ₃	H ₅	H ₆
TPPFe(apc) (1)	79.0	12.3, 11.3	-61.5	44.0	44.0	-61.5
TMPFe(apc) (2)	77.6	15.5, 13.9	-58.8 ^b	41.6	41.6	-58.8 ^b
TPPFe(dicyd)Tl (3)	78.1	12.5, 11.5	-35.2 ^b	34.4	34.4	-35.2 ^b
TMPFe(dicyd)Tl (4)	75.5	14.0, 12.6	-40.5	36.4 ^b	36.4 ^b	-40.5
TPPFe(adpc)Tl (5)	78.8	12.2, 11.2	-61.1 ^b	44.3	44.3	-61.1 ^b
TMPFe(adpc)Tl (6)	77.9	14.5, 13.1	-40.1	35.0	35.0	-40.1
TPPFe(dicyd)FeTPP (7)	75.3	11.8, 11.1	-35.4			-35.4
TMPFe(dicyd)FeTMP (8)	75.4	13.9, 12.6	-40.3			-40.3
TPPFe(adpc)FeTPP (9)	79.1	12.2, 11.2	-62.1 ^b	37.1	37.1	-62.1 ^b
TMPFe(adpc)FeTMP (10)	78.1	14.5, 13.2	с	35.1	35.1	с

^a In C₆D₆, data in ppm vs. TMS reference at 0.00 ppm at 300 K.

c Not observed.

For example, traces of **7** and **8** in Fig. 3 show only a signal at -35.4 and -40.3 ppm, respectively, so, the presence of only one signal for the hydrogen phenylcyanamides in the dinuclear complexes, provides evidence that hydrogens present in both position of ortho and meta cyanamide moieties on the phenyl ring are equivalent. Trace of **3** in Fig. 3 has shown a new signal low field region at 34.4 ppm with similar intensities of signal in -35.2 ppm. This signal in 34.4 ppm has been assigned to 3,5-H for compound **3**. In compound **1**, signals related to protons in 2,6 position in

phenyl ring appear in -61.5 ppm and protons in 3,5 position on phenyl ring have chemical shift of +36 ppm [43]. However, interaction of two iron atoms in dimers 7 and 8 cause spin transfer of both iron atoms on the protons of the phenyl ring and result in changing of chemical shift of protons in 2,6 position from -61.5 ppm in monomer to -35 ppm in dimer complexes. This 26.5 ppm chemical shift on protons of the phenyl on bridging phenylcyanamide shows that both irons have transferred spin to the bridging ligand. However, pyrrole protons in 1 and 2 are at 79.0 and 77.6 ppm, respectively. In dimers 7 and 8 pyrrole resonances are around 75 ppm. The pyrrole signal position is very sensitive to the magnetization state of the iron and antiferromagnetic coupling changes the pyrrole position dramatically [28]. There for little change of 3-4 ppm in pyrrole position of the dimmers, relative to the monomers indicates that there is a very weak antiferromagnetic coupling between two iron centers in these dimers.

The effect of temperature on the ¹H NMR spectrum of hydrogens of phenylcyanamide for **8** in chloroform solution is shown in Fig. 5, where the chemical shifts for the pyrrole proton and 2,6-H are plotted versus 1/T (K⁻¹). This plot shows Curie law behavior and confirms weak interaction between metal centers, since the plot is almost linear.

Trace of compound **1** in Fig. 4 with monoanion apc axial ligand shows two signals at -61.5 and 44.0 ppm which arises from two kinds of hydrogen, ortho and meta position with ratio of 1:1. When mononuclear complex **1** is replaced by dinuclear complex **9** of adpc

^b Very broad.



Fig. 5. Plot of the chemical shift versus 1/T (K) for the pyrrole (a), 2,6-H (b) resonances of **(8)** in chloroform solution

ligand, as expected, the same ¹H NMR pattern is seen, trace **9** of Fig. 4. It seems that in the case of azophenylcyanamide dimer complexes **9** and **10** larger distance between paramagnetic centers result in almost zero coupling between two iron centers, which are negligible. Their pyrrole positions are around 79 ppm similar to monomer complexes. Signals of phenyl of tetraphenylporphyrins in compounds **1–10** have been seen in almost the same place for TPPFeCl, Table 2.

The EPR of compound **1** in toluene at liquid nitrogen temperature has shown signals at g = 5.82 and 2.035. The signals for compound **8** are at g = 5.84 and 2.029, which is in the similar position to the monomer signals and these are indicative of iron(III) highspin species with S = 5/2 for monomers and dimers and confirm that the magnetic coupling for the iron centers in the dimeric complexes is weak or non-existent.

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