Fe₄S₄ Cubane Type Cluster Immobilized on a Graphene Support: A High Performance H₂ Evolution Catalysis in Acidic Water

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The development of alternate catalysts that utilize non-precious metal based electrode materials such as the first row transition metal complexes is an important goal for economic fuel cell design. In this direction, a new Fe₄S₄ cubane type cluster, [(PPh₄)₂][Fe₄S₄(DMET)] (1) (DMET = cis-1,2-dicarbomethoxyethylene dithiolate) and its composite with functionalized graphene, (1@graphene) have been synthesized and characterized. The presence of nanocrystalline structures on graphene matrix in TEM and SEM images of 1@graphene indicate that the cluster (1) has been immobilized. The composite, 1@graphene evolves H₂ gas from p-toluene sulfonic acid (TsOH) in a mixture of H₂O and CH₃CN under ambient conditions with a significant turnover number of 3200. 1@graphene electro-catalyzes H₂ evolution at Eₚ, −1.2 V with remarkable throughput, catalytic efficiency and stability in only H₂O or in only CH₃CN. The Fe₄S₄ cluster (1) alone electro-catalyzes hydrogen evolution at Eₚ, −0.75 V from TsOH in CH₃CN. The X-ray crystal structure of the Fe₄S₄ cluster (1) (λmax, CH2Cl2, 823 nm; ε, 2200 mol⁻¹ cm⁻¹) shows that it is dianionic with a cumulative oxidation state of +2.5 for the iron centers and short C-S bond distances (ca., 1.712 Å & 1.727 Å) indicating the presence of sulfur based radicals.

The presence of the dimetallic iron and heterodimetallic iron-nickel centers at the active sites of the hydrogenases has evoked the researchers to search for a non-platinum catalyst material for proton reduction and H₂ splitting. The nanocomposites of hydrogenase mimics with large surface area and versatile electronic behavior are expected to catalyze reduction of protons to hydrogen gas at lower electro-potentials than platinum based electrode materials. The three known classes of hydrogenases, [NiFe], [FeFe] and FeS—cluster free hydrogenases contain iron at their active site which is coordinated by thiolates, CO, CN⁻ or a light sensitive cofactor (Fig. 1a). Electro-catalytic H₂ generation involves reduction of protons to H₂ gas at lower reduction potentials towards Eₚ, 0.0 V under a catalyst that can performance-wise replace the platinum electrode (i.e., −0.413 V at pH 7.0). Several electro-catalysts for hydrogen evolution have been reported including a series of multinuclear iron sulfur complexes with benzene tetrathiolate bridges, iron carbonyl clusters, cobalt-dithiolene, metallo-porphyrins, low-valent transition metal complexes, diiron dithiolates, multinuclear Fe-S cluster with a Fe⁺ cubane(μ-SR)Fe⁺² sub-site linkedage, molybdenum-sulfur dimers, cobalt glyoximes, substituted iron glyoximes, carbon nanotube grafted nickel bisdiphosphine complexes, and mononuclear iron(II) polypyridyl complexes. Nickel(II) and iron(III) dithiolenes have been reported which electro-catalyze H₂ evolution at potentials comparable to that of platinum disc electrode. Recently the research on light driven H₂ production has gained momentum. Biomimetic chalcogels incorporating Fe₄S₄ cubane type clusters linked with (Sn₂S₁₂)⁻ blocks and iron dithiolene complexes have been reported as catalysts for light driven H₂ production from water and as solar fuel catalysts. The Fe₄S₄ cubane type cluster take part in many biological electron transfer processes which are also coupled with several other enzymatic reactions. The 6H⁺−6e⁻ reduction of N₂ to NH₃ by Fe₄S₄ cubane type cluster alone has been reported by van Tamelen et al. Hence, we are interested to find out the efficiency of Fe₄S₄ cubane type cluster alone as electrochemical hydrogen evolution catalysts. Since the Fe₄S₄ cubane type clusters are embedded in protein matrix in the biological active site, the stability and catalytic efficiency of the Fe₄S₄ clusters

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might be enhanced if they can be embedded or immobilized on a graphene support. Two dimensional nanomaterials of various compositions including graphene have been studied as catalysts in electrochemical reactions such as hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and carbon dioxide reduction. Recently 2D nanomaterials including functionalized graphene, their hybrids have gained interests in electrochemical energy conversion and storage devices. Defects existing in the 2D nanomaterials play an important role in tailoring of optical and electric properties. Functionalized graphene obtained by oxidation contains –COOH, –C=O, and –OH functional groups which can be used to immobilize metal ions and organic groups. Several graphene-photocatalyst composites have been developed recently for HER. Graphene as a matrix would enhance the catalytic performance of the electrocatalysts embedded on it due to its large surface area, excellent conductivity and indefinite durability. Graphene oxide gets folded to close like fisted form and entraps a large molecule such as tetraphenylporphyrin (TPP). Several graphene based hybrid electrocatalysts as anodic and cathodic fuel cell electrode materials have been reviewed. Herein we report a new Fe₄S₄ cubane type cluster, [PPh₄]₂[Fe₄(μ₃-S)₄(DMET)]₄ (1, Fig. 1b) and a functionalized graphene composite, 1@graphene (Fig. 1c) which react with protons and evolve H₂ gas in a mixture of CH₃CN and water under ambient conditions and electrochemically at Ep, −1.21 V in CH₃CN or in H₂O.

**Results and Discussion**

**Synthesis and X-ray structural data of the Fe₄S₄ cubane type cluster, [PPh₄]₂[Fe₄(μ₃-S)₄(DMET)]₄ (1).**

The cluster (1) was prepared by the reaction of iron(II) polysulfide, [PPh₄]₄[Fe₂(S)₁₂] with dimethylacetylene dicarboxylate (DMAD) and lithium sulfide (Li₂S) in CH₃CN under Schlenk conditions. The X-ray structure determination of (1) indicates the presence of dianionic, [Fe₄(μ₃-S)₄(DMET)]⁻² cluster and [PPh₄] cations in 1:2 ratio. The ORTEP view of the anionic part of the cluster (1) is shown in Fig. 2 which confirms the formation of Fe₄S₄ core with four bidentate DMET ligands coordinated to iron. The geometry around each iron atom is square pyramidal formed by three inorganic sulfurs (S²⁻) and two thiolates of the DMET ligand. The Fe–S bond lengths are similar at all iron centers, (Fe(1) and Fe(2)) and in the range 2.156 Å–2.250 Å. This is in contrast to the longer Fe–S bond distances (2.246 Å–2.383 Å) in the tetra anionic, super reduced cluster, [NBu₄]₄[Fe₃(μ₃-S)₄(mnt)]₄⁻² (2) (mnt = maleonitrile dithiolate). The Fe…Fe separations (Fe–Fe, 2.695 Å and 2.722 Å) are remarkably shorter in the cluster (1) in contrast to those observed in (2) (Fe–Fe, 2.843 Å–3.123 Å) and four of the C–S bond distances (S(2)–C(2) & S(2A)–C(2A), 1.718 Å and S(6)–C(6) & S(6A)–C(6A), 1.721 Å) are considerably shorter in (1) indicating oxidation of the dithiolene ligands to their monoanionic form containing sulfur based radicals. The lattice packing in the crystals of (1) indicates that the anionic Fe₄S₄ cluster is fully covered by a group four [PPh₄] cations with considerably short S²⁻ (cluster)...H–C(phenyl) (2.91 Å and 3.45 Å) and O(cluster)...H–C(phenyl), (2.43 Å). All of the four S²⁻ in the anionic part are involved in short contacts with C–H.
of the PPh₄ cations. These interactions might provide stability to the cluster skeleton and are reminiscent of the intermolecular interactions observed in native proteins.

The dianionic 1,2-dithiolenes coordinated to metal complexes are known to undergo oxidation resulting in monoanionic ligands with S-based radicals 41–47. The considerably shorter C−S bond distances in a previously reported [Fe₄(μ-3-S)₄(S₂C₂(CF₃)₂)₄]²⁻ dianion and in cluster (1) indicate that the four monoanionic dithiolates provide only four negative charges to the cluster whereas the four inorganic sulfurs (S²⁻) provide eight negative charges making up a total of 12 negative charges which are satisfied by the four iron ions and two [AsPh₄]⁺/[PPh₄]⁻ cations 48,49. This confirms that the four iron centers are in a comprehensive oxidation state of +2.5 and the four dithiolene ligands have been oxidized to form monoanionic ligands with four S-based radicals. The appearance of a peak at m/z, 1514 in electro spray ionization mass spectrum (Fig. 3) indicates the stability of [PPh₄][Fe₄(μ-3-S)₄(DMET)₄]⁻ complex ion in CH₃CN. The complex (1) is EPR silent both in the solid state and in CH₂Cl₂ solution. The diamagnetic nature of the cluster (1) is understood from the room temperature magnetic moment (μₑff) of <1 μₑ. The presence of a band around λ, 823 nm (ε, 2200 M⁻¹ cm⁻¹) in the electronic spectrum of (1) in CH₂Cl₂ (Fig. 3) can be assigned to an intervalence-charge transfer (IVCT) band which is observed in sulphur based radical containing complexes. This indicates the presence of S-based radicals and since the complex (1) is diamagnetic, the S-based radicals are expected to be coupled.

Synthesis and characterization of the composite, 1@graphene. The composite, 1@graphene was prepared by the ultrasonication of Fe₄S₄ cubane type cluster, (1) and functionalized graphene for 10 h in CH₂CN-H₂O under an argon atmosphere. It was then evaporated to dryness and the black residue was labelled as 1@graphene. The IR spectral peaks of 1@graphene show significant shifts to lower frequencies compared with the Fe₄S₄ cluster (1). The doublet at 1718 cm⁻¹ and 1690 cm⁻¹ observed in (1) due to –COO stretching of dithiolenes is shifted to 1616 cm⁻¹ and 1610 cm⁻¹ in 1@graphene and the doublet is also broadened (Supplementary information). This indicates the existence of the H-bonding interactions with –COOH of the f-graphene as shown in Fig. 1c. Furthermore, in 1@graphene, a broad band is observed at 3324 cm⁻¹ indicating the presence of hydrogen bonded –OH groups. Functionalized graphene and the composite, 1@graphene were further analyzed by scanning electron microscopy (SEM) and results are displayed in Fig. 4. The sample containing functionalized graphene displayed transparent and thin filmy structures as shown in the Fig. 4A and B. The sample containing
Graphene displayed a mixture of graphene and the Fe₄S₄ cubane type cluster (1) as shown in Fig. 4C (low magnification) and Fig. 4D (higher magnification). The red circled area in Fig. 4C has been magnified and shown in Fig. 4D which indicates that a cubic structure is embedded in a bed of transparent filmy structure. The functionalized graphene, Fe₄S₄ cluster (1) and the composite 1@graphene were dispersed in H₂O-CH₃CN, deposited onto carbon coated copper grids and analyzed by HR TEM. The results are displayed in Fig. 5 which indicates that the functionalized graphene solidifies as a film whereas the Fe₄S₄ cluster recrystallize as nanocrystals. The TEM images of 1@graphene displayed in Fig. 5C and D indicated the presence of dark crystals/particles of Fe₄S₄ cluster on the graphene matrix. The Fe₄S₄ crystals can be immobilized on a functionalized graphene matrix through H-bonding interactions with the –COOH, -OH functional groups which has also been corroborated by IR spectral studies as described above. Because the Fe₄S₄ cubane type clusters crystallize in the form of nanocubes and microcubes as confirmed by our unpublished results on the cluster, [NBu₄]₄[Fe₃ₓFeIV(µ₃–S)₄(mnt)₃ₓ(mnt)₄₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₁₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋ForeignKey:Figure 4. (A and B) SEM images of the functionalized graphene at low and higher magnifications on aluminium matrix. (C and D) SEM images of 1@graphene at low and higher magnifications on aluminium matrix. C, red circled area is magnified in D displaying the Fe₄S₄ cubane type cluster, 1 embedded in a bed of functionalized graphene.

Figure 3. ESI-MS (negative) of the cluster (1) in CH₃CN. (Inset: UV-VIS spectrum of (1) in CH₂Cl₂.
Cyclic voltammetric data and proton reduction. The Fe$_4$S$_4$ cubane type cluster (1) undergoes three reversible one electron redox processes around $E_{1/2}$, $+0.45$ V, $+0.11$ V and $-0.49$ V ($\Delta E$, 60 mV) and two quasi-reversible redox processes around $E_{p}$, $-1.01$ V and $-1.22$ V in CH$_2$Cl$_2$ (Fig. 6). The waves at $E_p$, $-0.49$ V, $-1.01$ V and $-1.22$ V can be assigned to the DMET ligand based redox processes since these were observed also in other related iron(III) dithiolene complexes and a nickel(II) complex of the DMET ligand$^{30–32}$. The reversible redox process occurring near zero ($E_{1/2}$, $+0.107$ V) can be assigned to Fe$^{3+}$/Fe$^{2+}$ and the one occurring at $E_{1/2}$, $+0.45$ V can be assigned to Fe$^{3+}$/Fe$^{4+}$ redox process. These assignments of the redox waves of the cluster (1) have been done based on comparison of cyclic voltammetric profiles of various Fe$_4$S$_4$ clusters, iron(II)/iron(III) and nickel(II)complexes of similar dithiolene ligands including classical tetrahedral Fe$_4$S$_4$ clusters of Holm et al.$^{50–59}$. 

The complex (1) electro-catalyzes hydrogen evolution from $p$-toluene sulfonic acid (TsOH) in CH$_3$CN. On addition of TsOH (0.25 M, 0.05 ml) to the cluster (1) in CH$_3$CN, the negative current at potential $E_p$, $-0.72$ V was increasing as shown in Fig. 6B. But the reversible redox couples around $E_p$, $+0.445$ V and $E_p$, $+0.107$ V were unaffected by the addition of TsOH. This indicates that the preferential sites of protonation could be the sulfur donors of the radical containing monoanionic dithiolate. The increase in current is due to the reduction of TsOH protons followed by the evolution of hydrogen gas. Controlled potential electrolysis of a mixture of the cluster (1) (0.025 mmol) and TsOH (0.25 mmol) was carried out in CH$_3$CN at $E_p$, $-0.8$ V. A net charge of 29 mC passed over a period of 2 minutes. Head space analysis of the electrochemical cell by gas chromatography confirmed the presence of H$_2$ gas. The cluster (1, 0.025 mmol) consumed 0.25 mmol of TsOH and the TON (turnover number) of (1) in CH$_3$CN is 400. The H$_2$ evolution occurring at $E_p$, $-0.8$ V using TsOH is proposed to be promoted by a S-radical based process. The iron bound monoanionic dithiolate type S-donor sites of DMET can be protonated upon addition of TsOH and reduce protons to H$_2$ on application of electric potential. In the process, the monoanionic dithiolate S- donors can in turn get oxidized to a fully oxidized, neutral di-radical ligand. The reduction of protons coupled to the oxidation of monoanionic dithiolate to neutral di-radical ligand is modulated by the iron center. Because similar DMET complexes of several other transition metal ions do not catalyze proton reduction at such a low reduction potential, viz., $E_p$, $0.72$ V.

The cyclic voltammogram of the composite, (1)@graphene is similar to that of the cluster (1) as shown in Fig. 7A. It displays three reversible one electron redox processes at $E_p$, $-0.41$ V, $+0.23$ V and $+0.57$ V in CH$_3$CN which are assigned to S-radical based Fe$^{3+}$/Fe$^{4+}$ redox processes as described above for the pure cluster in CH$_2$Cl$_2$ (vide supra).
The composite, 1@graphene electrocatalyzes TsOH-proton reduction to H2 at E0 = −1.19 V in CH3CN as a solvent. On addition of 0.4g of TsOH (2 mmol in 2 mL CH3CN), overall current of −0.95 mA passed at E = −1.19 V. The increase in current as a function of added TsOH solutions in CH3CN (1 M, 0.1 ml each) are shown in Fig. 7B and for clarity only the forward scans are displayed in Fig. 7C. The composite electrocatalyzes the above mentioned reduction to H2 at the same potential, E0 = −1.2 V as a solvent with better catalytic efficacy and higher current output. On addition of 0.1 g of TsOH (0.5 mmol in 1 mL H2O), overall current of −3.15 mA passed at E = −1.2 V as shown in Fig. 7D and for clarity only the forward scans are displayed in Fig. 7E. The composite (0.05 g, 0.025 mmol with respect to Fe4S4 cubane type cluster) consumed 2 mmol of TsOH with a turnover number of 3200. Formation of bubbles and brisk effervescence were observed upon addition CH3CN (1mL) to the electrochemical cell containing the composite 1@graphene and TsOH in water. This was confirmed to be H2 gas by head space analysis by gas chromatography. The stability of the Fe4S4 cubane type cluster and its composite, 1@graphene are confirmed in de-aerated water under argon due to the insolubility of (1) in water. The cluster (1) was extracted from the composite after cyclic voltammetric experiments by ultrasonication in CH3CN followed by centrifugation and evaporation to dryness. The elemental analysis of the residue indicated the presence of carbon, hydrogen, nitrogen and sulphur according to the percentage elemental composition of the cluster (1). The composite, 1@graphene isolated from water medium displayed an ESI-MS (−ve) signal at m/z, 1514. The IR spectrum of 1@graphene isolated after catalysis is dominated by peaks due to ν(−COO of dithiolene) and ν(C=S) (tosic acid) stretching at 1371 cm−1, 1177 cm−1 and 1120 cm−1. But weak signals at 1720 & 1644 cm−1 (C=O of dithiolene) at 1528 & 1490 cm−1 (C=C of dithiolene) coupled with the elemental analytical data indicate that the Fe4S4 cluster is intact. The cluster@graphene is confirmed to be stable in the solid state in water where as it is prone for attack only when it is dissolved in CH3CN or even in a mixture of H2O-CH3CN. This is due to the fact that in CH3CN, the composite functions as an emulsion of graphene in the CH3CN solution of (1) where as in water, it is an emulsion in graphene solution. The composite remains intact with indefinite durability and it is well behaved in pure water. But in a mixture of H2O-CH3CN, both the cluster (1) and graphene get into solution. The composite, 1@graphene shows an enhanced catalytic activity (TON, 3200) as compared to the pure Fe4S4 cluster (1) alone (TON, 400). This could be due to in situ reduction of the oxidized Fe4S4 cluster by graphene. As much as the cluster (1) gets oxidized after proton reduction, much can be reduced on the graphene matrix immediately. The graphene matrix can function similar to an external sacrificial electron donor. Only graphene in the absence of the Fe4S4 cubane type cluster electrocatalyzes proton reduction at a higher negative potential, ca, −1.7 V as shown in Fig. 7E. But the catalysis onset sets at the reduction potential, ca. Ep, −0.41 V itself. Under similar experimental conditions, only TsOH, did not show any response on a GCE in the potential range, E, 0.0 V to −1.8 V (supporting information).

In summary, an ideal catalytic material for the reduction of TsOH protons to H2 gas in water has been achieved by immobilizing the Fe4S4 cubane type cluster, [PPh4]2[Fe4S4(DMET)4] (1) on a functionalized graphene support. A high current output (3200 TON) and an extreme stability of the catalytic material in water was concluded from the cyclic voltammetric and ESI-MS experiments.Only Fe4S4 cluster (1), electrocatalyzes the same reduction reaction with low catalytic efficiency (400 TON) and concomitant decomposition to dimeric compound, [PPh4]2[Fe4S4(DMET)4]. The Fe4S4 cubane type cluster was synthesized in a novel synthetic route and structurally characterized. The cluster (1) is EPR silent and it displays reversible, one electron redox waves around E1/2, +0.107 V and at +0.45 V) which could be assigned to the Fe3+/Fe2+ and Fe2+/Fe3+ redox processes.

**Methods**

**Synthesis of [PPh4]2[Fe4S4(S2C2(COOC2H5)2)]4 (1)**. The reaction was done under Schlenk conditions. Acetonitrile (40 ml) was purged with argon gas for 30 min. and iron(II)-polysulfide, [PPh4]2[Fe4S4] (Electronic Supplementary information) (0.500 g) was added into it. The suspension was stirred for 20 min. followed by the addition of dimethyl acetylene carboxylate (0.5 ml) and freshly purchased lithium sulfide (Li2S, 0.15 g) under
argon. The black colored reaction mixture was stirred for 8h at room temperature and then diethylether (100 ml) was added. The reaction flask was closed tightly and allowed to stand at 10 °C for two days under argon. Dark green crystals were formed which were filtered and stored under argon. Dark green single crystals suitable for X-ray diffraction were obtained by layering of diethylether onto acetonitrile solution of the complex under argon. Data for (1): Yield, 0.6 g, C, H, N elemental analysis calculated for [PPh4]2[Fe4S4\((\mu_3-S)4(S2C2(COOCH3)2)4\)]2H2O, C, 45.72, H, 3.62; Found, C, 45.53, H, 3.82. ESI-MS (negative) in CH3CN; m/z, 1514 \([PPh4][Fe^{III}(\mu_3-S)4(S2C2(COOCH3)2)4]\); ESI-MS (positive), m/z, 339 \[PPh4]^+.

FT-IR (KBr disc, cm\(^{-1}\)): 3400(br), 2945(m), 1714 (s), 1693 (s), 1433(s), 1238 (s), 1212 (m), 1084 (m), 995(m), 722 (s), 688 (s), 526(s) (br, broad, w, weak, m, medium, s, strong). UV-visible in CH2Cl2 \([\lambda/\text{nm (}\varepsilon/\text{M}^{-1}\text{cm}^{-1})]\): 823 (2200), 582 (4500), 467 (5600). EPR silent, \(\mu_{eff} = 0.8\mu_B\) at 298K. E ½ = +0.445 V (\(\Delta E = +60 \text{ mV}\)), +0.107 V (\(\Delta E = +60 \text{ mV}\)) and −0.494 V (\(\Delta E = +60 \text{ mV}\)) vs. Ag/AgCl; E, (quasi-reversible), −1.005 V and −1.219 V vs. Ag/AgCl in CH2Cl2-0.2M NBu4ClO4 with GC working electrode.

**Preparation of functionalized graphene.** Graphite powder (0.5 g) was taken in THF (80 mL) and water (20 mL), stirred at 38 °C for 2 h and ultra-sonicated for 10 h. The solvents were decanted after centrifugation and the residue was dried thoroughly. This residue was treated carefully dropwise with concentrated H2SO4 (30 mL) and fuming nitric acid (10 mL) at 0 °C. The reaction mixture was heated under reflux for 12 h and allowed to stand at 38 °C for 10 h. The supernatant acid layer was decanted and the residue was washed thoroughly with water by centrifugation and dried. FT-IR (\(\nu, \text{ cm}^{-1}\)): 1718 (br), 1600 (w).

**Preparation of the Composite, 1@graphene.** The FeS4 cubane type cluster (1, 0.05 g) in degassed LC-MS grade CH3CN (12 mL) was mixed with functionalized graphene (0.05 g) in degassed LC-MS grade H2O (8 mL) and ultra-sonicated in closed sample vial under argon atmosphere for 3 h. The reaction mixture was heated under reflux for 12 h and allowed to stand at 38 °C for 10 h. The supernatant acid layer was decanted and the residue was washed thoroughly with water by centrifugation and dried. FT-IR (\(\nu, \text{ cm}^{-1}\)): 1718 (br), 1600 (w).

**X-ray crystallographic measurement of (1).** The dark green single crystals of the complex (1) were obtained by layering of diethylether onto acetonitrile solution of the complex under argon and isolated as [PPh4]2[Fe4\((\mu_3-S)4(DMET)2\)2\((DMET)\)2]2\((CH3CH2)2O\).2H2O. The intensity data for single crystals of (1) was collected at 120 K on a Bruker AXS Smart APEX CCD diffractometer with graphite monochromator MoKα radiation (0.71073 Å). Data reduction and absorption corrections were done using SAINTPLUS program package. The structure was solved by direct and conventional Fourier methods and refined on \(F^2\) by full-matrix
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Author Contributions
A. Begum and S. Sarkar designed and carried out most of the experiments. A. H. Sheikh and G. Moula carried out some of the experiments.

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