Supporting Information

for

Designing One-compartment H_2O_2 Fuel Cell Using Electroactive Phenalenyl-based $[Fe_2(hnmh\text{-}PLY)_3]$ Complex as the Cathode Material

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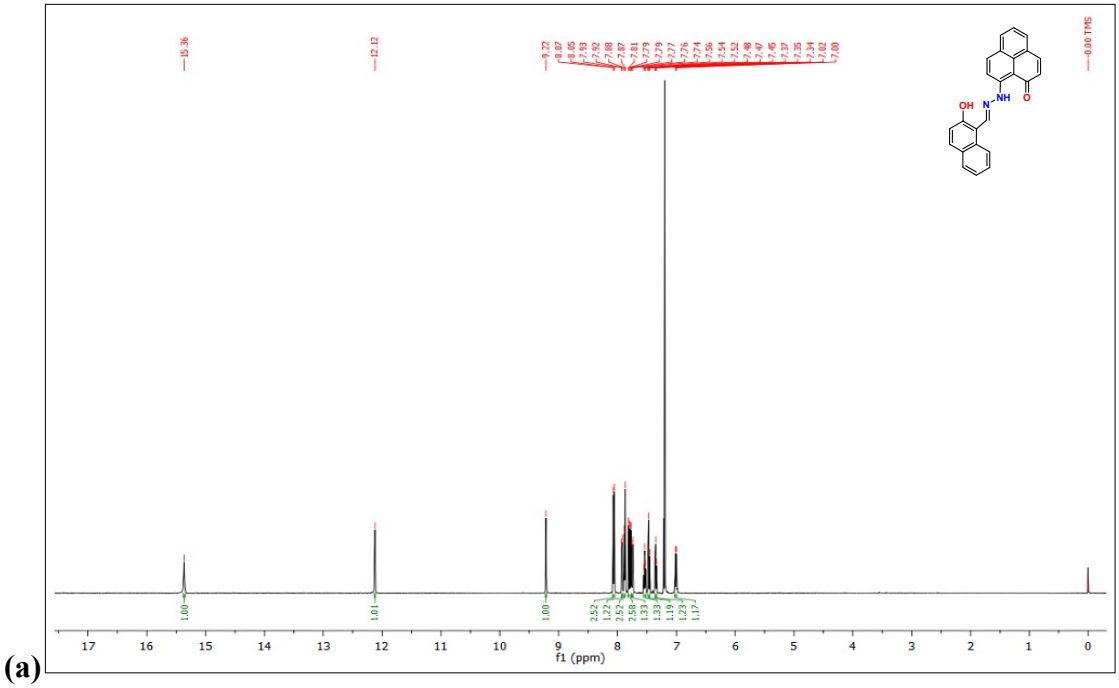
1. Crystallographic data for the hnmh-PLYH_2 ligand and complex 1.

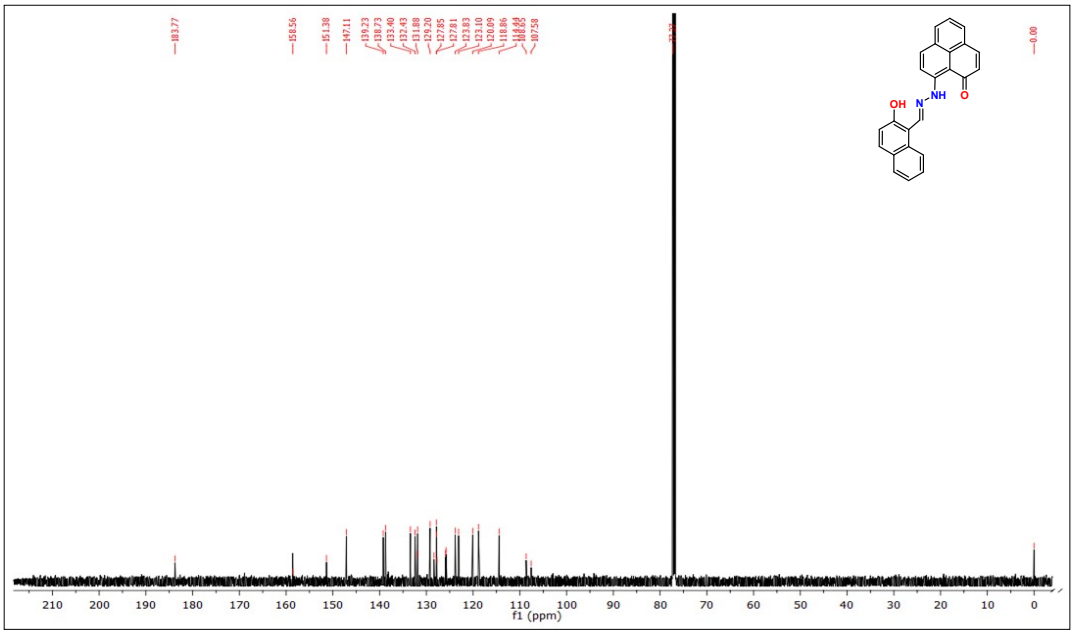
Table S1. Crystal data and structure refinement parameters for the ligand, hnmh-PLYH_2, and complex **1**.

Identification code	hnmh-PLYH_2	Complex **1**
Empirical formula	$C_{96}H_{64}N_8O_8$	$C_{72}H_{42}Fe_2N_6O_6$
Formula weight	1457.55	1198.82
Temperature/K	273	100
Crystal system	orthorhombic	triclinic
Space group	$P2_12_12_1$	P-1
a/Å	4.6410(8)	13.2008(16)
b/Å	13.252(3)	15.706(2)
c/Å	27.377(5)	16.0595(17)
α/°	90	81.353(4)
β/°	90	77.826(4)
γ/°	90	67.397(4)
Volume/Å^3	1683.8(5)	2995.9(6)
Z	1	2
ρ_{calc}g/cm^3	1.437	1.329
μ/mm^{-1}	0.093	0.544
F(000)	760.0	1232.0
Crystal size/mm^3	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.278 to 56.796	3.98 to 57.118
Index ranges	$-6 \le h \le 6$, $-17 \le k \le 17$, $-36 \le l \le 36$	$-16 \le h \le 17$, $-21 \le k \le 21$, $-20 \le l \le 21$
Reflections collected	23273	48330
Independent reflections	4229 [R_{int} = 0.1155, R_{sigma} = 0.0708]	15275 [R_{int} = 0.0518, R_{sigma} = 0.0615]
Data/restraints/parameters	4229/0/254	15275/0/765
Goodness-of-fit on F^2	1.140	1.221
Final R indexes [I>=2σ (I)]	R_1 = 0.0653, wR_2 = 0.1632	R_1 = 0.0773, wR_2 = 0.1880
Final R indexes [all data]	R_1 = 0.0966, wR_2 = 0.1897	R_1 = 0.1027, wR_2 = 0.2004
Largest diff. peak/hole / e Å^{-3}	0.36/-0.42	2.04/-0.55

2. General characterization of hnmh-PLYH$_2$ ligand and complex 1.



(a)



(b)

Figure S1. (a) ^{1}H and **(b)** ^{13}C NMR spectra of hnmh-PLYH$_2$ ligand recorded in $CDCl_3$ solvent.

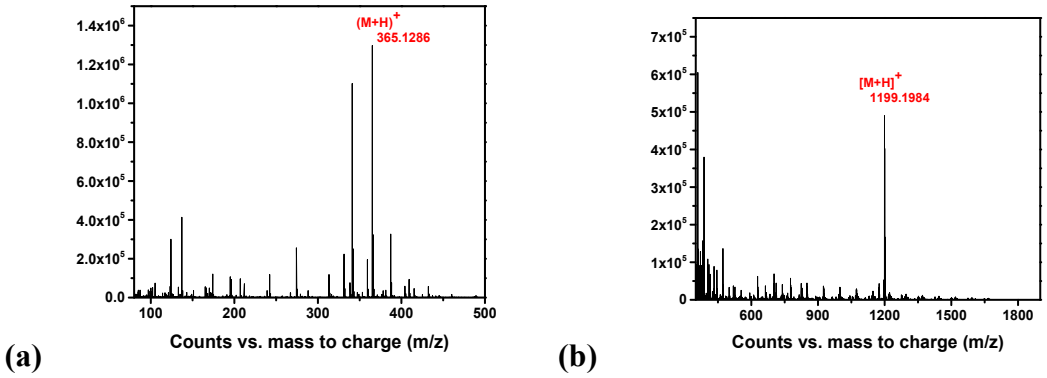


Figure S2. **(a)** HRMS spectrum of hnmh-PLYH_2 ligand. HRMS (CH_3CN, positive ionization): calcd. for $C_{24}H_{17}N_2O_2$ m/z = 365.1290 $[M+H]^+$, found 365.1286 $[M+H]^+$. **(b)** HRMS spectrum of complex **1**. HRMS (CH_3CN, positive ionization): calcd. for $C_{72}H_{42}Fe_2N_6O_6$ m/z = 1199.1943 $[M+H]^+$, found 1199.1984 $[M+H]^+$.

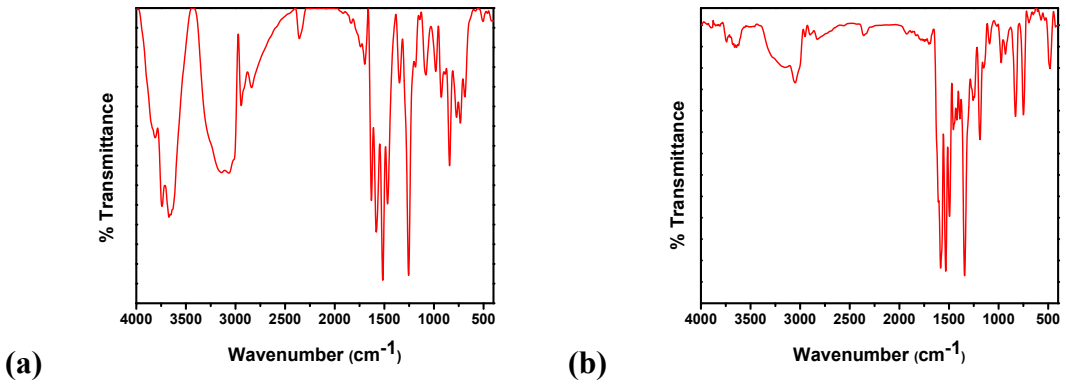


Figure S3. FT-IR spectrum of **(a)** hnmh-PLYH_2 and **(b)** complex **1**.

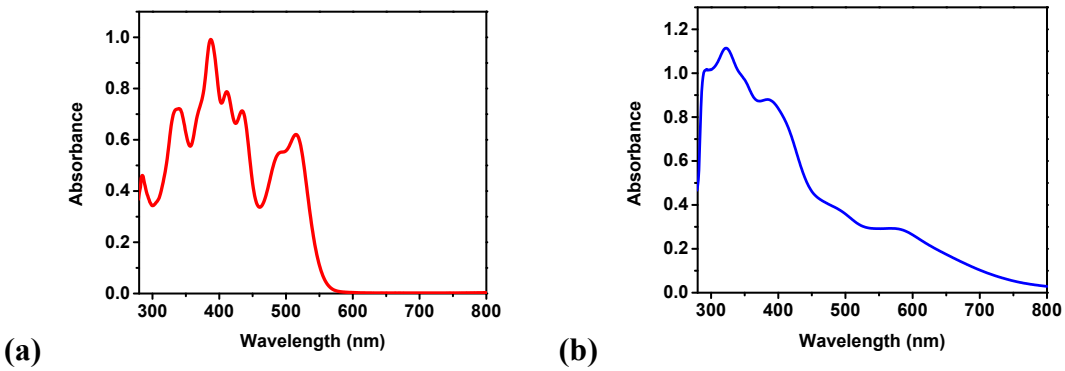
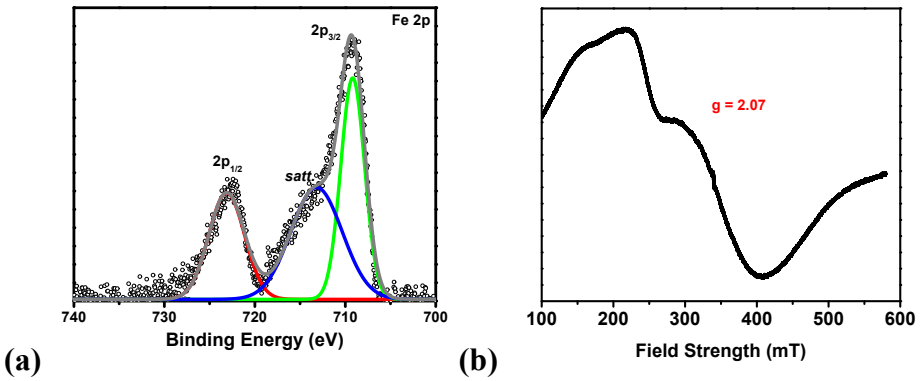
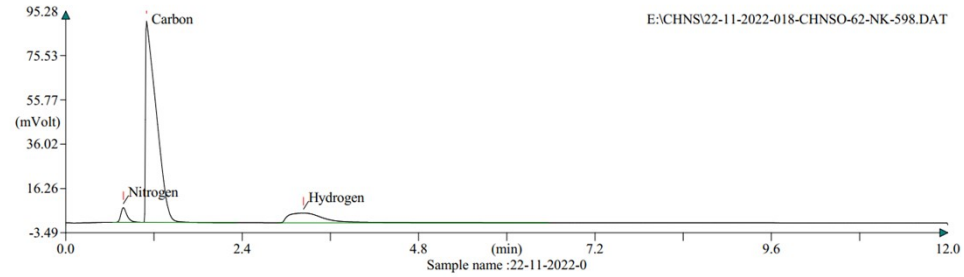


Figure S4. UV-vis spectrum of **(a)** hnmh-PLYH_2 and **(b)** complex **1** recorded in CH_2Cl_2 solvent.



(a) **(b)**



Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Element %	Component Name
1	0.783	383273	6.809	Nitrogen
2	1.100	9127306	71.453	Carbon
3	3.233	1477112	3.683	Hydrogen
		10987690	81.945	

(c)

Figure S5. (a) XPS, **(b)** solid state X-band EPR, and **(c)** elemental analysis of complex **1**.

3. H_2O_2 fuel cell performance test and CV experiments for mechanistic insights into H_2O_2 reduction by GC-1 electrode.

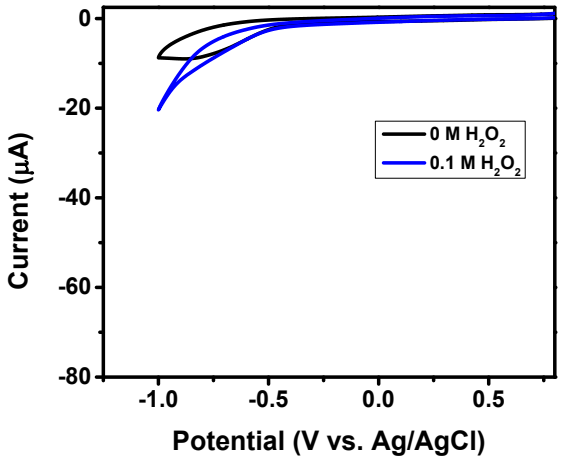
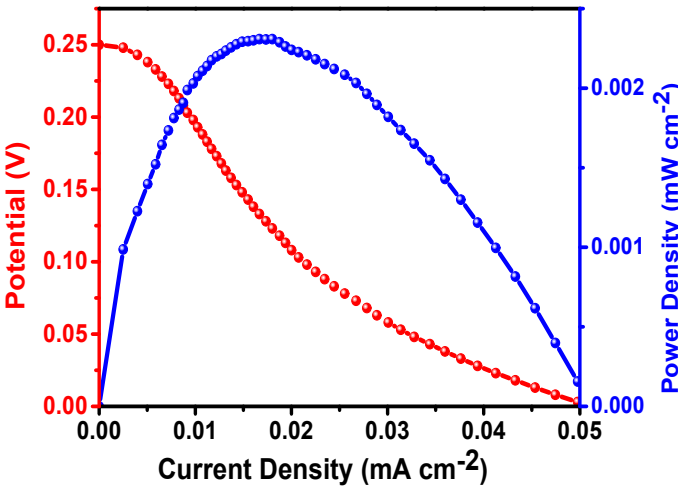


Figure S6. Electrocatalytic reduction of H_2O_2 with bare glassy carbon (GC) electrode in acetate buffer (pH 3) containing Ag/AgCl (3.0 M KCl) as the reference, and Pt-wire as the counter electrode at a scan rate of 100 mV s^{-1}.



(a)

Figure S7. *I-V* (red) and *I-P* (blue) curves of one-compartment H_2O_2 fuel cell with Ni anode and **GC-1** cathode. The performance tests were conducted in an acetate buffer (pH 3), containing 0.3 M H_2O_2.

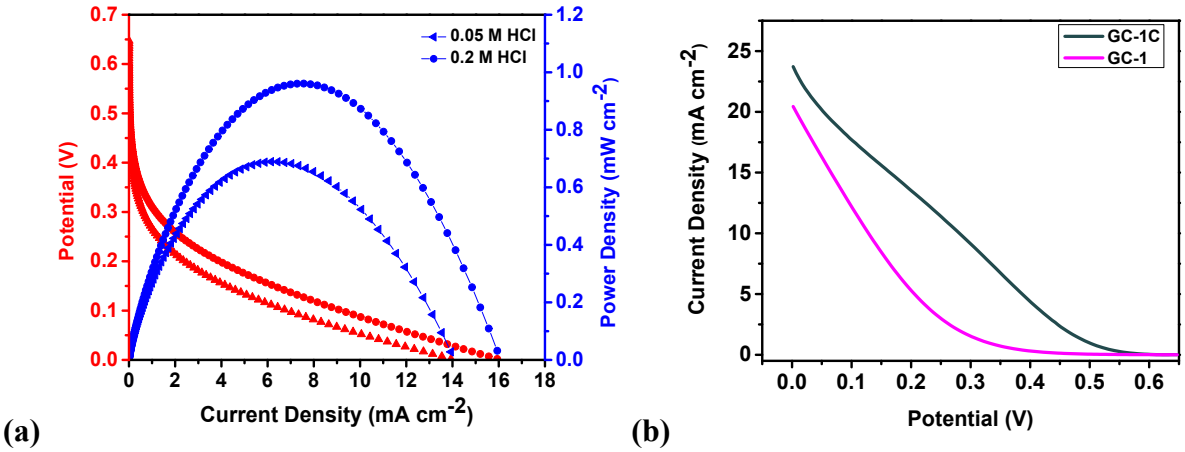
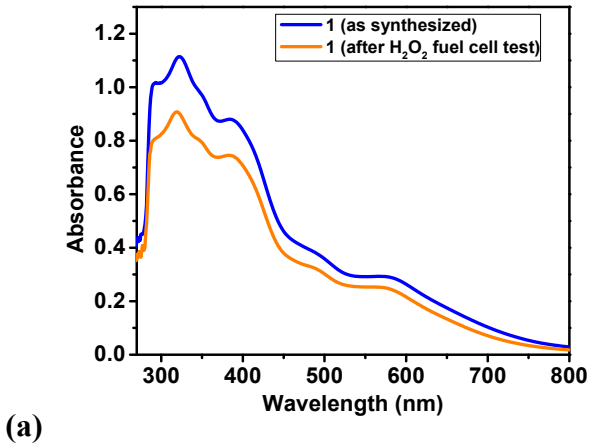


Figure S8. (a) Variation in *I-V* (red) and *I-P* (blue) curves for the one-compartment H_2O_2 fuel cell designed with **GC-1** cathode, and Ni foam anode with the change in concentration of aqueous HCl electrolyte. The concentration of H_2O_2 was maintained as 0.3 M. **(b)** Polarization curves for **GC-1** and **GC-1C** as a cathode in 0.1 M HCl containing 0.3 M H_2O_2, and Ni foam as the anode in one compartment H_2O_2 fuel cell. Current density is normalized by the geometrical area of the glassy carbon electrode.



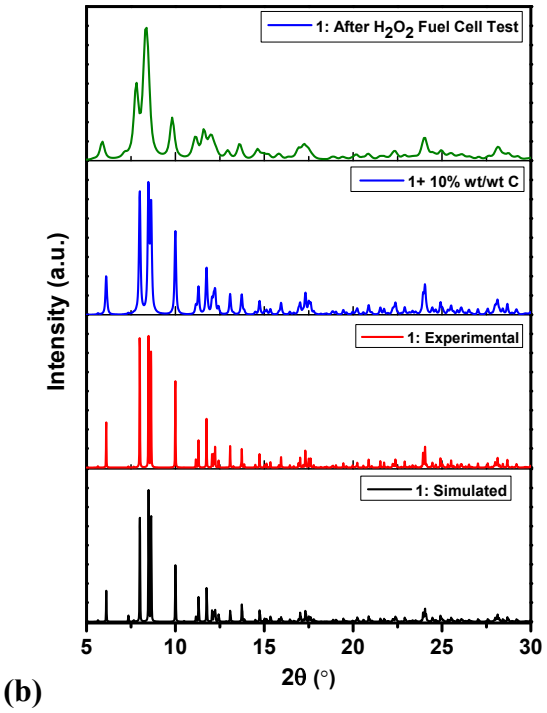
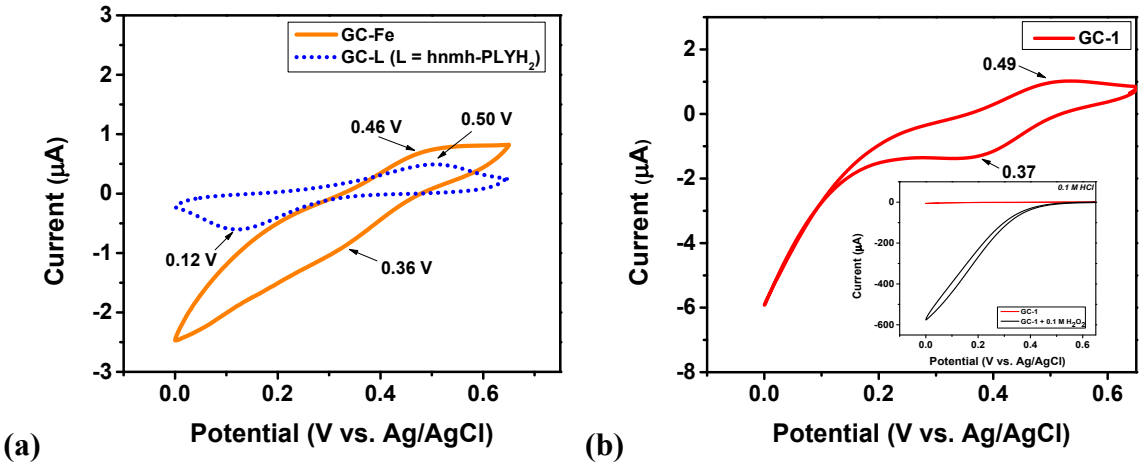
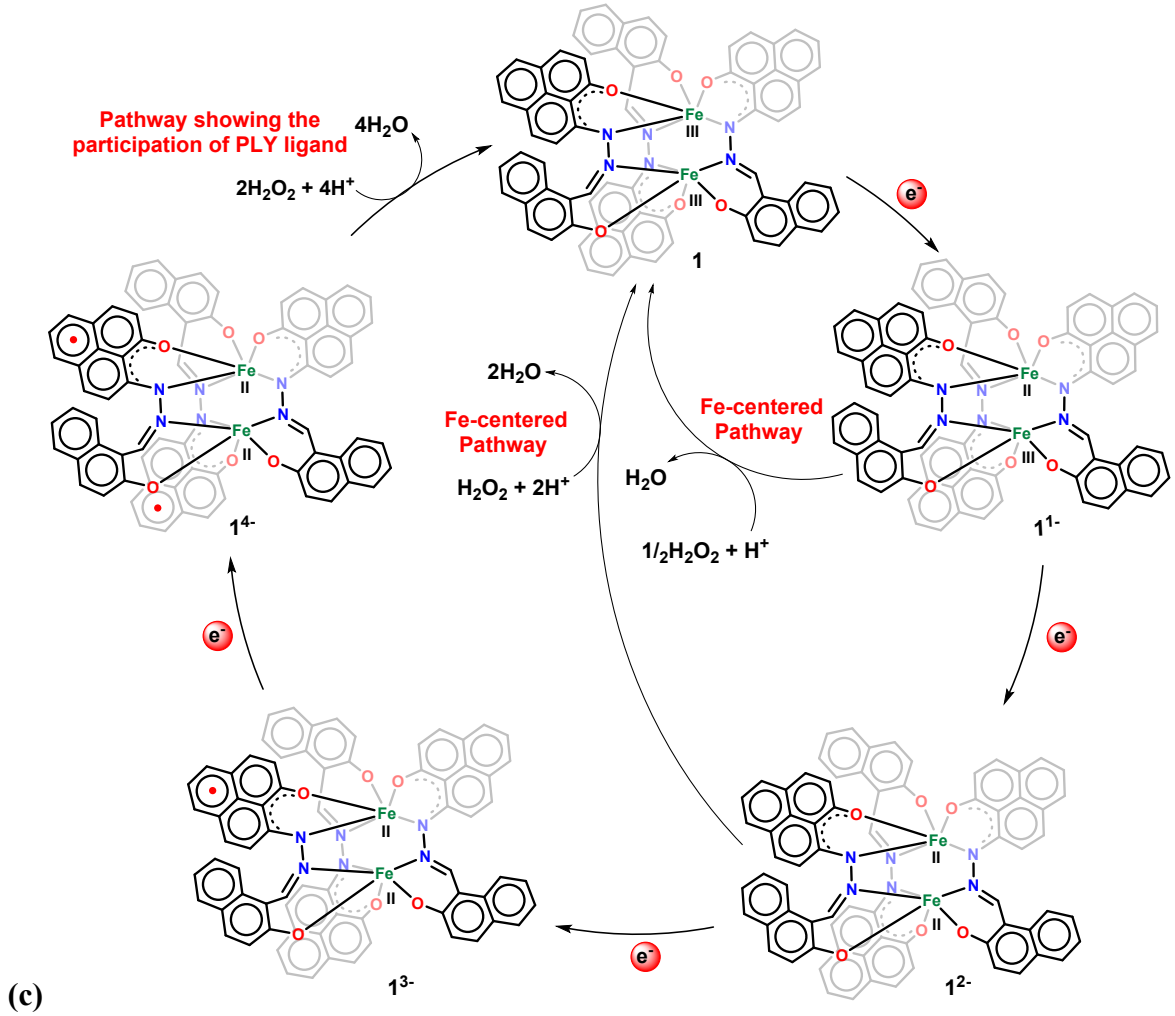


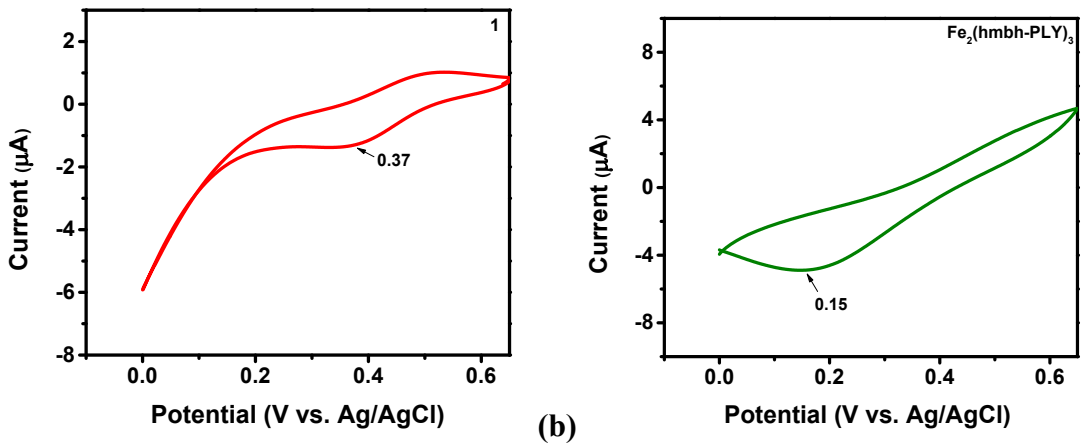
Figure S9. **(a)** UV-vis spectra of complex **1** and the recovered catalyst from the **GC-1** electrode after the one-compartment H_2O_2 fuel cell experiments. **(b)** PXRD pattern of complex **1**, **1** + 10% wt./wt. C, and recovered catalyst from **GC-1** after the one-compartment H_2O_2 fuel cell experiments.





(c)

Figure S10. Cyclic voltammogram of **(a)** $FeCl_3$ modified GCE, **GC-Fe**; hnmh-$PLYH_2$ ligand modified GCE, **GC-L**; and **(b) GC-1** recorded in 0.1 M HCl at a scan rate of 100 mV sec^{-1} (Inset shows the change in cyclic voltammogram on the addition of H_2O_2). **(c)** A generalized mechanism for H_2O_2 reduction by complex **1.**



(a) (b)

Figure S11. Solid-state CV of the complexes, **(a) 1** and **(b)** [Fe_2(hmbh-PLY)$_3$] immobilized over GCE in 0.1 M HCl electrolyte.

4. H_2O_2 Fuel Cell Demonstration Test

A demonstration setup was designed to test the application of complex **1** modified cathode **GC-1C** in the one-compartment H_2O_2 fuel cell. Four beakers containing 0.3 M H_2O_2 in 0.1 M HCl electrolyte were connected in a series setup using the conducting copper wire through the Ni foam as anode and **GC-1C** as the cathode. The OCP for the three setups in series was measured as ~2.5 V. As shown in Figure S11, the current flow in the designed H_2O_2 fuel cell setup has successfully glowed a red LED bulb (light emitting diode, 2 V), as a consequence of the reactions at the cathode and anode's surface.

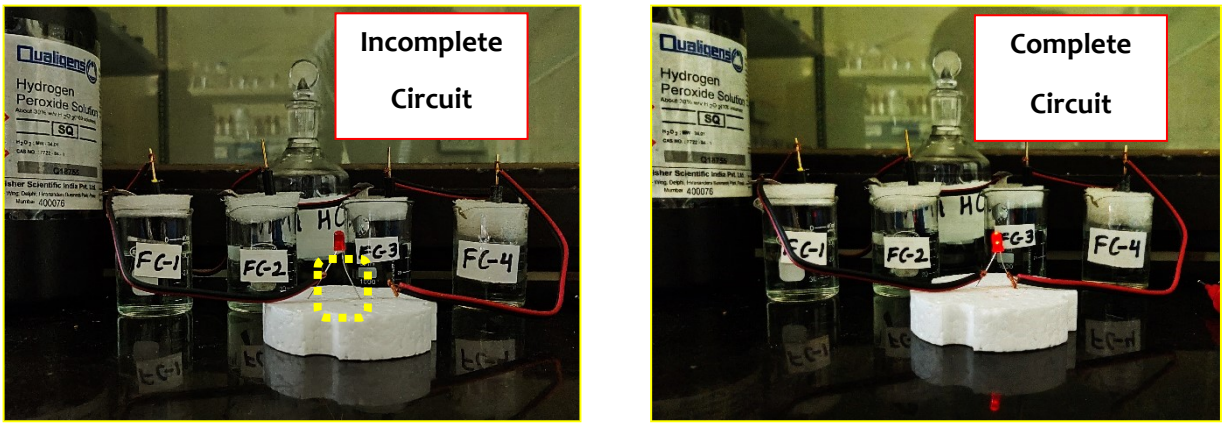


Figure S12. Demonstration setup of the one-compartment H_2O_2 fuel cell employing **GC-1** cathode and Ni foam as an anode.

5. DFT optimized atomic Cartesian coordinates of metal complex 1

Fe	13.40278321563452	12.40663045007605	3.38381576982838
Fe	15.36040268156612	9.50506586262461	4.90776043474558
O	15.50434839121535	7.78577397209173	3.99909515517464
O	12.41916932925645	12.13616207683466	1.72088177234550
O	11.94929017030265	13.22455577788315	4.37364359289031
O	14.29280548591336	14.05211316199941	2.81273896590917
O	14.85322159050611	8.84847146897547	6.66674541203073
O	17.27328835983996	9.66702812089816	5.28500449352787
N	14.79112682311064	11.00784028299603	2.42050020621097
N	12.65422421455948	10.59834096455075	4.38736594687717
N	14.78209371334551	11.41825589277245	5.80609619884536
N	15.92554698246721	10.66383798395257	3.16301655162129
N	14.89035638137707	12.51395370566529	4.94483334196206
N	13.34425285625267	9.41443411225680	4.10190328823627
C	14.80211933032047	7.05225092160531	3.21583124361553
C	14.26566499851428	9.27632982909758	7.73263282405410
C	11.82486214248620	10.54580171897554	5.38906892933446
H	11.69376661986243	9.56003460332993	5.84706349722167
C	13.38073336558981	10.27826314886301	0.56277202546480
C	12.37829231611200	11.27196212491440	0.76567969625101
C	11.09796481876210	11.64220800607641	5.95340125323399
C	12.78207879307198	8.57134476431300	3.24322027869892
C	13.84793646400829	10.62864281198146	7.91358530594221
C	17.08257428013474	11.20195692444256	2.79757672653437
C	13.12039281111876	11.00597233528767	9.11141968131676
C	15.46960788134164	14.54374678797729	2.93798608052471
C	13.47243971372434	7.37337085152113	2.78831108687530
C	14.15900422501033	11.62092377366071	6.92919413015459
H	13.84994390919306	12.65299830690347	7.12443110412251

C	16.39069595339570	14.15896943165396	3.96631325301131
C	11.18008917033549	12.94124105321352	5.36929696920050
C	13.19487757852803	9.25788918624125	-0.45251344901519
C	12.81766193061982	6.49290822182299	1.86447232312568
C	12.90721610555381	10.03014689709190	10.13648378139609
C	11.24672830514917	11.30505057210160	-0.11866882039983
H	10.51893599285684	12.10199593987149	0.04389374536359
C	14.53903066537930	10.24109805577673	1.39843427252784
H	15.29226060630758	9.47487614700169	1.18650964292634
C	18.31580070153274	10.19589994536993	4.75762341845548
C	16.04896926182738	13.16785233011274	4.97093622457755
C	19.55413311689478	12.43742925935779	1.97145494913879
C	10.26910875096276	11.42864844069971	7.12609183485564
C	12.02421828525099	9.29910803525111	-1.27512774828769
C	17.70877697225605	14.71824371299024	3.95434405649083
C	14.77123042173802	5.00160580839390	1.87437999599171
H	15.25943571857163	4.08815938692484	1.52257512849816
C	18.30307050792944	10.97600729270911	3.55658954817941
C	18.10696489588134	15.63858707358938	2.93535841369653
C	19.52138356008857	11.59530829355245	3.12638470727573
C	15.41627632980423	5.84019779105563	2.73597810827526
H	16.42477009053136	5.63602447775201	3.09953155555003
C	13.45693722254358	5.30085763853559	1.40242849955206
C	11.08131271866254	10.35737170599623	-1.08778178457126
H	10.20030354760992	10.38605707687041	-1.73603293658762
C	15.88056231962801	15.52179065620501	1.96340477287387
H	15.13548382590507	15.80079566977264	1.21638748799779
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H	10.85216799953900	9.36642147441164	7.53990841780981
C	9.48127892212768	12.51138749993244	7.63122105203968

C	20.73811481612497	11.41358704403119	3.85599083388738
C	14.02525625430337	8.33007080055946	8.78728160512562
H	14.37839901133780	7.31083095884408	8.62111106101258
C	17.14518659874386	16.03261871746903	1.95399324266740
H	17.44574718201773	16.75079287609725	1.18553163975609
C	13.38839763447412	8.69962028461891	9.93803697512900
H	13.21885983795477	7.96416860174163	10.73009085128906
C	18.67867916190897	14.34045849393804	4.93319104017213
C	20.71788278854293	10.59500985317291	5.02636020210018
H	21.64983200924706	10.44819797254134	5.58006710255483
C	8.68002193927936	12.33078930542567	8.78468684397128
H	8.08805881219071	13.17685068593784	9.14474168502514
C	10.36648406531387	13.99677765850975	5.90695481027913
H	10.43865547067995	14.96959683148455	5.41760201262540
C	9.54923520441012	13.78156107546476	6.98018442134849
H	8.93824641006344	14.59885817083968	7.37478783181287
C	20.74795634608627	13.05623037528571	1.58053955272758
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C	19.56142808849080	10.01257923933909	5.45649382275483
H	19.52189409220115	9.39602615333619	6.35615816572829
C	11.51804341905905	6.79589869322807	1.35311793015416
C	19.98433284966701	14.84473200313714	4.86645303130750
H	20.71063471061979	14.52447452128074	5.61747539323069
C	12.19444463167137	10.37552827128045	11.31051115195588
H	12.05128818916293	9.60886499794374	12.07714751160208
C	21.93301696168335	12.86187920385353	2.29786332500837
H	22.85550945981217	13.35199774349191	1.97923671939378
C	11.79711918096047	8.28956801981027	-2.24197660799638
H	10.89170969888215	8.34804276253467	-2.85263445557777
C	11.67366797784741	11.64279823836052	11.48102124254245

H	11.11308578152656	11.89737068212037	12.38325568112719
C	12.80137658709640	4.46096146148246	0.47769964831276
H	13.31341009750372	3.55504871371820	0.14165819165049
C	21.92187789642409	12.04733216038352	3.42316732747170
H	22.83886011621846	11.88879165619626	3.99744489994078
C	9.45079977112777	10.05986694967959	8.97978584195328
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C	14.08646328006279	8.17043462945917	-0.64911350189626
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H	19.71330756229400	16.81879780496732	2.10874814489454
C	12.68505765157411	7.24435511174538	-2.40355010786498
H	12.49410550628770	6.46088455159195	-3.14019496587947
C	12.56033217235657	12.29434611793519	9.31504878157175
H	12.64283210939264	13.05840912186786	8.54281398731991
C	8.65834026054391	11.12412287786188	9.45556282910525
H	8.05072627774939	10.99819880632816	10.35444445162909
C	10.90710007461840	5.94389686715909	0.42478658187088
H	9.92048196465723	6.21111950074738	0.03793659516126
C	20.36533458374464	15.72908143938136	3.85377035773752
H	21.39054791142171	16.10151853867269	3.80689415692557
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C	11.53984173079480	4.77507715783423	-0.01114749839682
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C	10.87805410186391	7.99987669957710	1.79979691180602

H	9.89774934768881	8.25137322111772	1.38714300006334
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H	18.34495639673018	13.31079337053818	0.38342260954808
C	17.16520458494231	12.06431879558900	1.63075920441324
H	16.25269528510360	12.26836180530726	1.07702198365171
C	17.04019295198447	12.87048886081937	5.98750104183429
H	16.78886247620951	12.14485186582850	6.75576661410733
C	18.28096857597649	13.42178285078127	5.95936328296476
H	19.01558845371859	13.14010553112224	6.71810323300915

….