Electronic Supporting Information (ESI)

Exploring a new dinuclear Fe(III) complex for fixation of atmospheric CO_2 and optical recognition of nano-molar Zn^{2+} ion

Seikh Taniya, Somnath Khanra, Sabyasachi Ta, Sudeshna Chatterjee, Noor Salam* and Debasis Das*

Department of Chemistry, The University of Burdwan, Burdwan, 713104, W.B., India

Materials and physical measurements

High-purity 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer, 3-ethoxysalicyaldehyde and hydrazine (98%) were purchased from Sigma−Aldrich (India). Analytical reagent grade, $FeCl_3.6H_2O$ and $Zn(OAc)_2$ have been purchased from Merck (India) and used without further purification. The spectroscopic grade solvents are used. Water was purified using Milli-Q Millipore system (18.2 MΩ cm^{-1}). The absorption spectra were recorded with Shimadzu Multi Spec 2450 spectrophotometer. The emission properties were monitored by Hitachi F-7000 spectrofluorimeter. The FTIR spectra were recorded on a Shimadzu FTIR (model IR Prestige 21 CE) spectrophotometer whereas mass spectra were collected using a QTOF 60 Micro YA 263 mass spectrometer in ES(+) mode Electrospray ionization mass spectra (ESI-mass) were recorded with the help of Thermo Fisher scientific Exactive Mass Spectrometer using HR positive/ negative mode. The pH was measured with a Systronics digital pH meter (model 335). The ^{1}HNMR spectra were collected with Bruker 400 MHz spectrometer using DMSO-d_6 as solvent. The chemical shift is represented in ppm using residual solvent peak as an internal reference. Multiplicity indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants (J, s) are reported in Hertz (Hz). The cyclic voltammetric (CV) studies were performed in dry acetonitrile using CHI620D potentiometer having three-electrode system: platinum disk working electrode, platinum wire auxiliary electrode and calomel reference electrode. The solution was extensively purged with N_2 prior to measurement. TBAP (0.1M) was used as supporting electrolyte. All potentials were measured at a scan rate of 100 mV s^{-1} at room temperature. The fluorescence lifetime is measured by time correlated single photon counting (TCSPC) technique using HORIBA Jobin Yvon Fluorocube-01-NL fluorescence lifetime spectrometer. The sample was excited using a picosecond diode laser of 336 nm. ZEISS Gemini Sigma 300 instrument was used to collect FESEM images. Finally, kinetic measurement was carried out with an Applied Photophysics SX 17MV stopped-flow spectrophotometer (model OPT-622) in the symmetric mixing mode at room temperature and ambient pressure.

Single crystal X-ray data were collected on a Bruker X8 APEX-II CCD diffractometer at 100(2) K using graphite-monochromated Mo-K_α radiation (0.71073Å) at 150K. Data were processed and corrected for Lorentz and polarization absorption effects. Crystal structure was solved by standard direct methods using the SHELXS,[1] and refined by full-matrix least-squares with SHELXL,[2] and OLEX2 software.[3] Significant crystal parameters and refinement data were presented in Table S1 (ESI). All non-hydrogen atoms were refined with anisotropic thermal displacements. Hydrogen atoms were included in the structure factor calculation in geometrically idealized positions, with thermal parameters depending on the parent atom, using a riding model. Images are generated by Mercury software.[4]

General method of UV-Vis and fluorescence measurement

The F1 (20 µM) was dissolved in in HEPES buffered EtOH/H_2O (4/1, v/v) media, pH 7. The absorption and emission spectrum of F1 was recorded in presence of all the metal ions *viz.* Zn^{2+}, K^+, Ca^{2+}, Mg^{2+}, Hg^{2+}, Pb^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ag^+. In a similar way competitive experiment have been performed for F2-Zn^{2+} system.

General method of UV-Vis and fluorescence titration

Stock solution of F1 are prepared (20 µM) in HEPES buffered EtOH/H_2O (4/1, v/v) media, pH 7 for UV-Vis and fluorescence titrations. Working solutions of F1 and Zn^{2+} are prepared from their respective stock solutions. The cells having path length 1 cm are used for absorption and emission studies. Fluorescence measurements have been performed using 5 nm x 5 nm slit width.

Job's plot from fluorescence experiment

A series of solutions containing F1 and $Zn^{2+}$are prepared such that the total concentration of Zn^{2+} and F1 remained constant (20 µM) in all the sets. The mole fractions (x) of Zn^{2+} are varied from 0.1 to 0.9.The fluorescence intensity at 400 nm for F1-Zn^{2+} are plotted against the mole fraction of Zn^{2+}.

Determination of binding constant

The binding constants of the compounds **F1** for analyte are determined using the following Benesi-Hildebrand equation[5].

$$\frac{F_{max} - F_{min}}{F_X - F_{min}} = 1 + \frac{1}{K[C]^n}$$

Here $\mathbf{F_{min}}$, $\mathbf{F_x}$, and $\mathbf{F_{max}}$ are the emission intensities of the compound **F1** in absence of analyte, at an intermediate analyte concentration, and at a concentration of complete interaction with analyte respectively. **K** is the binding constant, **C** is the concentration of analyte and **n** is the number of analyte bound per molecule (here, **n** = 1). The value of **K** can be determined from the slopes of different plot for different analytes.

Calculation of detection limit

The detection limit (**DL**) is determined from the following equation[6]:

$$DL = \frac{3\sigma}{S}$$

σ is the standard deviation of the blank solution, **S** is the slope of the calibration curve.

Calculation of quantum yield

Following equation[7-8] has been used to measure fluorescence quantum yield of the compound

$$\Phi_s = \Phi_r \frac{A_r F_s \eta_s^2}{A_s F_r \eta_r^2}$$

Where As and Ar are the absorbance of the sample and reference solutions, respectively, at the same excitation wavelength, Fs and Fr are the corresponding relative integrated fluorescence intensities, and η is the refractive index of the solvents.

References

1. M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 2005, **38**, 381-388.
2. G. M. Sheldrick, *ActaCry*st., 2008, **E**64, 112-122.
3. G. M. Sheldrick, *ActaCry*st., 2015, **A71**, 3-8.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.,* 2009, **42**, 339-341.
5. H. A. Benesi and J. H. Hildebrand,*J. Am. Chem. Soc.*, 1949, **71**, 2703-2707.
6. M. Zhu, M. Yuan, X. Liu, J. Xu, J. Lv, C. Huang, H. Liu, Y. Li, S. Wang and D. Zhu,*Org. Lett.*, 2008, **10**, 1481-1484.
7. W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229-235.
8. A. T. R. Williams, S. A. Winfield and J. N. Miller, *Analyst*, 1983, **108**, 1067-1071.

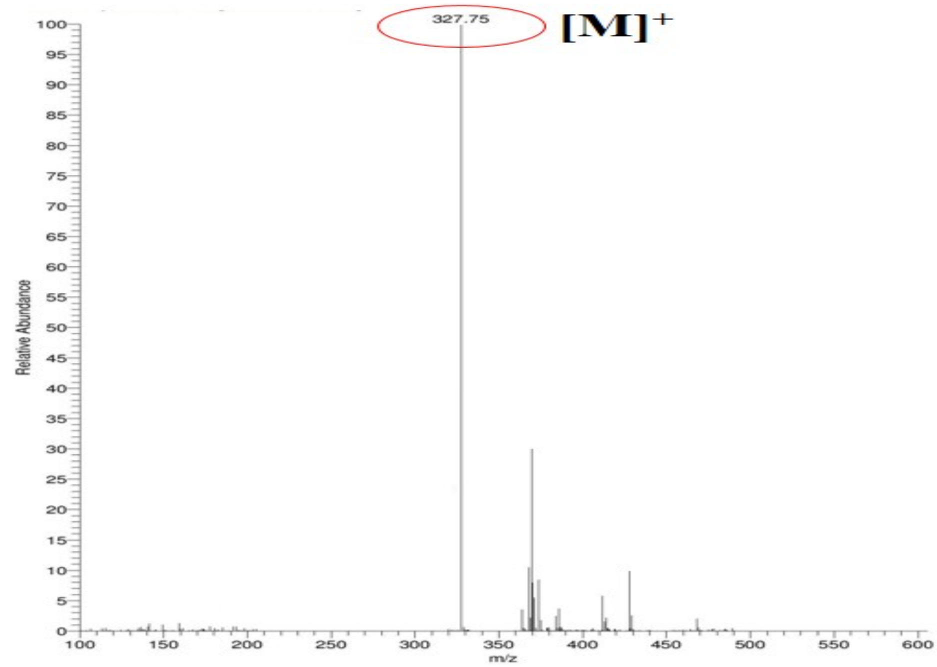


Figure S1a QTOF mass spectrum of **L1** in MeOH,

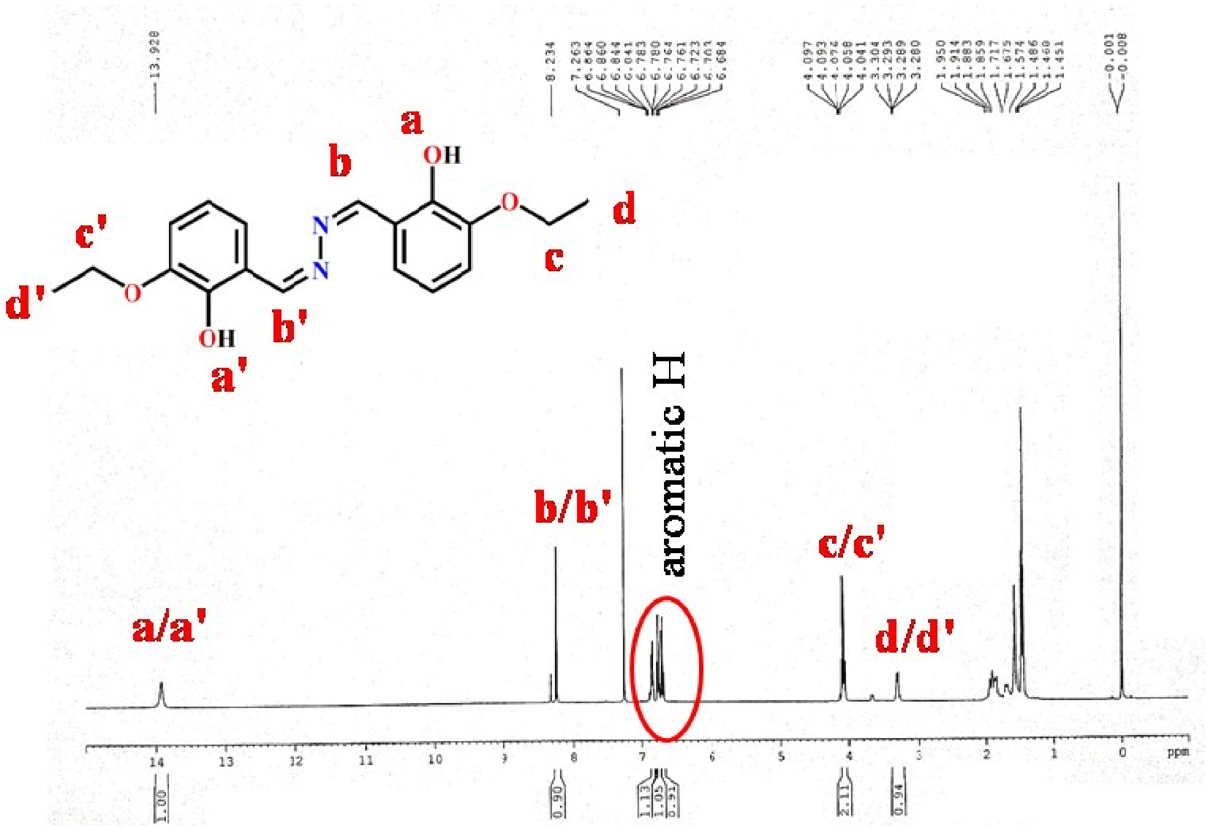


Figure S1b ^{1}H NMR spectrum of **L1** in DMSO-d_6.

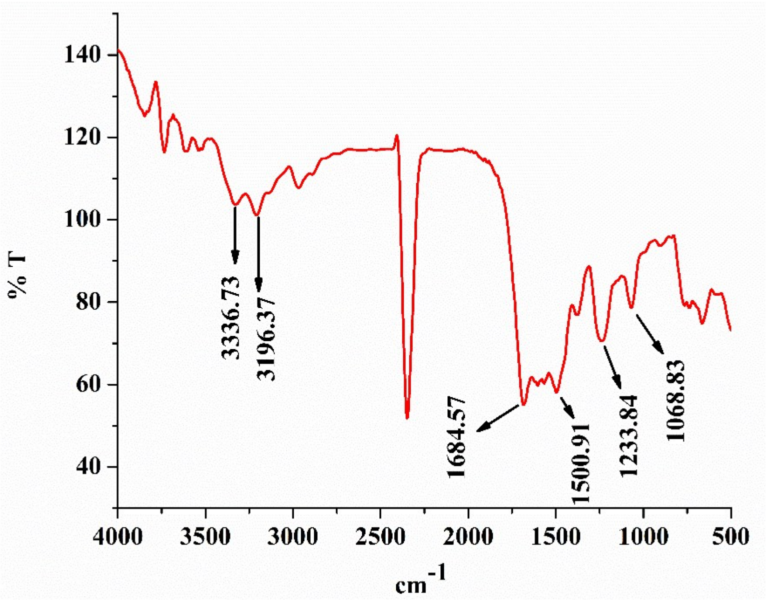


Figure S1c FTIR spectrum of **L1**

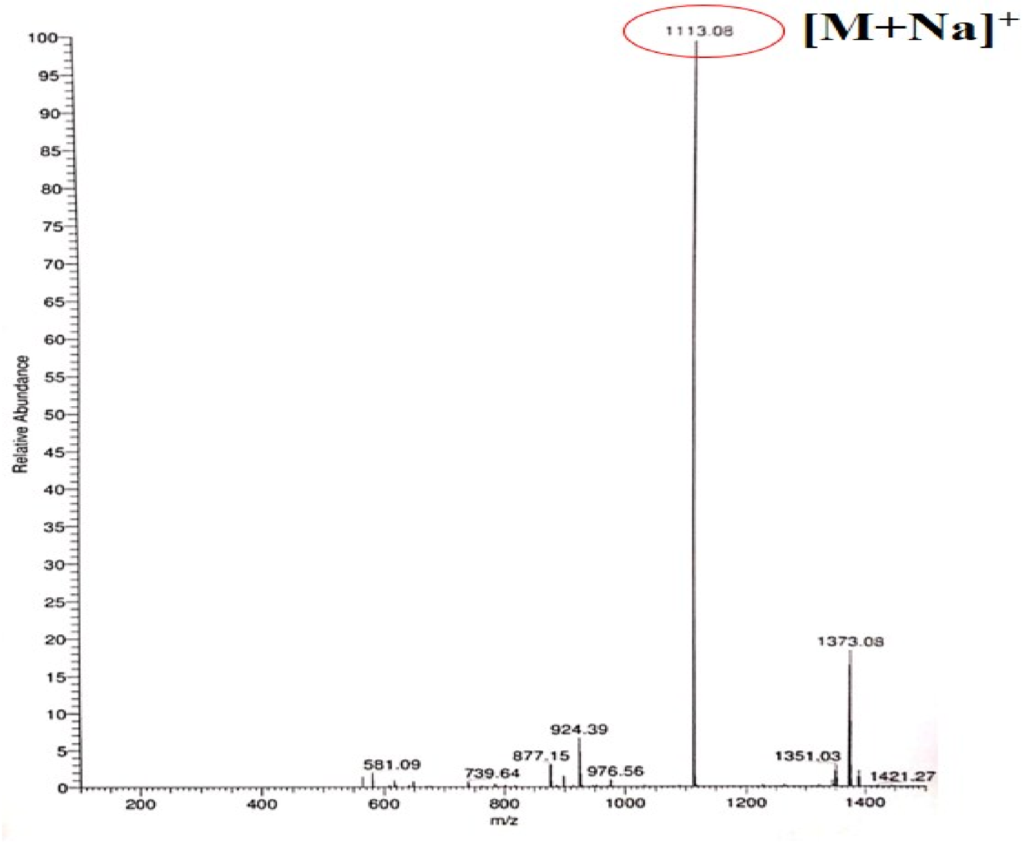


Figure S2a QTOF mass spectrum of **F1** in MeOH

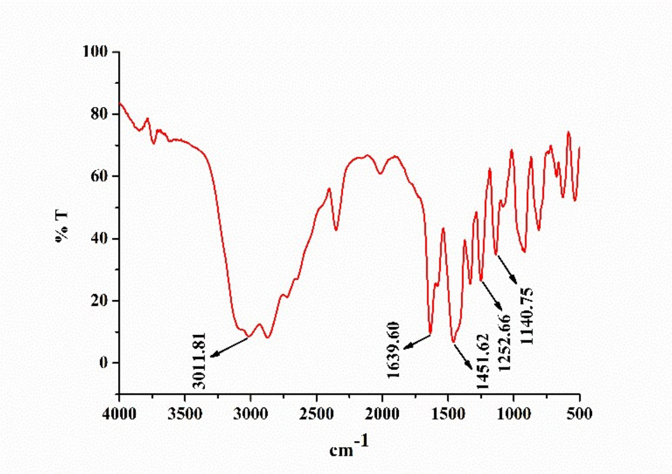


Figure S2b FTIR spectrum of **F1**

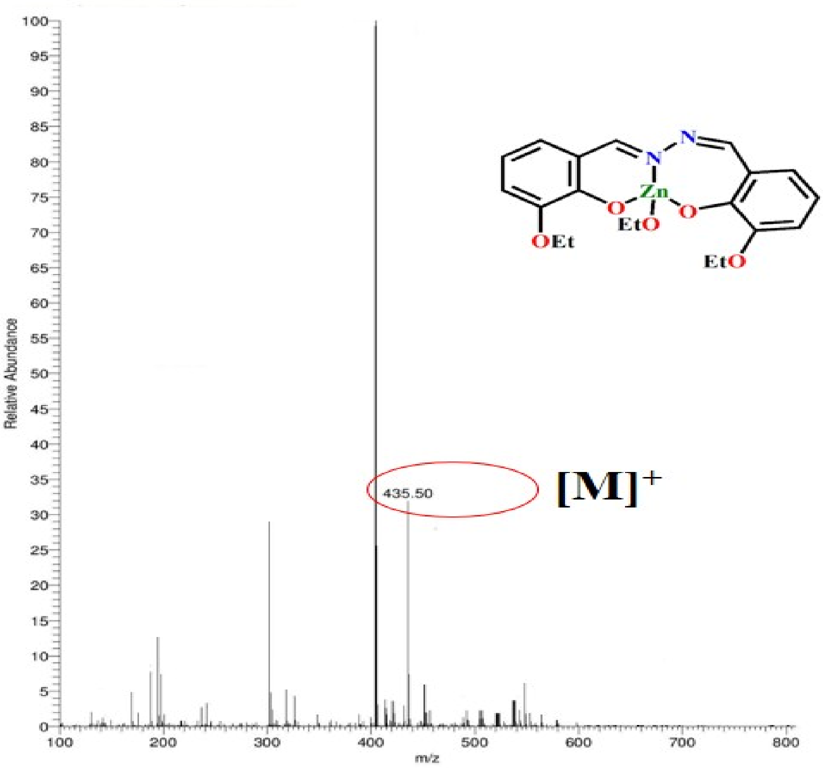


Figure S3a QTOF mass spectrum of **Z1** in MeOH

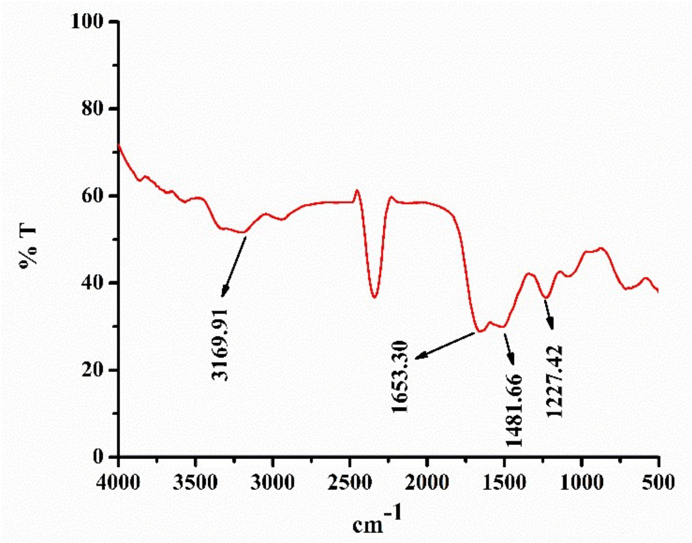


Figure S3b FTIR spectrum of **Z1**

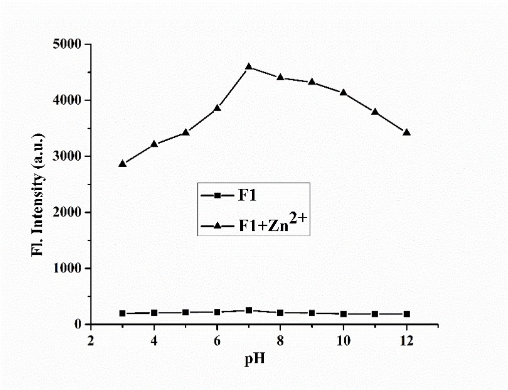


Figure S4 Effect of pH on the emission intensities of **F1** in presence and absence of **Zn^{2+}** (λ_{ex} = 332 nm, λ_{em} = 437 nm)

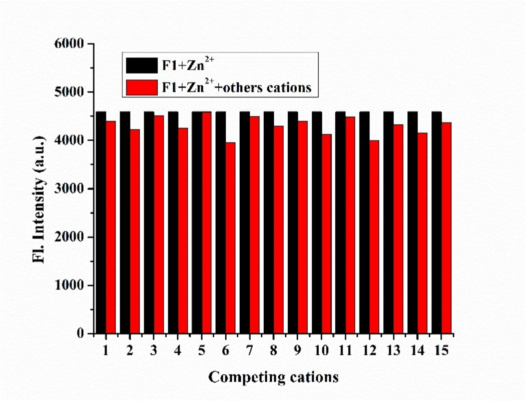


Figure S5 Interference diagram for determination of **Zn^{2+}** using **F1** (λ_{ex} = 332 nm, λ_{em} = 437 nm). 1 = Al^{3+}, 2 = K^{+}, 3 = Ca^{2+}, 4 = Mg^{2+}, 5 = Hg^{2+}, 6 = Pb^{2+}, 7 = Cr^{3+}, 8 = Fe^{3+}, 9 = Mn^{2+}, 10 = Co^{2+}, 11 = Ni^{2+}, 12 = Cu^{2+}, 13 = Zn^{2+}, 14 = Cd^{2+} and 15 = Ag^{+}

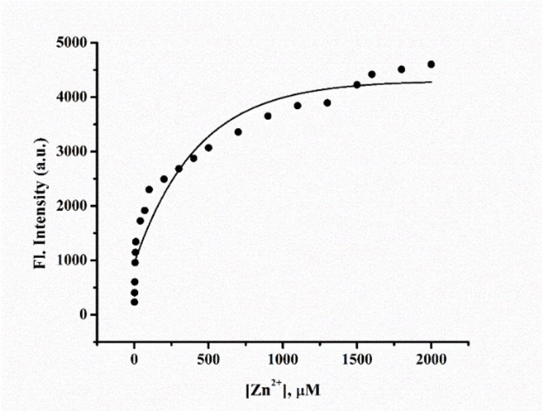


Figure S6 Plot of emission intensities of **F1** (20 µM, λ_{ex} = 332 nm, λ_{em} = 437 nm) as a function of externally added **Zn**$^{2+}$ (1.0-1500 µM).

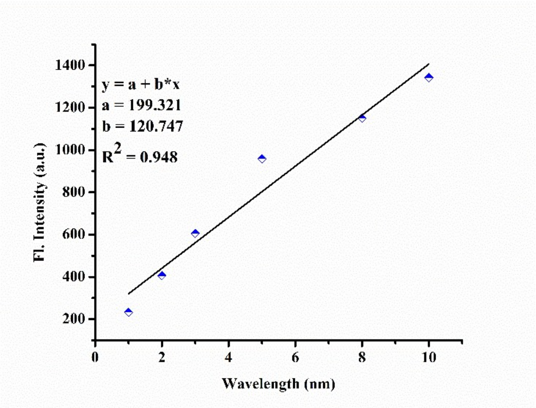


Figure S7 Determination of detection limit based on change of emission intensity at 437 nm (λ_{ex} = 332 nm) of **F1** (20 µM) upon addition gradual addition of **Zn**$^{2+}$.

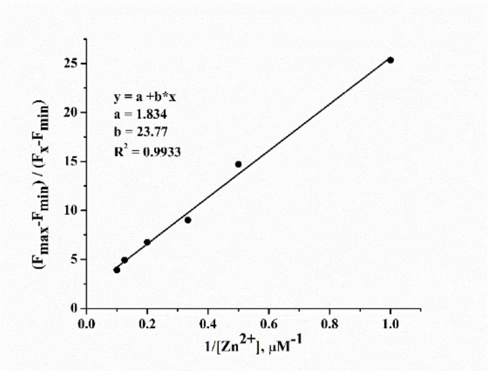


Figure S8 Benesi–Hildebrand plot for determination of interaction constant of **F1** with **Zn**$^{2+}$ (liner portion), λ_{ex} = 332 nm, λ_{em} = 437 nm.

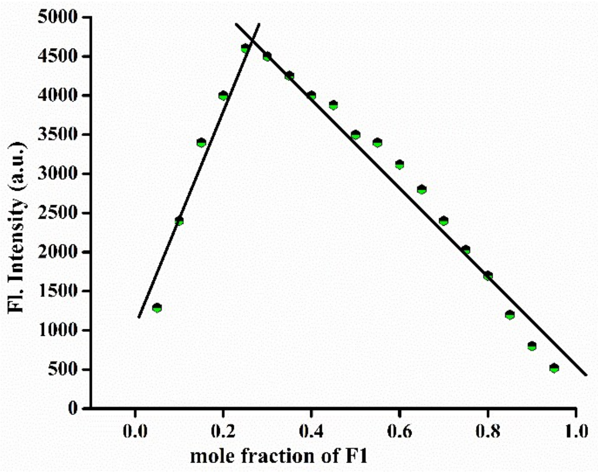


Figure S9 Job's plot for determination of stoichiometry of interaction between **F1** and **Zn^{2+}** (λ_{ex} = 332 nm λ_{em} = 437 nm).

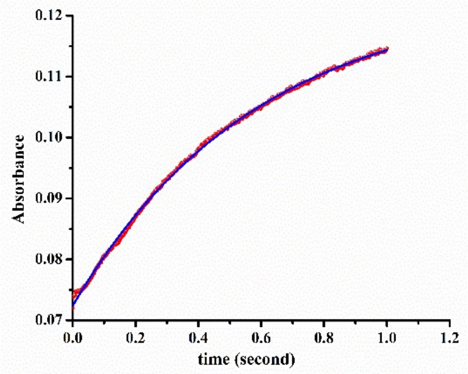


Figure S10 Changes in absorbance of F1 (20 µM) at 380 nm (pH 7.4), saturated with Zn^{2+} upon irradiation with 2 MeV electrons (noisy curve) and least-square fit of the first-order plot (blue line) using stopped flow spectrophotometry.

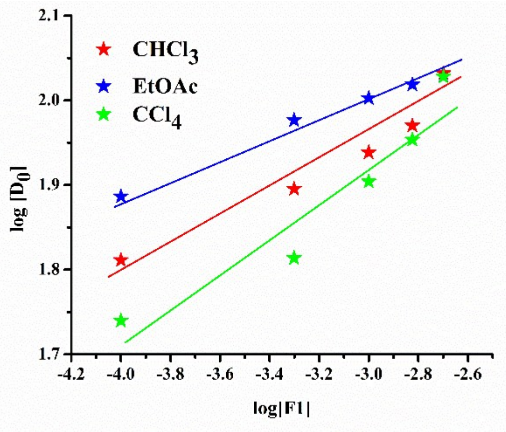


Figure S11a Plot of log[D_0] *vs.* log[F1]

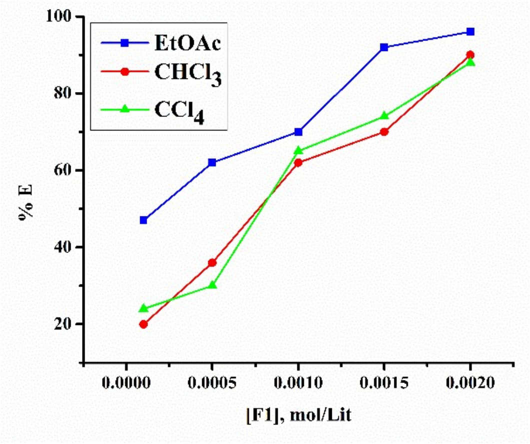


Figure S11b Plot of %E *vs.* [Zn^{2+}]

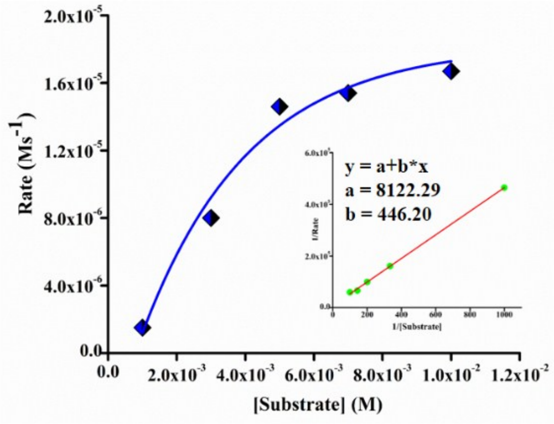


Figure S12a The plot of rate *vs.* substrate (catechol) concentration using F1 as bio-catalyst; Inset: Lineweaver–Burk plot.

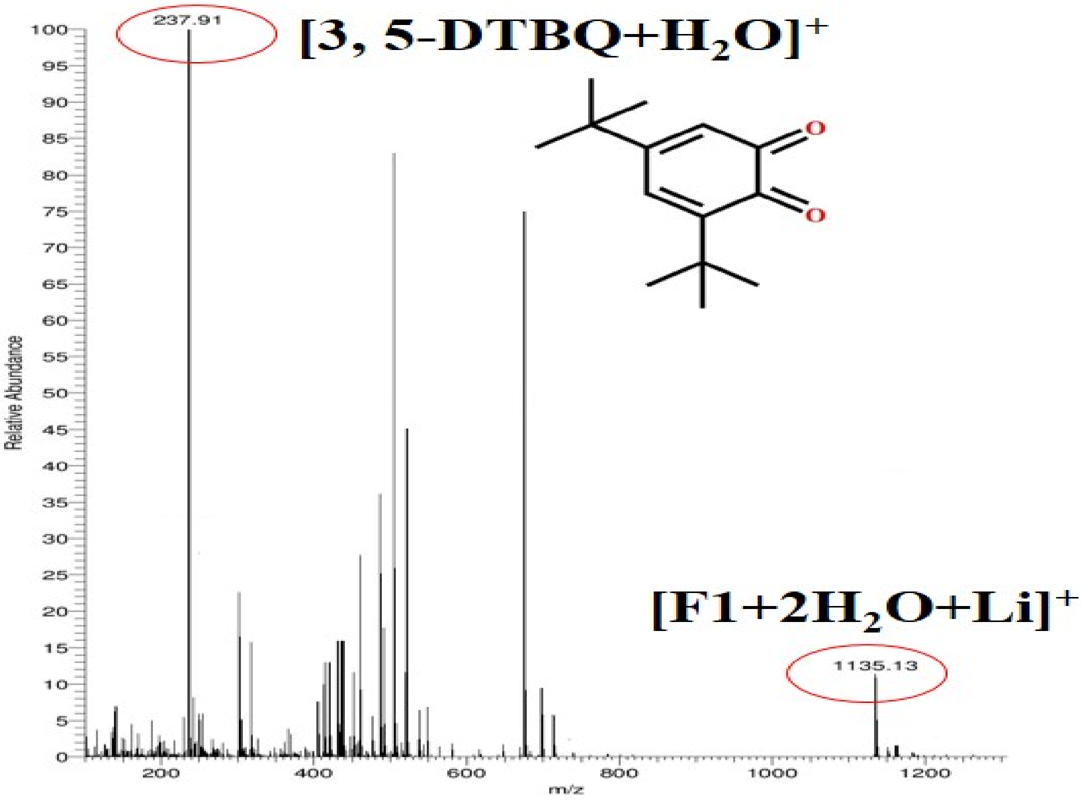


Figure S12b QTOF mass spectrum of the mixture of **F1** and **3, 5-DTBC**.

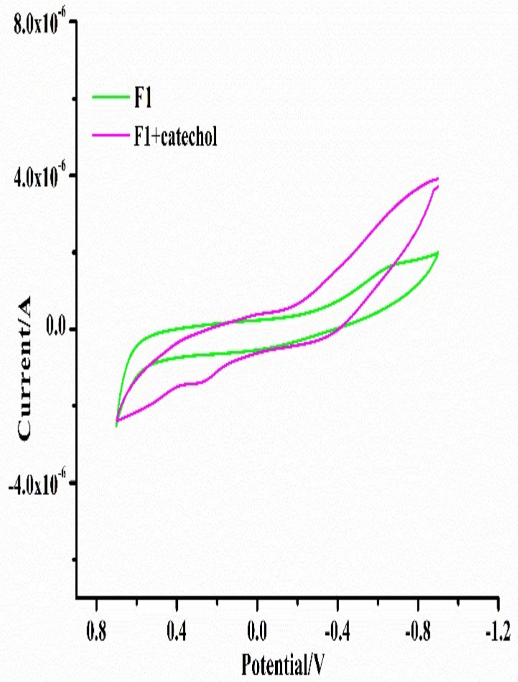


Figure S12c CV of F1 and F1-catechol system

Table S1 Crystal Refinement parameter

Molecule	**F1**
CCDC	1864282
Empirical formula	$C_{54}H_{54}Fe_2N_6O_{12}$
Formula weight	1089.73
Crystal system	Triclinic
Space group	P -1
Temparature	296 K
Wavelength	0.71073
a/Å	14.8885(7)
b/Å	15.0825(6)
c/Å	15.1336(6)
α/°	104.859(3)
β/°	104.285(3)
γ/°	117.418(3)
Volume/Å^3	2639.0(2)
Z	2
ρ_{calc} g/cm^3	1.371
μ/mm^{-1}	0.617
F(000)	1134.0
F(000′)	1135.87
Θmax	25.161
Index ranges (h,k,lmax)	17,18,18
Reflections collected	0.0773(4584)
wR$_2$ (Reflection)	0.2255(9457)

Table S2 Selected bond lengths and bond angles

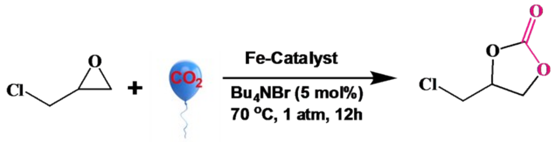
ATOMS	**LENGTH**	**ATOMS**	**ANGLE**
Fe01 O004	1.909(5)	O004 Fe01 O007	96.1(2)
Fe01 O007	1.913(5)	O004 Fe01 O003	94.2(2)
Fe01 O003	1.920(4)	O007 Fe01 O003	100.8(2)
Fe01 N3	2.142(6)	O004 Fe01 N3	173.2(2)
Fe01 N00J	2.178(5)	O007 Fe01 N3	84.9(2)
Fe01 N2	2.197(6)	O003 Fe01 N3	92.3(2)
N1 C00P	1.294(9)	O004 Fe01 N00J	83.9(2)
N1 N2	1.423(7)	O007 Fe01 N00J	93.6(2)
N1 Fe02	2.160(6)	O003 Fe01 N00J	165.5(2)
O1 C01G	1.371(10)	N3 Fe01 N00J	89.3(2)
O1 C4	1.400(13)	O004 Fe01 N2	89.5(2)
C1 C01Z	1.36(2)	O007 Fe01 N2	171.9(2)

Fe02 O009	1.903(5)	O003 Fe01 N2	84.5(2)
Fe02 O008	1.911(5)	N3 Fe01 N2	88.9(2)
Fe02 N4	2.138(5)	N00J Fe01 N2	81.2(2)
Fe02 N00F	2.208(6)	C00P N1 N2	116.8(6)
N2 C00U	1.284(9)	C00P N1 Fe02	125.4(5)
O2 C01V	1.371(14)	N2 N1 Fe02	117.4(4)
O2 C01L	1.383(10)	C01G O1 C4	115.5(8)
C2 C01V	1.521(17)	O009 Fe02 O005	100.2(2)
O003 C00V	1.312(8)	O009 Fe02 O008	95.5(2)
N3 C5	1.304(8)	O005 Fe02 O008	96.2(2)
N3 N4	1.421(7)	O009 Fe02 N4	84.9(2)
O3 C017	1.350(9)	O005 Fe02 N4	90.5(2)
O3 C01R	1.448(12)	O008 Fe02 N4	173.0(2)
C3 C4	1.423(16)	O009 Fe02 N1	94.0(2)
O004 C018	1.299(8)	O005 Fe02 N1	165.4(2)
N4 C00Q	1.287(8)	O008 Fe02 N1	85.7(2)
O4 C00W	1.365(9)	N4 Fe02 N1	87.3(2)
O4 C01S	1.426(9)	O005 Fe02 N00F	83.0(2)
O005 C019	1.314(9)	O008 Fe02 N00F	89.0(2)
C5 C00N	1.425(10)	N4 Fe02 N00F	90.1(2)
O5 C01A	1.352(10)	N1 Fe02 N00F	82.5(2)
O5 C01Z	1.463(16)	C00U N2 N1	118.1(6)
O007 C00M	1.310(9)	C00U N2 Fe01	121.4(5)
O008 C00R	1.301(9)	N1 N2 Fe01	119.6(4)
O008 C00R	1.301(9)	C01V O2 C01L	116.3(8)
O00B C010	1.376(10)	C00V O003 Fe01	126.4(4)
O00B C01U	1.436(10)	C5 N3 N4	116.3(6)
N00F C011	1.296(9)	C5 N3 Fe01	127.2(5)
N00F N00J	1.406(8)	N4 N3 Fe01	116.3(4)
N00J C00X	1.295(9)	C017 O3 C01R	121.1(7)
C00M C00N	1.384(11)	C018 O004 Fe01	138.3(5)
C00M C010	1.437(10)	C00Q N4 N3	118.1(5)
C00N C00Z	1.440(11)	C00Q N4 Fe02	126.6(5)
C00O C012	1.423(10)	N3 N4 Fe02	114.6(4)
C00O C00V	1.431(10)	C00W O4 C01S	120.5(7)
C00O C00U	1.437(10)	O1 C4 C3	114.6(12)
C00P C00S	1.441(9)	C019 O005 Fe02	130.5(5)
C00Q C00Y	1.432(9)	N3 C5 C00N	124.8(7)
C00R C00S	1.410(11)	C01A O5 C01Z	114.0(9)
C00R C01A	1.430(10)	C00M O007 Fe01	136.1(5)
C00S C01B	1.405(11)	C00R O008 Fe02	135.1(5)
C00T C011	1.412(10)	C014 O009 Fe02	134.5(5)
C00T C01C	1.418(10)	C010 O00B C01U	116.3(7)
C00T C019	1.434(11)	C011 N00F N00J	118.0(6)
C00V C00W	1.416(9)	C011 N00F Fe02	122.4(5)
C00W C01D	1.356(11)	N00J N00F Fe02	118.6(4)
C00X C015	1.413(10)	C00X N00J N00F	118.4(6)
C00Y C016	1.412(10)	C00X N00J Fe01	126.0(5)

C00Y C014	1.419(10)	O007 C00M C00N	123.3(7)
C00Z C013	1.369(11)	O007 C00M C010	118.4(8)
C010 C01I	1.385(12)	C00N C00M C010	118.3(7)
C012 C01E	1.343(10)	C00M C00N C5	123.5(7)
C013 C01I	1.362(13)	C00M C00N C00Z	120.4(7)
C014 C01L	1.392(10)	C5 C00N C00Z	115.9(8)
C015 C018	1.411(10)	C012 C00O C00V	120.2(7)
C015 C01F	1.413(11)	C012 C00O C00U	117.2(7)
C016 C01N	1.351(11)	C00V C00O C00U	122.6(7)
C017 C01J	1.375(11)	N1 C00P C00S	126.5(7)
C017 C018	1.421(11)	N4 C00Q C00Y	125.0(6)
C019 C01G	1.397(11)	O008 C00R C00S	123.8(6)
C01A C01H	1.382(12)	O008 C00R C01A	118.7(8)
C01B C01K	1.372(10)	C00S C00R C01A	117.4(7)
C01C C01M	1.367(12)	C01B C00S C00R	121.4(7)
C01D C01E	1.401(11)	C01B C00S C00P	116.8(7)
C01F C01O	1.361(12)	C00R C00S C00P	121.8(7)
C01D C01E	1.401(11)	C011 C00T C01C	117.9(8)
C01F C01O	1.361(12)	C011 C00T C019	123.0(7)
C01G C01P	1.368(12)	C01C C00T C019	118.9(8)
C01H C01K	1.376(12)	N2 C00U C00O	125.9(7)
C01J C01O	1.396(11)	O003 C00V C00W	120.9(7)
C01L C01Q	1.367(12)	O003 C00V C00O	122.3(6)
C01M C01P	1.389(13)	C00W C00V C00O	116.7(7)
C01N C01Q	1.388(12)	C01D C00W O4	125.4(7)
C01N C01Q	1.388(12)	C01D C00W C00V	121.3(8)
C01S C01Y	1.439(15)	O4 C00W C00V	113.3(7)
C01U C01W	1.504(16)	N00J C00X C015	127.0(7)
		C016 C00Y C014	119.2(7)
		C016 C00Y C00Q	117.7(7)
		C014 C00Y C00Q	123.1(7)
		O00B C010 C01I	127.1(8)
		C01I C010 C00M	119.7(9)
		N00F C011 C00T	125.5(8)
		C01E C012 C00O	120.1(8)
		C01E C012 C00O	120.1(8)
		O009 C014 C01L	120.3(7)
		O009 C014 C00Y	121.9(7)
		C01L C014 C00Y	117.7(7)
		C018 C015 C01F	119.7(8)
		C018 C015 C00X	122.2(7)
		C01F C015 C00X	118.1(7)
		C01N C016 C00Y	120.7(8)
		O3 C017 C01J	116.7(8)
		O3 C017 C018	123.4(7)
		C01J C017 C018	119.9(7)
		O004 C018 C015	122.6(7)
		O004 C018 C017	118.7(7)

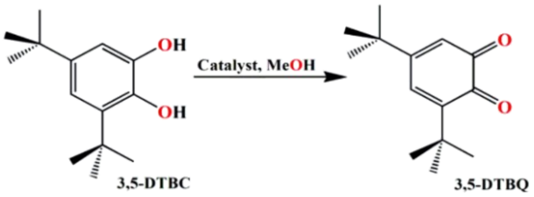
		C015 C018 C017	118.6(7)
		O005 C019 C01G	121.1(8)
		O005 C019 C00T	121.3(7)
		C01G C019 C00T	117.6(8)
		O5 C01A C01H	120.3(7)
		O5 C01A C00R	120.7(8)
		C01H C01A C00R	119.0(8)
		C01K C01B C00S	119.8(8)
		C01M C01C C00T	121.4(9)
		C00W C01D C01E	121.1(7)
		C012 C01E C01D	120.5(8)
		C01O C01F C015	120.4(8)
		C01P C01G O1	118.3(8)
		C01P C01G C019	121.6(9)
		O1 C01G C019	119.8(8)
		C01K C01H C01A	122.7(8)
		C013 C01I C010	121.0(9)
		C017 C01J C01O	120.9(8)
		C01B C01K C01H	119.6(8)
		C01Q C01L C014	121.8(8)
		C01C C01M C01P	119.0(9)
		016 C01N C01Q	120.4(8)
		C01G C01P C01M	121.4(9)
		C01L C01Q C01N	120.0(8)
		C01X C01R O3	112.7(10)
		O4 C01S C01Y	112.0(9)
		O00B C01U C01W	106.3(9)
		O2 C01V C2	107.0(13)
		C1 C01Z O5	112.5(17)

Table S3 Optimization of reaction conditions for the synthesis of styrene carbonate[a]



Entry	TBAB (mol %)	Temperature (°C)	Yield[b] (%)
1	6	70	78
2	4	70	54
3	2	70	34
4	**5**	**70**	**97**
5	5	50	32
6	5	80	75
7	-	70	20
8[c]	5	24	Trace

[a]**Reaction conditions:** epichlorohydrin (5 mmol), F1 (15mg); [b]GC yield of cyclic carbonate; [c]without catalyst



Scheme S1 Bio-catalytic oxidation of 3, 5-DTBC to 3,5-DTBQ by F1 in methanol