Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic supplementary information

The Giant Iron polyoxometalate that works as a catalyst for Water Oxidation

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1. Experimental section

1.1. Materials and Instrument:

All chemicals were of analytical grade and used without further purification. $FeCl_3.6H_2O$, $CH_3COONa.3H_2O$ and all the other chemicals were purchased from Sigma Aldrich.

1.2 Synthesis of catalyst $((NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ ~300 H_2O:

To a stirred solution of $(NH_4)_6Mo_7O_{24}.4H_2O$ (5.6 g, 4.5 mmol) and CH_3COONH_4 (12.5 g, 162.2 mmol) in 250 mL water $N_2H_6.SO_4$ (0.8 g, 6.1 mmol) was added and further stirred for 10 minutes. The color change of the solution was observed bluish green. Then 50% (v/v) CH_3COOH (83 mL) was mixed to it. The green solution was stored in an open 500-mL Erlenmeyer flask at 20°C undisturbed. The color of the solution slowly changed to dark brown. After 4/5 days the reddish-brown crystals were filtered off and finally dried in air. Yield: 3.0 g.

1.3 Synthesis of catalyst I:

The $FeCl_3.6H_2O$ (1.1 g, 4.1 mmol) was dissolved and stirred in 75 mL water and then $CH_3COONa.3H_2O$ (1.1 g, 8.1 mmol) was added to it. Next, the previously synthesized $((NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ ~300 H_2O (1.4 g, 0.05 mmol) was added in the solution. The mixture was vigorously stirred open in a 100-mL Erlenmeyer flask for 24 h. Then HCl (1M, 1 mL) was added to it followed by the addition of NaCl (2.0 g). The reaction mixture was heated to 90°C -95°C and stirred continuously then filtered hot. The golden yellow colour filtrate was cooled to room temperature, and after 2/3 days yellow crystals formed. The crystals along with golden yellow precipitate were collected by filtration and washed carefully with a little iced water followed by drying in air. Yield: 560 mg.

2. pH dependence:

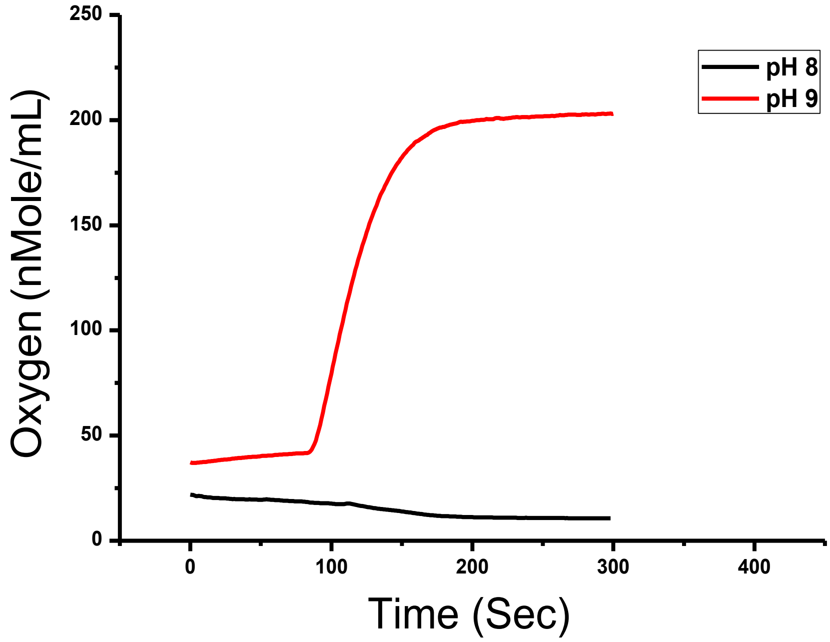

Figure S1: Oxygen evolution of catalyst **I** in pH 8 (black) and pH 9 (red) with catalyst (2 mg, in 2 mL). $Ru(bpy)_3^{2+}$(1 mM) and $Na_2S_2O_8$ (10 mM); Sodium borate buffer (10 mM, pH 9).

3. Table S1: Iron complexes/iron POMs catalysts reported for water oxidation process:

Iron complexes or iron POMs catalysts	Reaction condition applied	Instrument/method used to monitor the oxygen evolution	Turn over number/turnover frequency	Reference
cis-Fe(mcp)Cl_2 (mcp=N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)cyclohexane-1,2-diamine	$[Ru(bpy)_3(ClO_4)_3]$=0.75 mm, in 15 mm borate buffer (pH 8.5) at 23°C. Time=120 s.	Clark electrode	---	Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angewandte Chemie International Edition* **2013**, *52,* 1789-1791. **(Ref: 38)**
cis-Fe(mcp)Cl_2 (mcp=N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)cyclohexane-1,2-diamine	$[Ru(bpy)_3Cl_2]$=0.2 mm, $[Na_2S_2O_8]$=2 mm in 15 mm borate buffer (pH 8.5) at 23°C, λ>420 nm.	GC	194/--	Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angewandte Chemie International Edition* **2013**, *52*, 1789-1791. **(Ref: 38)**
$[Fe(bpy)_2Cl_2]$Cl (bpy=bipyridine)	$[Ru(bpy)_3(ClO_4)_3]$=0.75 mm, in 15 mm borate buffer (pH 8.5) at 23°C. Time=120 s.	Clark electrode	95/3.6 s^{-1}	Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angewandte Chemie International Edition* **2013**, *52*, 1789-1791. **(Ref: 38)**
$[Fe(bpy)_2Cl_2]$Cl (bpy=bipyridine)	$[Ru(bpy)_3Cl_2]$=0.2 mm, $[Na_2S_2O_8]$=2 mm in 15 mm borate buffer (pH 8.5) at 23°C, λ>420 nm.	GC	157/---	Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angewandte Chemie International Edition* **2013**, *52*, 1789-1791. **(Ref: 38)**
$[Fe(tpy)_2]Cl_2$ (tpy=2,2':6',2'' terpyridine	$[Ru(bpy)_3(ClO_4)_3]$=0.75 mm, in 15 mm borate buffer (pH 8.5) at 23°C. Time=120 s.	Clark electrode	19/1.5 s^{-1}	Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angewandte Chemie International Edition* **2013**, *52*, 1789-1791. **(Ref: 38)**
$[Fe(tpy)_2]Cl_2$ (tpy=2,2':6',2'' terpyridine	$[Ru(bpy)_3Cl_2]$=0.2 mm, $[Na_2S_2O_8]$=2 mm in 15 mm borate buffer (pH 8.5) at 23°C, λ>420 nm.	GC	376/---	Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angewandte Chemie International Edition* **2013**, *52*, 1789-1791. **(Ref: 38)**
cis-$[Fe(cyclen)Cl_2]$Cl (cyclen=1,4,7,10-tetraazacyclodecane)	$[Ru(bpy)_3(ClO_4)_3]$=0.75 mm, in 15 mm borate buffer (pH 8.5) at 23°C. Time=120 s.	Clark electrode	108/4.4 s^{-1}	Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angewandte Chemie International Edition* **2013**, *52*, 1789-1791. **(Ref: 38)**

cis-[Fe(cyclen)Cl_2]Cl (cyclen=1,4,7,10-tetraazacyclodecane)	[Ru(bpy)$_3$$Cl_2$]=0.2 mm, [$Na_2S_2O_8$]=2 mm in 15 mm borate buffer (pH 8.5) at 23°C, λ>420 nm.	GC	412/---	Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angewandte Chemie International Edition* **2013**, *52*, 1789-1791. **(Ref: 38)**
trans-Fe(tmc)Br_2 (tmc=1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)	[Ru(bpy)$_3$(ClO_4)$_3$]=0.75 mm, in 15 mm borate buffer (pH 8.5) at 23°C. Time=120 s.	Clark electrode	93/4.6	Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angewandte Chemie International Edition* **2013**, *52*, 1789-1791. **(Ref: 38)**
trans-Fe(tmc)Br_2 (tmc=1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)	[Ru(bpy)$_3$$Cl_2$]=0.2 mm, [$Na_2S_2O_8$]=2 mm in 15 mm borate buffer (pH 8.5) at 23°C, λ>420 nm.	GC	364/---	Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angewandte Chemie International Edition* **2013**, *52*, 1789-1791. **(Ref: 38)**
Fe(ClO_4)$_3$	[Ru(bpy)$_3$(ClO_4)$_3$]=0.75 mm, in 15 mm borate buffer (pH 8.5) at 23°C. Time=120 s.	Clark electrode	147/9.6 s^{-1}	Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angewandte Chemie International Edition* **2013**, *52*, 1789-1791. **(Ref: 38)**
Fe(ClO_4)$_3$	[Ru(bpy)$_3$$Cl_2$]=0.2 mm, [$Na_2S_2O_8$]=2 mm in 15 mm borate buffer (pH 8.5) at 23°C, λ>420 nm.	GC	436/---	Chen, G.; Chen, L.; Ng, S.-M.; Man, W.-L.; Lau, T.-C. *Angewandte Chemie International Edition* **2013**, *52*, 1789-1791. **(Ref: 38)**
{$PMo_{12}O_{40}$@$Mo_{72}Fe_{30}$}*n* ***(Heterogeneous catalyst)***	The reaction mixture was kept in a photo reactor under uv-light (300 Watt, λ_{max} = 280–400 nm, photon flux-77mW/cm^2 for 14 h.	YSI dissolved oxygen meter/ cyclic-voltammetry	20256/24.11 min^{-1}	Das, S.; Roy, S. Photochemical *Journal of Molecular and Engineering Materials* **2017**, *05*, 1750001. (**Ref: 32)**
[Fe^{III}(L1)Cl_2]$^+$ (L1=N,N'-dimethyl-2,11-diaza[3,3](2,6)pyridinophane) ***(Homogeneous catalyst)***	[NH_4]$_2$[Ce^{IV}(NO_3)$_6$] (CAN), as the oxidant; with 0.1 M HNO_3	GC	93/---	To, W.-P.; Wai-Shan Chow, T.; Tse, C.-W.; Guan, X.; Huang, J.-S.; Che, C.-M. *Chemical Science* **2015**, *6*, 5891-5903. (**Ref: 28)**
	$NaIO_4$ as the oxidant; with 0.1 M HNO_3		44/---	
	Oxone as the oxidant.; with 0.1 M HNO_3		113/---	

[Fe(TAML)(OH_2)] (TAML = tetraamido macrocyclic ligand) ***(Homogeneous catalyst)***	$[NH_4]_2[Ce^{IV}(NO_3)_6]$ (CAN), as the oxidant; pH 1.0	GC	18/1.3 s^{-1}	W. C. Ellis, N. D. McDaniel, S. Bernhard and T. J. Collins, *J. Am. Chem. Soc.*, **2010**, *132*, 10990-10991.
[Fe(OTf)$_2$(Me$_2$Pytacn)], (OTf = $CF_3SO_3^-$; Me$_2$Pytacn = 1-(2-pyridylmethyl)-4,7-dimethyl-1,4,7-triazacyclononane)) ***(Homogeneous catalyst)***	$[NH_4]_2[Ce^{IV}(NO_3)_6]$ (CAN)	GC	82/---	J. L. Fillol, Z. Codola`, I. Garcia-Bosch, L. Go´mez, J. J. Pla and M. Costas, *Nat. Chem*., **2011**, 3, 807.
[Fe(OTf)$_2$(mcp)] ***(Homogeneous catalyst)***	$[NH_4]_2[Ce^{IV}(NO_3)_6]$ (CAN)	GC	360/---	J. L. Fillol, Z. Codola`, I. Garcia-Bosch, L. Go´mez, J. J. Pla and M. Costas, *Nat. Chem*., **2011**, 3, 807.
	$NaIO_4$		1050/---	
[(Fe(mcp))$_2$(μ-O)(μ-OH)](OTf)$_2$ ***(Homogeneous catalyst)***	$[NH_4]_2[Ce^{IV}(NO_3)_6]$ (CAN)	GC	210/---	J. L. Fillol, Z. Codola`, I. Garcia-Bosch, L. Go´mez, J. J. Pla and M. Costas, *Nat. Chem*., **2011**, 3, 807.
[Fe(OTf)$_2$(bpbp)], (bpbp= N,N′-bis(2-pyridylmethyl)-2,2′-bipyrrolidine)_ ***(Homogeneous catalyst)***	$NH_4]_2[Ce^{IV}(NO_3)_6]$ (CAN)	GC	63/---	J. L. Fillol, Z. Codola`, I. Garcia-Bosch, L. Go´mez, J. J. Pla and M. Costas, *Nat. Chem*., **2011**, 3, 807.
[Fe(OTf)$_2$(mep)], (mep= N,N′-dimethyl-N,N′-bis-(2-pyridylmethyl)-ethane-1,2-diamine) ***(Homogeneous catalyst)***	$NH_4]_2[Ce^{IV}(NO_3)_6]$ (CAN)	GC	145/---	J. L. Fillol, Z. Codola`, I. Garcia-Bosch, L. Go´mez, J. J. Pla and M. Costas, *Nat. Chem*., **2011**, 3, 807.
[Fe(OTf)$_2$(tpa)] (tpa=tris-(2-pyridylmethyl)amine) ***(Homogeneous catalyst)***	$NH_4]_2[Ce^{IV}(NO_3)_6]$ (CAN)	GC	40/---	J. L. Fillol, Z. Codola`, I. Garcia-Bosch, L. Go´mez, J. J. Pla and M. Costas, *Nat. Chem*., **2011**, 3, 807.
Fe(Me$_3$tacn)Cl$_3$ (Me$_3$tacn=1,4,7-trimethyltriazacyclononane)	$NH_4]_2[Ce^{IV}(NO_3)_6]$ (CAN) in aqueous CF_3SO_3H solution (pH = 1)	Clark-type oxygen electrode	1.6/---	B. Zhang, F. Li, F. Yu, H. Cui, X. Zhou, H. Li, Y. Wang and L. Sun, *Chem. Asian J.*, **2014**, *9*, 1515-1518.
[Fe(L-N$_4$Me$_2$)(CH_3CN)$_2$](OTf)$_2$ (LN$_4$Me$_2$=N,N'-dimethyl-2, 11-diaza[3.3](2,6)pyridinophane),			65/---	
Fe^{III} (dpaq)(H_2O)](ClO_4)$_2$ (dpaq= 2-[bis(pyridine-2-	electrocatalyst; in propylene carbonate with H_2O as a limiting chemical agent	Electrocatalysis		M. K. Coggins, M.-T. Zhang, A. K. Vannucci, C. J. Dares and T. J. Meyer,

ylmethyl]amino-N-quinolin-8-yl-acetamido,				J. Am. Chem.Soc., **2014**, *136*, 5531-5534.
Fe(BQEN)$(OTf)_2$ (BQEN= N,N'-dimethyl-N,N'-bis(8-qunolyl)-ethane-1,2-diamine	$NH_4]_2[Ce^{IV}(NO_3)_6]$ (CAN)	GC	80/---	D. Hong, S. Mandal, Y. Yamada, Y.-M. Lee, W. Nam, A. Llobet and S. Fukuzumi, *Inorg. Chem.*, **2013**, *52*, 9522-9531.
Fe(BQCN)$(OTf)_2$; (BQCN= N,N-dimethyl-N,N-bis(8-quinolyl)-cyclohexanediamine,			20/---	
$[Fe(L_1)]^{2+}$ {L_1 = N,N-dimethyl-N,N- bis(pyridazin-3-ylmethyl)ethane-1,2-diamine} ***(Homogeneous catalyst)***	$NH_4]_2[Ce^{IV}(NO_3)_6]$ (CAN); pH=0.7	Electrocatalysis	---/141h^{-1}	W. A. Hoffert, M. T. Mock, A. M. Appel and J. Y. Yang, *Eur. J. Inorg. Chem.*, **2013**, *2013*, 3846-3857.
	$NaIO_4$; pH=4.7		---/24h^{-1}	
$[Fe_{11}(H_2O)_{14}(OH)_2(W_3O_{10})_2(\alpha\text{-}SbW_9O_{33})_6]^{27-}$ ***(Homogeneous catalyst)***	$[Ru(bpy)_3Cl_2]$=1.0 mm, $[Na_2S_2O_8]$=5 mm in 80 mm borate buffer (pH 10.0), λ>420 nm.	GC	1815/6.3s^{-1}	*Chem. Commun.*, **2015**, 51, 13925-13928

4. The turnover numbers and turnover frequencies:

Table S2:

S. No.	Catalyst I taken (mg)	Catalyst (nmoles)	Oxygen evolved (nmoles/ml)	Total Oxygen evolved for 2 ml	TON (moles of O_2/moles of catalyst)	Time taken for complete saturation (min)	TOF (TON / time) min^{-1}
1.	0.24	12.86	90	180	13.990	5	2.79
2.	0.58	31.10	125	250	8.038	5.5	1.46
3.	0.8	42.89	150	300	6.994	2.91	2.40
4.	1.0	53.62	164	328	6.117	1.8	3.39
5.	1.2	64.34	178	356	5.533	1.58	3.50

5. SEM images before and after catalysis:

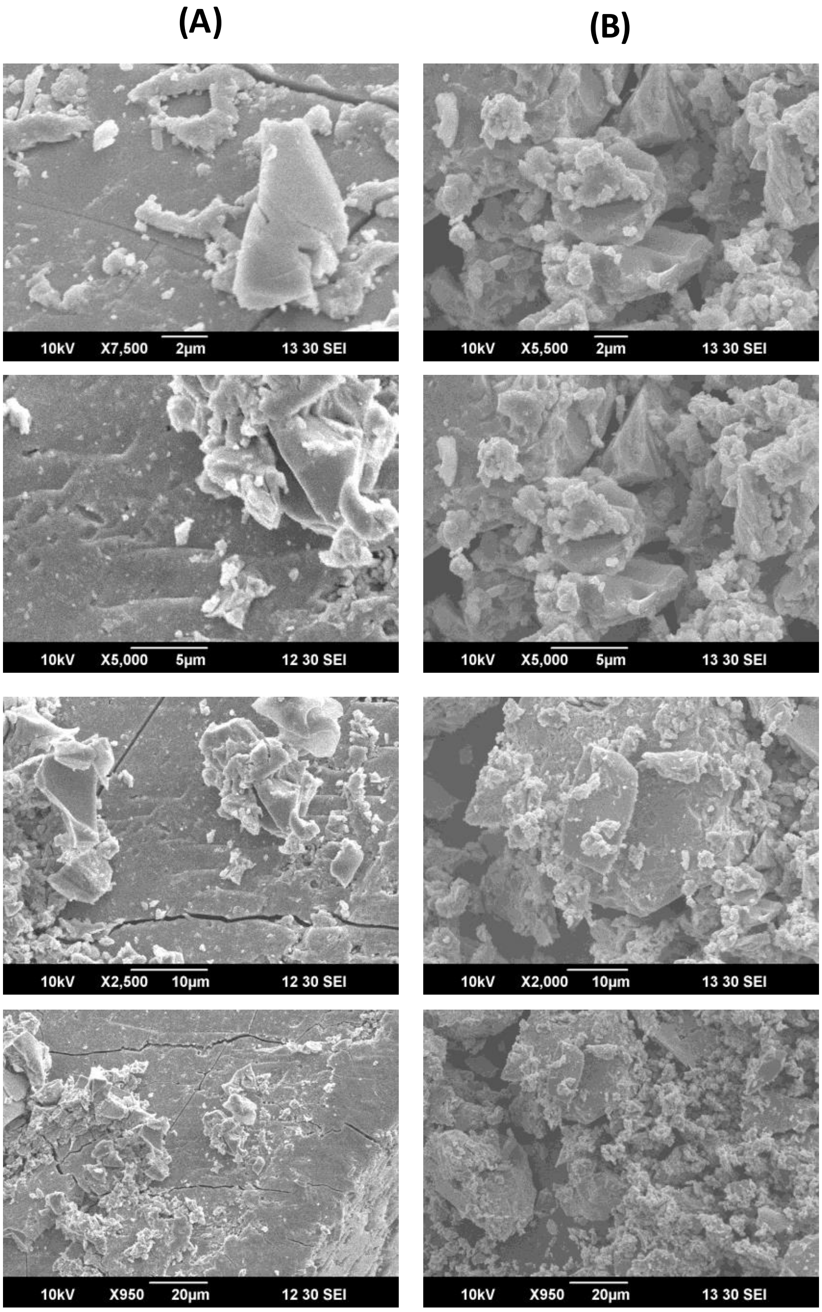

Figure S2: SEM images of the catalyst **I** at different resolution before catalysis **(A)** and after one catalytic cycle **(B)**.