Electronic Supplementary Information (ESI)

Three Metal Complexes Derived from 3-Methyl-1-*H*-Pyrazole-4-Carboxylic Acid: Synthesis, Crystal Structures, Luminescence and Electrocatalytic Properties

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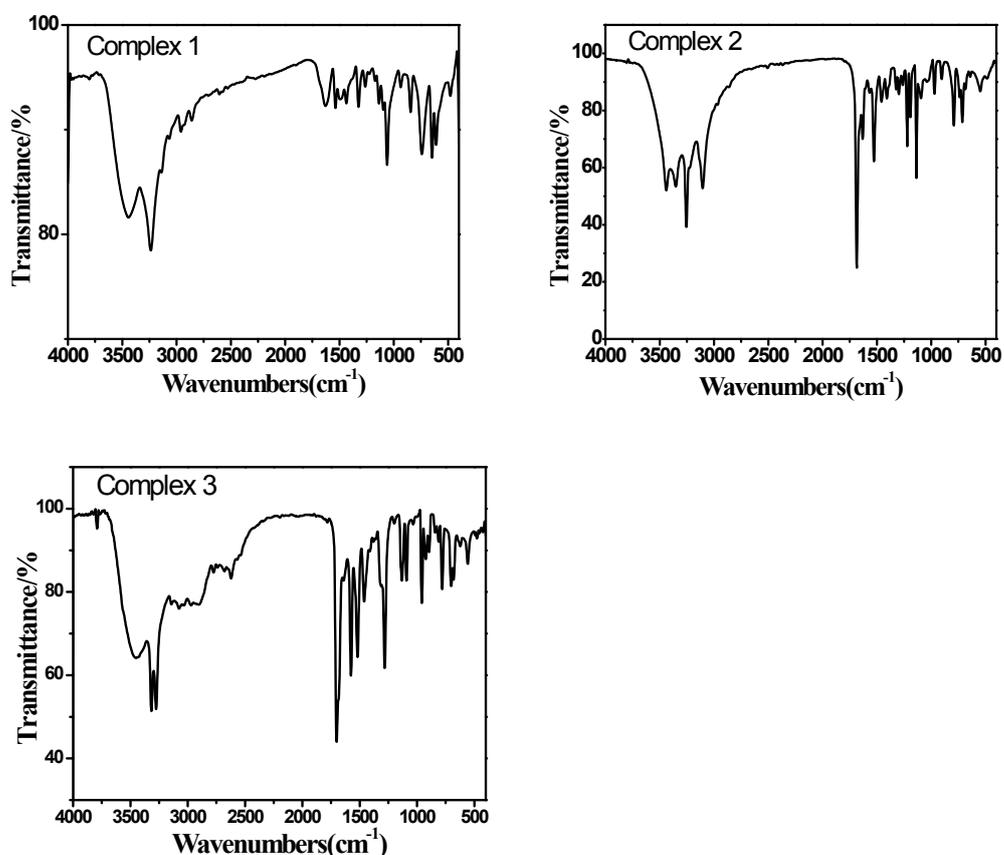
Fig. S1: The IR spectra of complexes 1-3

Crystallographic data:

The crystallographic data for the complexes **1-3** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internet) þ 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk. The CCDC numbers of complexes **1-3** are 977149, 1003672, 1003671 respectively.

Table S1. Selected bond lengths (Å) and angles (°) of complex **1, 2** and **3**.

Complex 1			
Cd1—O3	2.320 (4)	Cd1—N1^i	2.298 (4)
Cd1—O3^i	2.320 (4)	Cd1—O4	2.297 (4)
Cd1—N1	2.298 (4)	Cd1—O4^i	2.297 (4)
O3—Cd1—O3^i	180.0	O4^i—Cd1—N1^i	89.43 (16)
N1^i—Cd1—O3^i	90.00 (14)	O4—Cd1—N1	89.43 (16)
N1—Cd1—O3^i	90.00 (14)	O4^i—Cd1—N1	90.57 (16)
N1^i—Cd1—O3	90.00 (14)	O4^i—Cd1—O4	180.0
N1—Cd1—O3	90.00 (14)	O4—Cd1—O3	85.0 (2)
N1—Cd1—N1^i	180.0	O4^i—Cd1—O3	95.0 (2)
Symmetry code: (i) −x, −y, −z.			
Complex 2			
Co1—O3	2.089 (4)	Co1—O4	2.096 (4)
Co1—O3^i	2.089 (4)	Co1—N1^i	2.126 (5)
Co1—O4^i	2.096 (4)	Co1—N1	2.126 (5)
O3—Co1—O3^i	180.00 (1)	O4^i—Co1—N1^i	89.37 (18)
O3—Co1—O4^i	93.70 (18)	O4—Co1—N1^i	90.63 (18)
O3^i—Co1—O4^i	86.30 (18)	O4^i—Co1—N1	90.63 (18)
O3—Co1—O4	86.30 (18)	O4—Co1—N1	89.37 (18)
O3^i—Co1—O4	93.70 (18)	N1^i—Co1—N1	180.00(1)
O3^i—Co1—N1	90.23 (18)	O3—Co1—N1^i	90.23 (18)
O4^i—Co1—O4	180.00 (1)	O3—Co1—N1	89.77 (18)
Symmetry code: (i) −x+1, −y+1, −z+2.			
Complex 3			
Cd1—Cl3	2.653 (2)	Cd1—N3	2.286 (6)
Cd1—O1	2.346 (5)	Cd2—N1^v	2.280 (5)

Cd1—O2	2.418 (5)	Cd2—Cl3^{ii}	2.5920 (18)
Cd1—O4^{i}	2.221 (5)	Cd2—O3^{i}	2.455 (5)
Cd1—O5	2.372 (7)		
O1—Cd1—Cl3	88.91 (14)	O3^{i}—Cd2—Cl3^{ii}	93.93 (14)
O1—Cd1—O2	54.91 (17)	O3^{iii}—Cd2—O3^{i}	180.0
O1—Cd1—O5	89.1 (2)	N1^{v}—Cd2—Cl3^{ii}	87.66 (16)
O2—Cd1—Cl3	86.99 (14)	N1^{iv}—Cd2—Cl3^{ii}	92.34 (16)
O4^{i}—Cd1—Cl3	93.44 (16)	N1^{iv}—Cd2—Cl3	87.66 (16)
O4^{i}—Cd1—O1	150.2 (2)	N1^{iv}—Cd2—O3^{iii}	86.53 (19)
O4^{i}—Cd1—O2	95.5 (2)	N1^{v}—Cd2—O3^{iii}	93.47 (19)
O4^{i}—Cd1—O5	81.5 (2)	N1^{iv}—Cd2—O3^{i}	93.47 (19)
O4^{i}—Cd1—N3	121.1 (2)	N1^{v}—Cd2—O3^{i}	86.53 (19)
O5—Cd1—Cl3	166.1 (2)	N1^{iv}—Cd2—N1^{v}	180.0
O5—Cd1—O2	80.6 (2)	Cd2—Cl3—Cd1	97.98 (6)
N3—Cd1—Cl3	103.41 (16)	N3—Cd1—O1	87.05 (19)
N3—Cd1—O2	140.69 (19)	N3—Cd1—O5	90.3 (2)
Cl3—Cd2—Cl3^{ii}	180.00 (7)	O3^{iii}—Cd2—Cl3	93.93 (14)
O3^{i}—Cd2—Cl3	86.07 (14)	O3^{iii}—Cd2—Cl3^{ii}	86.07 (14)

Symmetry code: (i) −x+3/2, y+1/2, −z+3/2; (ii) −x+1, −y+1, −z+1; (iii) x−1/2, −y+1/2, z−1/2; (iv) x+1/2, −y+1/2, z−1/2; (v) −x+1/2, y+1/2, −z+3/2;

Table S2. Selected hydrogen bond distances (Å) and angles (°) in the complex **1, 2** and **3.**

D-H--A	D-H	H---A	D---A	D-H--A
Complex 1				
N(2)-H(2)---O(2)^{i}	0.86	1.96	2.785(6)	162.0
O(3)-H(3A)---O(1) ^{ii}	0.85(9)	1.95(10)	2.746(6)	156.0(9)
O(3)-H(3B)---O(1) ^{iii}	0.86(5)	1.90(5)	2.724(6)	161.0(7)
O(4)-H(4D)---O(2) ^{iii}	0.89	2.19	2.992(8)	150.0
O(4)-H(4E)---O(1)^{iv}	0.89	1.85	2.701(7)	160.0

Symmetry code: (i) -1+ x, y, z; (ii) -1+x, y, -1+z; (iii) 1-x, −y, − z; (iv) -1+x, −1+y, −1+ z;

D-H--A	D-H	H---A	D---A	D-H--A
Complex 2				
O(1)-H(1W)---Cl(1) ^{i}	0.90	2.17	2.975(4)	149.0
N(2)-H(2A)---Cl(1) ^{ii}	0.86	2.37	3.206(5)	165.0
O(3)-H(3A)---Cl(1) ^{iii}	1.07	1.99	3.058(5)	173.0
O(3)-H(3B)---Cl(1) ^{ii}	0.97	2.69	3.634(5)	165.0
C(3)-H(3)---O(2) ^{iv}	0.93	2.46	3.331(9)	157.0

Symmetry code: (i) 1+ *x*, *y*, 1+ *z*; (ii) 1+*x*, *y*, *z*; (iii) 1-*x*, −*y*, 1− *z*; (iv) 1−*x*, −*y*, 2− *z*;

Complex 3				
N(2)-H(2)---Cl(3) [i]	0.87	2.50	3.257(6)	145.0
O(5)-H(5A)---O(2) [ii]	0.89	2.08	2.789(8)	136.0
O(5)-H(5B)---O(6) [iii]	0.88	2.45	2.797(14)	104.0
O(6)-H(6A)---O(1) [i]	0. 85	1.98	2.829(14)	172.0
O(6)-H(6B)---O(5) [iv]	0.85	2.46	2.797(14)	105.0
C(5)-H(5C)---O(6)	0.96	2.39	3.199(14)	141.0

Symmetry code: (i) −1/2+ *x*, 1/2−*y*, 1/2+ *z*; (ii) 2−*x*, −*y*, 1−*z*; (iii) 1+*x*, *y*, *z*; (iv) −1+*x*, *y*, *z*;
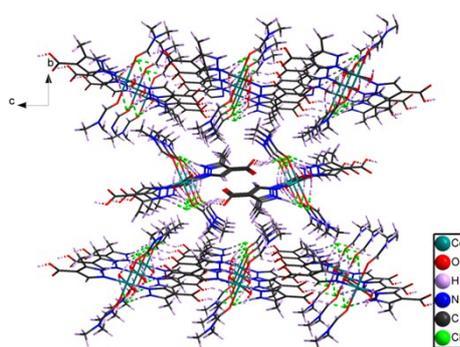
Fig. S2. 3D grids of complex **2**. (Dashed lines represent hydrogen bonds)
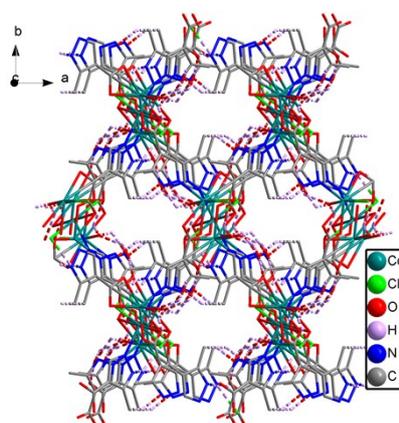
**Fig. S3.** 3D grids of complex **3**. (Dashed lines represent hydrogen bonds)
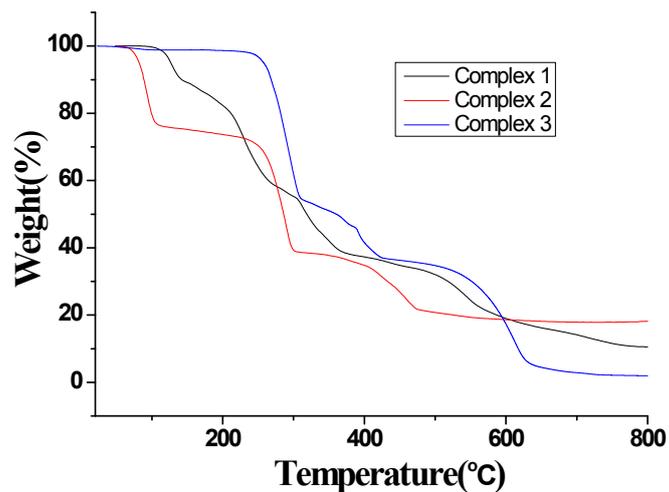
Fig. S4. TG curves of complexes **1**-**3**
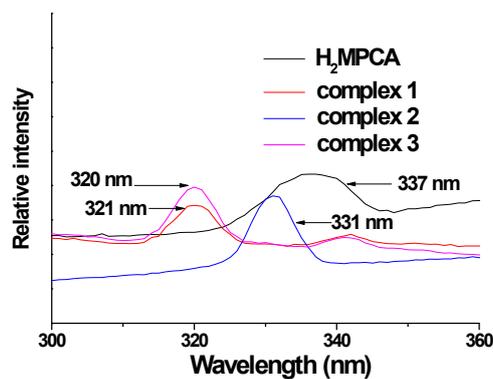
Fig. S5. The excitation spectra of H$_2$MPCA, complex **1, 2** and **3** in the solid state at room temperature
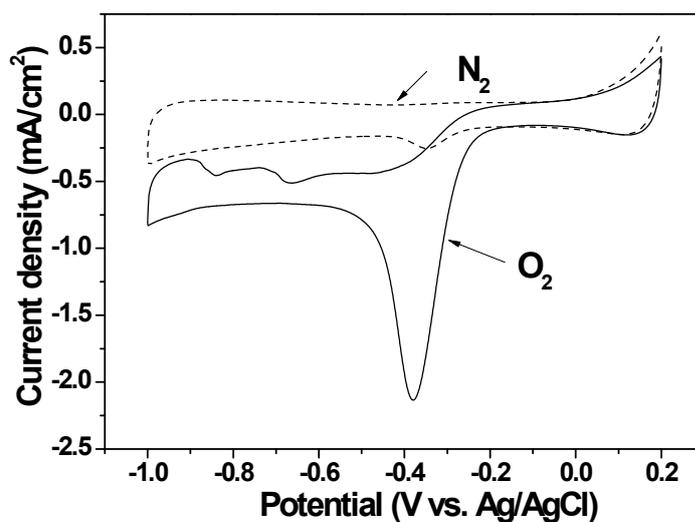

Fig. S6. CVs in N$_2$-saturated (dotted curve) and O$_2$-saturated (solid curve) 0.1M KOH. Scan rate, 50 mV s^{-1}.

The electrode transfer number for ORR using complex 2 as electrocatalyst

Often, the electrode transfer number was obtained using the Koutecky-Levich (K-L) equation, the process is as follows:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} + \frac{1}{j_f} \tag{1}$$

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} \tag{2}$$

$$j_d = 0.62nFD^{2/3}C_0v^{-1/6}\omega^{1/2} \tag{3}$$

$$j_k = nFkC_0 \tag{4}$$

j was current density, j_k and j_d were dynamic current density and limiting diffusion current density, respectively, j_f was diffusion current density through Nafion, n was the electrode transfer number of every O_2, k was rate constant of ORR, F was Faraday constant (96485 C/mol), ω was the angular velocity of rotating disk electrode ($\omega = 2\pi N$, N was rotate speed), C_0 was the concentration of O_2 in the electrolyte, (0.1 M KOH, 1.2×10^{-3} mol/L), D was diffusion coefficient of O_2 in the electrolyte, (0.1 M KOH, 1.9×10^{-5} cm/s), v was viscous drag coefficient in the electrolyte (0.1 M KOH, 0.1 m^2/s)。

The impedance could be ignored owing to the thickness of Nafion membrane in adhesive electrode was too small. So the equation (1) was approximately equal to equation (2).

In alkaline electrolyte, there are two electron transfer way for ORR:

(i) Direct 4 electron transfer process:

$$O_2 + H_2O + 4e^- \rightarrow 4OH^-$$
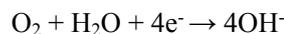
(ii) Indirect 2 electron transfer process:

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad or \quad 2HO_2^- \rightarrow 2OH^- + O_2$$
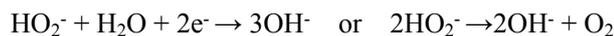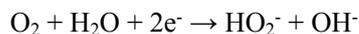
Through calculation, the average electron transfer was 3.37 in the ORR with complex **2** as electrocatalyst.

The current density was normalized to the geometrical surface area and the measured

potentials *vs*.Ag/AgCl were converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.205$)
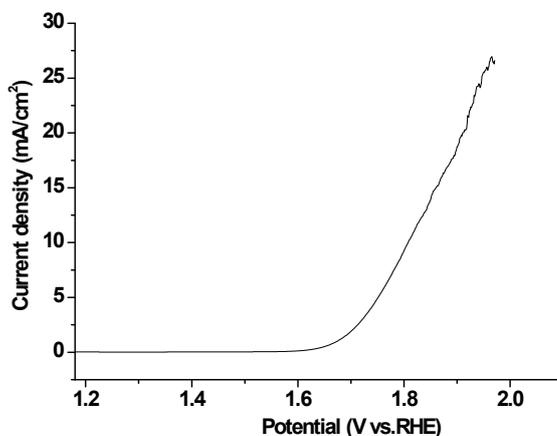

Fig. S7. OER polarization curve for complex **2**

For rotating ring-disk electrode (RRDE) measurements, a rotating ring disk electrode with a glassy carbon disk (5 mm in diameter) was used (Pine Instruments, model: AFMSRCE). The ring potential was constantly set at 0.5 V vs Ag/AgCl. The electron transfer number (*n*) and the percentage of H_2O_2 produced during the catalyzed ORR can be determined by the following equations:

$$n = 4 \frac{I_d}{I_d + I_r/N} \qquad (1)$$

$$mol\%H_2O_2 = 100(\frac{I_r}{I_d/N}) \qquad (2)$$

where I_d was the disk current, I_r was the ring current, and N was the collection efficiency of the ring electrode that was determined to be 0.4 of our electrode.
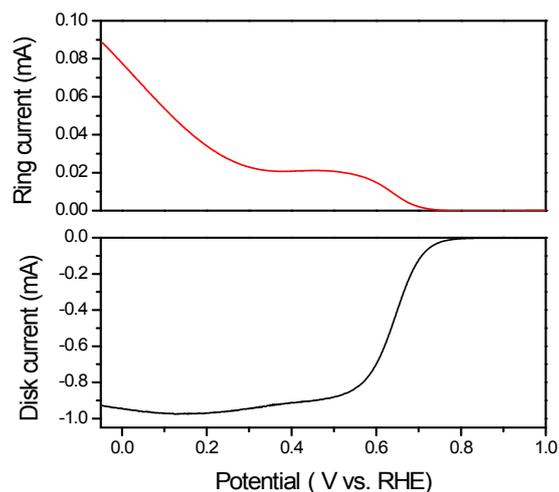
Fig. S8. Rotating ring-disk electrode (RRDE) curves of complex **2** in O_2-saturated 0.1MKOH. All the scanning rates were 50 mV/s.


$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$$
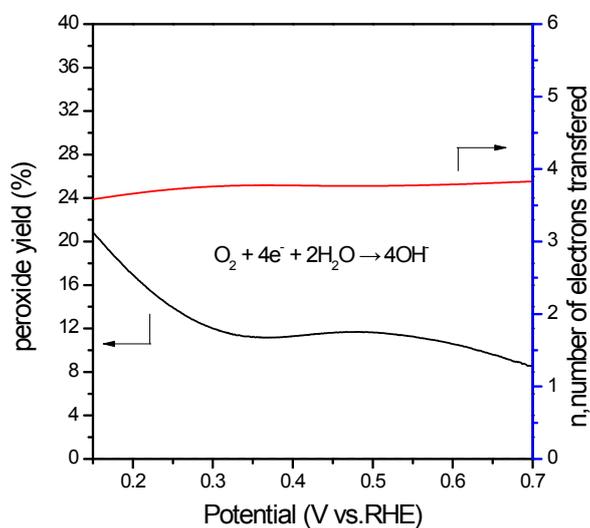
Fig. S9. Electron transfer numbers for the ORR catalyzed complex **2** and the corresponding % H_2O_2 produced. Data obtained using rotating ring -disk electrode.

Table S3. Comparison of the OER activity for several active catalysts supported on different substrates

catalyst	Overpotential @ 10 mA cm^{-2} (mV)	Catalyst loading (mg cm^{-2})	Electrolyte	Substrate	Ref.
Complex **2**	578	0.24	0.1M KOH	Glassy carbon	This work
meso-Co$_3$O$_4$	426	0.1	0.1M KOH	Glassy carbon	[S1]
Co$_3$O$_4$C-NA	290	~0.2	0.1M KOH	Cu foil	[S2]
Co$_3$O$_4$/N-doped graphene	310	1.0	1M KOH	Ni foam	[S3]
N-doped graphene-CoO	340	0.7	1M KOH	Glassy carbon	[S4]
IrO$_2$/C	370	0.2	0.1M KOH	Glassy carbon	[S5]
CoO/CNT	550	0.05	1M KOH	ITO	[S6]
Mesoporous Co$_3$O$_4$	525	0.13	0.1M KOH	gold disk	[S7]
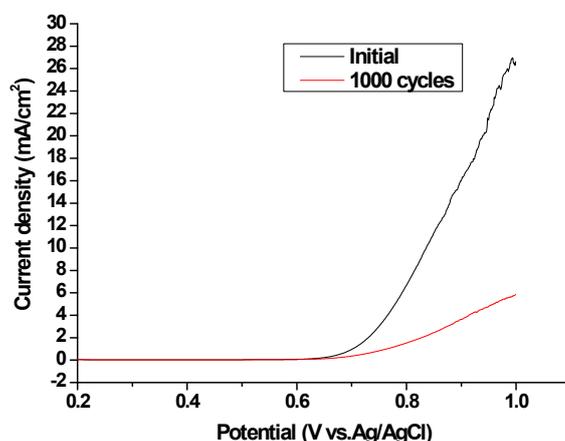
Fig. S10. OER stability test of complex **2** catalyst dispersed on glassy carbon electrode in 0.1M KOH electrolyte. Cycles were swept between 0.2 V and 1.0 V at 5 mV/s.

References for Table S1

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