Multicomponent Self-Assembly of a Pentanuclear Ir-Zn Heterometal-Organic Polyhedron for Carbon Dioxide Fixation and Sulfite Sequestration

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1. Materials and Methods

Unless stated otherwise, all chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Acetonitrile (CH$_3$CN; Aldrich, 99.9+% ) were distilled over CaH$_2$ prior to use. $^{13}$CO$_2$, 99%, (1% $^{18}$O) was purchased from Beijing Gaisi Chemical Gases Center. All reactions were carried out under a nitrogen atmosphere, unless stated otherwise. The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. $^1$H NMR and $^{13}$C NMR spectra were measured on a Varian INOVA 400 M and 100 M spectrometer. ESI mass spectra were carried out on a HPLC-Q-Tof MS spectrometer using methanol as mobile phase. Uv-vis spectra were measured on a HP 8453 spectrometer. The solution fluorescent spectra were measured on JASCO FP-6500. Abbreviations: ppy = 2-(4-Nitrophenyl)pyridine; nm = nanometres; min = minute(s); h = hour(s); rt = room temperature (20 °C).
2. Syntheses and Characterizations

2.1 Synthesis of fac-Ir-NH₂

Ligand fac-Ir-NH₂ was synthesized according to the reported procedure with modifications to improve both yields and purities. All synthetic procedures involving IrCl₃·xH₂O and other Ir(III) species were performed under an inert N₂ atmosphere and dark environment.

![Scheme S1. Synthesis of fac-Ir-NH₂.](image)

**Synthesis of [Ir(ppy)₂(μ-Cl)]₂ (M-1)**

IrCl₃·xH₂O (0.6 g, 2 mmol) was refluxed with 2.5 equiv of cyclometalating ligand L₁ (1.0 g, 5 mmol) in a 3:1 mixture of 2-methoxyethanol and water, and the reaction mixture was stirred for 24 h at 120 °C. The reaction mixture was filtered, washed with water and ethanol. The red solids were collected and dried under vacuum to give the product M-1 (0.96 g, yield 77%). ¹H NMR (CD₂Cl₂-d₂, ppm): δ 9.23 (d, J = 4.6 Hz, 1H, HA), 8.14 (d, J = 7.1 Hz, 1H, HG), 8.05 (m, 1H, HE), 7.73 (d, J = 8.6 Hz, 1H, HF), 7.68 (m, 1H, HB), 7.09 (m, 1H, HC), 6.59 (d, J = 2.2 Hz, 1H, HD).

**Synthesis of [Ir(ppy)₂(NCCH₃)₂]OTf (M-2)**

Compound M-1 (0.25 g, 0.2 mmol) in 75 mL of dry acetonitrile was heated to dissolve all of the chloro-bridged dimer. A 50 mL acetonitrile solution of AgOTf (0.1 g, 0.41 mmol) was added to the solution. The mixture was kept at 60°C in the dark for 2 h resulted in a gray precipitate. The gray AgCl precipitate was filtered over a Celite pad resulted a yellow solution. The solution was concentrated in vacuo, then redissolved in a minimal amount of acetonitrile and precipitating with diethyl ether. The yellow crystal precipitate were collected and dried under vacuum to give the product M-2 (0.3 g, yield 91%). ¹H NMR (CD₃CN-d₃, ppm): δ 9.20 (d, J = 8.0 Hz, 1H, HA), 8.29 (d, J = 8.0 Hz, 1H, H₃), 8.05 (m, 1H, H₆), 7.73 (d, J = 8.6 Hz, 1H, H₇), 7.68 (m, 1H, H₈), 6.75 (d, J = 4.0 Hz, 1H, H₉), 1.96 (s, 3H, H₅).
Synthesis of *fac*-Ir-NO₂

Compound M-2 (0.25 g, 0.3 mmol) and L₁ (0.066 g, 0.33 mmol) were combined in 15 mL of o-dichlorobenzene and heated at 120 °C under N₂ atmosphere for 100 h. After cooling to room temperature, the reaction solution was chromatographed on a silica gel column packed with petroleum ether to first elute o-dichlorobenzene. Switching to 1 : 1 dichloromethane / petroleum ether eluted the product, as a bright red band in 40% yield. 

\[ ^1H \text{NMR (CDCl}_3, \text{ppm): } \delta 8.05 (d, J = 8.0 \text{ Hz}, 1H, H_A), 7.80 (m, 3H, H_{B,C,D}), 7.58 (d, J = 8.0 \text{ Hz}, 1H, H_E), 7.44 (s, 1H, H_G), 7.07 (m, 1H, H_F). \]

ESI-MS \[ [M^+ = 790.2701, (M+Na)^+ = 813.2615]. \]

Synthesis of *fac*-Ir-NH₂

The catalyst Pd/C(10%) and hydrazine hydrate (80%, 15 equiv) were used for reduction *fac*-Ir-NO₂ to *fac*-Ir-NH₂, and dichloromethane was chosen as the solvent (~100% yield). 

\[ ^1H \text{NMR (CDCl}_3, \text{ppm): } \delta 7.65 (d, J = 8.0 \text{ Hz}, 1H, H_A), 7.37-7.45 (m, 3H, H_{C,D,E}), 6.67 (m, 1H, H_B), 6.28 (s, 1H, H_G), 6.23 (d, J = 8.0 \text{ Hz}, 1H, H_F), 4.12 (m, 2H, H_H). \]

ESI-MS \( (M^+ = 700.1412). \)

2.2. Synthesis of compound Ir-Zn₁

To a Schlenk tube was added *fac*-Ir-NH₂ (35 mg, 0.05 mmol, 2 equiv.), 2-formylpyridine (15 μL, 0.15 mmol, 6 equiv.), Zn(BF₄)₂·6H₂O (25 mg, 0.075 mmol, 3 equiv.) in acetonitrile (40 mL). The solution was refluxed for 24 h under the protection of N₂. Then the solution was placed in a sealed tank full of N₂ and diffused with diethyl ether then the dark wine crystals was obtained (yield 90%, based on the crystal dried vaccum). 

\[ ^1H \text{NMR (C}_2\text{D}_2\text{Cl}_4-d_2, \text{ppm): } \delta 7.54 (m, 1H, H_E), 8.59 (m, 1H, H_C), 8.34 (d, J = 8.0 \text{ Hz}, 1H, H_A), 7.77 (t, 1H, J = 8.0 \text{ Hz}, H_B), 7.58 (m, 1H, H_D), 7.53-7.45 (m, 3H, H_{1,3,4}), 7.17-7.01 (m, 3H, H_{2,5,7}), 6.8 (m, 1H, H_G). \]

ESI-MS \( m/z = 541.5710 \) [Zn₃(Ir-PY)₂·OH·F⁺], 751.1100 [Zn₃(Ir-PY)₂·OH·F·BF₄⁻]³⁻ and 1170.1512 [Zn₃(Ir-PY)₂·OH·F·2BF₄⁻]⁵⁻. Anal. Calc. for \[ [Zn₃(C_{51}H_{36}N₈Ir)₂(OH)(F)(H₂O)](BF₄)₅·H₂O: \] H, 3.04; C, 48.05; N, 9.89. Found: H, 2.95; C, 48.08; N, 10.06.
2.3. Synthesis of compound Ir-Zn2

This complex was synthesized following the same procedure as described for compound Ir-Zn1, the solution was exposed on air over one week or placed in a sealed tank full of CO2 and then diffused with diethyl ether, the dark wine crystals were obtained (yield 92%, based on the crystal dried vacuum). 1H NMR (C2D2Cl4-d2, ppm): δ 9.39 (m, 1H, H1), 8.48 (m, 1H, H2), 8.26 (d, J = 8.0 Hz, 1H, H3), 7.90 (m, 1H, H4), 7.69 (m, 1H, H5), 7.51-7.46 (m, 3H, H6, H7, H8), 7.16-7.04 (m, 3H, H9, H10), 6.81-6.69 (m, 1H, H11). ESI-MS: [Zn3(Ir-PY)2·CO3]2- 547.6038, [Zn3(Ir-PY)2·CO3·BF4]- 759.1555, [Zn3(Ir-PY)2·CO3·2BF4]- 1182.2535. Anal. Calc. for [Zn3(C51H36N9Ir)2·CO3](BF4)4·(H2O): H, 2.92; C, 48.41; N, 9.87. Found: H, 2.99; C, 47.83; N, 9.73.

2.4. Synthesis of compound Ir-Zn2’

Control experiments using a labeled 13CO2 source to synthesise compound Ir-Zn2’. An amount of Cage 1 (30 mg, 0.01 mmol) was dissolved in CH3CN (100 mL) under N2 in a septum-sealed Schlenk flask, and excess 13CO2 was injected by gas-tight syringe. Then the mixed solution was placed in a sealed tank full of 13CO2 and crystals of compound Ir-Zn2’ were obtained over one week (yield 86%, based on the crystal dried vacuum). ESI-MS: [Zn3(Ir–PY)2·13CO3]2- 547.8039, [Zn3(Ir–PY)2·13CO3·BF4]- 759.4199, [Zn3(Ir–PY)2·13CO3·2BF4]- 1182.5814.

2.5. Synthesis of compound Ir-Zn3

To a Schlenk tube was added fac-Ir-NH2 (35 mg, 0.05 mmol, 2 equiv.), 2-formylpyridine (15 μL, 0.15 mmol, 6 equiv.), Zn(BF4)2·6H2O (25 mg, 0.075 mmol, 3 equiv.) in acetonitrile (40 mL). The solution was refluxed for 24 h under the protection of N2. A 6% solution of sulphur dioxide in water (266 μL, 0.25 mmol, 10 eq.) was added dropwise to the solution of Ir-Zn1 with 0.25 mmol triethylamine. The mixture was stirred at room temperature overnight. Then the solution was diffused with diethyl ether then the wine red crystals was obtained (yield 91%, based on the crystal dried vacuum). 1H NMR (C2D2Cl4-d2, ppm): δ 9.41 (d, J = 8.0 Hz, 1H), 8.57 (dd, J = 12.0, 8.0 Hz, 1H), 8.39 (dd, J = 12.0, 8.0 Hz, 1H), 7.86 (m, 1H), 7.65 (m, 1H), 7.36 (m, 1H), 7.18 (m, 1H), 6.69 (m, 1H). ESI-MS: [Zn3(Ir–PY)2·SO3]2+ 552.5938, [Zn3(Ir–PY)2·SO3·2BF4]- 765.7897, [Zn3(Ir–PY)2·SO3·2BF4]- 1192.1641. Anal. Calc. for [Zn3(C51H36N9Ir)2·SO3](BF4)4·(H2O): H, 2.95; C, 47.23; N, 9.72. Found: H, 2.87; C, 47.68; N, 9.79.
2.6 ESI-MS spectra of the compound Ir-Zn1.

![ESI-MS spectra of the compound Ir-Zn1.](image)

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<td>6</td>
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**Figure S1**  ESI-MS spectra of compound Ir-Zn1 in acetonitrile
2.7 ESI-MS spectra of the compound Ir-Zn2.

![ESI-MS spectra](image)

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**Figure S2** ESI-MS spectra of compound Ir-Zn2 in acetonitrile
2.8 $^{13}$C NMR spectra of the compound Ir-Zn1 and Ir-Zn2.

Figure S3 $^{13}$C NMR of compound Ir-Zn2 (red) and compound Ir-Zn1 (black), showing the presence of a peak at 164.0 ppm for CO$_3^{2-}$. (Solvent C$_2$D$_2$Cl$_4$ signals were marked using *).

2.9 $^{13}$C NMR spectra of the compound Ir-Zn2'.

Figure S4 $^{13}$C NMR of compound Ir-Zn2', showing the presence of a peak at 164.0 ppm for $^{13}$CO$_3^{2-}$. (Solvent C$_2$D$_2$Cl$_4$ signals were marked using *).
2.10 ESI-MS spectra of the compound Ir-Zn2'.

![ESI-MS spectra of compound Ir-Zn2']

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**Figure S5** ESI-MS spectra of compound **Ir-Zn2’** in acetonitrile.
Figure S6 The simulation results obtained on the basis of natural isotopic abundance for [Zn$_3$(Ir–PY)$_2$\(\supset\)CO$_3$\(^{2-}\)\cdot 2BF$_4$]\(^{2+}\) and [Zn$_3$(Ir–PY)$_2$\(\supset\)^{13}CO$_3$\(^{2-}\)\cdot 2BF$_4$]\(^{2+}\), respectively.
2.11 ESI-MS spectra of the compound Ir-Zn3

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**Figure S7** ESI-MS spectra of compound **Ir-Zn3** in acetonitrile.

3.1 Crystallography

Intensities of the crystal data were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo-Kα (\(\lambda = 0.71073\) Å) using the SMART and SAINT programs. The structures were solved by direct methods and refined on \(F^2\) by full-matrix least-squares methods with SHELXTL version 5.1. Crystallographic data have been deposited with the CCDC number being 1001631, 1001629 and 1442696.

For the crystal data of compound Ir-Zn1, six carbon atoms in one of the imine-pyridine moiety on the ligand backbone were disordered into two parts with the site occupancy factors (s.o.f.) of each parts being fixed as 0.5, respectively. The coordinated fluoride atom on one zinc center was disordered into two parts with the s.o.f. of each part being fixed as 0.67 and 0.33, respectively. Totally seven fluoride atoms in two BF\(_4^−\) anions were disordered into two parts with the s.o.f. of each parts being refined with free variables. Except the disordered parts and the partly occupied solvent molecules, the other non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones and the solvent acetonitrile molecules were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. The distances of the B-F bond in each anion were restrained to be same. Thermal parameters on adjacent atoms of the disordered carbon atoms and the disordered BF\(_4^−\) groups were restrained to be similar. CCDC 1001631.

For the crystal data of compound Ir-Zn2, the non-hydrogen atoms in the backbone of the cage complex were refined anisotropically. Hydrogen atoms within the ligand backbones and the solvent molecules were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. The three oxygen atoms of the carbonate ion were disordered into two parts with the s.o.f. of each parts being refined with free variables. Three of the four fluoride atoms in one BF\(_4^−\) anions were disordered into two parts with the s.o.f. of each parts being fixed as 0.5, respectively. Thermal parameters on adjacent atoms of the disordered BF\(_4^−\) groups were restrained to be similar. CCDC 1001629.

For the crystal data of compound Ir-Zn3, except the partly occupied solvent molecules, the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones and the solvent molecules were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. The SO\(_3^2−\) ion was disordered into two parts with the s.o.f. of each part being fixed as 0.5. Some distances of the solvent molecules were restrained as ideal geometry. Thermal parameters on adjacent atoms of the solvent molecules were restrained to be similar. CCDC 1442696.
<table>
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<th>Ir-Zn1</th>
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<th>Ir-Zn3</th>
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<td><strong>Formula</strong></td>
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$R_1 = \sum |F_o| - |F_c| / \sum |F_o| \cdot wR_2 = \left[ \frac{\sum w(F_o^2 - F_c^2)}{\sum(F_o)^2} \right]^{1/2}$
Figure S8  Coordination geometry of the Zn(1) atom in Ir-Zn1. Selected bond distances (Å) and angles (°): Zn(1)−N(12) 2.174(3), Zn(1)−N(13) 2.037(3), Zn(1)−N(22) 2.169(3), Zn(1)−N(23) 2.057(3), Zn(1)−O(1) 1.863(4); O(1)−Zn(1)−N(13) 126.40(15), O(1)−Zn(1)−N(23) 122.42(15), O(1)−Zn(1)−N(22) 88.72(18), O(1)−Zn(1)−N(12) 93.16(18), N(13)−Zn(1)−N(23) 111.16(14), N(13)−Zn(1)−N(22) 100.20(13), N(13)−Zn(1)−N(12) 78.72(13), N(23)−Zn(1)−N(22) 79.39(12), N(23)−Zn(1)−N(12) 99.56(12), N(22)−Zn(1)−N(12) 178.12(12).
Figure S9  Coordination geometry of the Zn(2) atom in Ir-Zn1. Selected bond distances (Å) and angles (°):
Zn(2)–N(15) 2.159(3), Zn(2)–N(16) 2.039(3), Zn(2)–N(25) 2.133(3), Zn(2)–N(26) 2.039(4), Zn(2)–O(2) 1.921(5);
O(2)–Zn(2)–N(16) 124.07(18), O(2)–Zn(2)–N(26) 124.33(17), O(2)–Zn(2)–N(25) 89.46(16), O(2)–Zn(2)–N(15)
90.07(16), N(26)–Zn(2)–N(16) 111.56(14), N(26)–Zn(2)–N(25) 79.96(14), N(26)–Zn(2)–N(15) 98.44(13),
N(16)–Zn(2)–N(25) 102.91(12), N(16)–Zn(2)–N(15) 79.24(12), N(25)–Zn(2)–N(15) 177.66(12).

Figure S10  Coordination geometry of the Zn(3) atom in Ir-Zn1. Selected bond distances (Å) and angles (°):
Zn(3)–N(18) 2.133(3), Zn(3)–N(19) 2.032(4), Zn(3)–N(28) 2.153(3), Zn(3)–N(29) 2.030(4), Zn(3)–F(1) 1.888(6),
Zn(3)–F(1’) 1.882(14); F(1)–Zn(3)–N(19) 122.3(2), F(1)–Zn(3)–N(29) 124.6(2), F(1)–Zn(3)–N(18) 88.0(2),
F(1)–Zn3–N(28) 91.9(2), F(1’)–Zn(3)–F(1) 39.9(4), F(1’)–Zn(3)–N(19) 158.8(3), F(1’)–Zn(3)–N(29) 86.2(4),
F(1’)–Zn(3)–N(18) 105.7(4), F(1’)–Zn(3)–N(28) 73.9(4), N(19)–Zn(3)–N(29) 113.06(16), N(19)–Zn(3)–N(18)
80.86(14), N(19)–Zn(3)–N(28) 99.67(14), N(29)–Zn(3)–N(18) 99.11(13), N(29)–Zn(3)–N(28) 80.48(13),
N(18)–Zn(3)–N(28) 179.42(14).
Figure S11  Coordination geometry of the Zn(1) atom in \textit{Ir-Zn2}. Selected bond distances (Å) and angles (°): 
Zn(1)--N(12) 2.197(6), Zn(1)--N(13) 2.069(6), Zn(1)--N(22) 2.186(6), Zn(1)--N(23) 2.082(6), Zn(1)--O(1) 1.952(8), 
Zn(1)--O(1') 1.931(16); O(1)--Zn(1)--N(13) 111.2(3), O(1)--Zn(1)--N(23) 140.7(3), O(1)--Zn(1)--N(22) 107.8(3), 
O(1)--Zn(1)--N(12) 81.7(3), N(13)--Zn(1)--N(12) 77.7(2), N(13)--Zn(1)--N(22) 97.0(2), N(13)--Zn(1)--N(23) 106.3(2), 
N(23)--Zn(1)--N(22) 78.2(2), N(23)--Zn(1)--N(12) 95.5(2), N(22)--Zn(1)--N(12) 170.4(2), O(1')--Zn(1)--O(1) 40.9(5), 
O(1')--Zn(1)--N(13) 144.6(4), O(1')--Zn(1)--N(23) 107.1(5), O(1')--Zn(1)--N(22) 79.0(5), O(1')--Zn(1)--N(12) 110.0(4).
Figure S12  Coordination geometry of the Zn(2) atom in Ir-Zn2. Selected bond distances (Å) and angles (°):
Zn(2)−N(15) 2.176(6), Zn(2)−N(16) 2.075(6), Zn(2)−N(25) 2.140(6), Zn(2)−N(26) 2.077(7), Zn(2)−O(2) 1.951(9),
Zn(2)−O(2') 1.966(17); O(2)−Zn(2)−N(16) 110.7(3), O(2)−Zn(2)−N(26) 139.1(3), O(2)−Zn(2)−N(25) 108.4(3),
O(2)−Zn(2)−N(15) 79.6(3), N(26)−Zn(2)−N(16) 107.7(3), N(26)−Zn(2)−N(25) 78.7(3), N(26)−Zn(2)−N(15) 94.8(2),
N(16)−Zn(2)−N(25) 98.6(2), N(16)−Zn(2)−N(15) 78.7(2), N(25)−Zn(2)−N(15) 172.0(2), O(2')−Zn(2)−O(2) 42.2(5),
O(2')−Zn(2)−N(16) 144.0(5), O(2')−Zn(2)−N(26) 106.3(5), O(2')−Zn(2)−N(25) 76.7(5), O(2')−Zn(2)−N(15) 110.0(5).

Figure S13  Coordination geometry of the Zn(3) atom in Ir-Zn2. Selected bond distances (Å) and angles (°):
Zn(3)−N(18) 2.194(7), Zn(3)−N(19) 2.072(7), Zn(3)−N(28) 2.168(6), Zn(3)−N(29) 2.099(6), Zn(3)−O(3) 1.985(9),
Zn(3)−O(3') 1.996(17), O(3)−Zn(3)−N(19) 109.7(3), O(3)−Zn(3)−N(29) 140.5(3), O(3)−Zn(3)−N(18) 79.4(3),
O(3)−Zn(3)−N(28) 110.6(3), N(19)−Zn(3)−N(29) 106.8(3), N(19)−Zn(3)−N(18) 78.3(3), N(19)−Zn(3)−N(28) 97.3(3), N(29)−Zn(3)−N(18) 93.9(3), N(29)−Zn(3)−N(28) 78.7(2), N(18)−Zn(3)−N(28) 170.0(2), O(3')−Zn(3)−O(3) 43.4(5),
O(3')−Zn(3)−N(19) 143.7(5), O(3')−Zn(3)−N(29) 107.4(4), O(3')−Zn(3)−N(18) 110.8(5),
O(3')−Zn(3)−N(28) 78.1(5).
Figure S14  Coordination geometry of the Zn(1) atom in Ir-Zn3. Selected bond distances (Å) and angles (°): Zn(1)-O(1) 1.930(9), Zn(1)-N(19) 2.061(6), Zn(1)-N(28) 2.074(5), Zn(1)-N(27) 2.180(5), Zn(1)-N(18) 2.189(5); O(1)-Zn(1)-N(19) 145.8(3), O(1)-Zn(1)-N(28) 105.5(3), N(19)-Zn(1)-N(28) 107.6(2), N(19)-Zn(1)-N(27) 97.41(19), N(28)-Zn(1)-N(27) 78.94(17), O(1)-Zn(1)-N(18) 106.5(3), (19)-Zn(1)-N(18) 79.1(2), N(28)-Zn(1)-N(18) 95.00(18), N(27)-Zn(1)-N(18) 171.87(19).
Figure S15  Coordination geometry of the Zn(2) atom in Ir-Zn3. Selected bond distances (Å) and angles (°): Zn(2)-O(2) 1.905(8), Zn(2)-N(13) 2.049(4), Zn(2)-N(22) 2.055(6), Zn(2)-N(21) 2.173(4), Zn(2)-N(12) 2.177(4); O(2)-Zn(2)-N(13) 145.9(3), O(2)-Zn(2)-N(22) 104.5(3), N(13)-Zn(2)-N(22) 108.6(2), O(2)-Zn(2)-N(21) 79.5(2), N(13)-Zn(2)-N(21) 98.87(17), N(22)-Zn(2)-N(21) 78.89(19), O(2)-Zn(2)-N(12) 105.2(2), N(13)-Zn(2)-N(12) 79.41(16), N(22)-Zn(2)-N(12) 96.22(19), N(21)-Zn(2)-N(12) 174.1(2).

Figure S16  Coordination geometry of the Zn(3) atom in Ir-Zn3. Selected bond distances (Å) and angles (°): Zn(3)-O(3) 1.859(8), Zn(3)-N(16) 2.055(5), Zn(3)-N(25) 2.064(4), Zn(3)-N(15) 2.187(5), Zn(3)-N(24) 2.192(5); O(3)-Zn(3)-N(16) 144.8(3), O(3)-Zn(3)-N(25) 104.7(3), N(16)-Zn(3)-N(25) 109.01(19), O(3)-Zn(3)-N(15) 107.6(3), N(16)-Zn(3)-N(15) 78.24(19), N(25)-Zn(3)-N(15) 7.25(19), O(3)-Zn(3)-N(24) 78.7(3), N(16)-Zn(3)-N(24) 98.2(2), N(25)-Zn(3)-N(24) 78.29(19), N(15)-Zn(3)-N(24) 173.17(18).
**Figure S17** Coordination geometry of the SO$_3^{2-}$ in Ir-Zn$_3$. Selected bond distances (Å) and angles (°): S(1)-O(1) 1.427(8), S(1)-O(2) 1.449(9), S(1)-O(3) 1.491(9), S(1')-O(1') 1.384(19), S(1')-O(3') 1.416(16), S(1')-O(2') 1.642(16); O(1)-S(1)-O(2) 114.0(5), O(1)-S(1)-O(3) 116.7(5), O(2)-S(1)-O(3) 114.7(5), S(1)-O(1)-Zn(1) 127.8(6), S(1)-O(2)-Zn(2) 126.4(5), S(1)-O(3)-Zn(3) 128.3(5), O(1')-S(1')-O(3') 117.3(12), O(1')-S(1')-O(2') 101.6(10), O(3')-S(1')-O(2') 101.6(9), S(1')-O(1')-Zn(1) 130.1(8), S(1')-O(2')-Zn(2) 126.4(8), S(1')-O(3')-Zn(3) 117.7(8).
4. Luminescence Spectra of the Compounds and the Tracing of the Transformation

4.1 Luminescence spectra of Ir-Zn1 and Ir-Zn2 (1.0×10⁻⁵ M in deaerated acetonitrile solution, excited at 360nm).

**Figure S18**  Luminescence spectra of Ir-Zn1 and Ir-Zn2
4.2  Luminescence spectra change upon the bubbling of CO2 (under a deoxident sieve sorbent) into the Ir-Zn1 solution (1.0x10^{-5} M acetonitrile solution, luminescence spectra were recorded at time intervals of 2 min, excited at 360 nm).

![Figure S19](image1.png)

**Figure S19**  Time-dependent luminescence spectra of Ir-Zn1 (10 µM) in a CH3CN solution after the bubbling of CO2.

![Figure S20](image2.png)

**Figure S20**  Time-dependent luminescence intensity tracing at 508 nm of Ir-Zn1 (10 µM) in a CH3CN solution after the bubbling of CO2.
4.3 Rate Constant Calculation.

Generally, for the formation of Host-Guest complexation species formed by the cage compound host (H) and the guest (G), the original concentration of the cage being fixed at \( C_0 \), and we assume \( xC_0 \) to the concentration of complexes species Host-Guest (H-G),

\[
\begin{align*}
H + G & \rightleftharpoons H - G \\
\text{t = 0 min, cage only} & C_0 \\
\text{when G was added, t = t min,} & (1-x)C_0 \quad xC_0
\end{align*}
\]

The measurements are performed under the conditions where the luminescence intensity of the free host (H) in such a concentration is \( F_0 \). After addition of a given amount of G, the luminescence intensity \( F \) of the system is close to (in the dilute solution):

\[
F = F_0(1-x) + xF_T \quad (1)
\]

Where \( F_T \) is the luminescence of the saturated value in the presence of excess guest.

It is easy to derive the usual equation:

\[
\frac{(F_0-F)}{(F_0-F_T)} = x \quad (2)
\]

The first-order dynamics equation:

\[
\ln(1-x) = -kt + N \quad (3)
\]

From eqs (2) and (3), we can obtain the equation:

\[
\ln\left[\frac{(F-F_T)}{(F_0-F_T)}\right] = -kt + N \quad (4)
\]

\( k \) can be obtained by a linear analysis of \( X \) t versus \( Y \) ln \([F-F_T]/(F_0-F_T)\].

\[Y = -0.6279 - 0.09216X\]
\[R = -0.99513\]

**Figure S21** First-order dynamics fitting of luminescence tracing of Ir-Zn1 upon the bubbling of CO2. The rate constant calculated \( k = 0.092 \text{ min}^{-1} \).
5. References

