Electronic Supplementary Information

for

A Triangular Prismatic Hexanuclear Iridium(III) Complex Bridged by Flavin Analogues Showing Reversible Redox Processes

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Table S1. X-ray crystallographic data for **1**•PF_6.

formula	$C_{90}H_{99}Cl_6F_{18}Ir_6N_{12}O_9P_3$
fw	3293.78
crystal system	trigonal
space group	*R*3*c*
T (K)	123
a (Å)	16.0783(6)
c (Å)	74.528(6)
V (Å^3)	16685.1(15)
Z	6
no. of reflections measured	31593
no. of observations	2214
no. of parameters refined	211
$R1^a$	0.0965
$R_W{}^b$	0.2415 ($I > 2.0\sigma(I))^c$
GOF	1.092
CCDC no.	888985

[a] $R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|$. [b] $Rw = [\Sigma (w (F_0{}^2 - F_c{}^2)^2) / \Sigma w(F_0{}^2)^2]^{1/2}$. [c] $w = 1 / [\sigma^2(F_0{}^2) + (0.1361P)^2 + 1691.4005P]$, where $P = (\mathrm{Max}(F_0{}^2, 0) + 2F_c{}^2) / 3$

Table S2. Selected bond lengths (Å) and angles (deg) of **1**

Ir1 – O1	2.14(4)	N1 – Ir1 – O1	72.5(11)
Ir1 – N1	2.17(3)	N1 –Ir1 – N3	87.1(14)
Ir2 – N2	1.98(3)	O1– Ir1 – N3	82.7(13)
Ir2 – O2	2.22(4)	Ir1 – O1 – C12	119 (3)
Ir2 – O3	2.13(4)	Ir1 – N1 – C11	111.7(17)
Ir1 – N3	2.16(2)	Ir1 – N3 – C13	118.1(18)
O1 – C12	1.23(4)	Ir1 – N3 – C14	121 (2)
N1 – C11	1.35(4)	O1 – C12 – C11	116 (3)
N1 – C20	1.35(4)	N1 – C11 – C12	116(2)
N2 – C12	1.39(5)	N2 – Ir2 – O2	60.6(12)
N2 – C13	1.39(4)	N2 – Ir2 – O3	91.0(13)
O2 – C13	1.10(5)	Ir2 – N2 – C13	92.3(19)
N3 – C13	1.39(5)	Ir2 – O2 – C13	89(3)
N3 – C14	1.39(5)	O2 – C13 – N2	118(3)
N4 – C14	1.35(4)	O2 – C13 – N3	122(3)
N4 – C15	1.35(4)		
C11 – C12	1.39(5)		

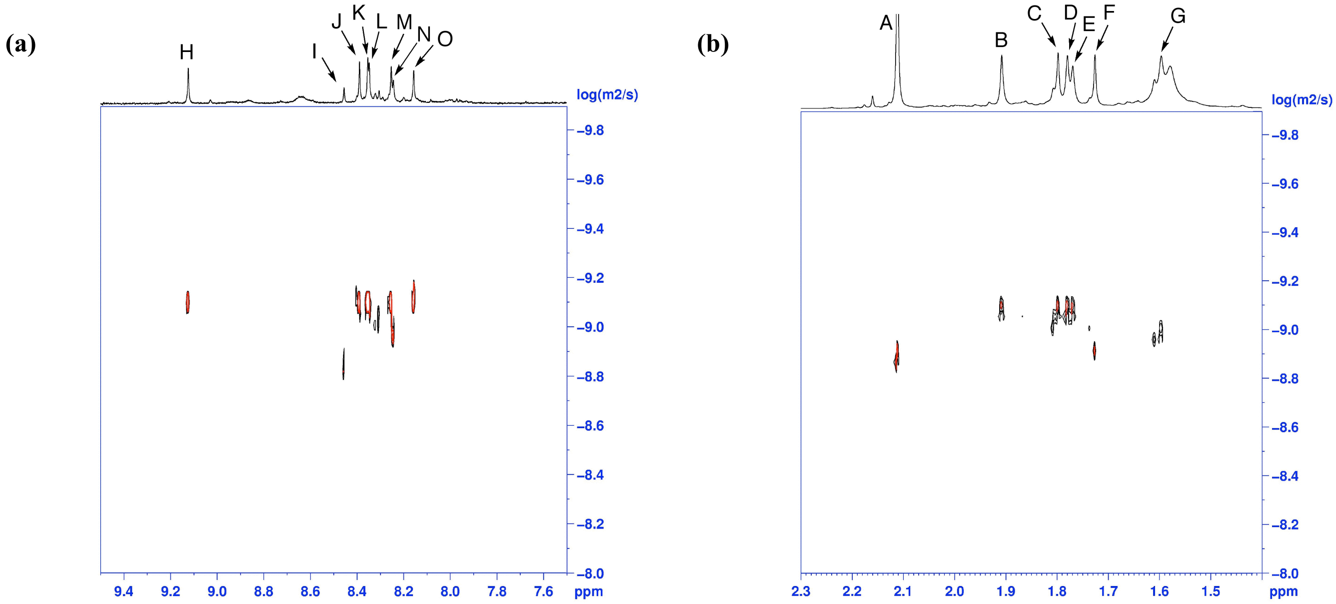

Fig. S1 DOSY spectra of **1** (2.8 mM) at room temperature in CD_2Cl_2 after 48 h since making sample: (a) Low magnetic field; (b) high magnetic field.

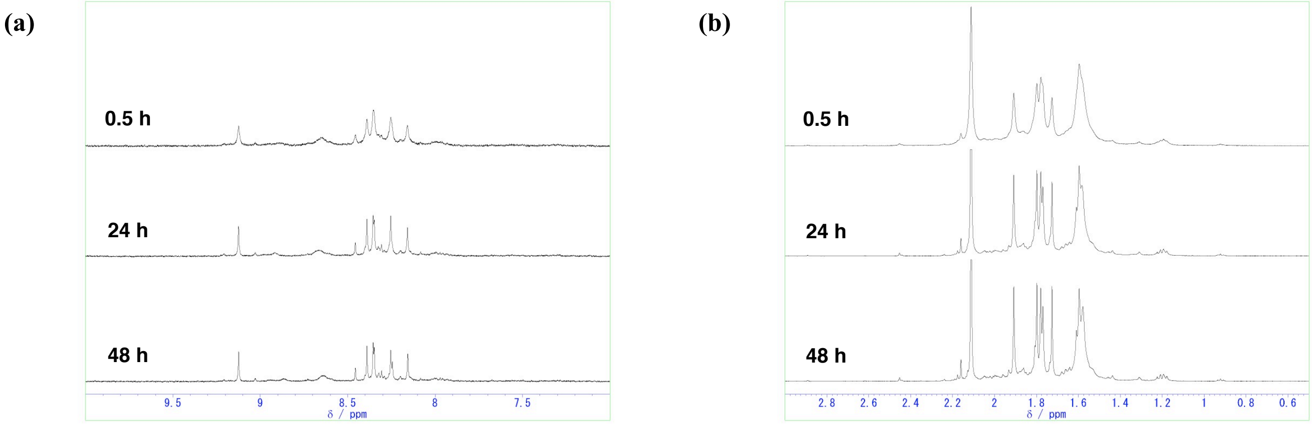

Fig. S2 ^{1}H NMR spectra of **1** (2.8 mM) at room temperature in CD_2Cl_2 after 0.5 h, 24 h and 48 h: (a) Low magnetic field; (b) high magnetic field.

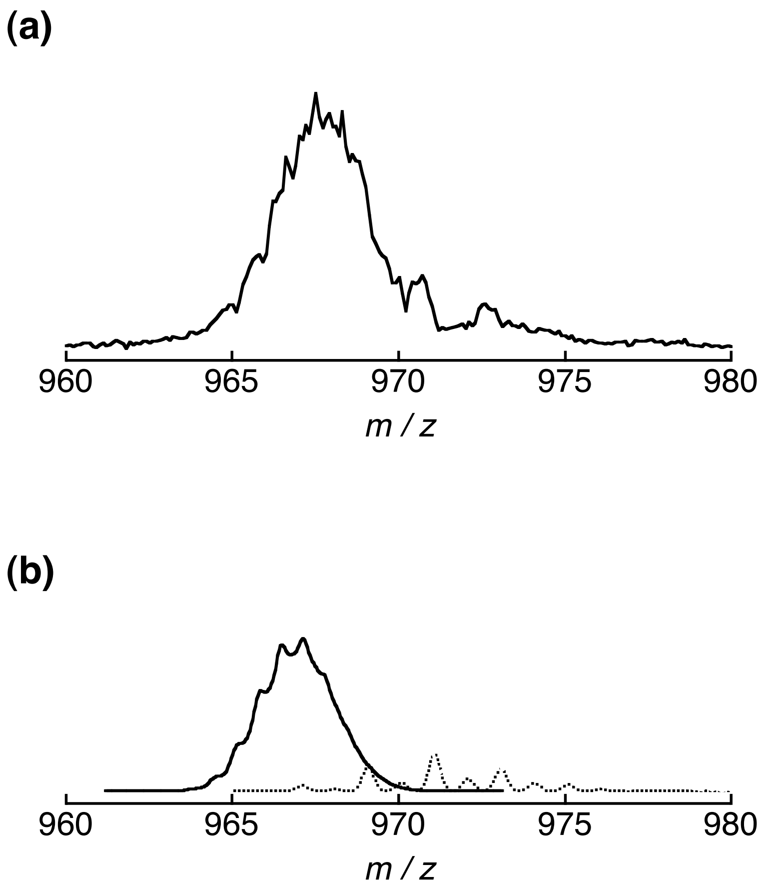

Fig. S3 (a) ESI-MS spectrum of **1** in CH_3OH at room temperature. (b) Calculated mass number of $[\{Ir(Cp^*)\}_6(alloCl_2)_3(CH_3O)_3]^{3+}$ (black line) and $[\{Ir(Cp^*)\}_2(alloCl_2)Cl]^{+}$ (dotted line).

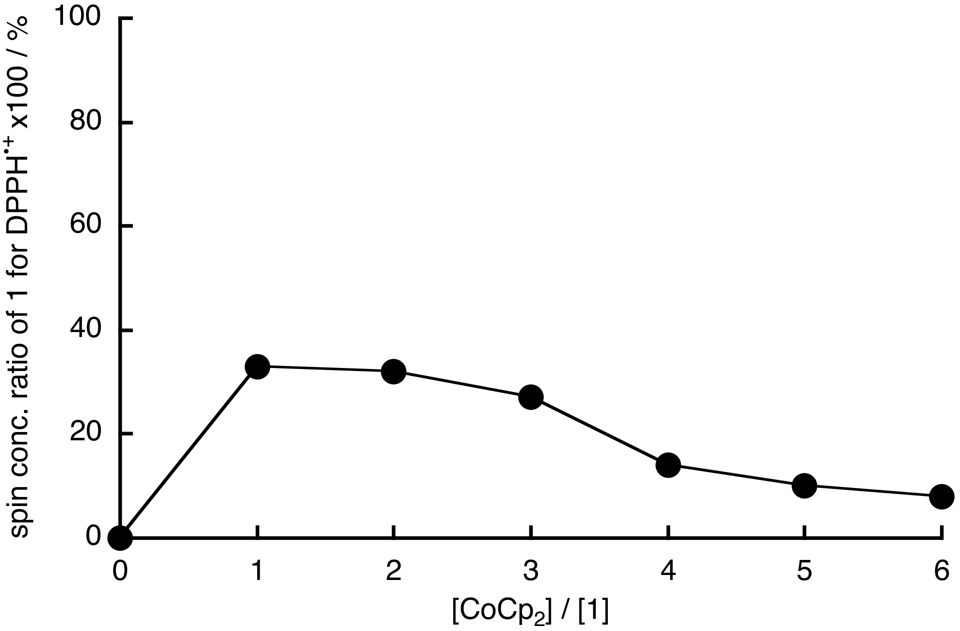

Fig. S4 Change of spin concentration of reduced species of **1** relative to the ratio of [CoCp$_2$]/[**1**]. The spin concentration was represented by the percentage of double integration of the signals due to the reduced species of **1** relative to that of the same concentration of DPPH (2,2-diphenyl-1-picrylhydrazyl).

References

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