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Supplementary Material

Controlling emission energy in metal–organic frameworks featuring cyclometalated iridium(III) linkers

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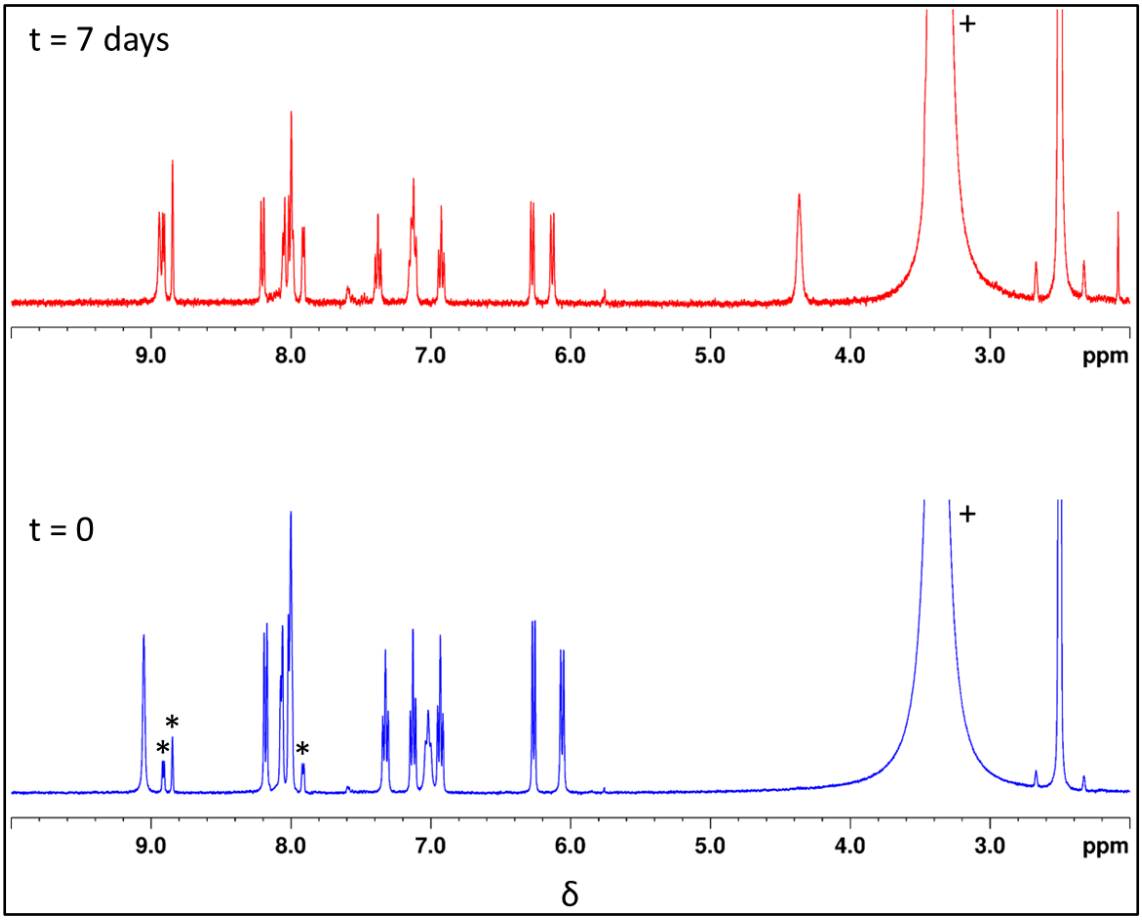

Figure S1. Partial ^{1}H NMR spectra (400 MHz, d_6-DMSO, 298 °K) of [Ir(bt)$_2$(Hdcbpy)] immediately after preparation (blue) and measured again after seven days (red). Asterisks (*) denote free H_2dcbpy ligand, plus symbols (+) denote residual water.

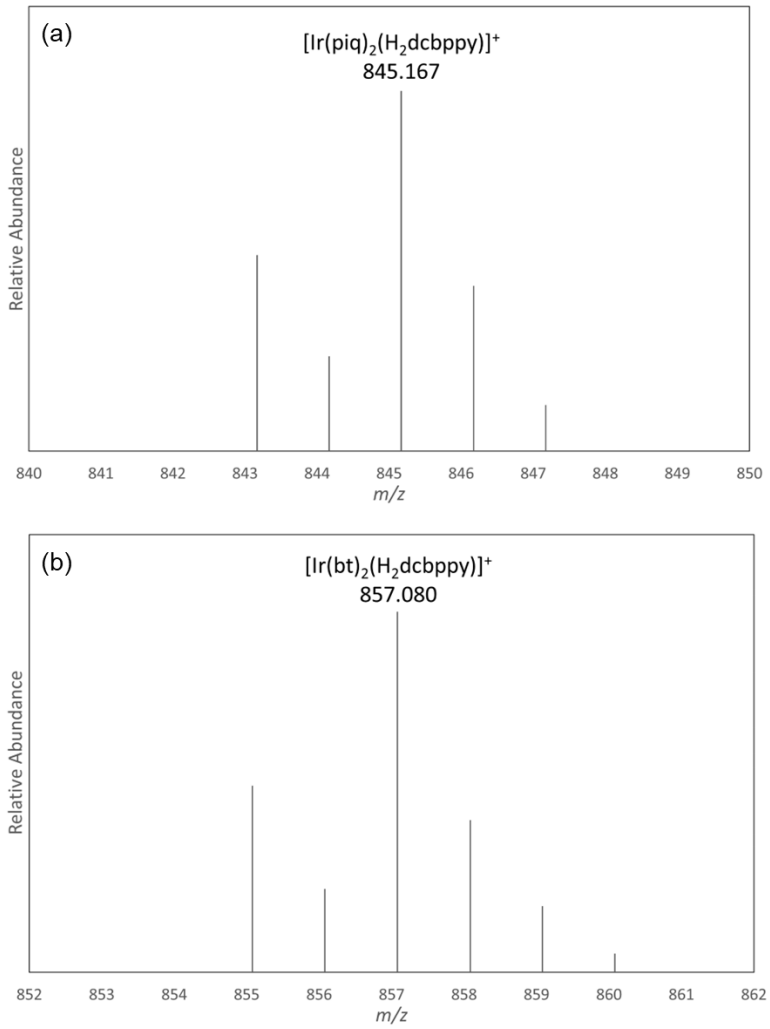

Figure S2. Mass spectra (positive ion) of (a) $[Ir(piq)_2(H_2dcbpy)]^+$ and (b) $[Ir(bt)_2(H_2dcbpy)]^+$.

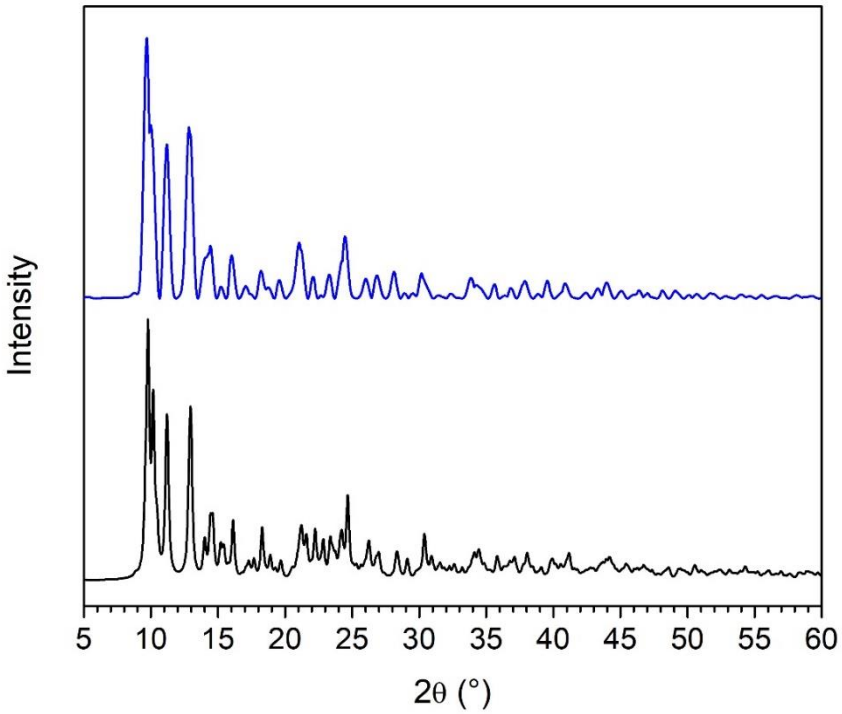

Figure S3. Powder X-ray Diffraction (PXRD) of {Ca[(Ir(ppy)$_2$(dcbpy)]$_2$ (DMF)$_2$}·2H$_2$O (**1**) (blue) between 2 and 60° 2θ *v*. the calculated pattern (black).

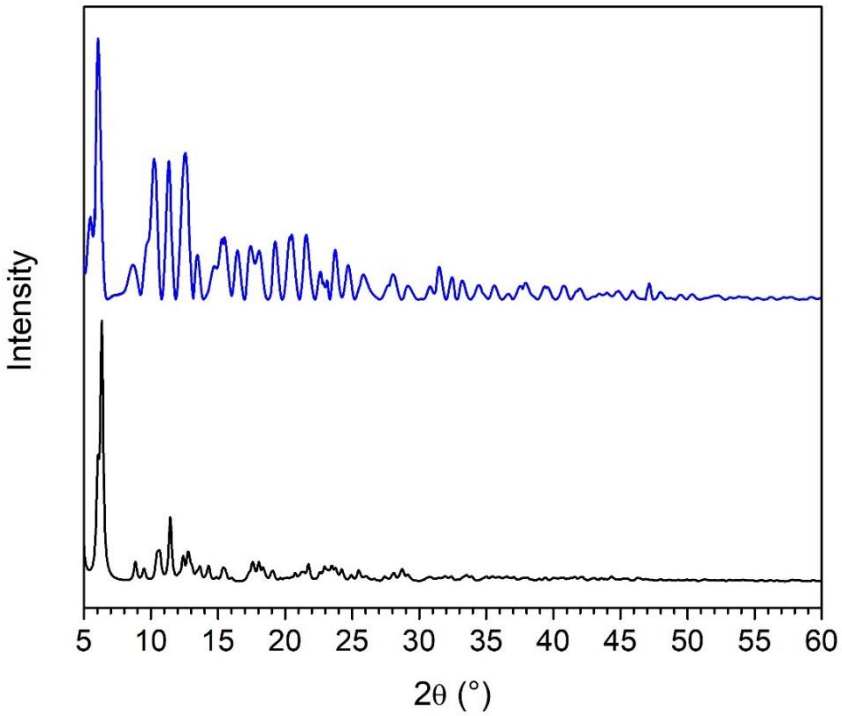

Figure S4. PXRD of {Ca[(Ir(piq)$_2$(dcbpy)]$_2$ (DMF)$_2$}·2H$_2$O (**2**) (blue) between 5 and 60° 2θ *v*. the calculated pattern (black).

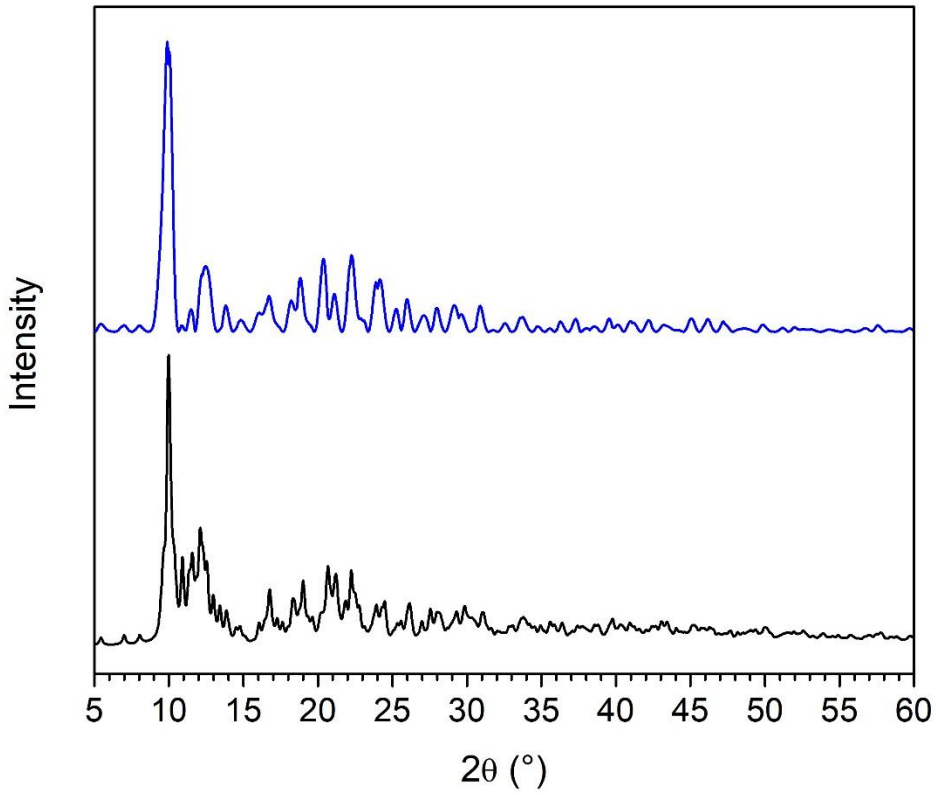

Figure S5. PXRD of {Ca[Ir(bt)$_2$(dcbpy)]$_2$(dcbpy)(H$_2$O)$_2$]}·2DMF (**3**) (blue) between 5 and 60° 2θ *v.* the calculated pattern (black).

Table S1. Crystallographic parameters for compounds **1-3** in this study.

Compound	**{Ca[(Ir(ppy)$_2$(dcbpy)]$_2$ (DMF)$_2$}·2H$_2$O (1)**	**{Ca[(Ir(piq)$_2$(dcbpy)]$_2$ (DMF)$_2$}·2H$_2$O (2)**	**{Ca[Ir(bt)$_2$(dcbpy)]$_2$ (dcbpy)(H$_2$O)$_2$]} ·2DMF (3)**
Formula	$C_{74}H_{62}CaIr_2N_{10}O_{12}$	$C_{90}H_{68}CaIr_2N_{10}O_{12}$	$C_{91}H_{61}Ca_2Ir_2N_{11}O_{15}S_4$
Formula Weight	1707.81	1906.02	2141.30
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space Group	$P2_1/c$	P-1	P-1
a (Å)	8.8330(18)	8.8580(18)	9.6380(19)
b (Å)	36.811(7)	16.029(3)	18.941(4)
c (Å)	10.533(2)	19.758(4)	22.687(5)
α (°)	90	106.75(3)	75.51(3)
β (°)	100.29(3)	96.19(3)	88.64(3)
γ (°)	90	105.00(3)	88.30(3)
Cell Volume (Å^3)	3369.8(12)	2543.8(10)	4007.5(15)
Z	2	1	2
ρ_{calc} (g cm^{-3})	1.683	1.244	1.775
μ (mm^{-1})	4.093	2.719	3.628
F(000)	1692.0	948.0	2124.0
Crystal size (mm^3)	0.1 × 0.08 × 0.05	0.1 × 0.03 × 0.02	0.1 × 0.05 × 0.05
Radiation	Synchrotron (λ = 0.71073)	Synchrotron (λ = 0.71073)	Synchrotron (λ = 0.71073)
Reflections collected	59450	44897	72417
Independent reflections	9892 [R_{int} = 0.0253, R_{sigma} = 0.0138]	12997 [R_{int} = 0.0583, R_{sigma} = 0.0562]	20723 [R_{int} = 0.0215, R_{sigma} = 0.0196]
Data/restraints/ parameters	9892/0/453	12997/0/525	20723/0/1130
GooF	1.074	1.053	1.079
R_1, wR_2 ($I > 2\sigma(I)$)	R_1 = 0.0463, wR_2 = 0.1285	R_1 = 0.0478, wR_2 = 0.1381	R_1 = 0.0326, wR_2 = 0.0917
R_1, wR_2 (all)	R_1 = 0.0476, wR_2 = 0.1303	R_1 = 0.0523, wR_2 = 0.1424	R_1 = 0.0336, wR_2 = 0.0927
Largest diff. peak/hole (eÅ^{-3})	1.66/−3.98	2.84/−1.61	2.68/−2.93

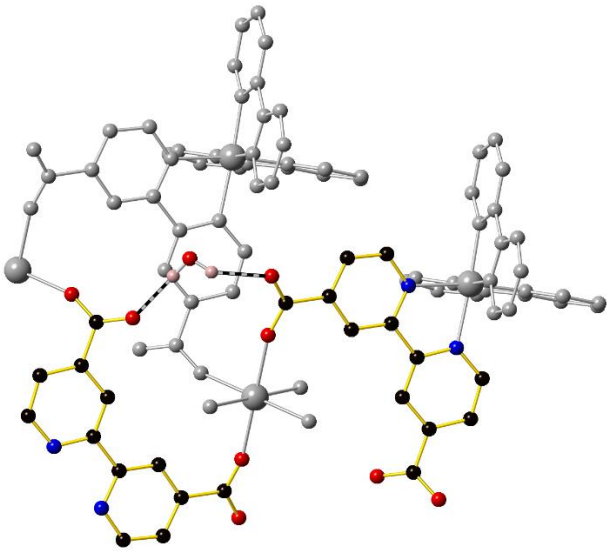

Figure S6. Structure of {Ca[Ir(ppy)$_2$(dcbpy)]$_2$(DMF)$_2$}·2H$_2$O (**1**) showing the position of the water molecule sitting within a "pocket" in the framework structure with hydrogen bonds (shown in black and white) to oxygen atoms of two dcbpy ligands.

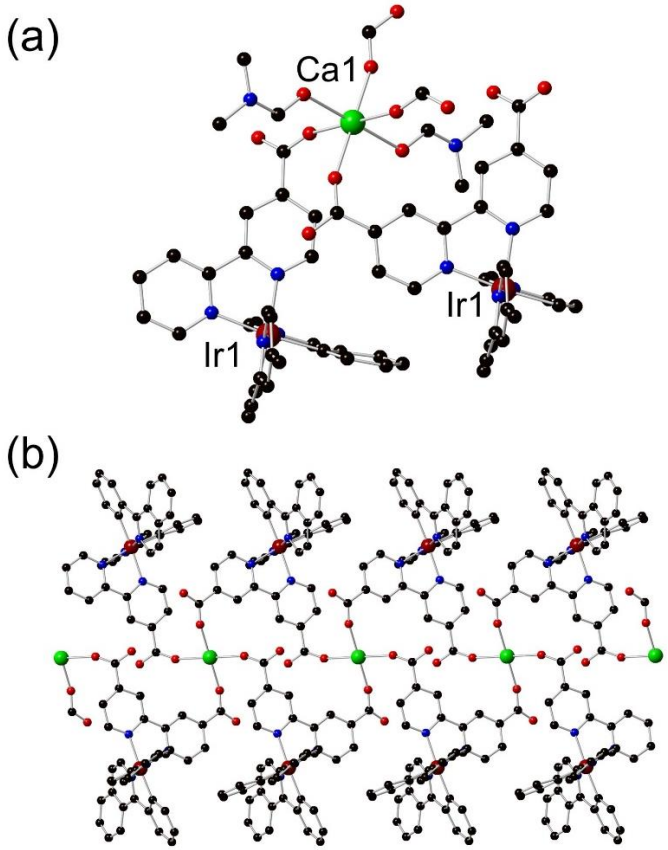

Figure S7. Structure of {Ca[Ir(piq)$_2$(dcbpy)]$_2$(DMF)$_2$}·2H$_2$O (**2**) showing (a) the coordination environment around the Ca^{2+} ion (black, carbon; red, oxygen; blue, nitrogen; maroon, iridium; green, calcium), (b) the 1-D chain containing the iridium(III) metalloligand on the top and bottom of the chain (the coordinated DMF molecules have been hidden for clarity).

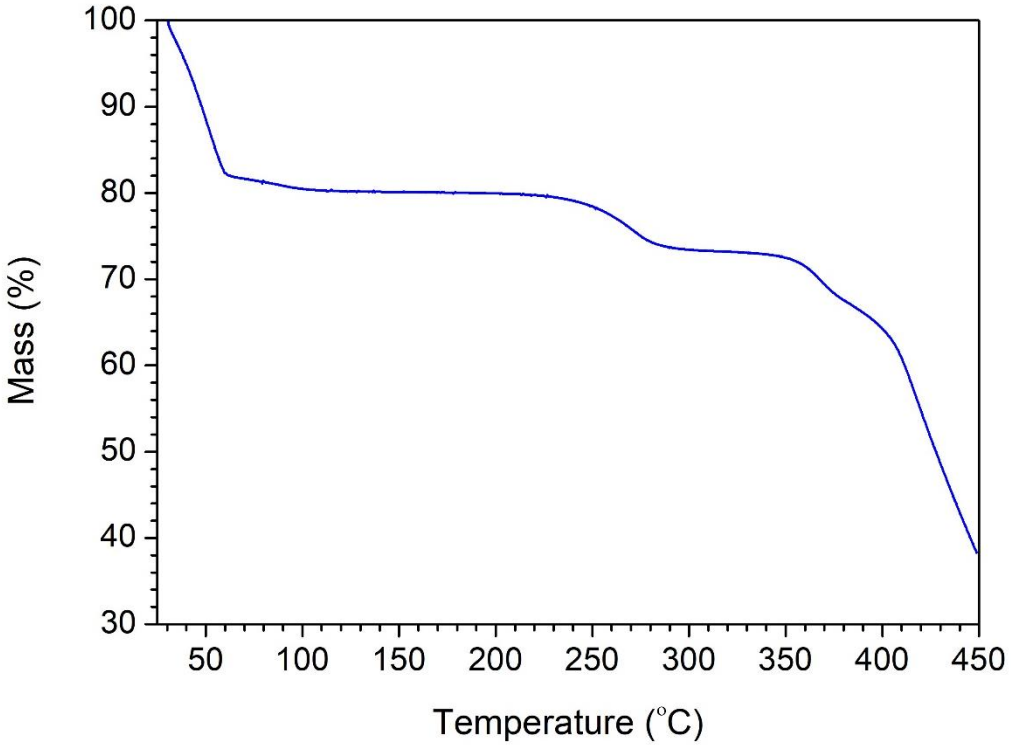

Figure S8. Thermal Gravimetric Analysis of {Ca[(Ir(ppy)$_2$(dcbpy)]$_2$(DMF)$_2$}·2H$_2$O (**1**) between 25 and 400°C measured under nitrogen gas with a ramp rate of 10°C min^{-1}.

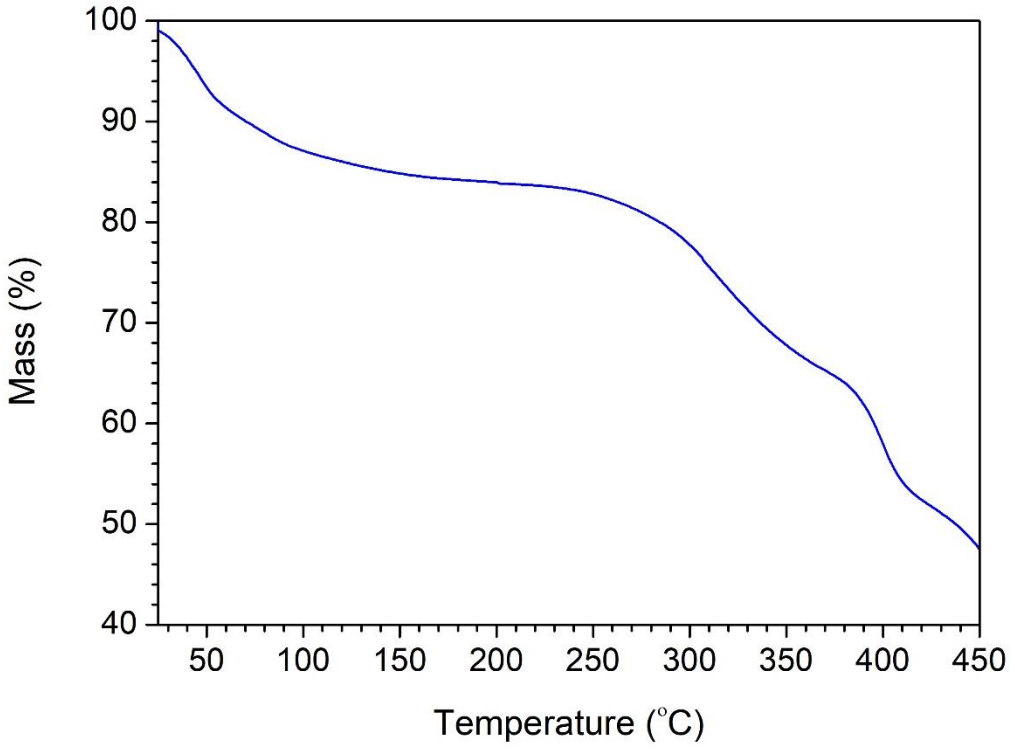

Figure S9. Thermal Gravimetric Analysis of {Ca[(Ir(piq)$_2$(dcbpy)]$_2$(DMF)$_2$}·2H$_2$O (**2**) between 25 and 400°C measured under nitrogen gas with a ramp rate of 10°C min^{-1}.

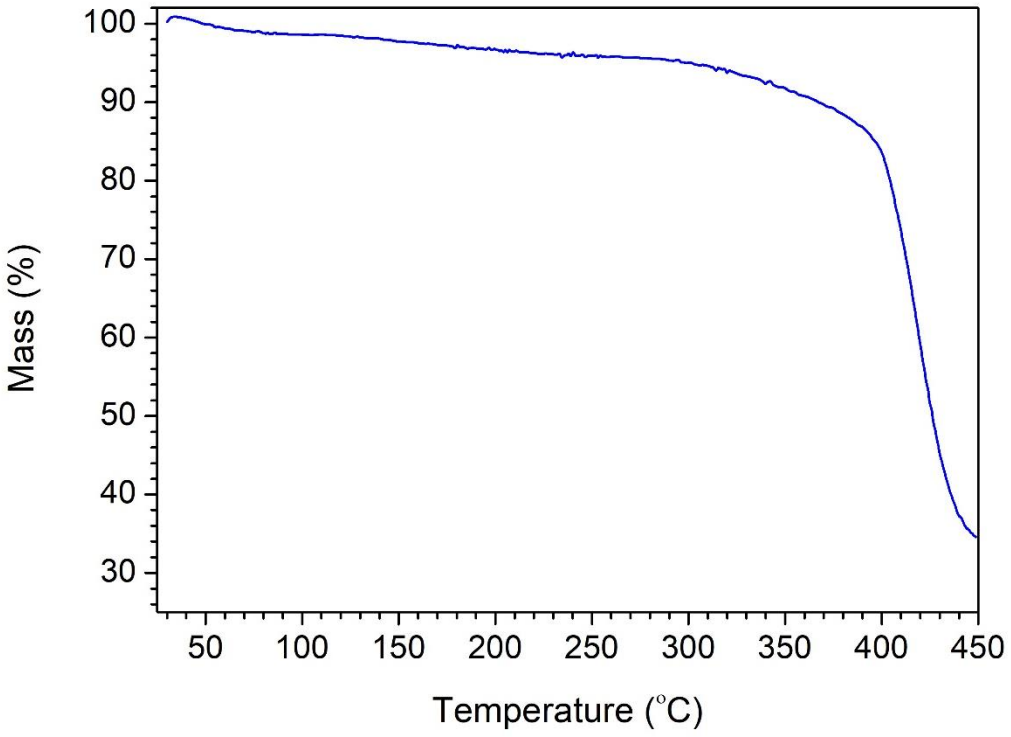

Figure S10. Thermal Gravimetric Analysis of {Ca[Ir(bt)$_2$(dcbpy)]$_2$(dcbpy)(H$_2$O)$_2$]}·2DMF (**3**) between 25 and 400°C measured under nitrogen gas with a ramp rate of 10°C min^{-1}.

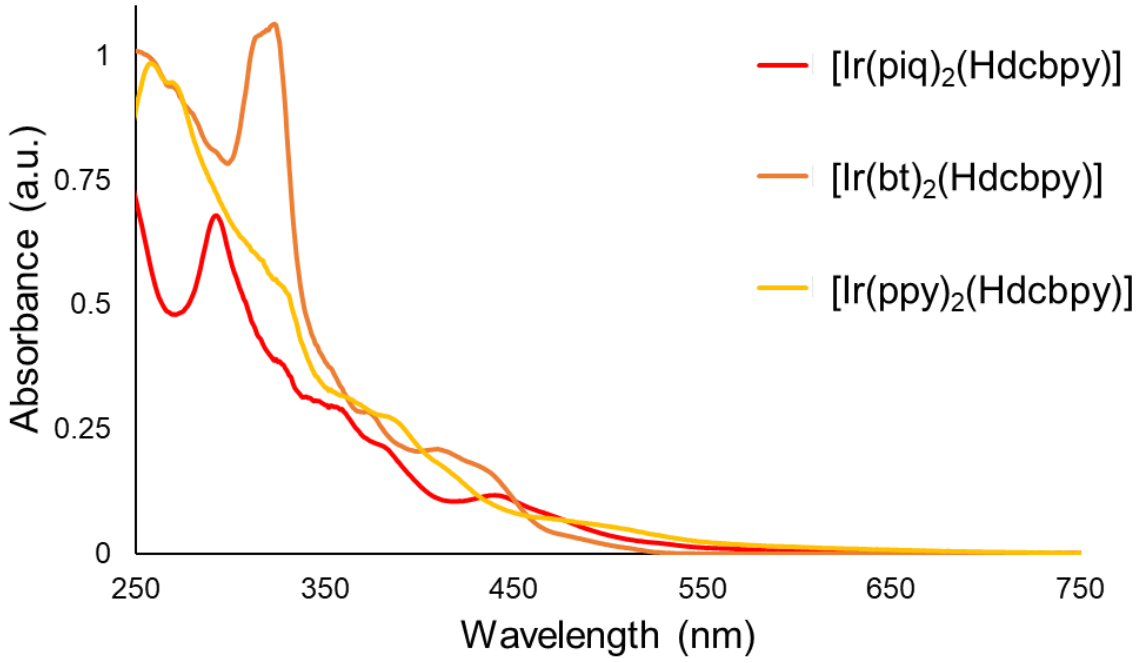

Figure S11. Absorption spectra of iridium(III) metalloligands in a dichloromethane solution (25 μM).

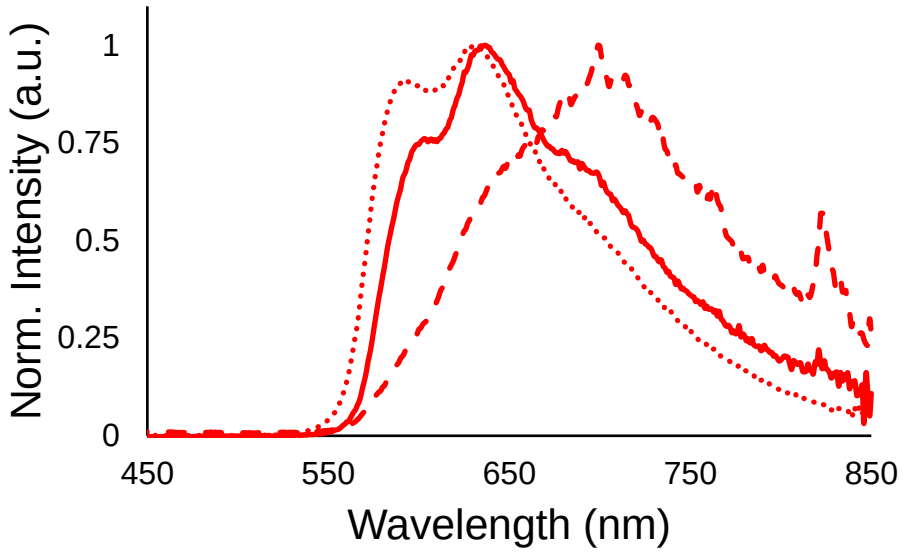

Figure S12. Normalised emission spectra of [Ir(piq)$_2$(Hdcbpy)] in a dichloromethane solution (25 μM, 350-nm excitation, dotted line), solid state powder (380-nm excitation, dashed line) and synthesised calcium(II) MOF (380-nm excitation, solid line).

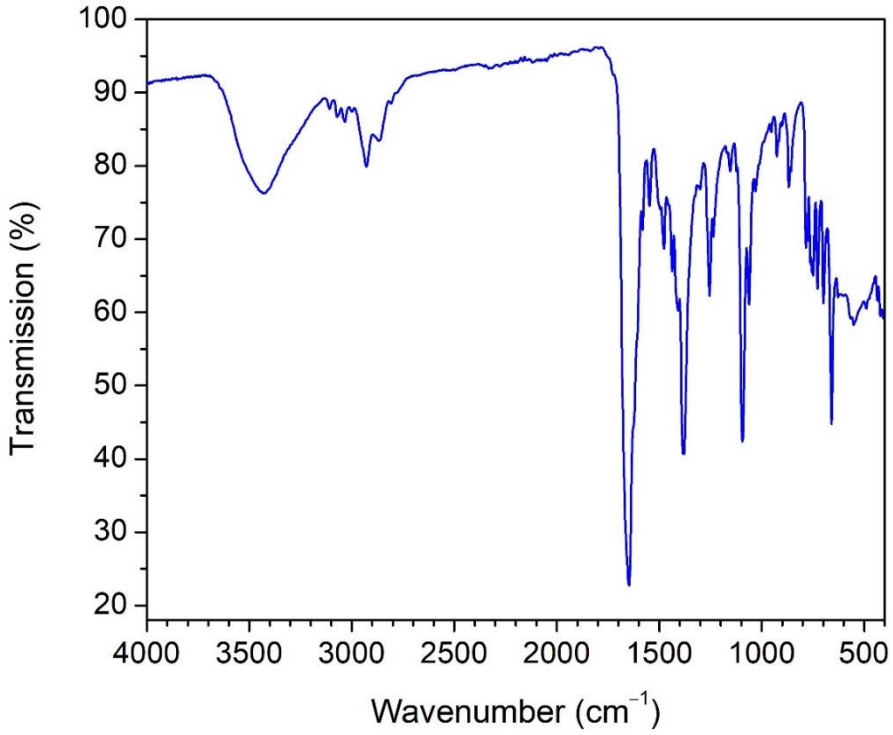

Figure S13. ATR FT-IR spectra of {Ca[(Ir(ppy)$_2$(dcbpy)]$_2$(DMF)$_2$}·2H$_2$O (**1**) between 4000 and 400 cm^{-1}.

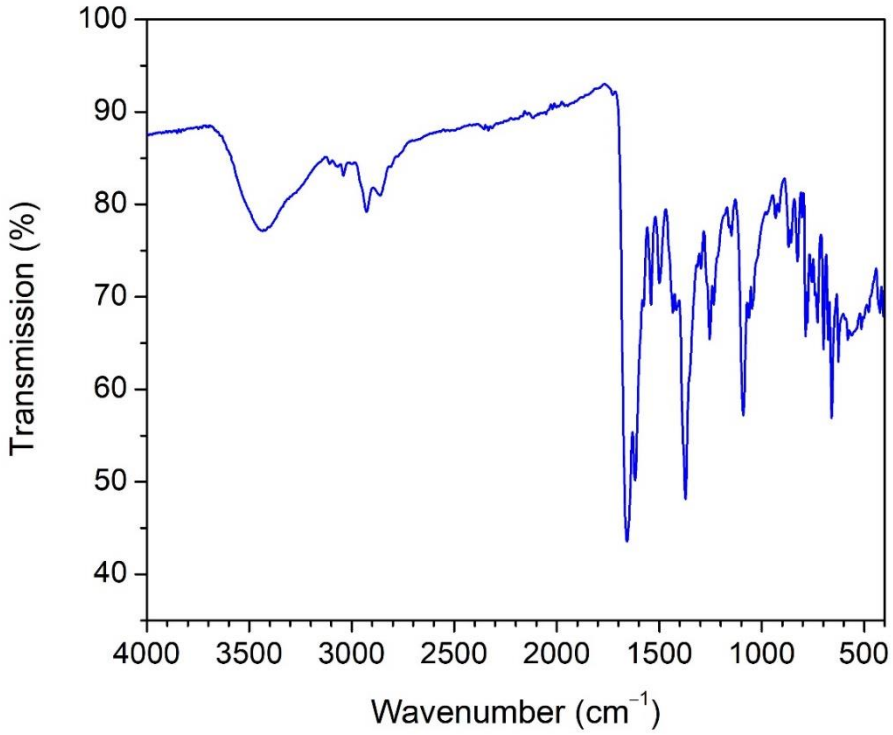

Figure S14. ATR FT-IR spectra of {Ca[(Ir(piq)$_2$(dcbpy)]$_2$(DMF)$_2$}·2H$_2$O (**2**) between 4000 and 400 cm^{-1}.

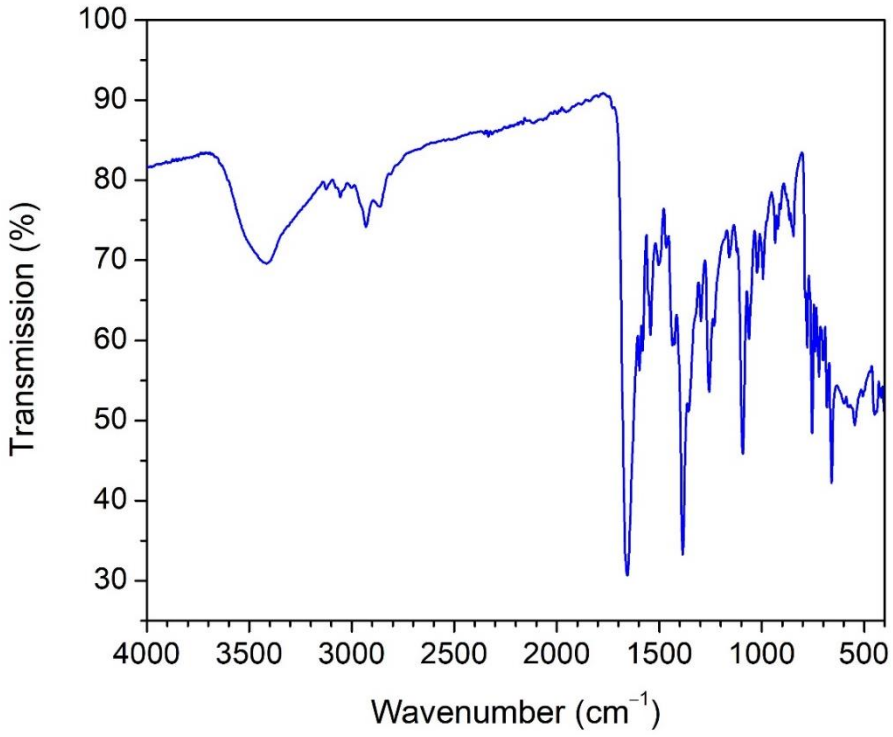

Figure S15. ATR FT-IR spectra of {Ca[Ir(bt)$_2$(dcbpy)]$_2$(dcbpy)(H$_2$O)$_2$]}·2DMF (**3**) between 4000 and 400 cm^{-1}.