Supplementary Material (ESI) for Chemical Communications

Supplementary Information

For

A Tetranuclear Iridium(III) Complex Having a Flavin Analogue as Bridging Ligands in Different Coordination Modes and Exchangeable Anion Encapsulation in a Supramolecular Cage

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Experimental Section

Preparation of 1-PF_6. **1**-PF_6: To a suspension of $[IrCl_2(Cp^*)]_2$ (161 mg, 0.202 mmol) in acetonitrile (20 ml) was added $AgPF_6$ (103 mg, 0.408 mmol). After 30 min of stirring at RT, the white precipitate of AgCl was filtered off through a Celite pad and yellow powder was obtained by removing acetonitrile. After dissolving the yellow powder into methanol (30 cm^3), alloxazine (87.8 mg, 0.410 mmol) was added to the solution under Ar. The mixture was stirred for 24 h at RT and then the solvent was removed by a rotary evaporator. The residue was dissolved in a small volume of acetone and the solution was filtered and then orange powder precipitated by adding a large amount of diethyl ether to the filtrate. The orange powder was stirred overnight in chloroform. After that the orange precipitate of $[Ir(Cp^*)(Hallo)Cl]PF_6$ (**A**) was collected by filtration, washed with chloroform and then dried in vacuo (yield: 33%). Elemental analysis (%) calcd for $C_{20.5}H_{21.5}O_2N_4IrCl_{2.5}PF_6(A\cdot 0.5(CHCl_3))$: C 31.50, H 2.77, N 7.17; found: C 31.80, H 2.94, N 6.62.

The precursor complex **A** was dissolved into acetone and vapour diffusion of $CHCl_3$ into the solution gave crude crystalline **1**-PF_6 which was contaminated by alloxazine.

This crude product was dissolved into acetone and the solution was filtered to remove alloxazine. To the solution, $CHCl_3$ vapour was diffused again to obtain red single crystals of **1**-PF_6. Elemental analysis (%) calcd for $C_{73}H_{81}N_{12}O_8Cl_{11}P_2F_{12}Ir_4$ (**1**-PF_6•$3CHCl_3$•$2H_2O$): C 32.43, H 3.02, N 6.22; found: C 32.40, H 2.97, N 6.30. Absorption maxima in acetone (λ_{max}, nm (ε, mol^{-1} dm^3 cm^{-1})): 358 (2.4×10^4), 400 (2.4×10^4), 455 and 535 (shoulder).

Preparation of 1-ClO_4. To a solution of **1-PF_6** in acetone, 20-fold excess amount of [(*n*-butyl)$_4$N]ClO_4 was added as solids. Vapour diffusion of $CHCl_3$ into the solution gave red single crystals of **1-ClO_4**. Elemental analysis (%) calcd for $C_{72.5}H_{76.5}N_{12}O_{14}Cl_{11.5}Ir_4$ (**1**-ClO_4•$2.5CHCl_3$): C 34.60, H 3.06, N 6.68; found: C 34.60, H 3.16, N 6.89.

Notes on X-ray crystallography. Severe disorder of the solvent molecules of crystallization was observed in both crystals and those molecules were treated with isotropic thermal parameters. Considerably large R values might be due to imperfectness of the disordered models of the solvents. The cations in **1**-ClO_4 and **1**-PF_6 were also disordered: the alloxazine ligand bridging between Ir2 and Ir4 could be resolved in two

disordered moieties, which were treated as rigid groups. Hydrogen atoms of waters in **1**-PF_6 could not be located in the final d-Fourier map.

The crystals contain large solvent-accessible voids. However, we could not locate residual solvent molecules in the final d-Fourier map. The SQUEEZE procedure was not applied.

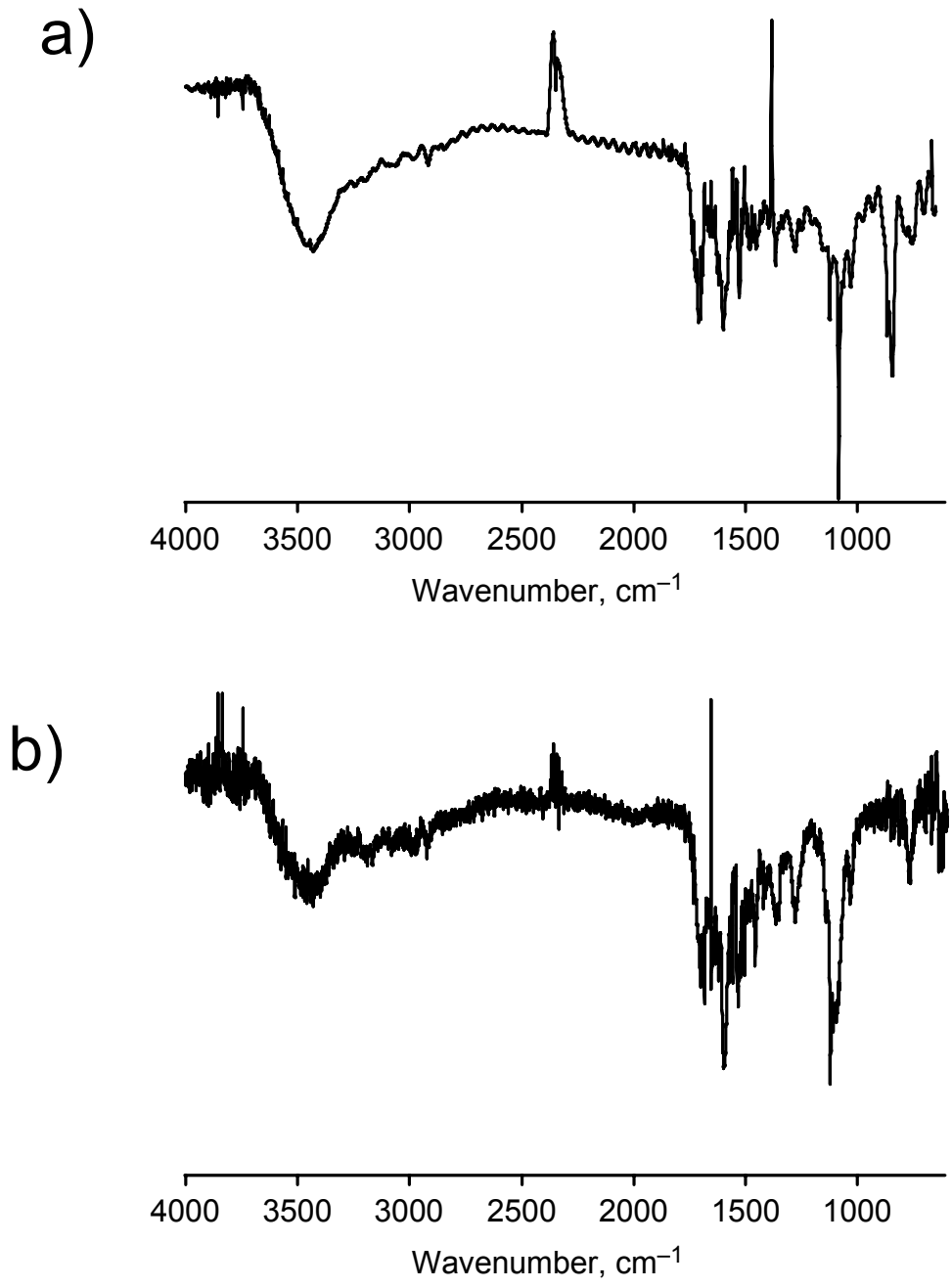

Fig. S1 IR spectra of **1**-PF_6 (a) and **1**-ClO_4 (b) measured in KBr pellets at room temperature.

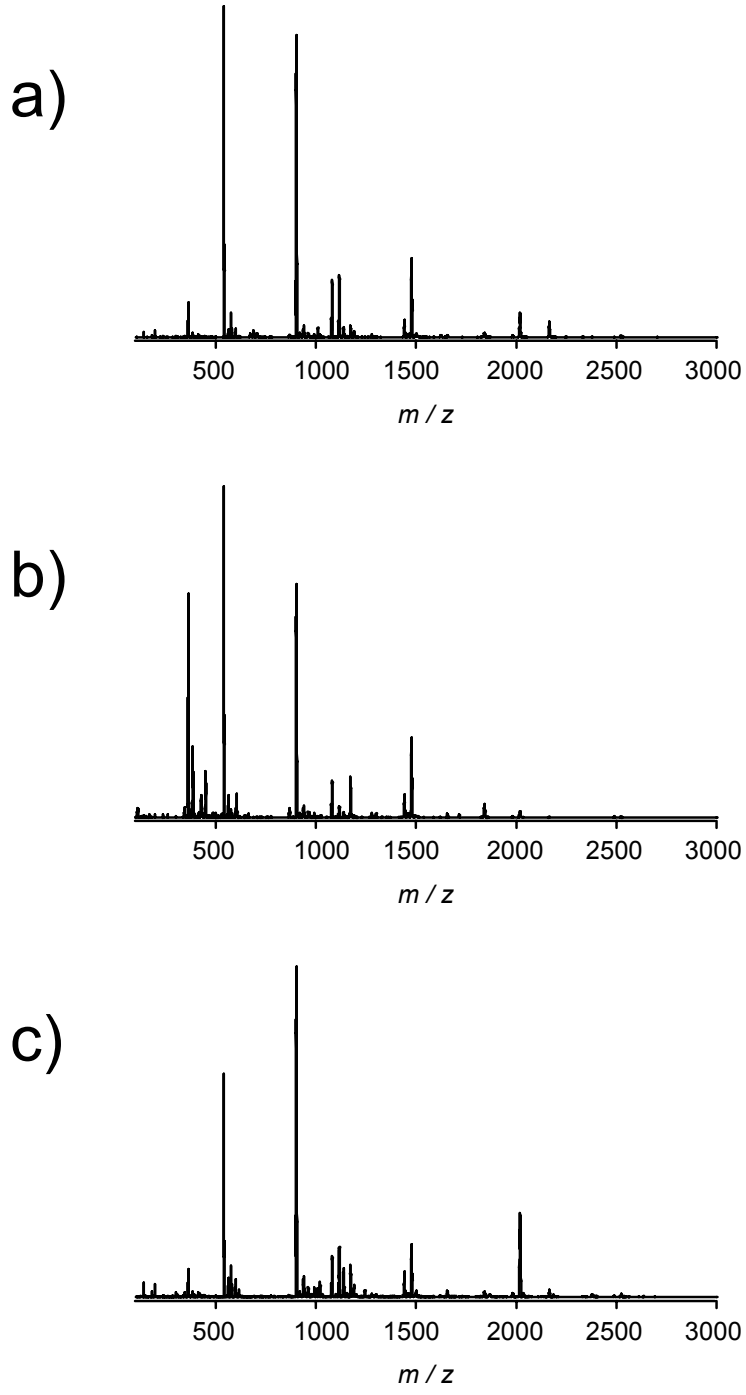

Fig. S2 ESI-MS spectra of **1**-PF_6 just after dissolving into acetone (a), 24h later after dissolving crystals of **1**-PF_6 into acetone (b), and recrystallized sample of **1**-PF_6 just after dissolving into acetone.