Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information (ESI)

for

A Water-Soluble Iridium(III) Porphyrin

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Synthesis of $[Ir^{III}(TSPP)(OH_2)_2][Na(benzo\text{-}18\text{-}crown\text{-}6\text{-}ether)]_3$. A reaction of sodium tetra-*p*-sulfonatophenyl porphyrin ($TSPPH_2Na_4$, 102 mg, 0.1 mmol) with $[Ir^{I}Cl(COD)]_2$ (67.2 mg, 0.1 mmol) in ethylene glycol (10 mL) at 140 ˚C for 5 h was provided the dark red solution. The resultant solution was evaporated under reduced pressure and the obtained dark red powder was dissolved in water. The excess of iridium was removed by elution with water through a short column of Dowex 50X8 (Na^+). The water-soluble iridium(III) diaqua porphyrin **1** was isolated as an red powder of **1**·[Na(benzo-18-crown-6-ether)]$_3$ by addition of benzo-18-crown-6-ether (80 mg, 10.5 μmol) in acetone (200 μL) to the aqueous solution of crude **1** (yield: 14.6% based on $TSPPNa_4$). ^{1}H NMR of **1**·[Na(benzo-18-crown-6-ether)]$_3$ (300 MHz, in D_2O, reference to TSP in D_2O, 25 ˚C): δ 8.93 (s, 8H, pyrrole *H*), 8.25-8.44 (dd, 16H, phenyl *H*). UV-vis spectroscopy (H_2O, λmax): 406 nm (ε = 335000 $M^{-1}cm^{-1}$) and 519 nm (ε = 27000 $M^{-1}cm^{-1}$). Anal. Calcd for $[Ir^{III}(TSPP)(OH_2)_2][Na(benzo\text{-}18\text{-}crown\text{-}6\text{-}ether)]_3(H_2O)_8$: Anal. Calcd for C, 47.89; H, 5.06; N, 2.43; S, 5.56. Found: C, 47.89; H, 5.23; N, 2.40; S, 5.40.

Crystallization of $[Ir^{III}(TSPP)(OH_2)_2][Na(benzo\text{-}18\text{-}crown\text{-}6\text{-}ether)]_3$. A red crystal of **1**·[Na(benzo-18-crown-6-ether)]$_3$ used for single crystal X-ray analysis was obtained by diffusion of acetone into an aqueous solution of **1**·[Na(benzo-18-crown-6-ether)]$_3$ at pH 5.5 with the excess of benzo-18-crown-6-ether in acetone at 25 ˚C. A single crystal with dimensions of 0.13 x 0.16 x 0.11 x mm^3 was mounted on the tip of a glass rod. One of the counter-cation $[Na(benzo\text{-}18\text{-}crown\text{-}6\text{-}ether)]^+$ was bonded to one of the sulfonyl groups in **1**. The solvents (water) had positional disoder. The hydrogens attached to the disordered atoms were not added.

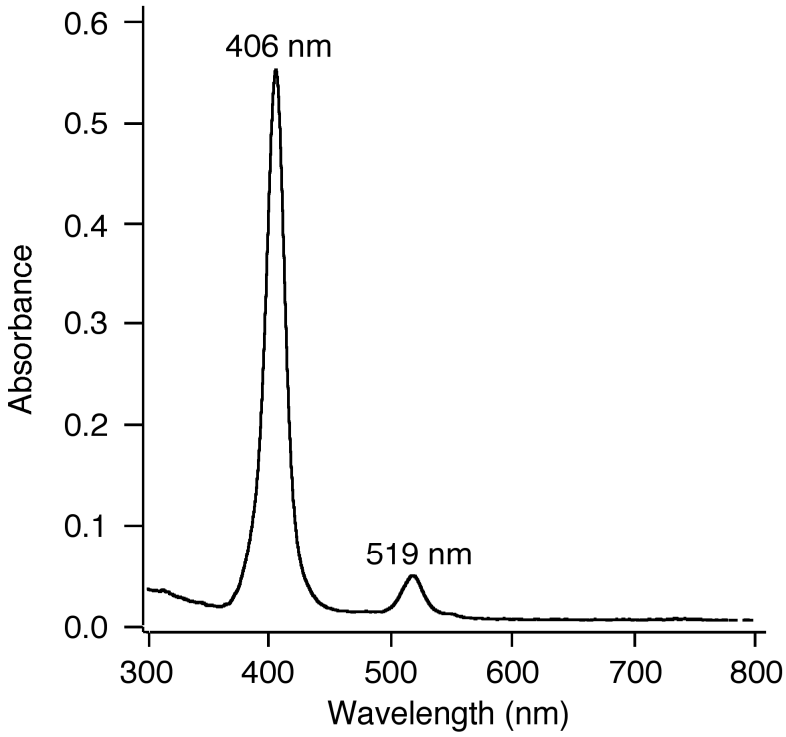

Figure (S1). UV-vis spectrum of **1**·[Na(benzo-18-crown-6-ether)]$_3$.

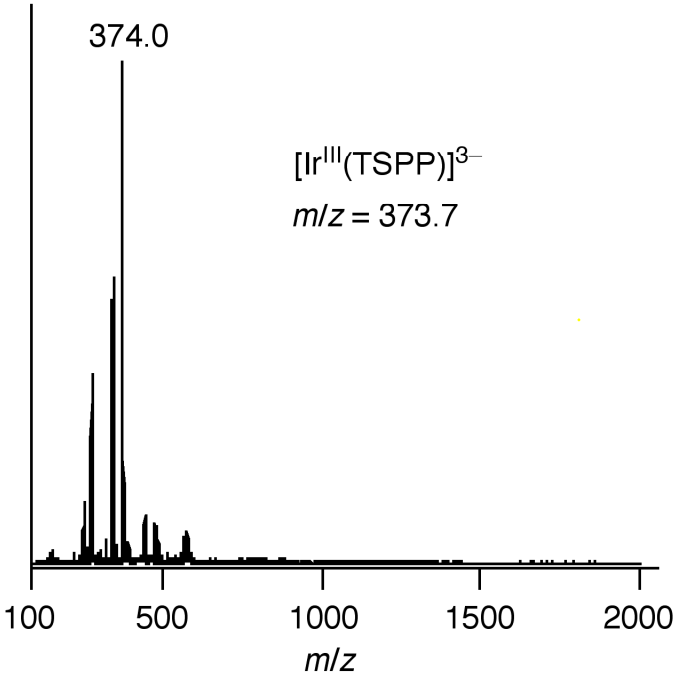

Figure (S2). Negative-ion ESI mass spectrum of **1**·[Na(benzo-18-crown-6-ether)]$_3$.

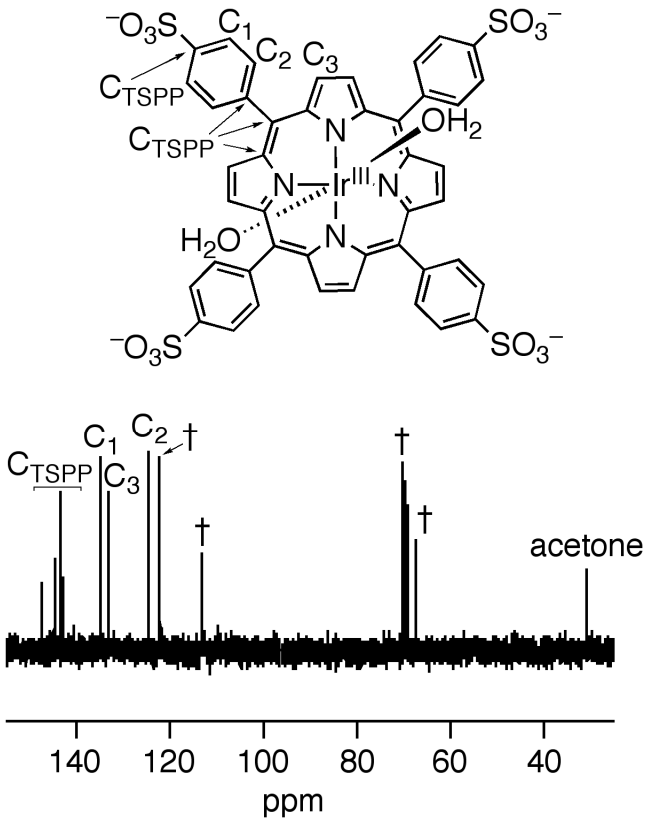

Figure (S3). $^{13}C\{^1H\}$ NMR spectrum of **1**·[Na(benzo-18-crown-6-ether)]$_3$. †, benzo-18-crown-6-ether.

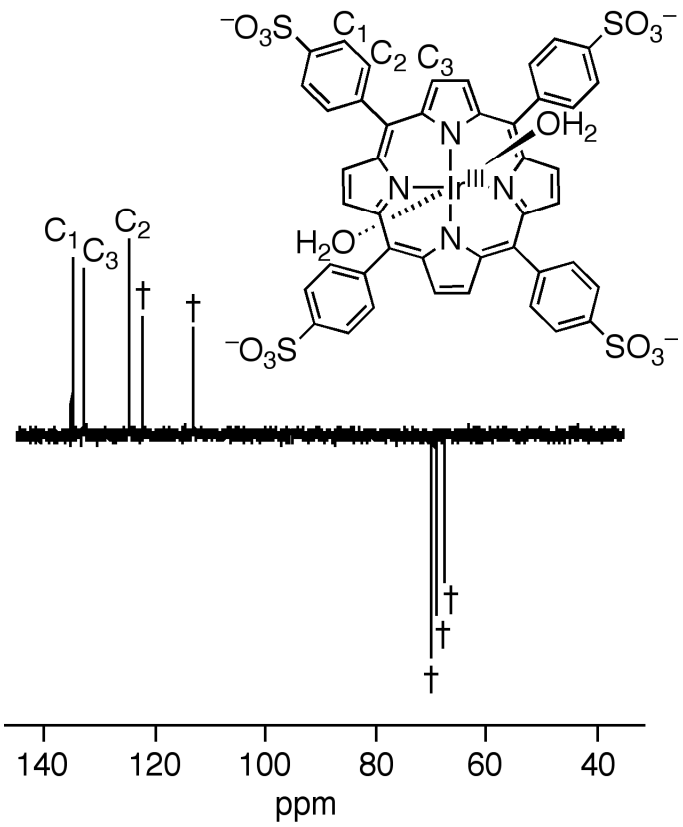

Figure (S4). DEPT spectrum of **1**·[Na(benzo-18-crown-6-ether)]$_3$. †, benzo-18-crown-6-ether.

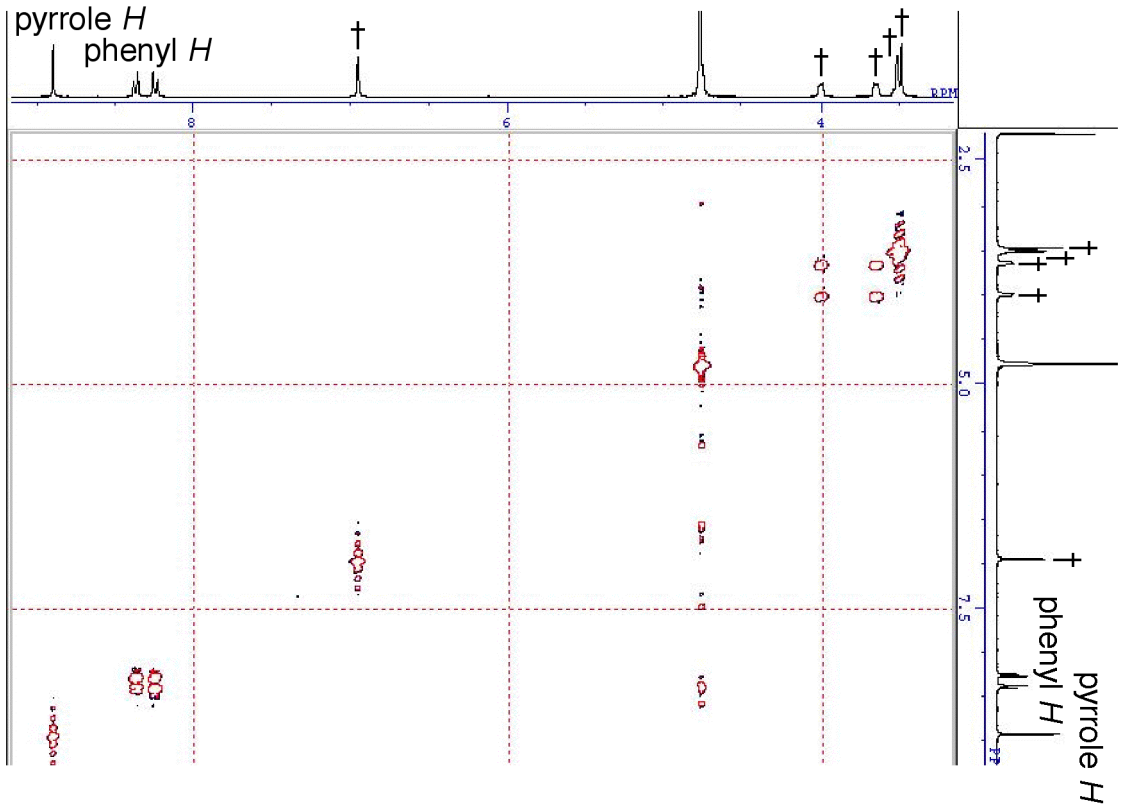

Figure (S5). H-H COSY spectrum of **1**·[Na(benzo-18-crown-6-ether)]$_3$. †, benzo-18-crown-6-ether.

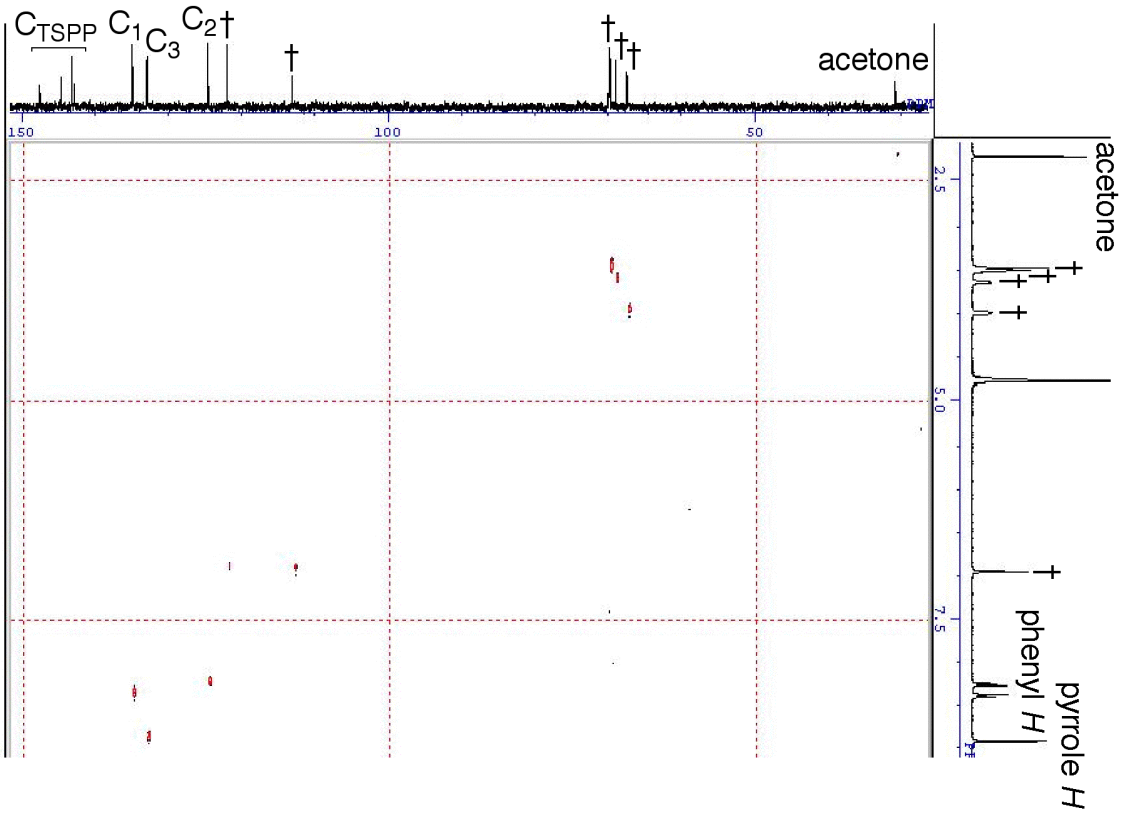

Figure (S6). C-H COSY spectrum of **1**·[Na(benzo-18-crown-6-ether)]$_3$. †, benzo-18-crown-6-ether.

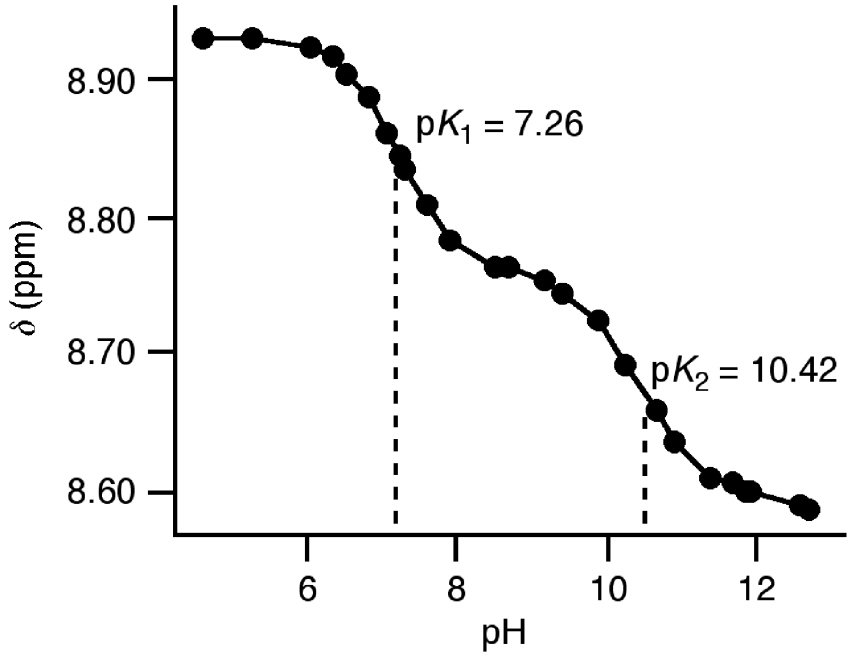

Figure S7. The pH dependence of pyrrole ^{1}H NMR chemical shifts for **1**·[Na(benzo-18-crown-6-ether)]$_3$ in a pH range of 4.6–12.7. Experiments were performed by the titration of **1**·[Na(benzo-18-crown-6-ether)]$_3$ with 0.1 M NaOH/H_2O at 25 ˚C. At pH 7.26, the iridium diaqua complex **1** was deprotonated to form the corresponding iridium aqua hydroxo complex. Similarly, the iridium aqua hydroxo complex was deprotonated to form the corresponding iridium dihydroxo complex at pH 10.42.

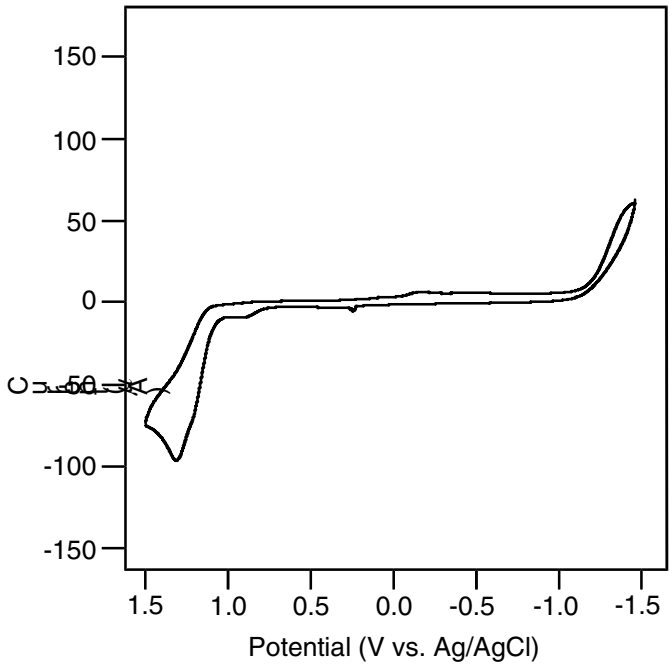

Figure S8. Cyclic Voltammogram of **1**·[Na(benzo-18-crown-6-ether)]$_3$ (1.0 mM) in H_2O (pH 5.5) at a glassy carbon electrode (υ = 50 mV s^{-1}).