Electronic Supporting Information

Belonging to

Photolytic water oxidation catalyzed by molecular carbene iridium complexes

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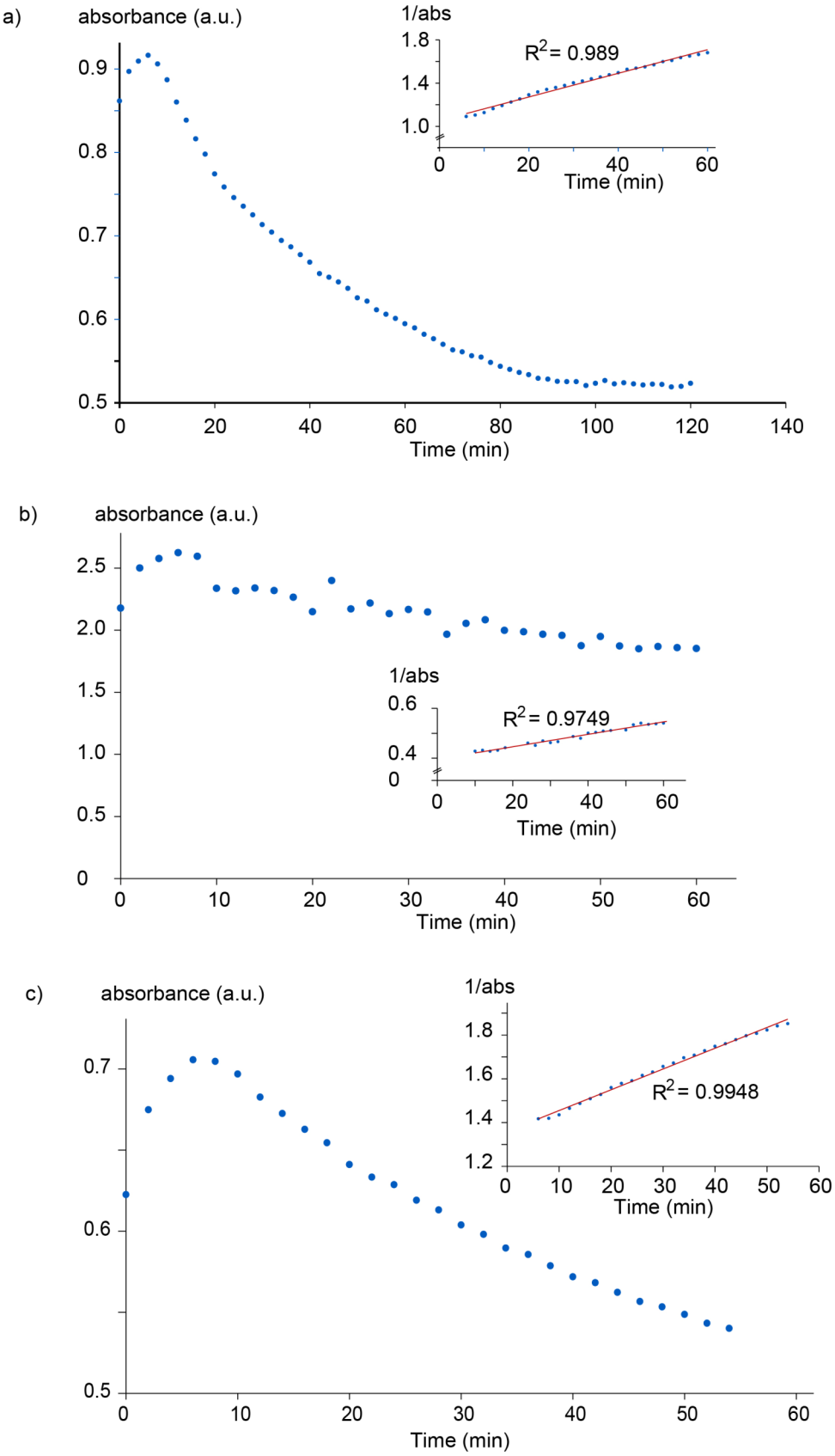

Fig. S1 Change of absorbance in CAN-mediated water oxidation using complex **2** at different concentrations: a) 1.4 mM **2**, 10 molequiv CAN; b) 1.4 mM **2**, 80 molequiv CAN; c) 0.7 mM **2**, 20 molequiv CAN (for 1.4 mM **2**, 20 molequiv CAN, see main text).

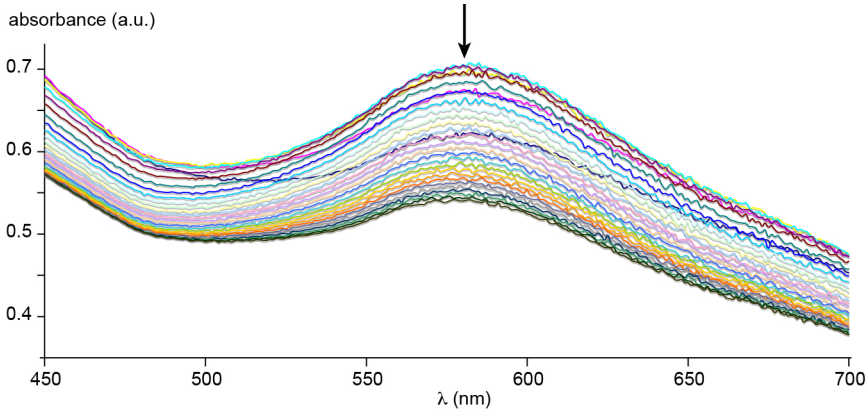

Fig. S2 Stacked plot of UV-vis spectra in the 450–700 nm range of complex **2** in the presence of Ce^{IV} (1.4 mM catalyst, 20 molequiv CAN in 2.0 mL H_2O); spectra were recorded every 2 min and reveal the gradual non-linear decrease of the absorbance at 580 nm.

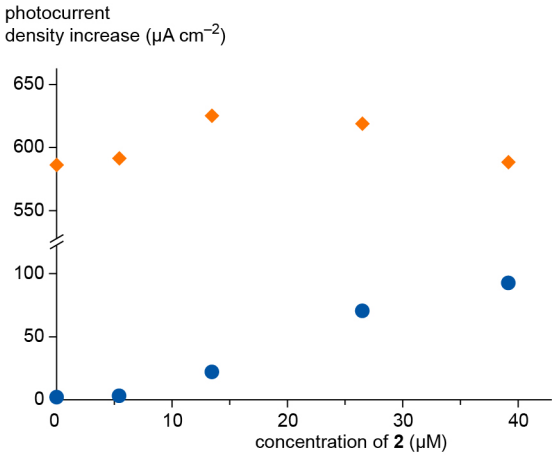

Fig. S3 Photocurrent (orange diamonds) and dark current (blue circles) induced by different concentrations of **2** (pH 3.3, 3.5% NaCl as supporting electrolyte). The plot shows that at higher concentrations, complex **2** is mediating electrocatalytic water oxidation, while the photoelectrochemical response disappears, likely due to electrodeposition of complex on the electrode.

Table S1. Crystal data for complex **2**

CCDC No.	867256
Molecular formula	$C_{20}H_{26}Cl_2IrN_3 \times CH_2Cl_2$
Formula weight	656.46
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P–1 (#2)
Unit cell dimensions	a = 8.96981(5) Å α = 86.2178(4)°
	b = 9.18519(5) Å β = 76.6774(4)°
	c = 14.95269(7) Å γ = 77.1641(4)°
Volume	1168.690(11) $Å^3$
Z	2
Density (calcd)	1.865 g cm^{-3}
Absorption coefficient	6.183 mm^{-1}
F(000)	640
Crystal size	0.245 × 0.175 × 0.102 mm^3
Reflections collected	75290
Independent reflections	8215 (R_{int} = 0.0268)
Absorption correction	analytical
Max., min. transmission	0.712, 0.454
Data, restraints, parameters	8215, 0, 269
Goodness–of–fit on F^2	1.038
Final R indices for I>2σ(I)	R1 = 0.0142, wR2 = 0.0323
R indices (all data)	R1 = 0.0153, wR2 = 0.0328
Largest diff. peak, hole	0.614, –0.953 e $Å^{-3}$