

Synthesis and Characterization of a Trinuclear Iridium(III) based Catalyst for the Photocatalytic Reduction of CO₂ under Visible Light Irradiation.

Richard O. Reithmeier,^a Simon Meister,^a Armin Siebel,^b Bernhard Rieger*^a

^a WACKER-Chair of Macromolecular Chemistry, Technische Universität München, Lichtenbergstr. 4, 85748 Garching b. München, Germany.

^b Department of Technical Electrochemistry, Technische Universität München, Lichtenbergstr. 4, 85748 Garching b. München, Germany.

* E-Mail for B.R.: rieger@tum.de, Fax: (+49)-89-289-13562;

Supporting Information

Contents

1. Analytical Data
2. Photoexperiments

Figures

Figure S1: Fluorescence spectra of complex **3** in dependence on the quencher concentration.

Figure S2: UV/Vis spectra of complex **3**.

Figure S3: NMR spectrum of complex **3**, measured in deuterated acetonitrile.

Figure S4: IR-spectrum of complex **3**.

Figure S5: Rotating disk electrode voltammograms of complex **3** recorded in Ar-saturated acetonitrile, containing 0.1 M TBABF₄ using a scan rate of 100 mV/s and different rotation rates.

Figure S6: Photoreduction of CO₂ to CO using various concentrations of complex **3**.

Figure S7: Determination of the reaction order in catalyst for complex **3**.

Tables

Table S1: Determination of the reaction order in catalyst for complex **3**.

1. Analytical Data

Fluorescence

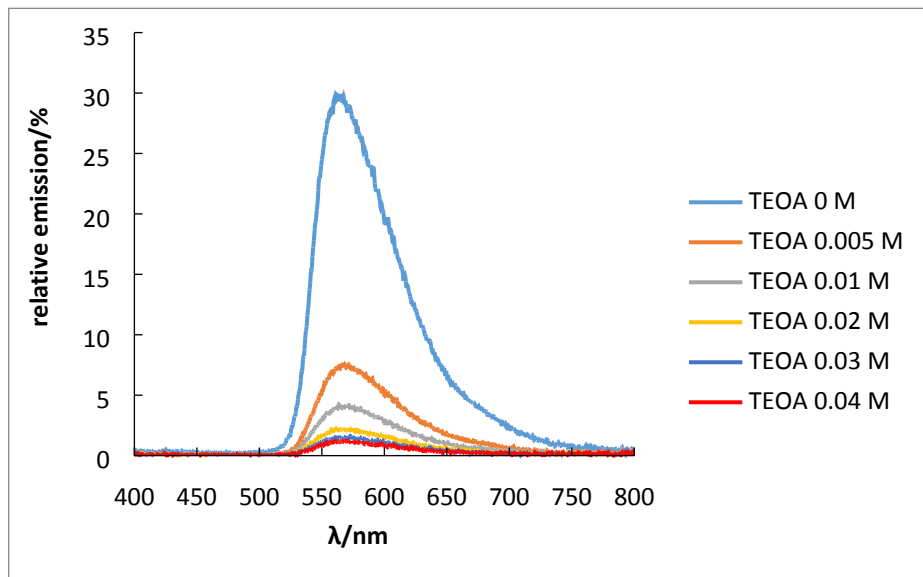


Figure S1: Fluorescence spectra of complex 3 in dependence on the quencher concentration.

UV/Vis

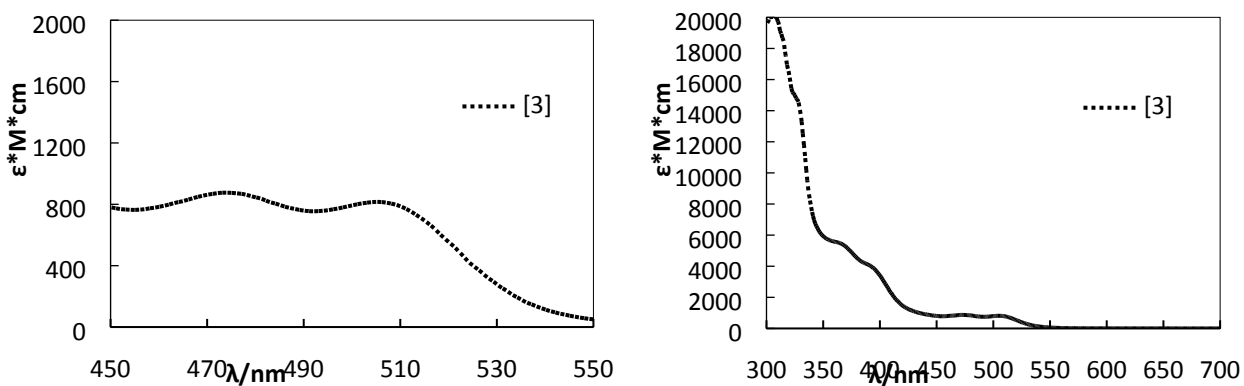


Figure S2: UV/Vis spectra of complex 3.

NMR

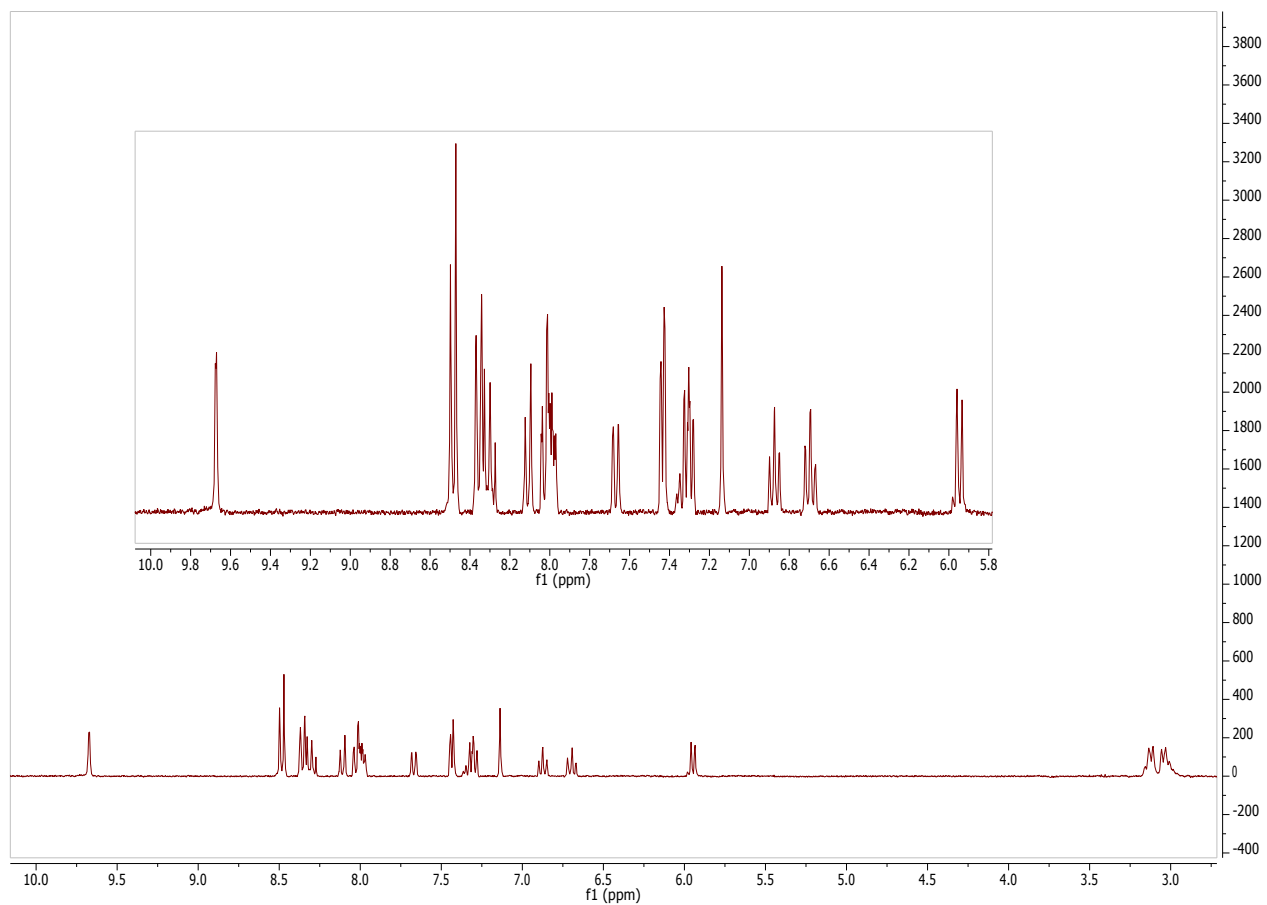


Figure S3: NMR spectrum of complex 3, measured in deuterated acetonitrile.

IR

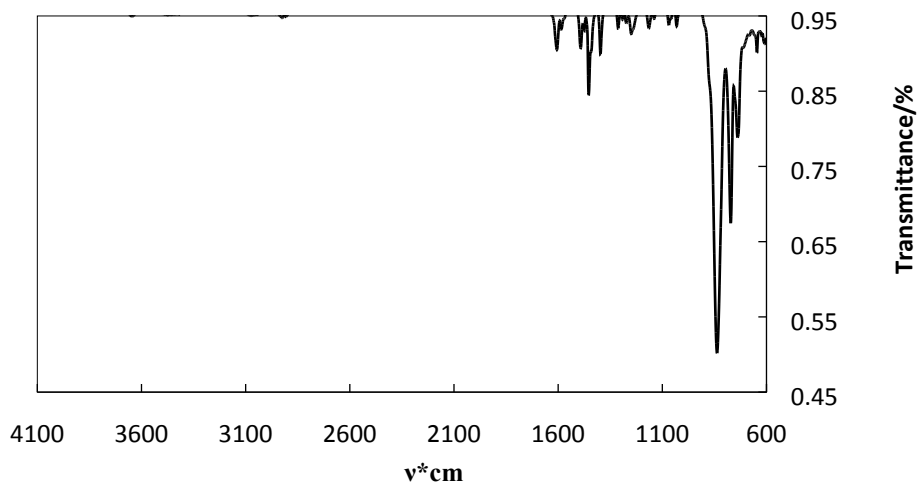


Figure S4: IR-spectrum of complex 3.

Cyclic voltammetry

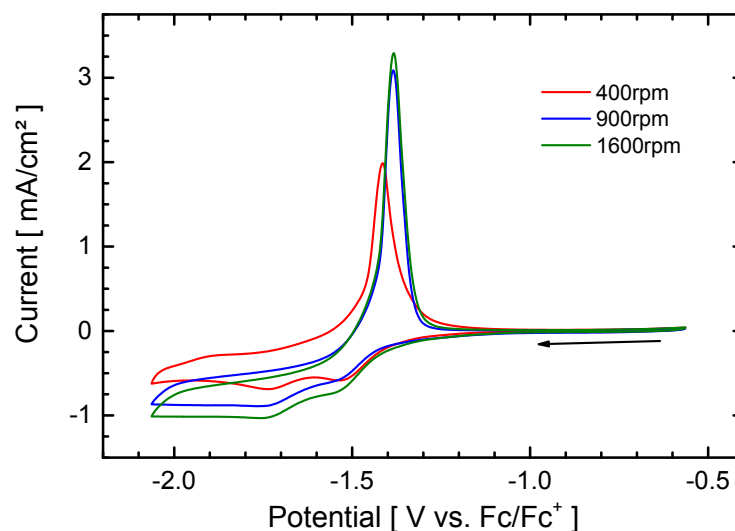


Figure S5: Rotating disk electrode voltammograms of complex 3 recorded in Ar-saturated acetonitrile, containing 0.1 M TBABF₄ using a scan rate of 100 mV/s and different rotation rates.

2. Photoexperiments

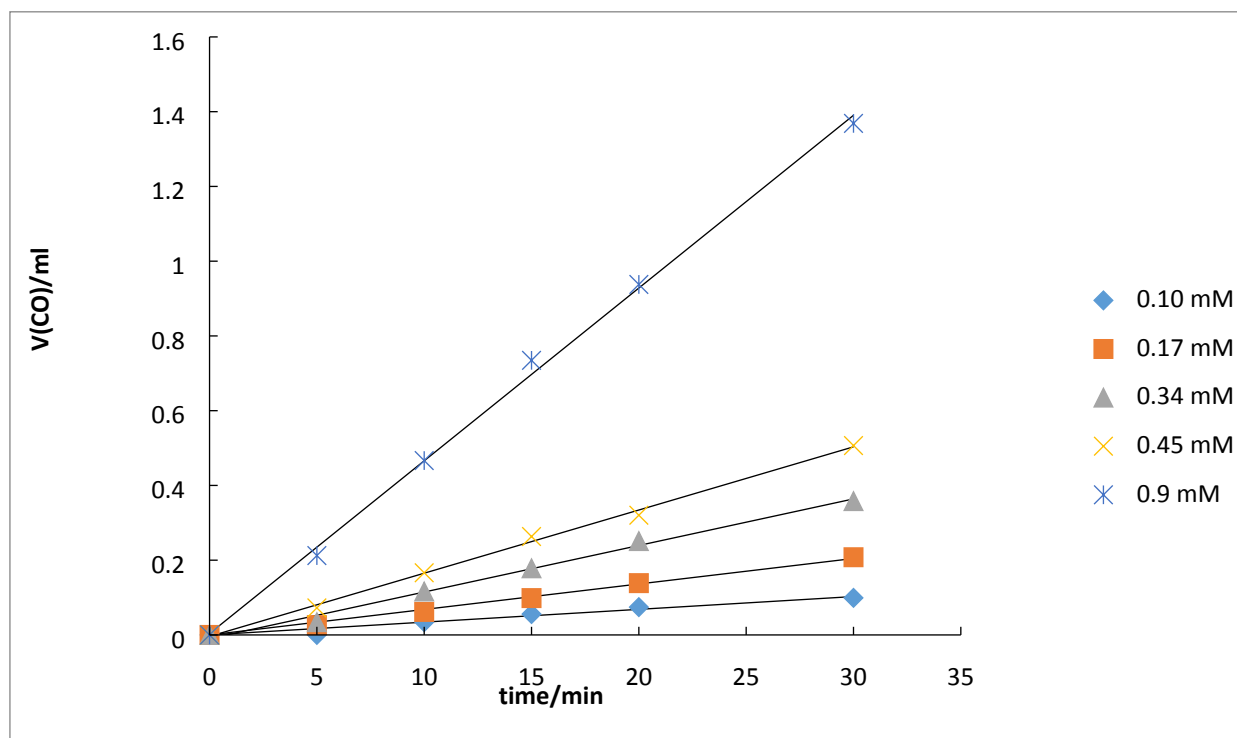


Figure S6: Photoreduction of CO₂ to CO using various concentrations of complex 3, 5 ml CH₃CN, 1 ml TEOA, light intensity 3.35×10^{-7} einstein/s, 450 nm, CO₂ atmosphere.

Determination of the Reaction order in catalyst

The reaction order in catalyst was determined by varying the catalyst concentration at otherwise identical reaction conditions. TEOA as well as CO₂ are added in excess to the reaction solution and therefore the reaction rate is only influenced by the amount of catalyst at the beginning (0 – 30 min) of the catalysis. Besides, the number of emitted photons by the light source, stirring and the distance of the reaction vessel to the light source are kept constant. A summary of the overall reaction rate in dependence on the catalyst concentration is given in Table S1. Double logarithmic plotting gives an order of 1 in catalyst below catalyst concentrations of 0.9 mM Ir centers. Above this value the order switches to 0, because the number of emitted photons by the light source becomes the limiting factor for the overall reaction rate (Figure S7).

Table S1: Determination of the reaction order in catalyst for complex 3, 0.1 – 2.0 mM Ir(III) centers, 5 ml CH₃CN, 1 ml TEOA, light intensity 3.35×10^{-7} einstein/s, 450 nm, CO₂ atmosphere.

Ir(III) center [mM]	ln(Ir(III) center) [mM]	V(CO)/time [ml min ⁻¹]	ln(V(CO)/time) [ml min ⁻¹]
0,1	-2,30258509	0,0034	-5,68397985
0,17	-1,77195684	0,0068	-4,99083267
0,34	-1,07880966	0,0125	-4,38202663
0,45	-0,7985077	0,0169	-4,08044166
0,9	-0,10536052	0,0462	-3,07477548
1,2	0,18232156	0,0467	-3,06401111
1,4	0,33647224	0,0464	-3,07045582
2	0,69314718	0,0468	-3,06187208

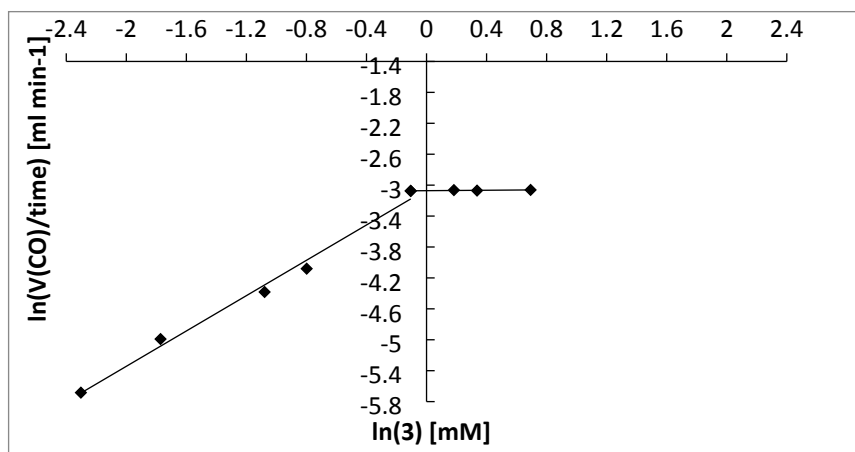


Figure S7: Determination of the reaction order in catalyst for complex 3, 0.1 – 2.0 mM Ir(III) centers, 5 ml CH₃CN, 1 ml TEOA, light intensity 3.35×10^{-7} einstein/s, 450 nm, CO₂ atmosphere.