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Electronic supplementary information

Ionic Liquid Mediated Deposition of Ruthenium Mirrors on Glass under Multiphase Conditions

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Table of Content S1

Experimental Section

General information and instrumentations

^{1}H NMR spectra were recorded on 400 and 300 MHz NMR spectrometer using TMS as the internal standard. Chemical shifts are reported in parts per million (ppm). Peak multiplicities are described according to the following abbreviations: s, singlet; br s, broad singlet; d, doublet; t, triplet; m, multiplet. ^{13}C NMR spectra were proton decoupled and recorded on a 100 or 75 MHz spectrometer using TMS as the internal standard.

ICP-OES analyses were run on a Perkin Elmer Optima 5300DV.

Transmission Electron Microscopy (TEM) images were acquired on JEOL JEM 3010 TEM operating at 300 kV; the powder specimens were suspended in isopropyl alcohol and then sonicated, 5 μL of this suspension were deposited on a copper grid (300 mesh) coated with holey carbon film. The copper grids were allowed to dry in air.

Scanning Electron Microscopy (SEM) measurements were performed using a Sigma-VP Field Emission (FE-SEM) from Zeiss. The microscope is equipped with an on-axis in-lens secondary electron detector as well as a high efficiency off- axis secondary electron detector. Chemicals and solvents were purchased from commercial sources and were used as such, unless otherwise mentioned.

Methyl trioctyl ammonium bistriflimide ($[N_{8881}][NTf_2]$). The title compound was prepared according to a two-step procedure already described by us:[1] i) a mixture of *n*-trioctylamine (TOA, 25 mL, 20.8 g, 56 mmol), DMC (30 mL, 32 g, 356 mmol) and methanol (30 mL) was set to react in a steel autoclave for 20 h at 140 °C and under magnetic stirring. A N-methylation reaction occurred to produce methyl trioctyl ammonium methyl carbonate $[N_{8881}][CH_3OCOO]$. This salt was isolated as a viscous clear colourless liquid (m.p. < 0 °C) in a quantitative yield (27.5 g). ii) in a second step, an aqueous solution of $LiNTf_2$ (2.33 g. 8.13 mmol in 50 mL) was added to $[N_{8881}][CH_3OCOO]$ (4.0 g) dissolved in water (70 mL). The mixture was stirred at 70 °C for 2 h. The resulting white precipitate was extracted with CH_2Cl_2 to afford pure dry ($[N_{8881}][NTf_2]$) in a 65% yield (2.72 g). This was characterized by both ^{1}H and ^{13}C NMR. Spectroscopic properties were in agreement with those previously reported.

Dichloro acetylacetonato acetylacetone ruthenium (III) [$RuCl_2$(acac)(acacH)]. The title compound was prepared and characterized according to an already reported procedure:[2] a mixture of $RuCl_3$ (0.73 mmol, 0.15 g) and acetyl acetone (15.0 mmol, 1.5 g) was set to react at 90 °C for 3 hours. Then, at rt, the violet final solution was added with diethyl ether (20 mL). An oily brown phase was observed on the bottom of the flask. After decanting of the supernatant solution, the residual oil was added with additional diethyl ether (10 mL) which induced the precipitation of a violet solid. This was purified by treatment with a mixture of CH_2Cl_2 (3 mL) and exane (3 mL). $RuCl_2$(acac)(acacH) was obtained as a red-violet solid (0.19 g, 70%). Characterization data were in agreement with those previously reported.

IR (KBr pellet, cm^{-1}) ν: 1625, 1548, 1518, 465, 357 (Figure S1).

Conductivity measures were carried out in a 10^{-3} M solution (25 mL) of the complex in acetone as a solvent: a conductivity as low as 10.2 μS was found.

Tris-acetylacetonate ruthenium (III) [Ru(acac)$_3$]. The title compound was prepared and characterized according to an already reported procedure:[3] a mixture of $RuCl_3$ (0.73 mmol, 0.15 g), acetyl acetone (22 mmol, 2.2 g), and $NaHCO_3$ (2.5 mmol, 0.21 g) was set to react at 120 °C for 3 hours. Then, at rt, the dark red final solution was added with diethyl ether (20 mL). An oily brown phase was observed on the bottom of the flask. After decanting of the supernatant solution, the residual oil was added with additional diethyl ether (10 mL) which induced the precipitation of a red solid. This was purified by treatment with mixture of CH_2Cl_2 (1 mL) and exane (5 mL). Ru(acac)$_3$ was obtained as a red solid (0.18 g, 62%). Characterization data were in agreement with those previously reported.

IR (KBr pellet, cm^{-1}) ν: 1516, 1423, 1364, 1269, 1018, 355 (Figure S2).
Conductivity measures were carried out in a 10^{-3} M solution (25 mL) of the complex in acetone as a solvent: a conductivity as low as 1.0 μS was found.

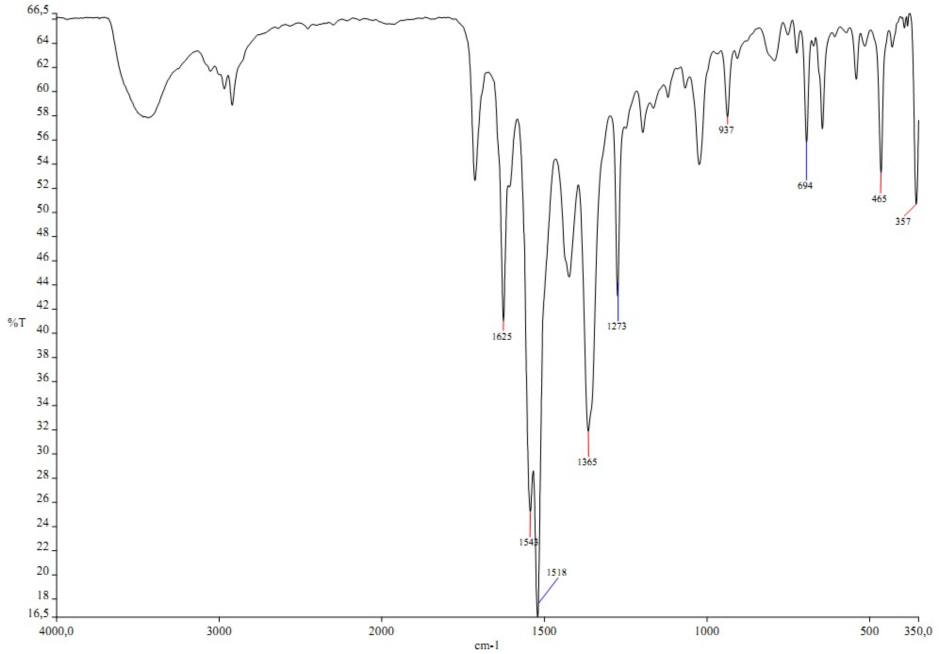


Figure S1. IR spectrum of $RuCl_2(acac)(acacH)$

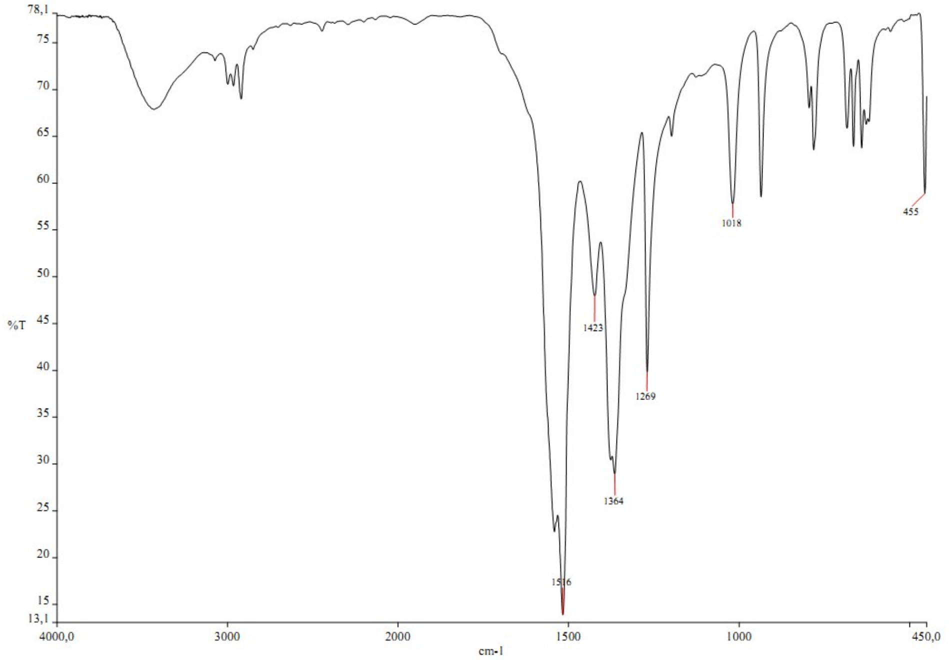


Figure S2. IR spectrum of $Ru(acac)_3$

Chemical treatments of Ru-deposits on glass. The chemical stability of Ru deposits on glass was tested under a number of different conditions. The treatment of mirrors with concd. HNO_3 (68%, 5 mL) or aqua regia (5 mL) did not produce any Ru leaching (as confirmed by ICP analyses) nor it removed the IL (organic support) from the deposits. They were stable even at the refluxing temperature. Analogously, the treatment of mirrors with organic solvents including acetone, methanol, and CH_2Cl_2 did not affect the deposits.

Mirrors however, were rapidly dissolved by aq. NaOCl (1% wt; 5 mL) at rt: under such conditions, an initial pale yellow solution was obtained which turned to brown on standing. Both the metal and IL were removed from the glass, the first (Ru) being converted to RuO_4.[4]

ICP analysis. ICP-OES analyses allowed to evaluate the amount of Ru present in the liquid mixtures recovered at the end of deposition experiments. Analyses were run in axial direction at 240.272 nm. A calibration curve was obtained by using seven aqueous solutions containing 0, 200, 500, 1000, 2000 ppb of Ru. These solutions were all prepared by dilution of a 1000 mg/L standard solution of $RuCl_3$ in HCl. The linear fit was automatically calculated by the ICP software resulting with interceptor= -2170.8, slope= 39.671 and correlation coefficient= 0.9976.

A total of six samples were considered for Ru-analyses. They were obtained according to the procedure described in the main text: three samples (A-C) derived from deposition experiments carried out in the presence of AcOH (Table 1, entry 2, main text), while other three samples (D-E) derived from tests with acetylacetone (Scheme 2, main text). Table S1 reports the results.

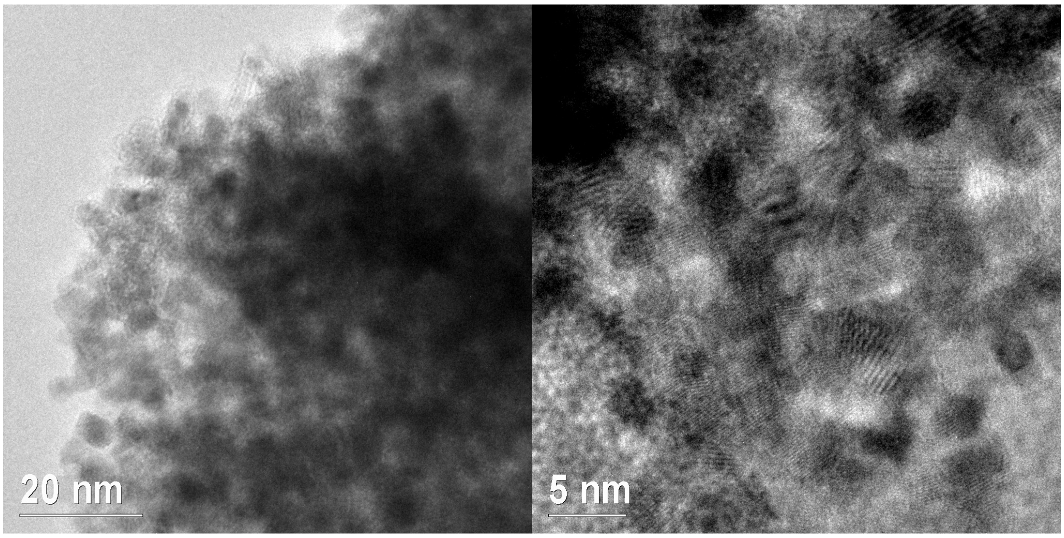
Table S1. ICP-OES analyses of the Ru content

Entry	Sample	Deposition procedure [a]	Ru content	
			(μg/L)[b]	Deposition yield (%)[c]
1	A	AcOH	2570	69
2	B	AcOH	2487	70
3	C	AcOH	2320	72
4	D	Acetyl acetone	2238	73
5	E	Acetyl acetone	1825	78
6	F	Acetyl acetone	1661	80

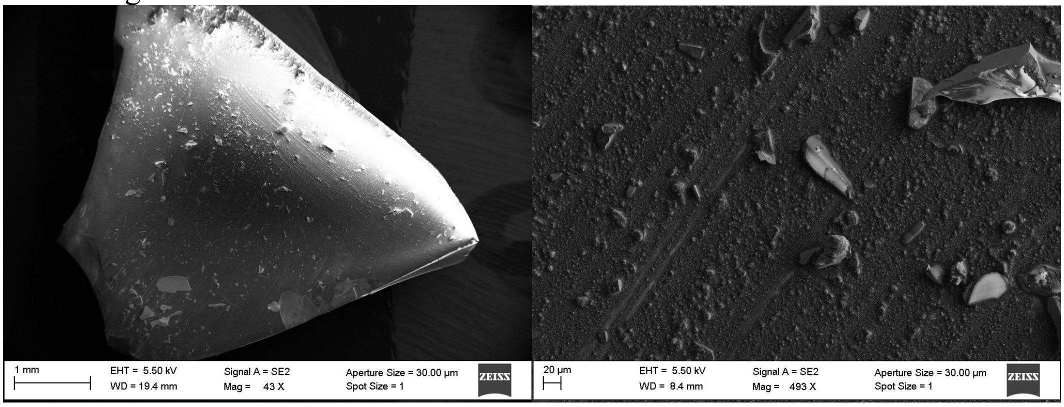
[a] Samples A-C: conditions of entry 2, Table 1 (main text); Samples D-E: conditions of Scheme 2 (main text). [b]Amount of Ru determined in the liquid mixtures recovered at the end of deposition tests. [c]Amount of Ru on mirrors: this was estimated by the difference between the total quantity of the used metal (from starting $RuCl_3$) and the quantity of residual Ru in the liquid mixtures after the formation of mirrors.

Selection of TEM and SEM Images.

*Specimen **A** (Table S1)*
TEM images:

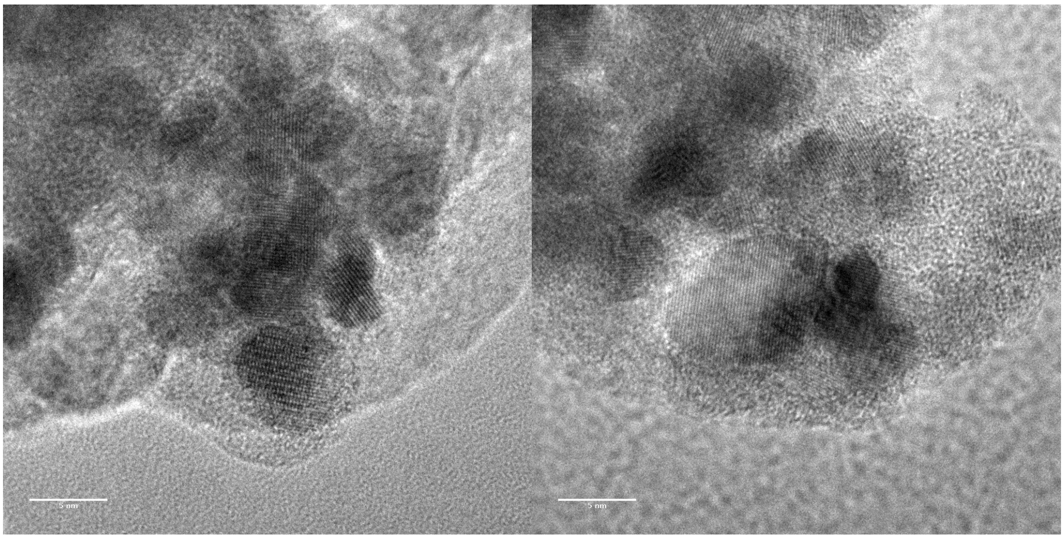


SEM images:



*Specimen **D**, Table S1*

Tem images:



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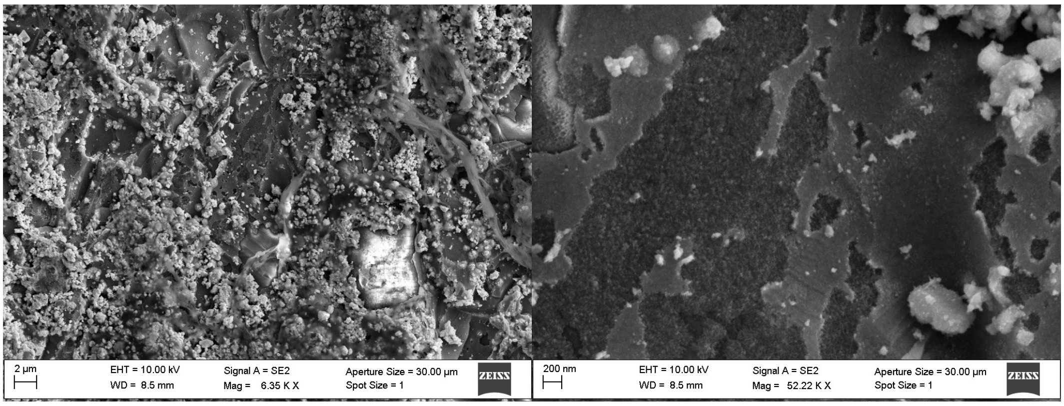

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