

**Design and Performance of a Dual-Polarity Instrument for Ion Soft landing**

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## Experimental Section

### Chemicals

Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ( $\text{Ru}(\text{bpy})_3 \cdot 6\text{H}_2\text{O}$ , CAS: 50525-27-4), Neutral Red ( $\text{C}_{15}\text{H}_{17}\text{ClN}_4$ , CAS: 553-24-2), sodium phosphotungstate tribasic hydrate ( $\text{Na}_3[\text{PW}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ , CAS: 12026-98-1), sodium phosphomolybdate hydrate ( $\text{Na}_3[\text{PMo}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ , CAS: 1313-30-0) and 1H,1H,2H,2H-perfluorodecanethiol (FSAM,  $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{SH}$ , CAS: 34143-74-3) were purchased from Sigma-Aldrich (St. Louis, MO) and were used to demonstrate the instrument performance.

### FSAM Surface Preparation

An FSAM on a gold surface was prepared as follows: a 10 × 10 mm gold coated silicon wafer (100 nm Au layer and 5 nm Ti adhesion layer, Platypus Technologies, Madison, WI) was ultrasonically washed in methanol, cleaned by a UV Ozone cleaner and immersed in a glass scintillation vial containing a 15 mM solution of FSAM in methanol. The monolayer was allowed to assemble for at least 12 h and then ultrasonically washed for 5 min in methanol. The surface was subsequently rinsed with methanol, dried under nitrogen and mounted on the sample holder in the soft landing chamber.

### Surface Characterization

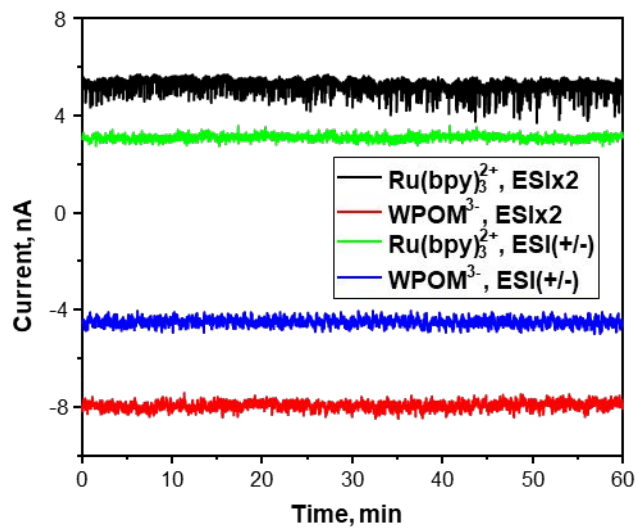
Infrared reflection absorption spectroscopy (IRRAS) measurements were performed using a Bruker Tensor II FTIR spectrometer (Bruker Optics, Billerica, MA) equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. Surfaces were mounted onto an 80° reflection unit in the chamber of the spectrometer. IRRAS spectra were acquired at a spectral resolution of 4  $\text{cm}^{-1}$  using p-polarized light. Each spectrum was collected by averaging 2000 scans corresponding to a 5-minute acquisition time. The experimental IRRAS plots were processed using water subtraction and baseline-correction options of the OPUS software.

Visible spectroscopy characterization of on the surfaces was performed using

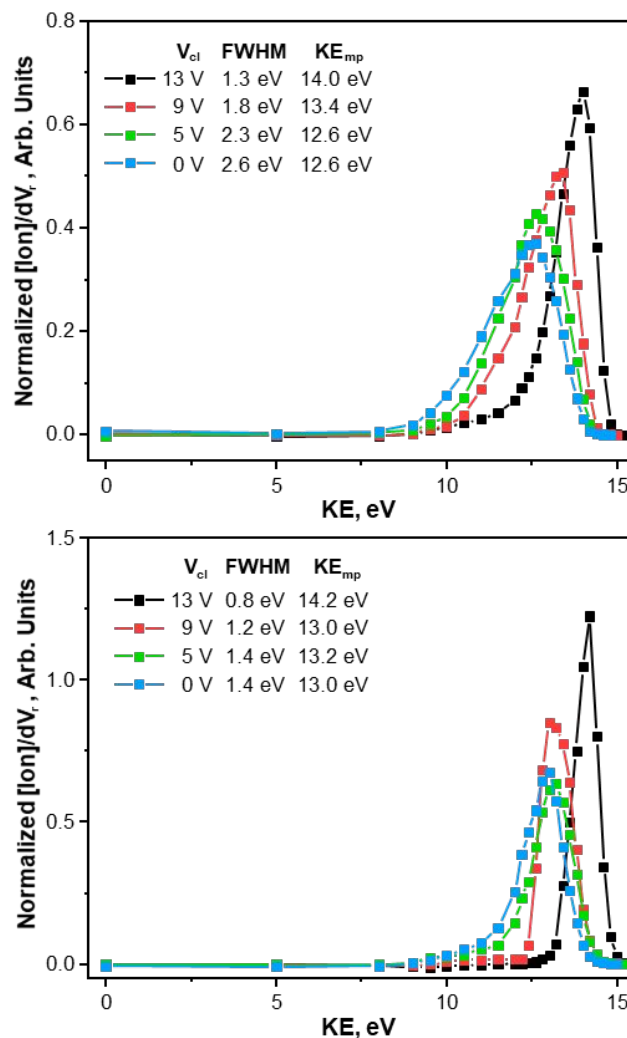
a R600-8-VisNIR reflectance probe connected to a BLK-CXR spectrometer and a SL1 Tungsten-Halogen visible-NIR light source (Stellarnet, Tampa, FL). Visible spectrum of a clean Au-FSAM surface was used as the reference. The spectra were collected using the SpectraWiz software.

Visible spectroscopy characterization of solutions was performed using an QP450-1-XSR optical fiber patch cords connected to USB2000+UV-VIS spectrometer and a DH-2000-DUV-TTL Deuterium Halogen light source (Ocean Optics, Largo, FL). Visible spectrum of methanol was used as the reference. The spectra were collected using the OceanView software.

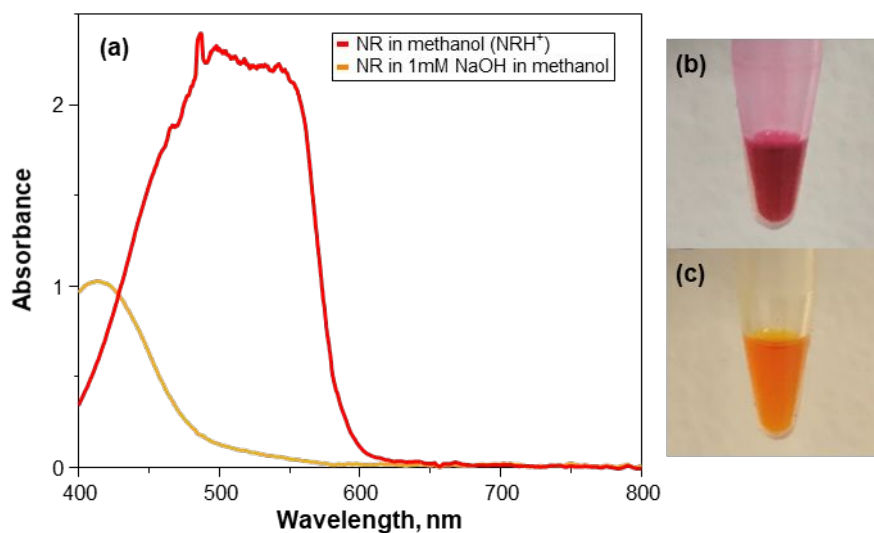
Extraction ESI-MS analysis of the surface was performed by dissolving the deposited material with 80  $\mu\text{L}$  methanol and analyzed using Q-Exactive HF-X Hybrid Quadrupole-Orbitrap Mass Spectrometer (Thermo Fisher Scientific GmbH, Bremen, Germany). Sample was introduced into the MS inlet by direct infusion from a capillary (50  $\mu\text{m}$  ID, 150  $\mu\text{m}$  OD) at a flow rate of  $\sim 0.5$   $\mu\text{L}/\text{min}$ . Typical mass spectrometer conditions on Q-Exactive were as follows: electrospray voltage:  $\pm 3$  kV, capillary temperature: 250  $^{\circ}\text{C}$ , RF funnel level: 100. Mass spectra were acquired over 150-2000  $m/z$  at 240000 resolution ( $m/z$  400).



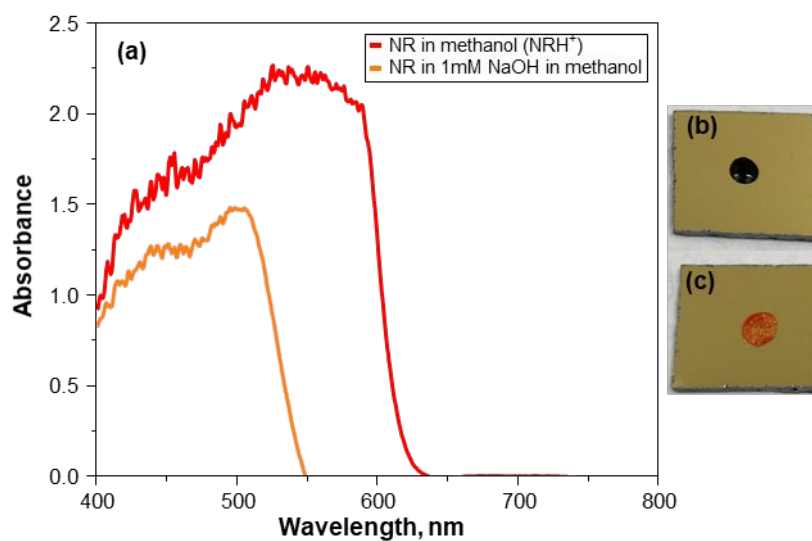
**Figure S1.** Ion current stabilities of mass-selected  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{WPOM}^{3-}$  in  $\text{ESI}\times 2$  or  $\text{ESI}(+/-)$  modes over one hour time period.



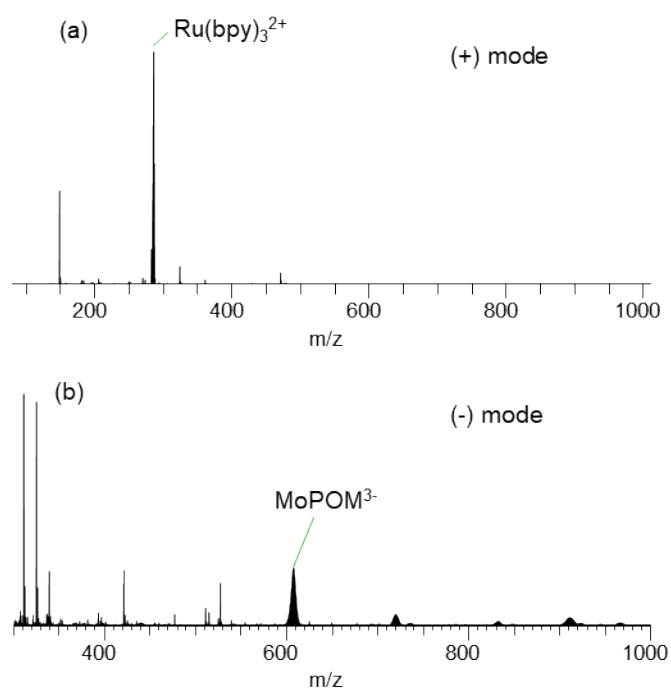
**Figure S2.** Ion kinetic energy distributions (KEDs) of Ru(bpy)<sub>3</sub><sup>2+</sup> (a) and WPOM<sup>3-</sup> (b) acquired at different voltages on the conductance limit ( $V_{cl}$ ). The flatapole bias was kept at +14 V/-14 V for Ru(bpy)<sub>3</sub><sup>2+</sup> and WPOM<sup>3-</sup>, respectively. The FWHM and most probable kinetic energy (KE<sub>mp</sub>) of each KED plot was shown on the top left corner of each figure.



**Figure S3.** (a) Visible spectra of 1 mM Neutral Red in methanol (red) and in a solution of 10 mM NaOH in methanol (yellow). Optical images of the solutions are shown on the right: (b) NR in methanol, (c) NR in 10 mM NaOH in methanol.



**Figure S4.** (a) Visible spectra of solutions of 1 mM Neutral Red in methanol (red) and in a solution of 10 mM NaOH in methanol (yellow) dropcasted onto FSAM surfaces. Optical images of the dropcasted spots are shown on the right: (b) NR in methanol, (c) NR in 10 mM NaOH in methanol.



**Figure S5.** Extraction ESI-MS spectra of the layer prepared by co-deposition of  $\text{Ru(bpy)}_3^{2+}/\text{MoPOM}^{3-}$  in positive (a) and negative (b) modes.