

Supplementary Information:
Ultrafast excited states dynamics of $[\text{Ru}(\text{bpy})_3]^{2+}$
dissolved in ionic liquids

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S1: Cross-Correlation on the bare Ionic Liquid:

Temporal Resolution

To reveal possible contributions from the bare ionic liquid (IL) to the transient signal of the sample containing the metal complex, pump-probe measurements on the bare IL were conducted. These test measurements facilitate to determine the time response in experiment as well as to ensure that the presence of contamination is negligible. Without the presence of resonant excited states, the process of non-resonant multiphoton ionization occurs when pump and probe pulses overlap in time. This effect, also called laser-assisted photoelectric effect from a surface^{1,2}, involves absorption of an XUV probe photon simultaneously with absorption or emission of one or more pump photons. Hence, sidebands in the XUV photoemission spectrum arise and their magnitude as a function of the pump-probe time delay represents the cross correlation (CC) signal of the pump and the probe beams. The CC width, determined by the widths convolution of the pump and probe pulses, constitutes the time response. The CC signal recorded with the bare IL sample is shown in Fig. S1. A fit of the experimental data to a Gaussian profile yields a width of 110 ± 5 fs (FWHM).

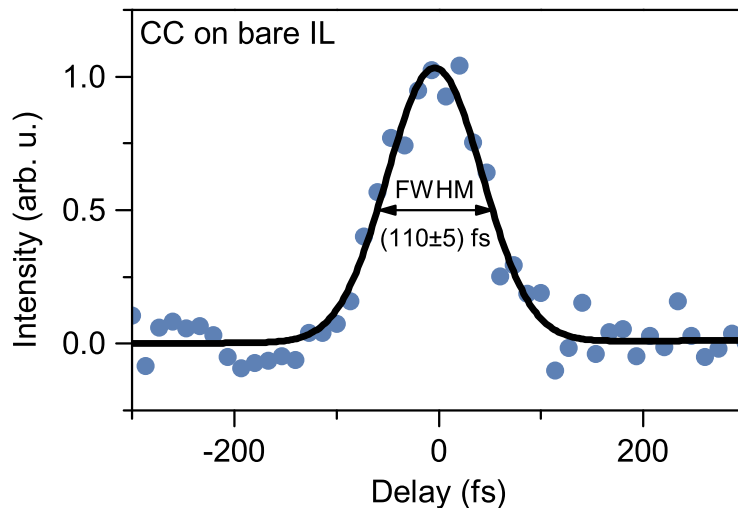


Figure S1: Cross correlation measurements performed with the bare IL sample. The background-subtracted transient signal is shown by circles. The solid curve represents the fit of the CC trace to a Gaussian profile, yielding a CC width of 110 ± 5 fs (FWHM).

It is important to note that the CC trace appears to be highly symmetric. This ensures

that the pump beam does not initiate any fast or slow electron population dynamics in the bare sample. Any dynamics of transient excited states would lead to an asymmetric shape. Thus, it is concluded that laser assisted ionization is the only process that takes place in the bare IL.

S2: Long-term Stability and Sample Damage

The stability of IL under exposure to XUV radiation represents an important issue in the present study. Sample damage or diffusion might be possible effects giving rise to unintended spectral changes. Therefore, XUV spectra for the bare IL and the solute-containing sample were recorded over a time span of several hours.

Results obtained for the bare IL are presented below first. Fig. S2(a) shows exemplary spectra acquired after three different XUV exposure times: 0h (fresh sample), 1h exposure, and 14h exposure. The signal was normalized according to the applied XUV intensity which was monitored during the experiment. In the binding energy range between 4.5 and 7 eV, the spectra exhibit no distinct differences. The photoemission yield integrated over this energy range is shown in Fig. S2 (b) by red dots as a function of the exposure time (also denoted by int1). Note that the integrated yield is normalized to the value of the fresh sample and is assigned to 1. The absence of any variation in the shown dependence confirms the stability of XUV spectra in this energy range.

In contrast, a variation of the XUV spectra in the range of binding energies between 4.5 and 1eV can be observed. To quantify the spectral changes as a function of the exposure time, the photoemission yield was integrated over this range of binding energies. The results are shown in Fig S2 (b) by blue dots (also denoted by int2). The changes exhibit no distinct structure. From the dependence of the integrated yield on the exposure time, it can be seen that the appearance of the additional shoulder in the spectrum (see Fig. S2(a)) is randomly distributed in time. Approximately after one hour of illumination, it starts to grow on a timescale of less than 30 minutes. Afterwards, the yield stabilizes for one hour before it starts

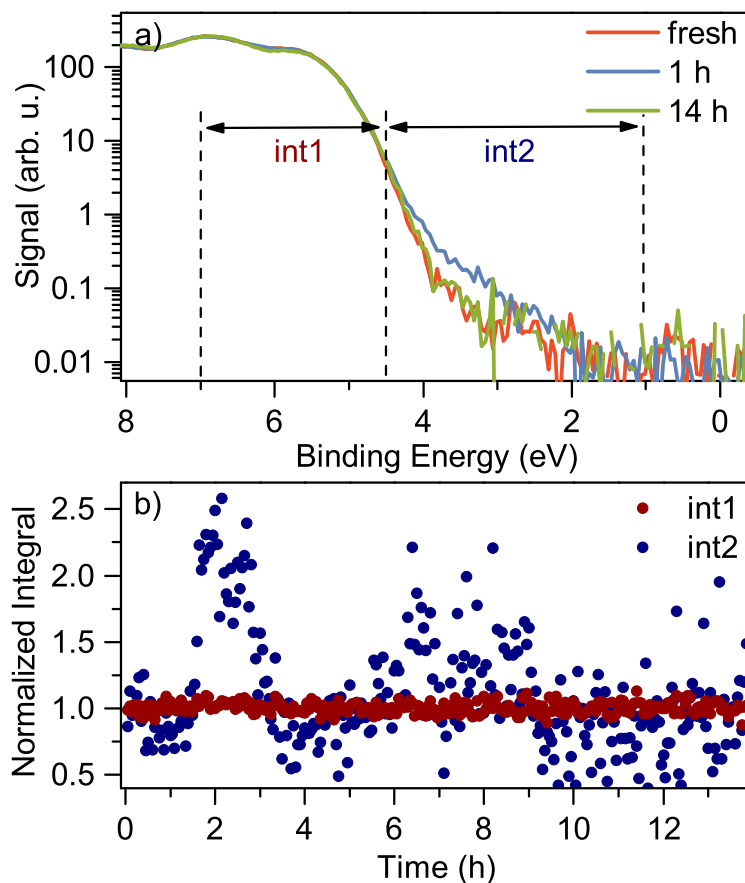


Figure S2: Steady-state XUV spectra of the bare IL obtained in the beginning of exposure to the XUV beam (red line, fresh), after an exposure time of 1 hour (blue line, 1h) and 14 hours (green line, 14h). Bottom panel: Ionization yield integrated over the range of binding energies between 7 and 4.5 eV (int1, red dots) and between 4.5 and 1 eV (int2, blue dots) as a function of the XUV exposure time.

to decrease again. Such a behavior is repeated again at later time. However, the spectra acquired with the fresh sample and after 14h of exposure appear to be identical. This finding leads to the conclusion that the spectral changes are reversible. A possible origin can lie in the fact that the liquid sample consists of ions which are able to randomly move from the bulk to the surface and vice versa. Since IL is an ionic conductor, a directed transport in the form of ion flow is required to recharge the photo-ionized sample surface. This might lead to a continuous ion exchange in the probed sample. Thermal instabilities and other experimental circumstances can influence the formation of a steady flow.

The obtained results do not reveal any clear indications of sample damage in terms of

chemical changes. One should not exclude that the above mentioned ion exchange can lead to a refreshment of the sample surface in a continuous way and, thus, to the surface recovery from damages in single molecules.

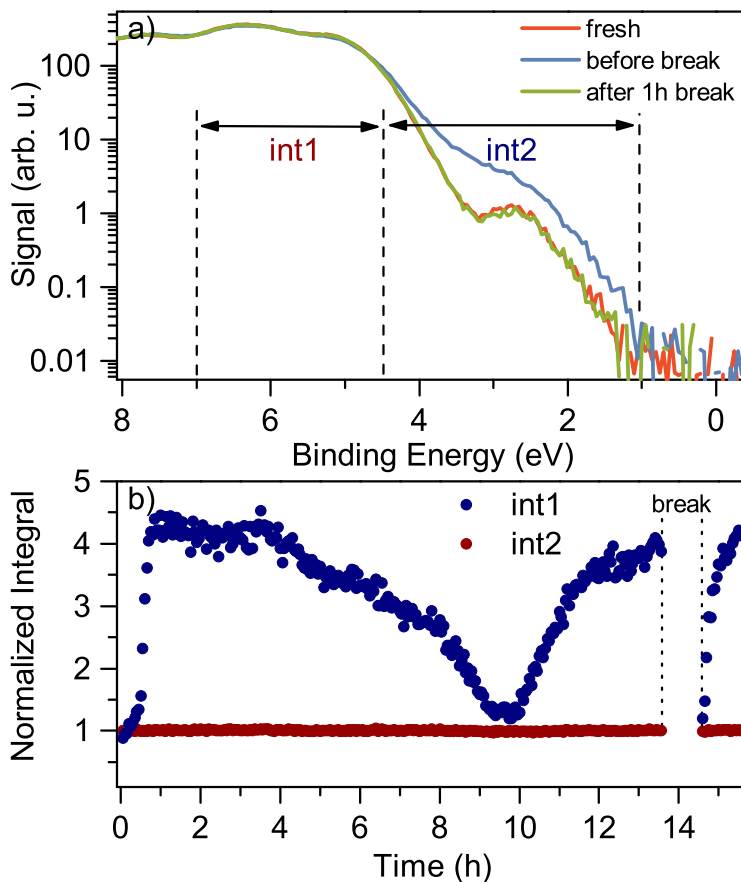


Figure S3: Steady-state XUV spectra of the IL containing $[\text{Ru}(\text{bpy})_3]^{2+}$ obtained in the beginning of the exposure to the XUV beam (red line, fresh), after an exposure time of 13 hours (blue line, before break) and after a break of 1 hour (green line, after 1h break). Bottom panel: Ionization yield integrated over the range of binding energies between 7 and 4.5 eV (int1, red dots) and between 4.5 and 1 eV (int2, blue dots) as a function of the XUV exposure time.

Figure S3 illustrates the steady state spectra recorded for the solute-containing IL. For this sample, the HOMO band contribution of the dye is clearly apparent in the spectra. One can see that the spectra exhibit changes which are very similar as in the previous investigation. The same two energy intervals were used to calculate the integrated yield which is shown in Fig. S3(b). For the range of higher binding energies (int1) a constant

yield is observed, whereas for the lower energy part (int2) variations in the integrated yield are present. As a supplementary measurement, the XUV exposure was interrupted for one hour after 13.5 hours of continuous illumination. The spectra recorded immediately after the break appeared to be rather identical to the spectrum of the fresh sample. However, the same tendency in spectral changes starts arising again, and after one hour of exposure the deviation of the integrated yield reaches similar amplitude as before the break. This finding provides further support for the conclusion that irradiation by XUV beam induces an ion flow which neutralizes the deficiency of negative charges at the samples surface caused by photoemission. However, the charge equilibrium seems to be unstable, leading to the observed fluctuations. Another finding is the fact that the dyes HOMO band appears identical in the spectrum after enduring XUV exposure (see Fig. S3(a)). This implies that the spectral changes are related solely to ionization of IL. Even if degradation of the dye is present, the continuous ion flow at the surface seems to renew the surface coverage.

The found instabilities complicate investigation of the electron dynamics in solute molecules. Nevertheless, the spectral changes appear on a much longer timescale than a typical duration of 20 minutes of pump-probe scans. This yields the possibility to perform a proper background correction.

S3: Time dependence of the transient signal at different binding energies

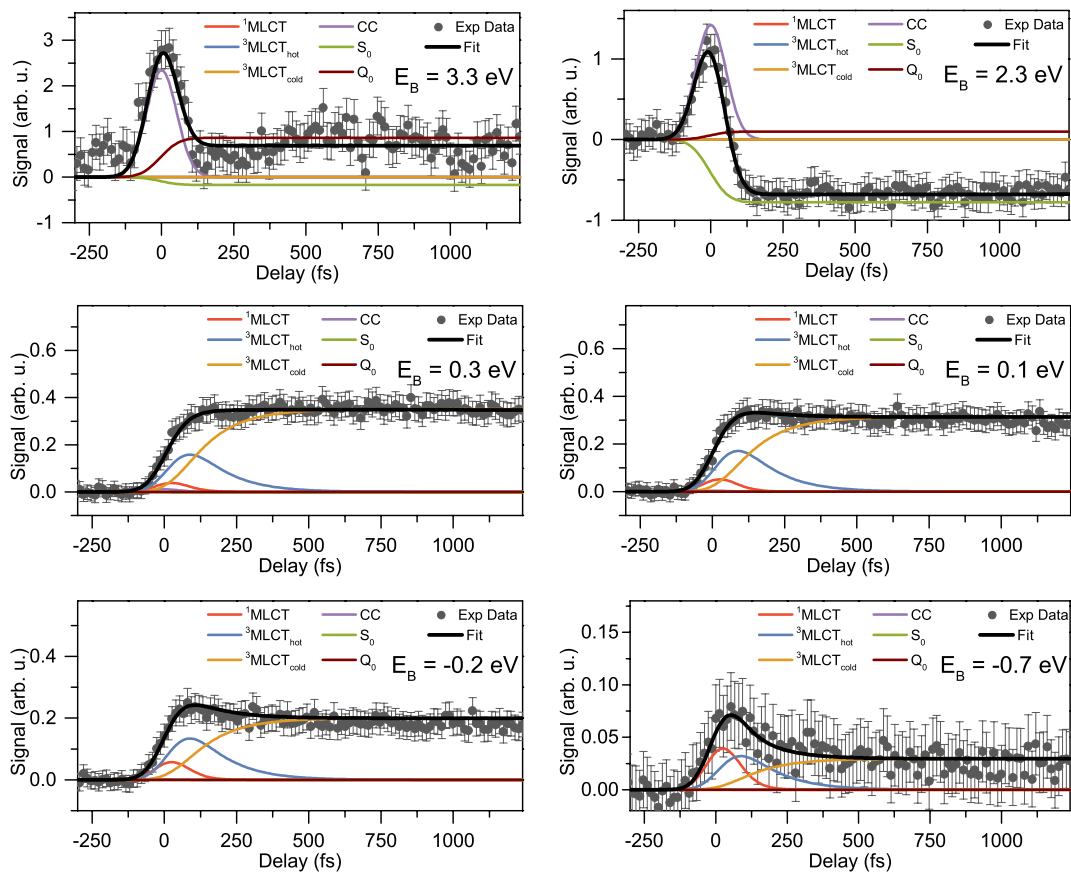


Figure S4: Time dependence of the transient signal at different binding energies indicated in each panel individually.

S4: Energy dependence of the transient signal for different pump-probe time delays

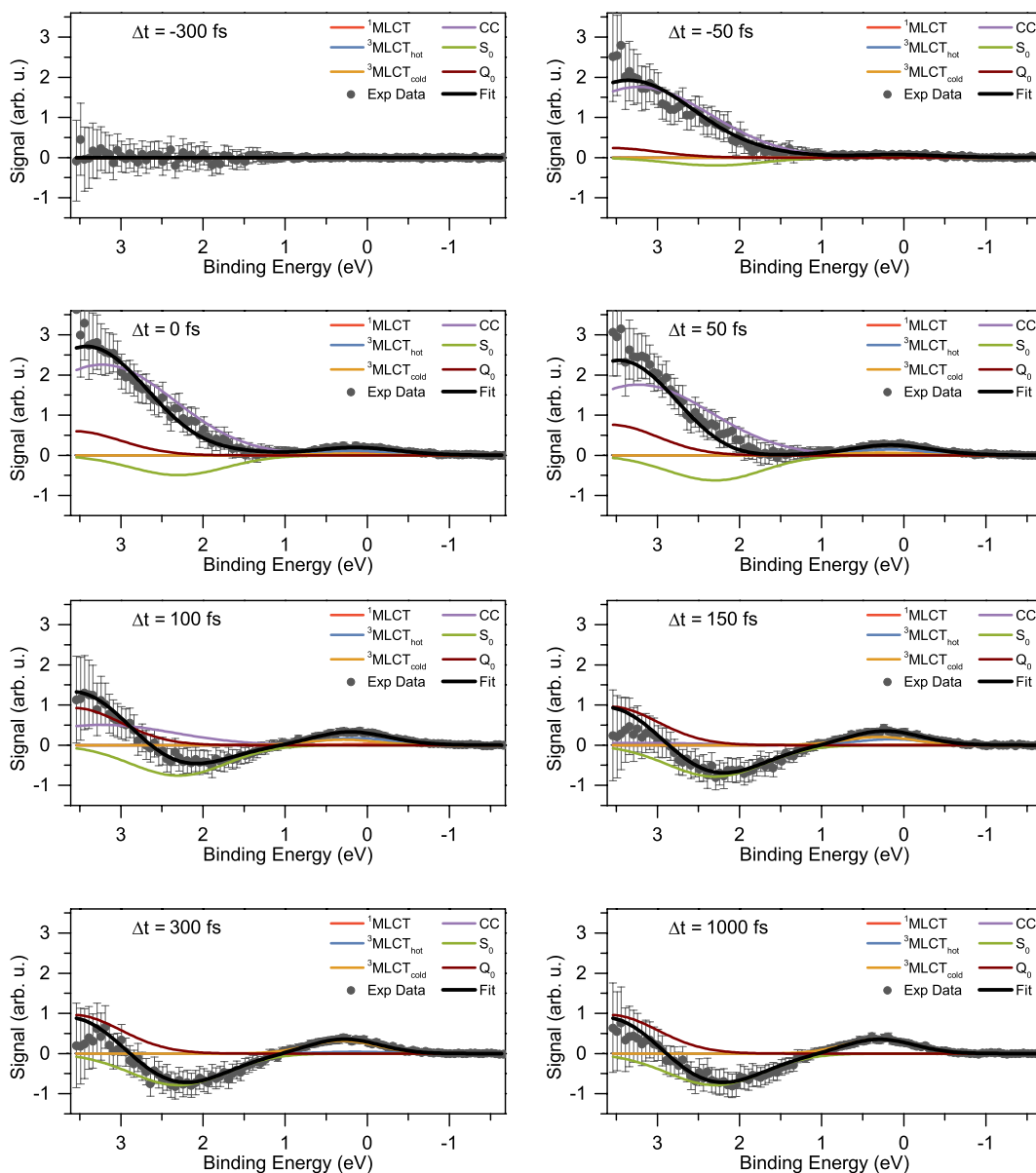


Figure S5: Energy dependence of the transient signal at different pump-probe time delays indicated in each panel individually.

References

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