

## SUPPLEMENTARY INFORMATION

### A. Sodium K-edge X-ray absorption spectra of NaI and NaBr

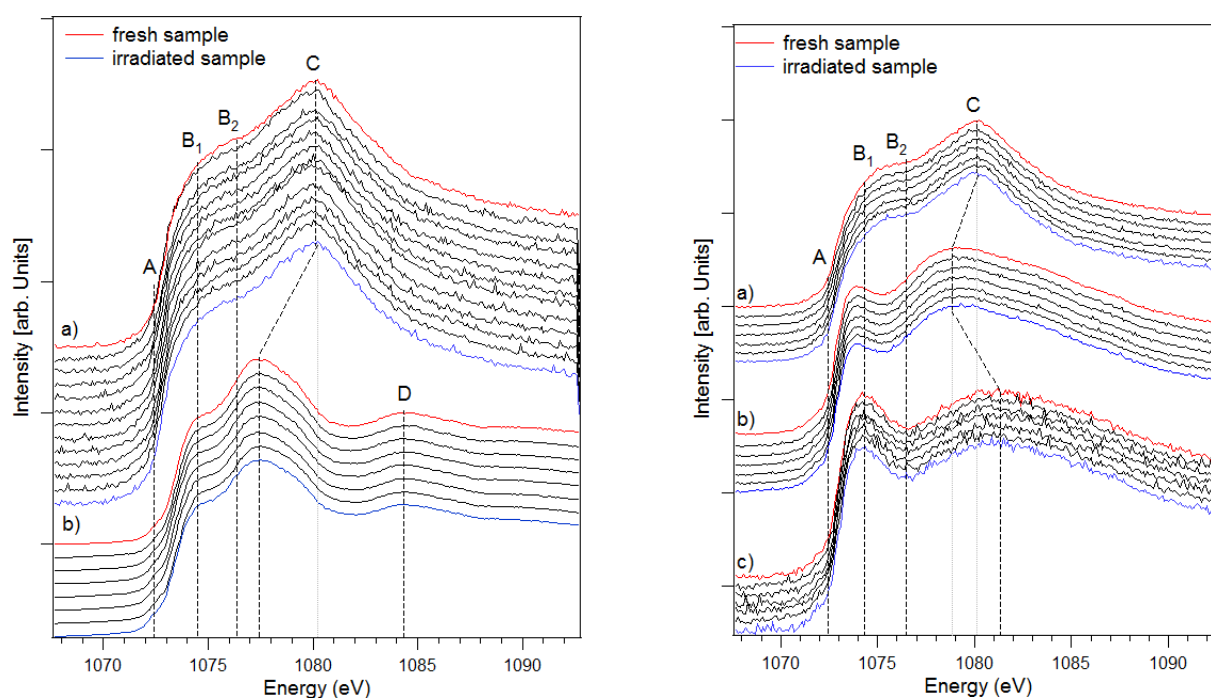


Fig S. 1: Time dependent spectral measurement of NaI in a) water and b) propanol (left), and NaBr in a) water, b) methanol and c) ethanol as solvents (right). The shape and positions of the peaks (A;B<sub>1</sub>;B<sub>2</sub>;C;D) are characteristic for each solvent. The series of spectra of NaI and NaBr are displayed for increasing stages of irradiation, beginning with the spectra of the fresh samples (red).

### B. XA Spectroscopy

NEXAFS measurements at the sodium K-edge were performed at the U-41 PGM beamline at BESSY II, Berlin. The liquid samples were circulated with a flow of 1 l/min through a flow cell (made of stainless steel), directly behind a 150 nm thick Si<sub>3</sub>N<sub>4</sub> membrane window allowing the irradiation by soft X-rays. The Na K-edge spectra were measured with a resolution of 200 meV. Due to the soft X-ray attenuation length in the liquids in the range of a few microns, the detection was primarily bulk sensitive and surface effects were neglected. The absorption spectra were recorded in the total fluorescence yield mode using a 25 mm<sup>2</sup> GaAsP photodiode (type Hamamatsu G1127-04). The diode was mounted in a distance of 4 mm from the membrane window and with an angle of 45° relative to the X-ray beam. The solutions measured were, nominally 1 M NaI dissolved in water, in ethanol, and in methanol. Due to the low solubility of NaI in propanol, a lower actual concentration of 0.1775 M NaI was chosen for this measurement. For comparison, the spectra of 1 M NaBr in water, in ethanol and in methanol were recorded as well. Between measurements of different solutions, the flow cell was cleaned by flushing it with deionized water. To avoid uncertainties in the electrolyte concentration, the cell was rinsed once with the solution to be measured before each measurement. The setup allowed us to probe the solutions as a function of irradiation time. Therefore, each sample circulated several times through the flow cell and was measured in fixed time intervals. The data

collection time for a single spectrum was 251 seconds. To increase the effect of the X-ray on the liquid, the cell was continuously irradiated between the measurements as well, thus giving the respective direct X-ray irradiation time dependence.

### C. Mass spectroscopy

For the investigation of the solvents with gas chromatography/ mass spectrometry (HP G1800 A GCD system, Agilent, Waldbronn), 50 l of the reaction mixture were placed in a sealed glass vial and equilibrated to 50 °C for ten minutes. From the headspace, 0.5 l were injected onto a HP5-MS column (30 m, 0.25 mm) which was maintained at 25 °C for two minutes, then heated to 50 °C during the next minute. Hydrogen served as carrier gas at a flow rate of 1 ml/min with an inlet temperature of 50 °C.

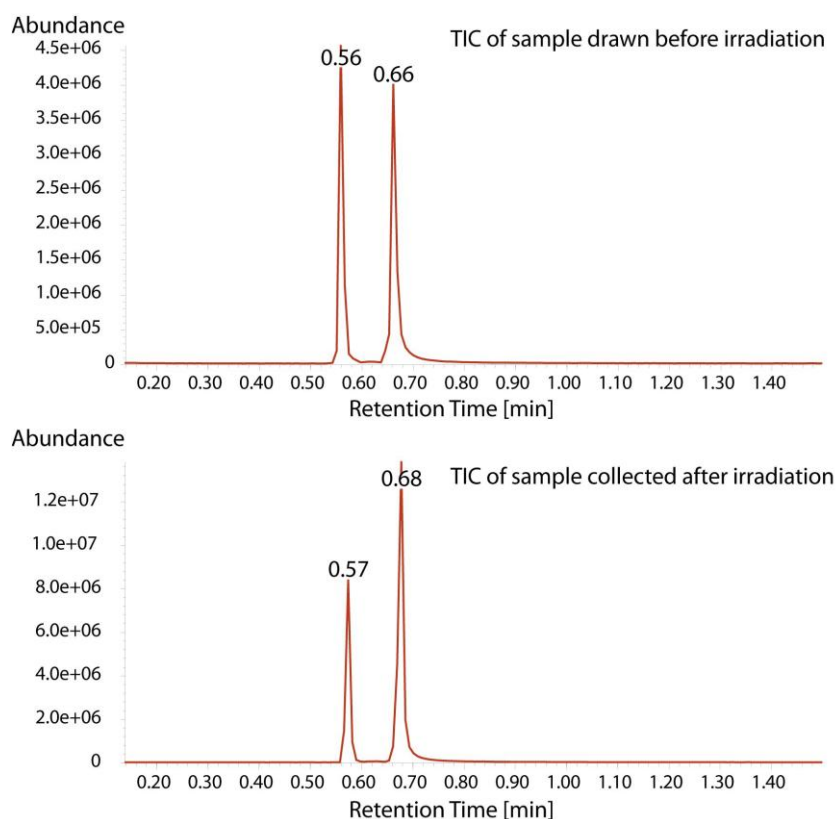


Fig S. 2: The total ion chromatograms (TIC) of the GCMS analyses show only one peak at 0.67 min arising from the neat solvent. At 0.56 min, the system peak is detected which indicates the void time of the system and which is also present in blank runs. No other peaks are detectable, indicating that the solvent is not affected by irradiation.

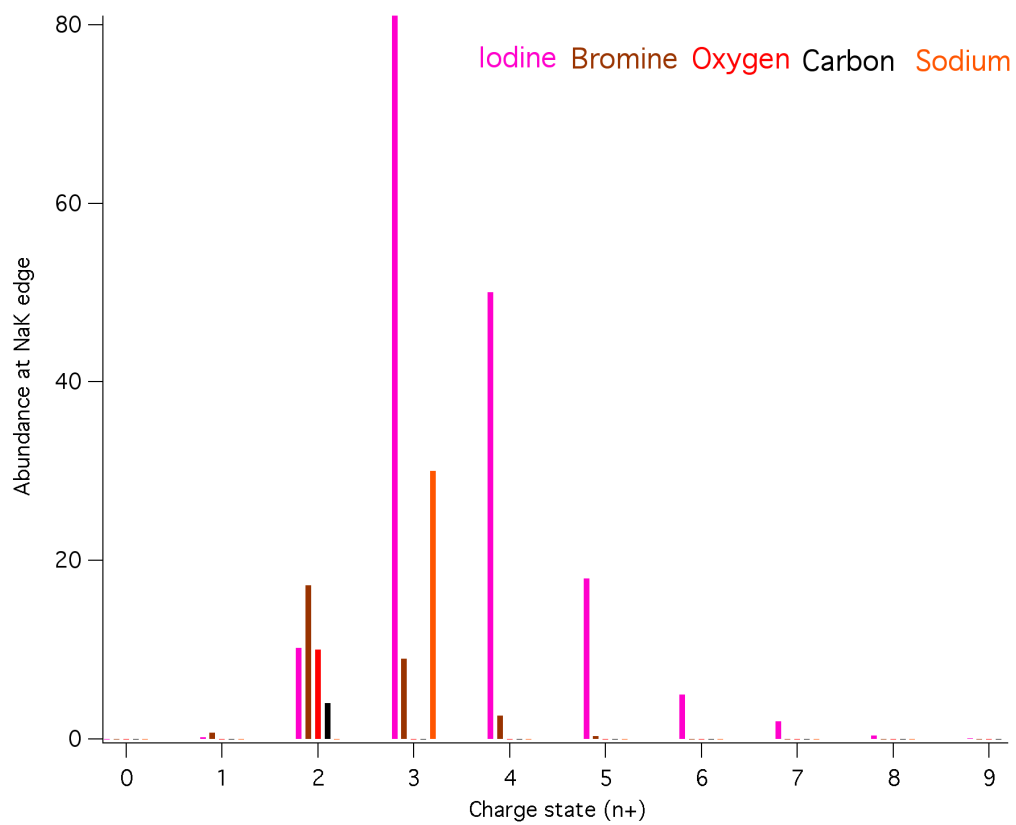


Fig S. 3: Charge states of iodine, bromine, oxygen, carbon and sodium at the sodium K-edge.