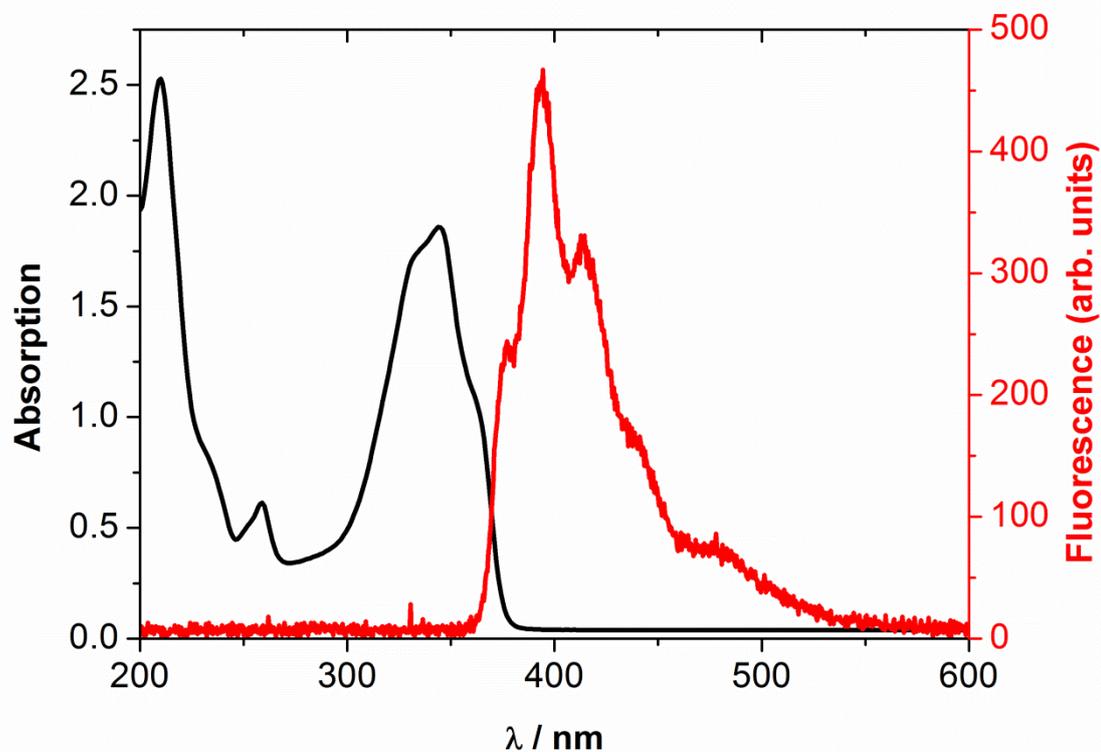
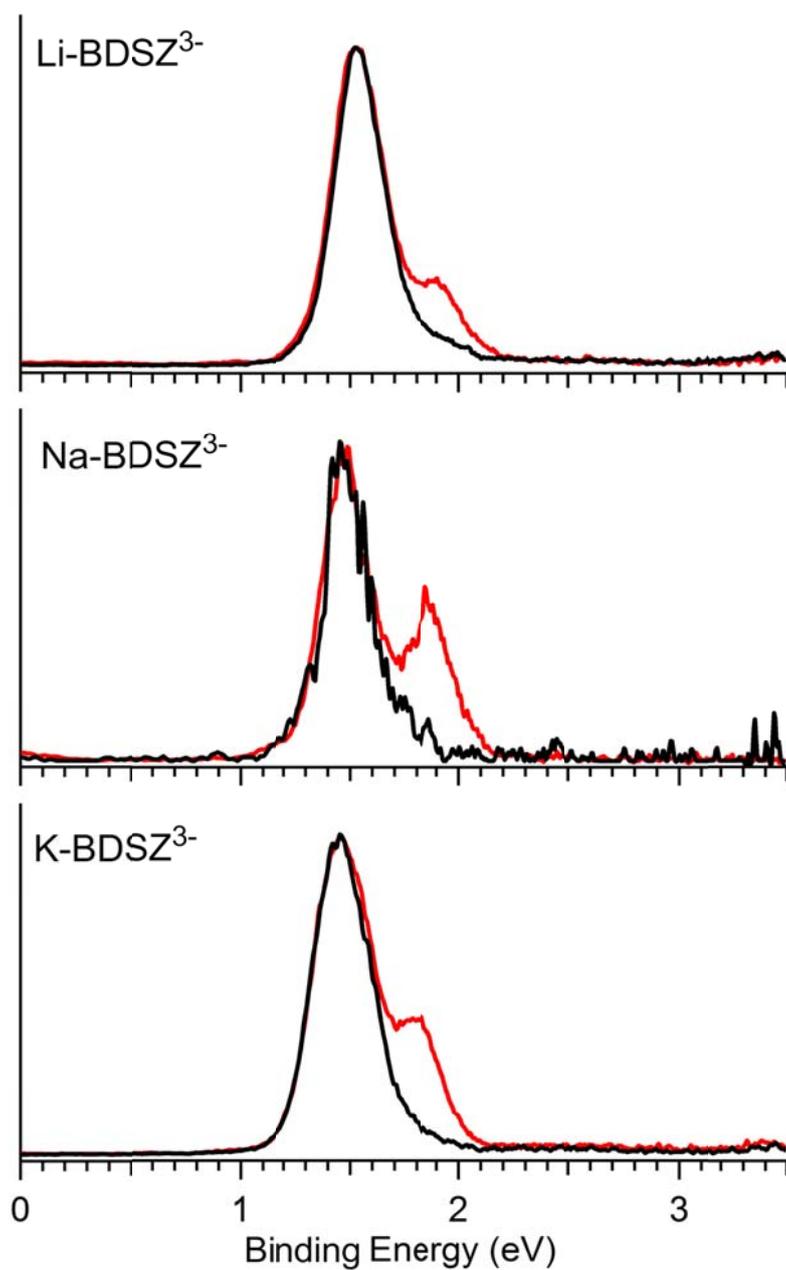


"Electron Tunneling from Electronically Excited States of Isolated Bisdisulizole-Derived Trianion Chromophores Following UV Absorption", M.-O. Winhart et al., Electronic Supplementary Information (PCCP C3CP50497B)

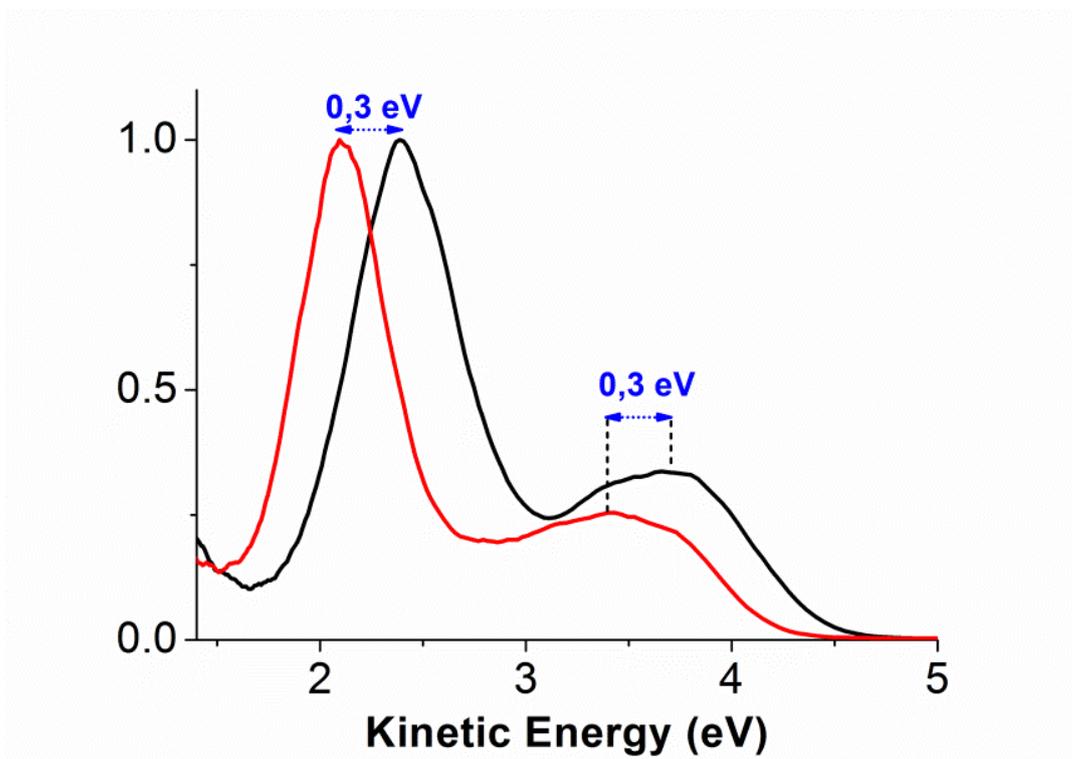
Supplemental Figures (S=supplemental data)



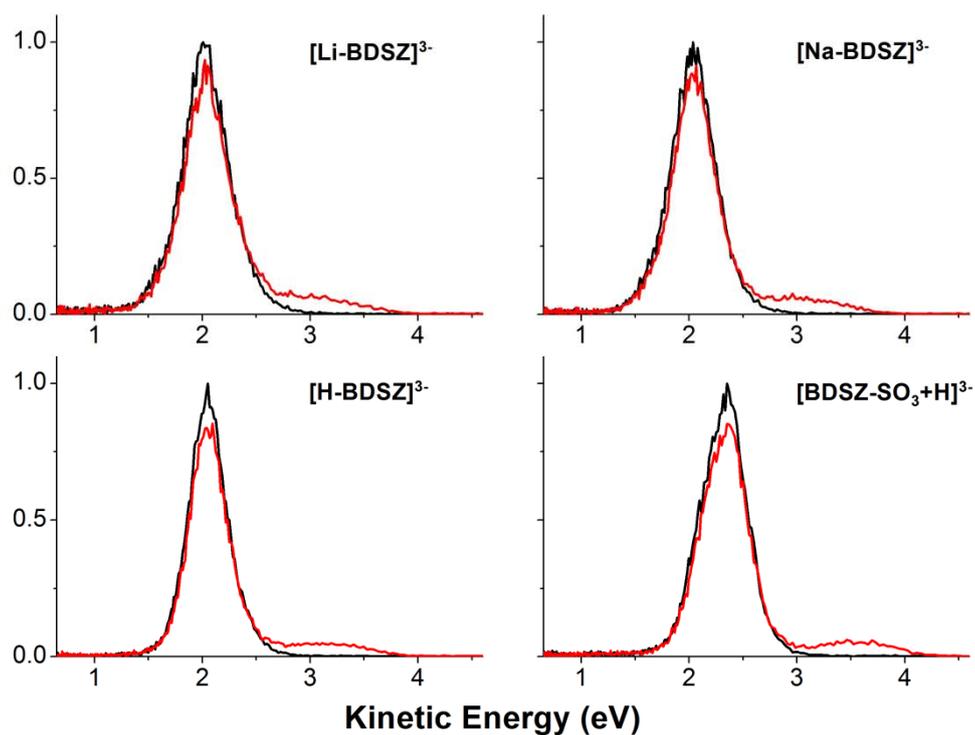
**Figure S1.** Absorption and fluorescence measurements of Na<sub>2</sub>H<sub>2</sub>-BDSZ in water/methanol at room temperature (absorption measurement: 0.4 mM; fluorescence measurement: 2 mM).



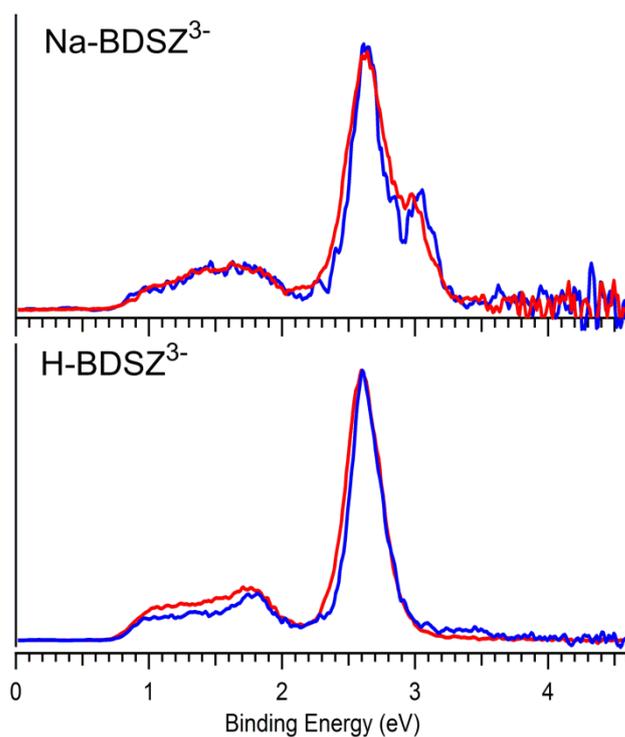
**Figure S2.** Single-photon 355 nm PES spectra of  $[M\text{-BDSZ}]^{3-}$  ( $M = \text{Li, Na, K}$ ) acquired under two different ESI source temperature conditions. When the dissolution capillary was operated at room temperature, only one conformer was observed. At 57 °C, two conformers were observed (red). All time-resolved data reported in this study were measured under conditions in which only one conformer was present.



**Figure S3.** Comparison of the single-photon PES measurement (258nm detachment wavelength) obtained for  $[\text{BDSZ-SO}_3+\text{H}]^{3-}$  (black curve) with a typical PES recorded for  $[\text{M-BDSZ}]^{3-}$  (represented here by  $[\text{K-BDSZ}]^{3-}$ , red curve). Note a systematic energy shift of both the tunneling signal and ADE by 0.3 eV.



**Figure S4.** Comparison of pump + probe PE spectra at maximum temporal overlap (red) with pump only PE spectra (black) - for several  $[M\text{-BDSZ}]^{3-}$  and  $[\text{BDSZ-SO}_3\text{+H}]^{3-}$ . Laser pulse energies were 40/190  $\mu\text{J}$  at 388/775 nm, respectively. Note the observation upon probe irradiation of a depletion peaking at ca. 2.1 eV - together with a two-photon enhancement at an electron kinetic energy near 3.5 eV. In all cases, integral depletions of the 2.1 eV feature were comparable to integrated two photon transients in the 2.6-4.0 eV range, indicating that ESETD is the dominant decay process.



**Figure S5.** Single-photon PES measurements of  $[M\text{-BDSZ}]^{3-}$ ,  $M = \text{H}$  and  $\text{Na}$ , at 266 nm and two different ion trap temperatures: blue - 20 K; red - room temperature. Note that only slight differences in band widths were observed for cold anions.