Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

Preparation and Luminescence of the Homoleptic Cluster Cation $[(W_6I_8)(CH_3CN)_6]^{4+}$

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Figure S1. Crystals of **III** under VIS (left side) and UV (right side) irradiation

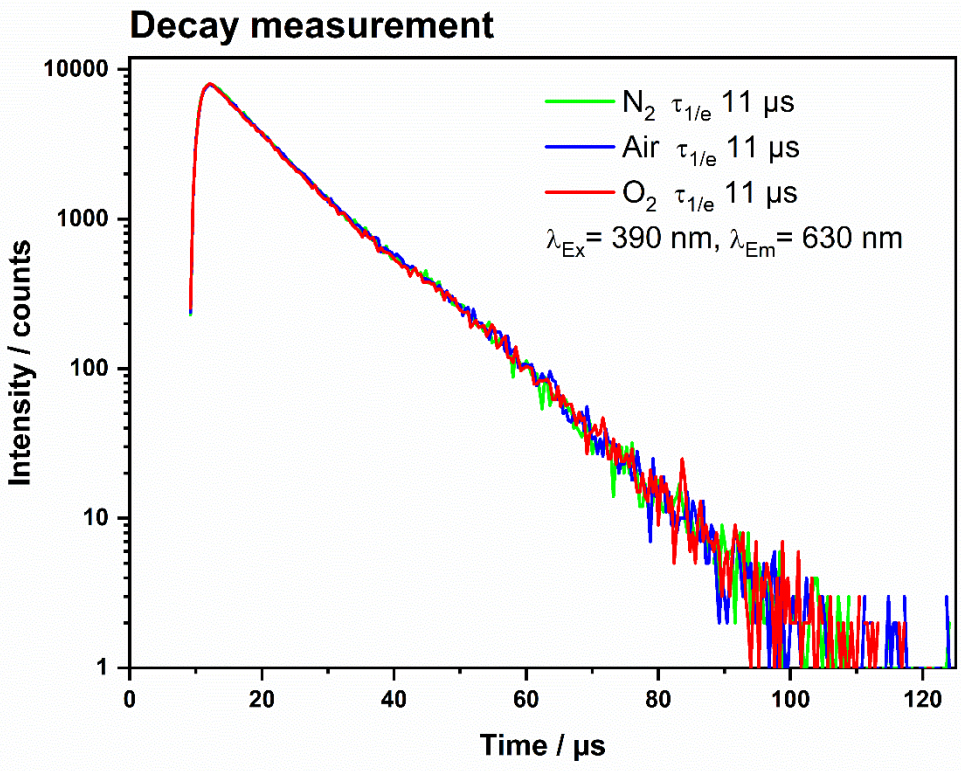

Figure S2. Decay measurement of solid **III**.

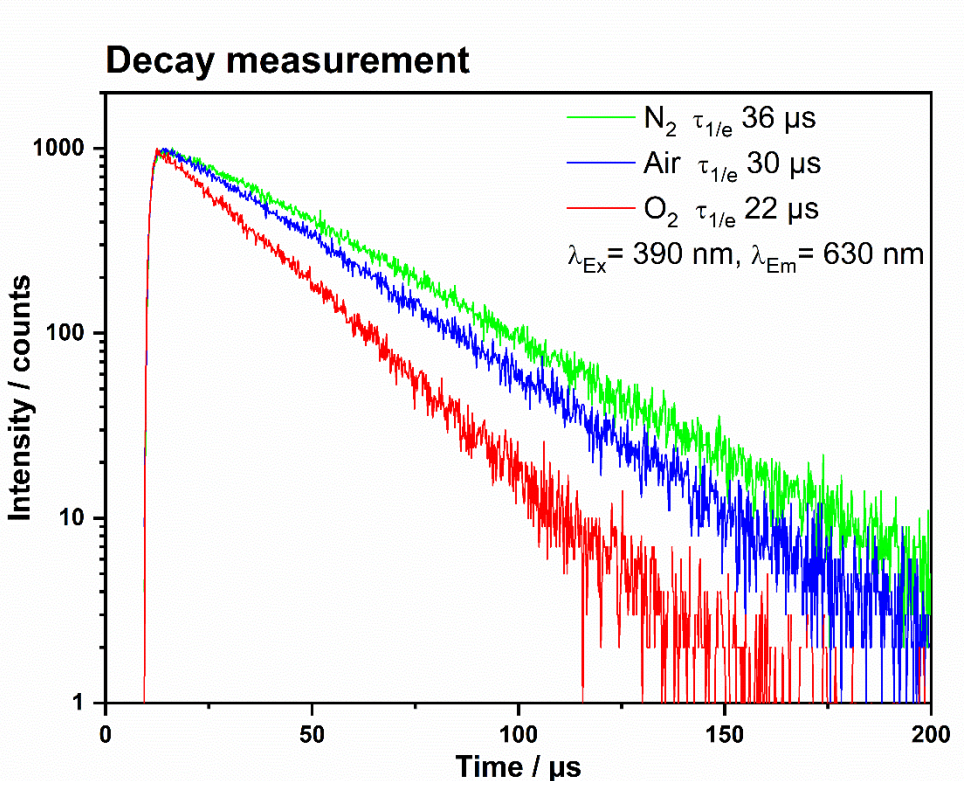

Figure S3. Decay measurement of solid $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$.

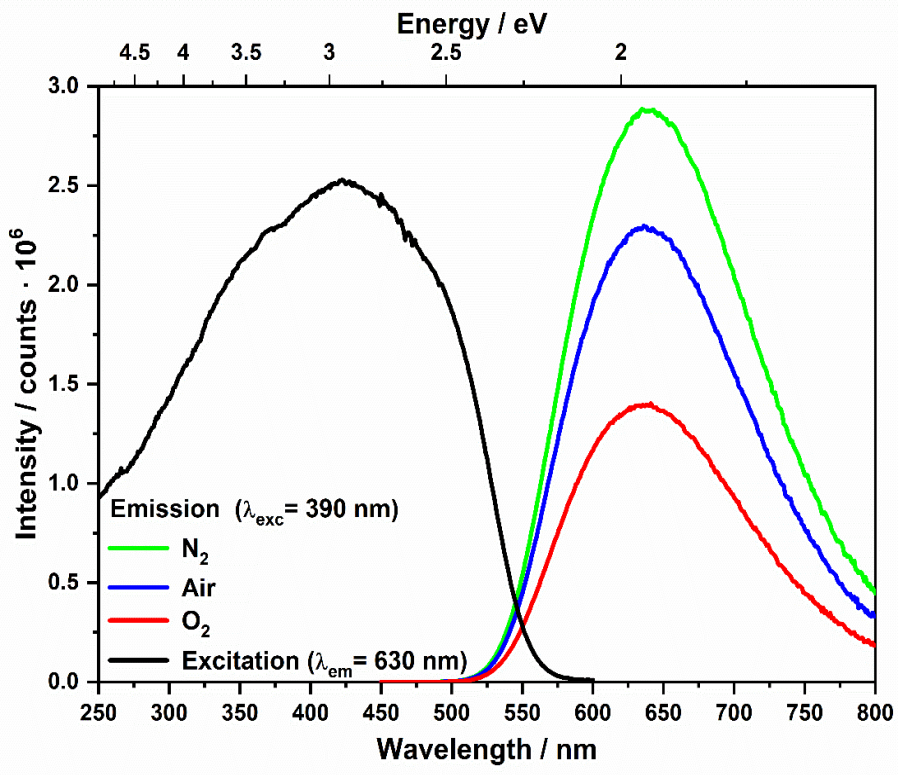

Figure S4. Excitation and emission spectra of solid $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$ under nitrogen, air and oxygen atmosphere.

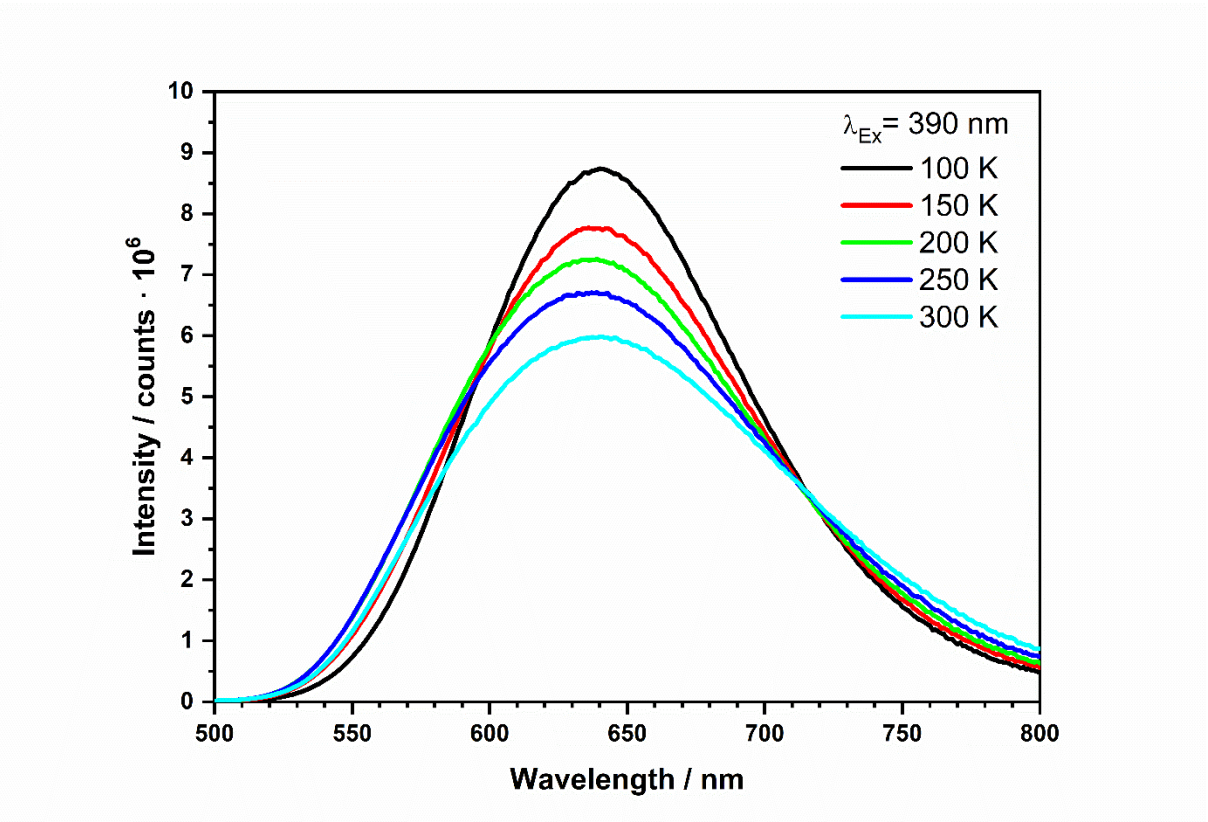

Figure S6. Emission spectra of solid $(TBA)_2[W_6I_8(CO_2C_3F_7)_6]$ at different temperatures.

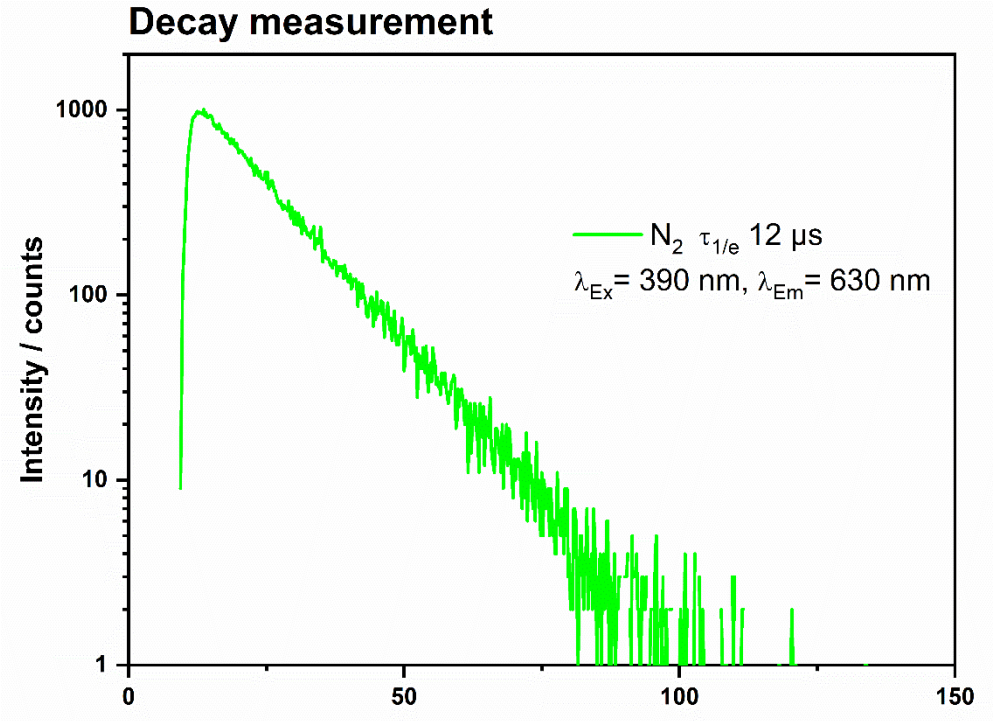

Figure S5. Decay measurement of **III** in acetonitrile.

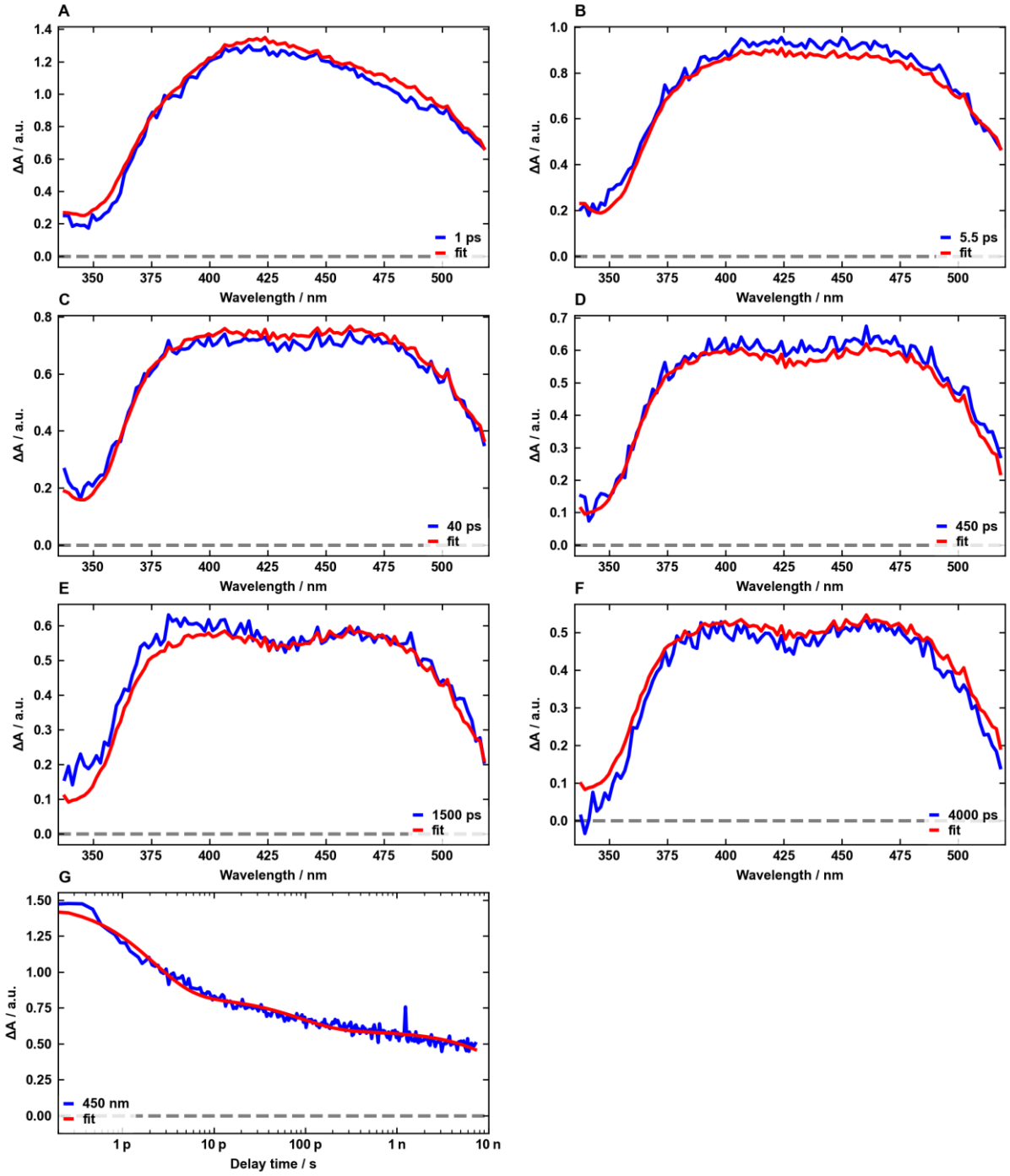

Figure S7. Selected ΔA spectra (A-F) of **III** at different time delays (blue) after excitation at 300 nm and kinetic trace at 450 nm (G). The corresponding fit spectra and traces of the global analysis are shown in red.

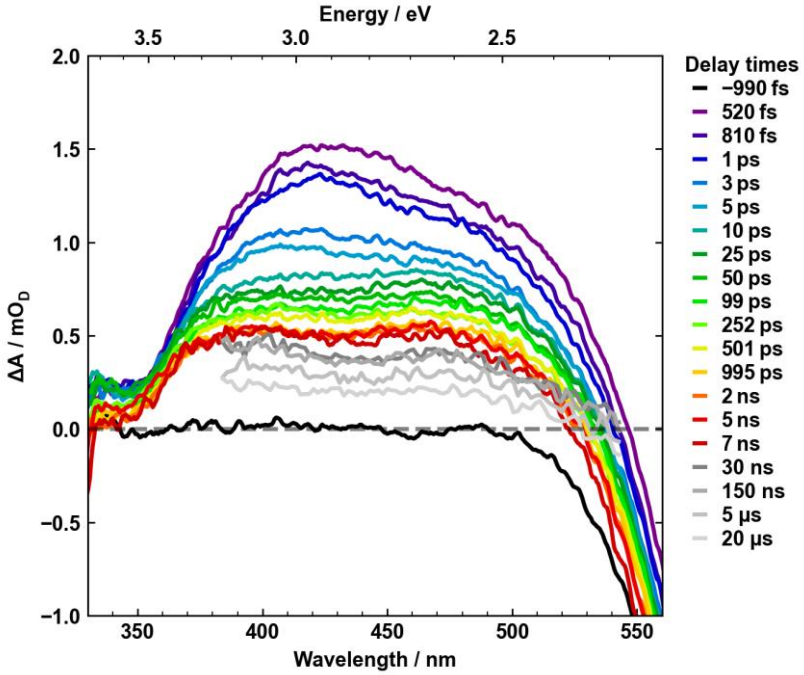

Figure S8. Selected ΔA spectra of **III** at different delay times after excitation at 300 nm. A femtosecond transient absorption spectrometer was used for delay times up to 7.5 ns. For the long-lived species longer than 7 ns, a different nanosecond pump probe spectrometer was used (grey scale). The negative signals at wavelengths higher than 520 nm are due to strong luminescence.

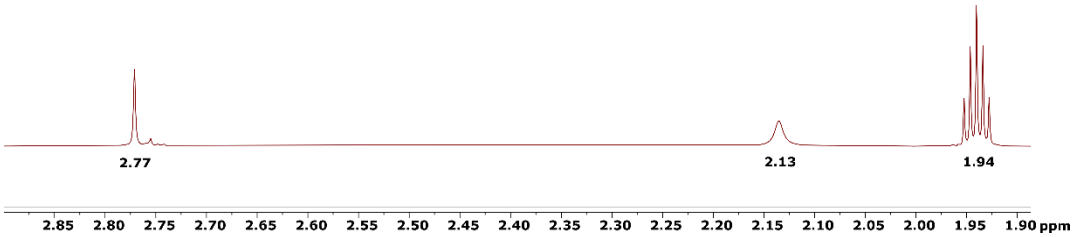

Figure S9. Section of the ^{1}H-NMR of **III** in CD_3CN showing the signal for the CH_3-group at 2.77 ppm and a signal of H_2O at 2.13 ppm.

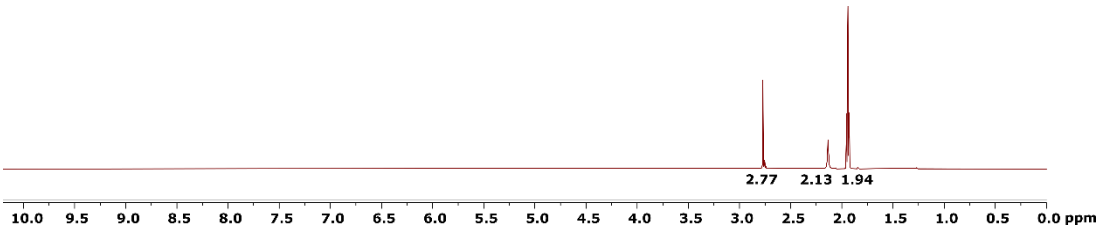

Figure 10. Greater section of the ^{1}H-NMR of **III** in CD_3CN between 0.0 and 10 ppm.

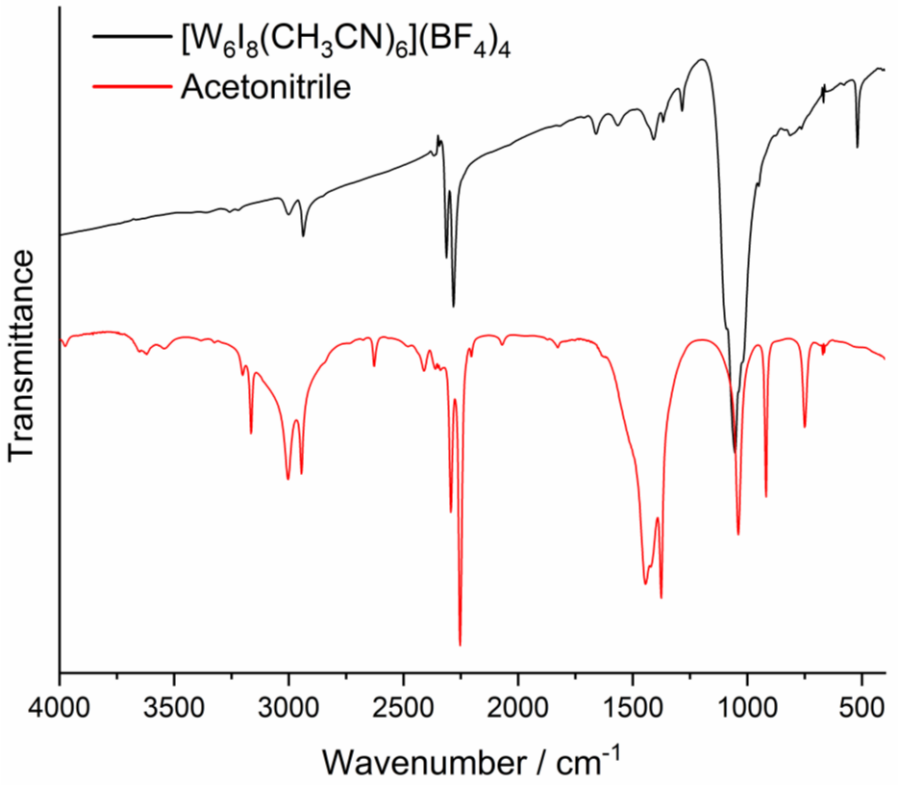

Figure 11. Infrared spectrum of **III** in black and of acetonitrile in red.