Comparative study of the redox and excited states properties of $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6X_{14}}]$ and $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6X_8(CF_3COO)_6}]$ (X = Cl, Br, or I)

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Figure S4.	Time profile of the $O_2(^1\Delta_g)$ phosphorescence.
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Figure S7.	Electrospray ionization-mass spectrum of **5**.

Figure S1. Transient absorption spectra of $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Mo}_6\mathrm{Cl}_{14}]$ **(1)** (A) in acetonitrile measured 1-5 μs after excitation (negative *ΔA* above 570 nm is due to intensive luminescence). The samples were excited at 308 nm.

B: Comparison of normalized luminescence (red, recorded at 720 nm) and transient absorption (recorded at 410 nm) kinetics for cluster **1**.

C: Comparison as in the panel B; kinetics of cluster **4** (transient absorption recorded at 530 nm).

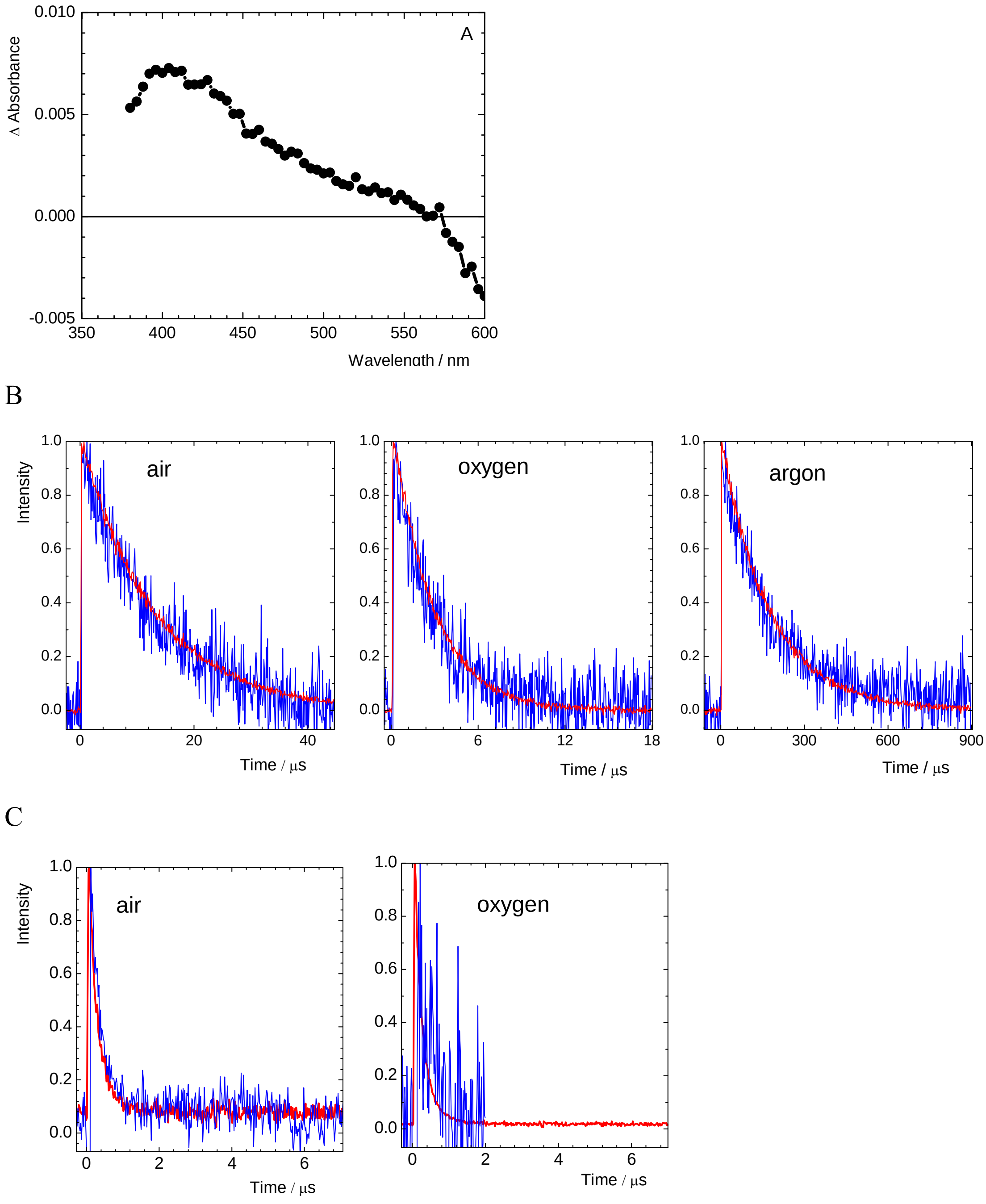

Figure S2. Transient absorption spectra of (nBu$_4$N)$_2$[Mo$_6$Br$_{14}$] **(2)** (A) and (nBu$_4$N)$_2$[Mo$_6$Br$_8$(CF$_3$CO$_2$)$_6$] **(5)** (B) in acetonitrile measured 1-5 μs after excitation. The samples were excited at 308 nm.

C: Comparison of normalized luminescence (red, recorded at 720 nm) and transient absorption (recorded at 425 nm) kinetics of cluster **2**.

D: Comparison as in the panel C; kinetics of cluster **5** (transient absorption recorded at 410 nm).

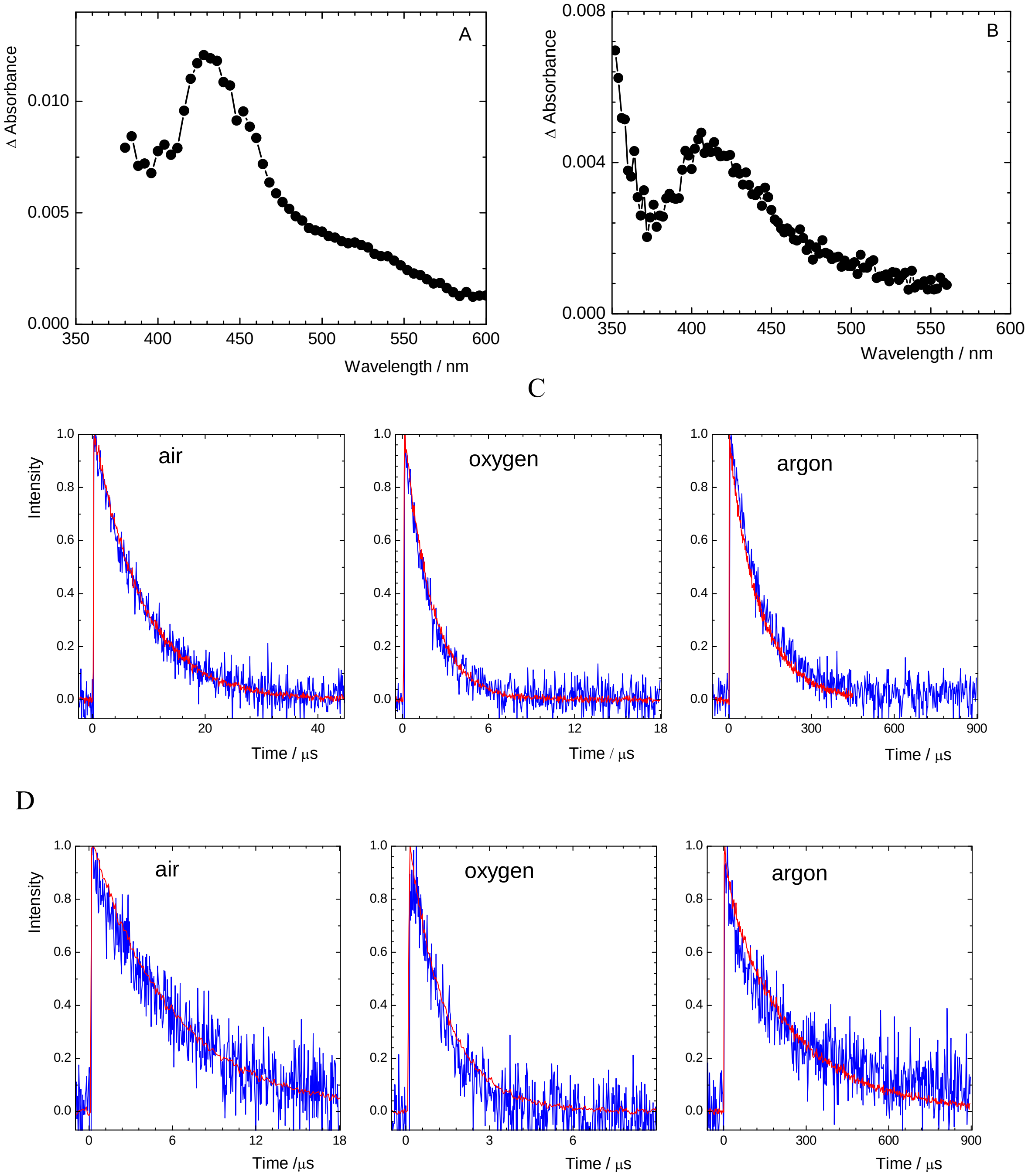

Figure S3. Transient absorption spectra of $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6I_{14}}]$ **(3)** (A) and $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6I_8(CF_3CO_2)_6}]$ **(6)** (B) in acetonitrile measured 1-5 μs after excitation (negative ΔA above 570 nm in B is due to intensive luminescence). The samples were excited at 308 nm.

C: Comparison of normalized luminescence (red, recorded at 720 nm) and transient absorption (recorded at 600 nm) kinetics for cluster **3**.

D: Comparison as in the panel C; kinetics of cluster **6** (transient absorption recorded at 520 nm).

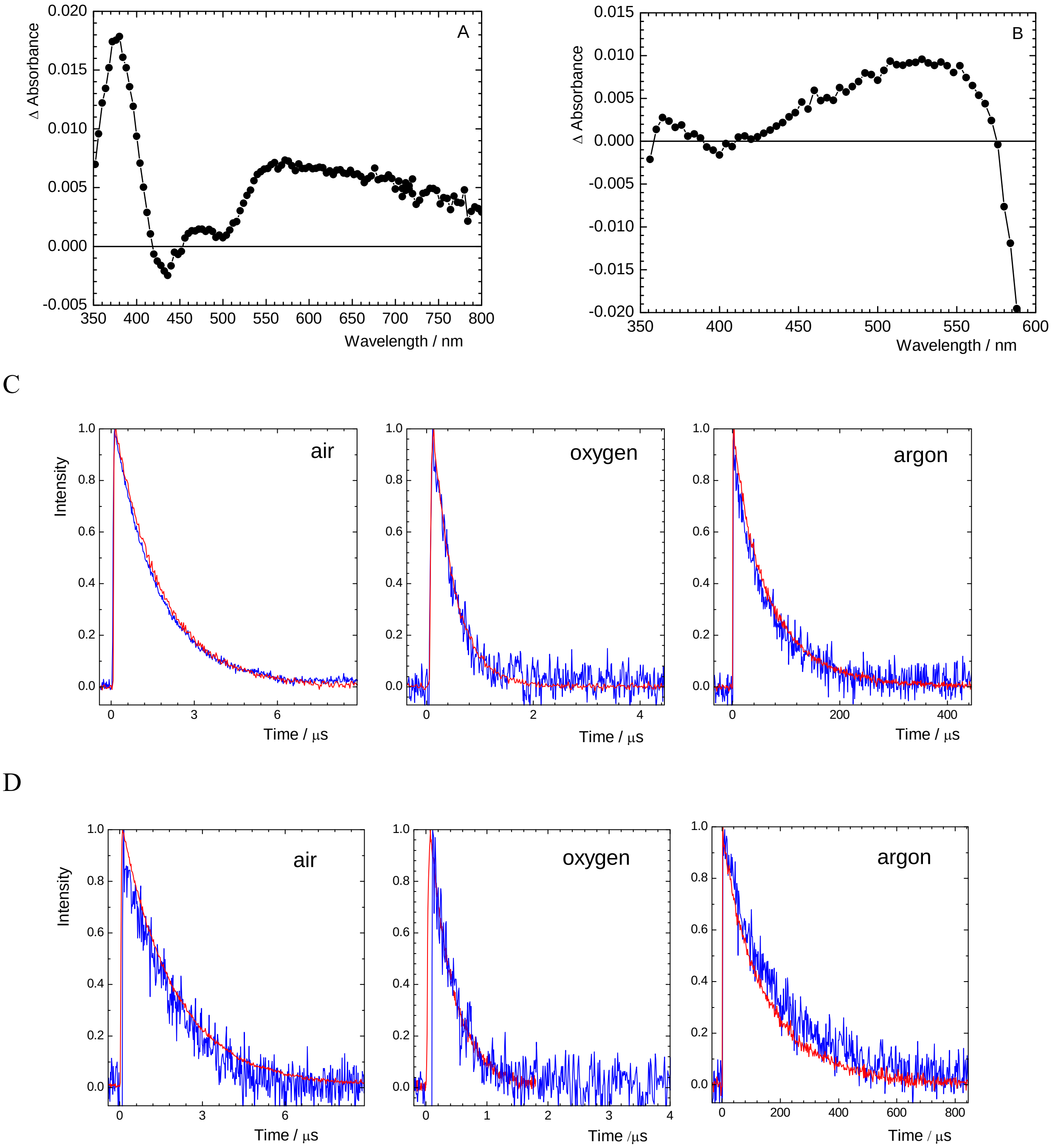

Figure S4. Time profile of the $O_2(^1\Delta_g)$ phosphorescence signal produced by anthracene (used as a standard) (black), $[Mo_6I_8(CF_3CO_2)_6]^{2-}$ **(6)** (red), and $[Mo_6Cl_8(CF_3CO_2)_6]^{2-}$ **(4)** in oxygen-saturated acetonitrile. The samples were adjusted to the same absorption at the excitation wavelength (308 nm) and the phosphorescence of $O_2(^1\Delta_g)$ was recorded at 1270 nm.

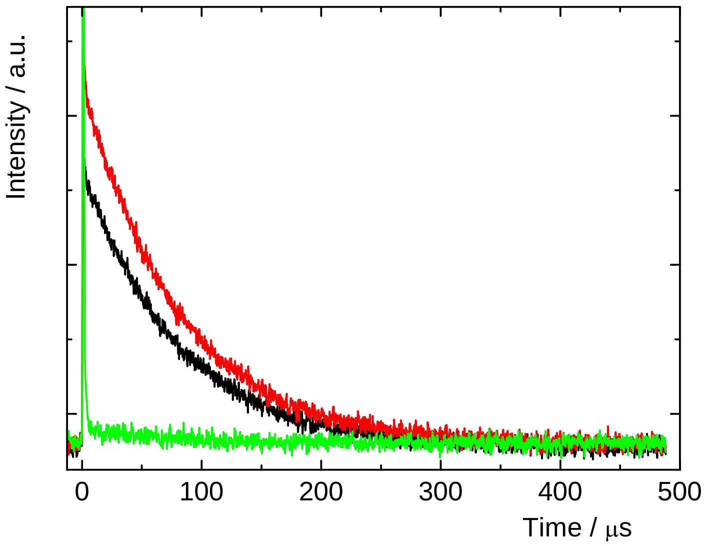

Figure S5. Evolution-associated decay spectra (EADS) obtained from global fitting of the data after excitation at 397 nm for **1**, **2**, **5**, and **6**. For **1**, **5** and **6**, the first components are not shown, because their lifetimes extracted from global fitting are shorter than 120 fs, which is the limit of the time resolution of our system. Consequently, the spectra of these components do not correspond to true states as they are significantly affected by the device response function. Thus, we cannot determine the spectral shapes of the initial states, but we can conclude that these states decay with time constants less than 120 fs. The numbers represent time constants of the decay of the corresponding component (inf means that the component did not decay within 1.5 ns, the time scale of the femtosecond transient absorption experiment).

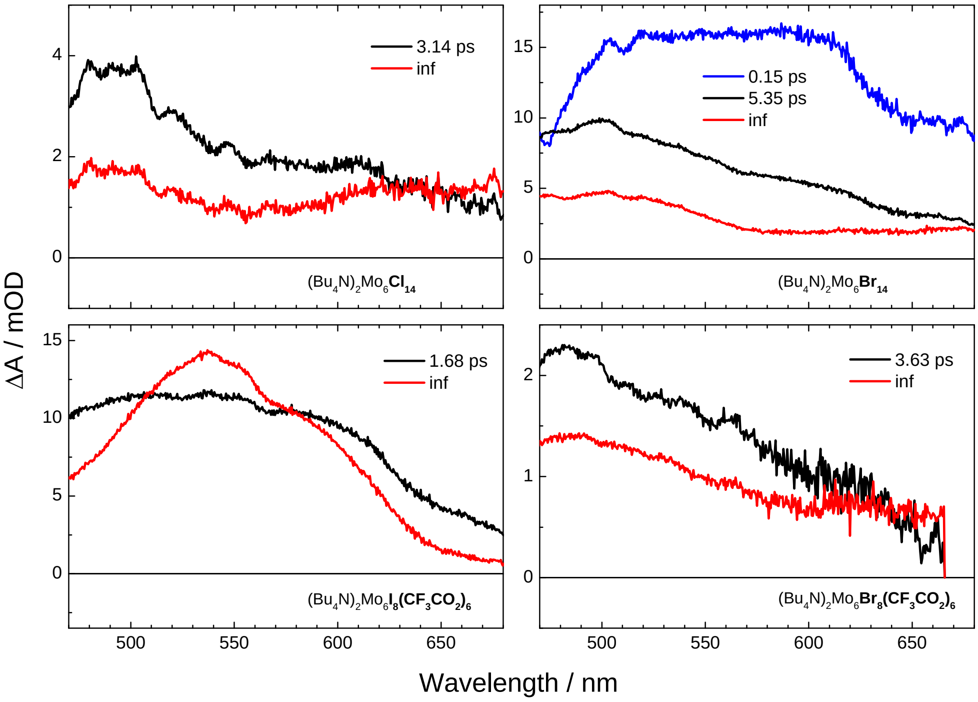

Figure S6. Spectra associated with the longest (infinite) component from the global analysis of ultrafast measurements. Black, red, green, and blue lines correspond to clusters **1**, **2**, **3**, **5**, and **6** respectively. In order to reasonably compare these spectra they were normalized to the illumination (5.6 × 10^{15} photons/cm^2 per pulse) and to the absorbance at the excitation wavelength.

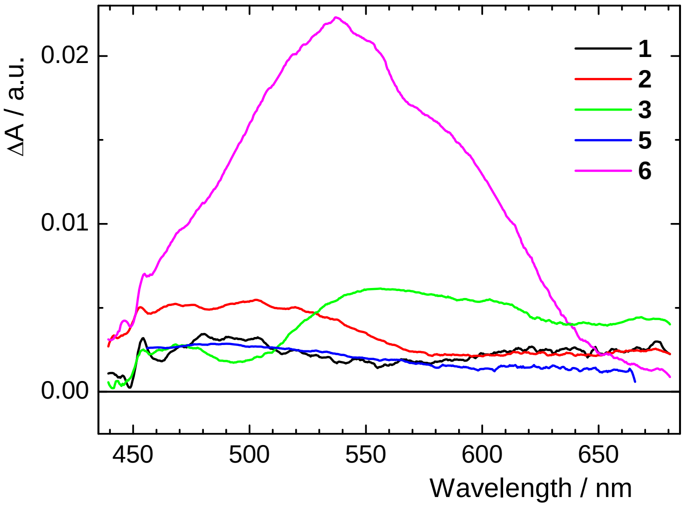

Figure S7. Electrospray ionization-mass spectrum of $(n\mathrm{Bu}_4\mathrm{N})_2[\mathrm{Mo}_6\mathrm{Br}_8(\mathrm{CF}_3\mathrm{CO}_2)_6]$ (**5**).