Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information:

Electron transfer between carbon dots and tetranuclear Dawson-derived sandwich polyanions

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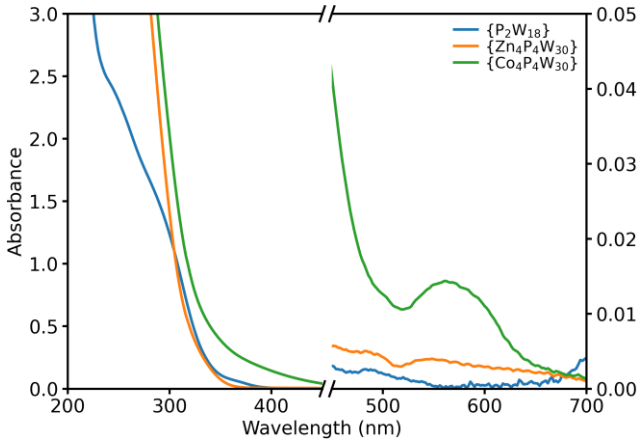

Figure S1: Absorbance spectra of aqueous solutions of the polyoxometalates used in this work at a 50 µM concentration. While both $\{P_2W_{18}\}$ and $\{Zn_4P_4W_{30}\}$ only present spectral features found below 400 nm, polyoxometalate $\{Co_4P_4W_{30}\}$ displays an absorbance tail extending up to 500 nm and a weak band peaking at 565 nm.

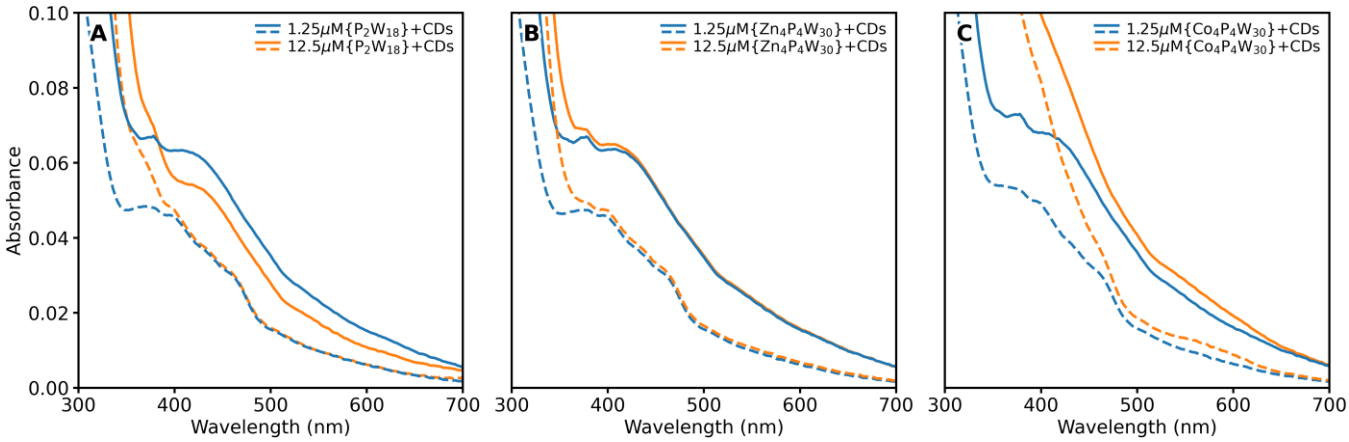

Figure S2: Comparison between the absorption spectra of CDs aqueous solutions to which either 1.25 µM or 12.5 µM POM were added (continuous curves) and the absorption expected if the resulting spectra were only caused by additive contributions (dashed lines); the latter was calculated as sum between the absorbance of an aqueous solution only containing CDs and the absorbance of an aqueous solution only containing POMs at the indicated concentration; data is relative to polyoxometalates: A) $\{P_2W_{18}\}$, B) $\{Zn_4P_4W_{30}\}$, and C) $\{Co_4P_4W_{30}\}$.

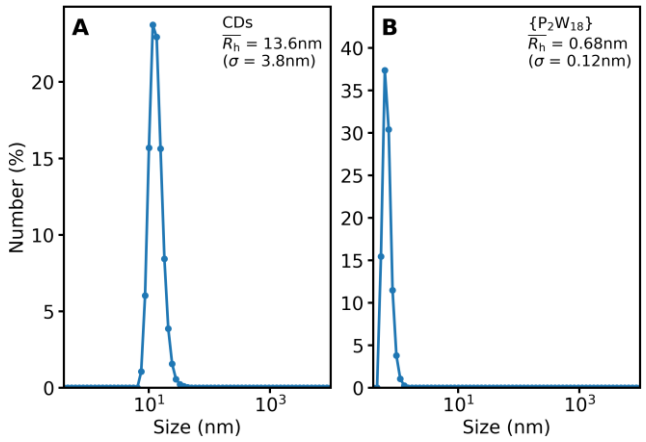

Figure S3: Size number distribution of A) CDs and B) $\{P_2W_{18}\}$ as obtained via DLS measurements; the indicated hydrodynamic radii R_h have been calculated from the average size weighed on the distribution; the relative standard deviation σ is reported.

R_{CDs} (nm)	R_{POM} (nm)	D_{CDs} (m^2s^{-1})	D_{POM} (m^2s^{-1})	K (M^{-1})
13.6 ± 0.4	0.683 ± 0.012	$(181 \pm 5)\times10^{-13}$	$(360 \pm 6)\times10^{-12}$	271 ± 12

Table S1: Diffusion limited quenching constant (K) and the parameters used to obtain it relative to the interaction between $\{P_2W_{18}\}$ and CDs; the interacting species radii (R) corresponds to the hydrodynamic radii obtained from the DLS size distribution; diffusion coefficients (D) have been calculated from the Einstein equation; diffusion limited quenching constant calculated from the Smoluchowski equation.

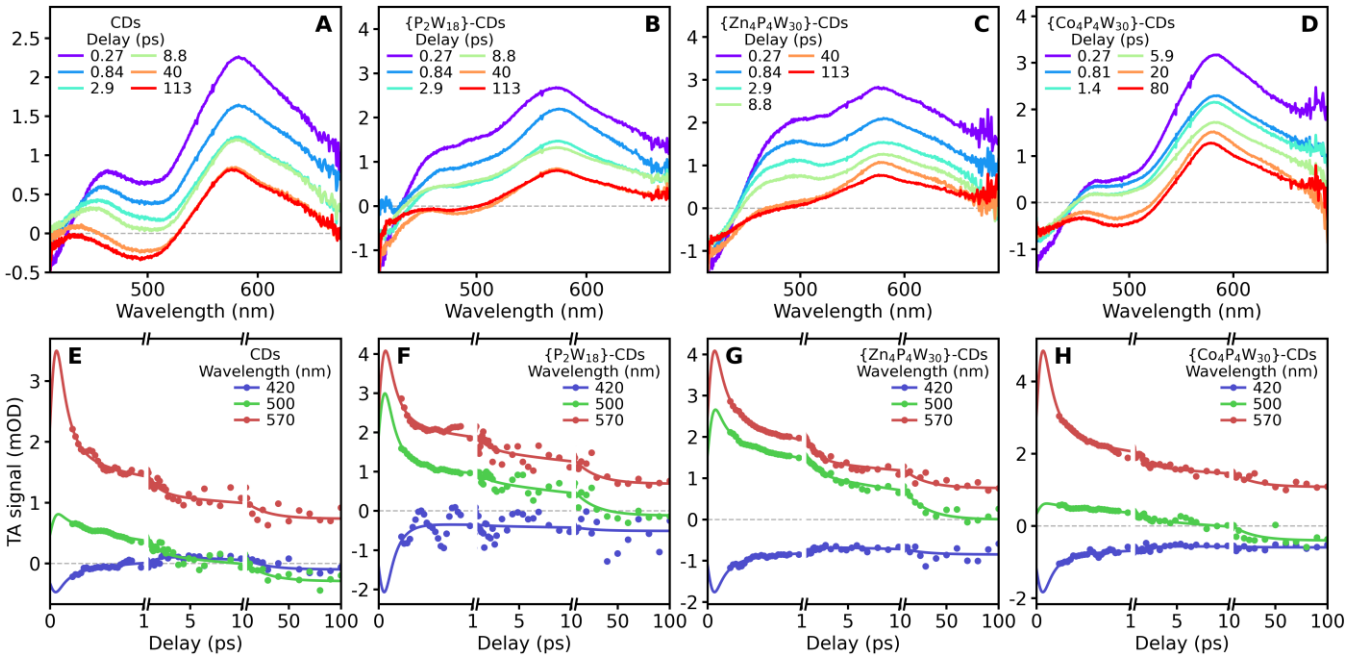

Figure S4: Ultrafast transient absorbance spectra at different delays from excitation (A, B, C and D) and traces taken at different wavelengths (E, F, G and H) of a CDs solution excited by a 400 nm femto-second laser pulse, either in the absence of POMs (A and E), in the presence of 125 µM of $\{P_2W_{18}\}$ (B and F), in the presence of 125 µM of $\{Zn_4P_4W_{30}\}$ (C and G) or in the presence of 125 µM of $\{Co_4P_4W_{30}\}$ (D and H). The best fitting multi-exponential decay curves obtained via a global least-squares minimization procedure are shown.

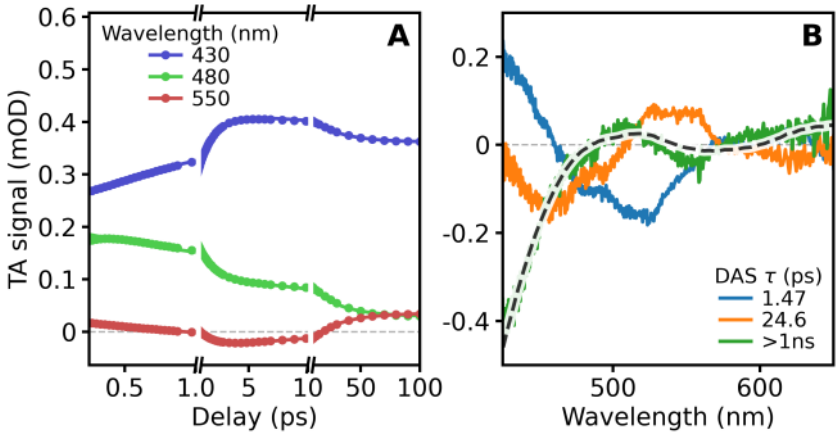

Figure S5: A) Traces and relative least-squares fitting curves taken at different wavelengths and B) decays associated spectra of the difference between the TA of a 125 μM $\{Co_4P_4W_{30}\}$-CDs complexes solution and the TA of a bare CDs solution.

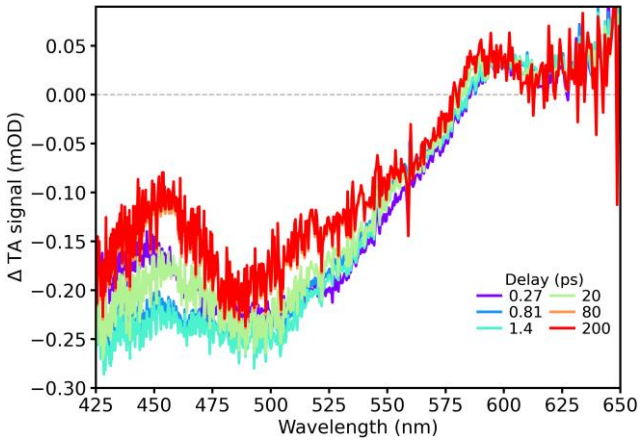

Figure S6: Spectra at different delays from excitation obtained as difference between the TA signal of $\{Co_4P_4W_{30}\}$-CDs complexes obtained at a 1.25 μM $\{Co_4P_4W_{30}\}$ concentration and the TA signal of CDs.