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SUPPLEMENTARY INFORMATION

Polymeric carbon nitride coupled with a molecular thiomolybdate catalyst: exciton and charge dynamics in light-driven hydrogen evolution

Ashwene Rajagopal,[a] Elham Akbarzadeh,[a,j] Chunyu Li,[b,c] Dariusz Mitoraj,[d] Igor Krivtsov,[d,*] Christiane Adler,[d] Thomas Diemant,[e] Johannes Biskupek,[f] Ute Kaiser,[f] Changbin Im,[d] Magdalena Heiland,[a] Timo Jacob,[d,g,h] Carsten Streb,[a,g,h]* Benjamin Dietzek,[b,c,i] * Radim Beranek[d,*]

[a] Institute of Inorganic Chemistry I, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany

[b] Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich Schiller University Jena, Lessingstr. 10, 07743 Jena, Germany

[c] Department Functional Interfaces, Leibniz Institute of Photonic Technology (IPHT), Albert-Einstein-Str. 9, 07745 Jena, Germany

[d] Institute of Electrochemistry, Ulm University, Albert-Einstein-Allee 47, 89081 Ulm, Germany

[e] Institute of Surface Chemistry and Catalysis, Ulm University, Albert-Einstein-Allee 47, 89081 Ulm, Germany

[f] Electron Microscopy of Materials Science, Central Facility for Electron Microscopy, Ulm University, Albert-Einstein-Allee 11, 89081, Ulm, Germany

[g] Helmholtz-Institute-Ulm (HIU), Helmholtzstr. 11, 89081, Ulm, Germany

[h] Karlsruhe Institute of Technology (KIT), P.O. Box 3640, 76021, Karlsruhe, German

[i] Center for Energy and Environmental Chemistry Jena (CEEC Jena), Philosophenweg 7a, 07743 Jena, Germany

[j] Department of Chemistry, Sharif University of Technology, Tehran, Iran

*Corresponding authors: igor.krivtsov@uni-ulm.de, carsten.streb@uni-ulm.de, benjamin.dietzek@uni-jena.de, radim.beranek@uni-ulm.de

Preliminary photocatalytic study:

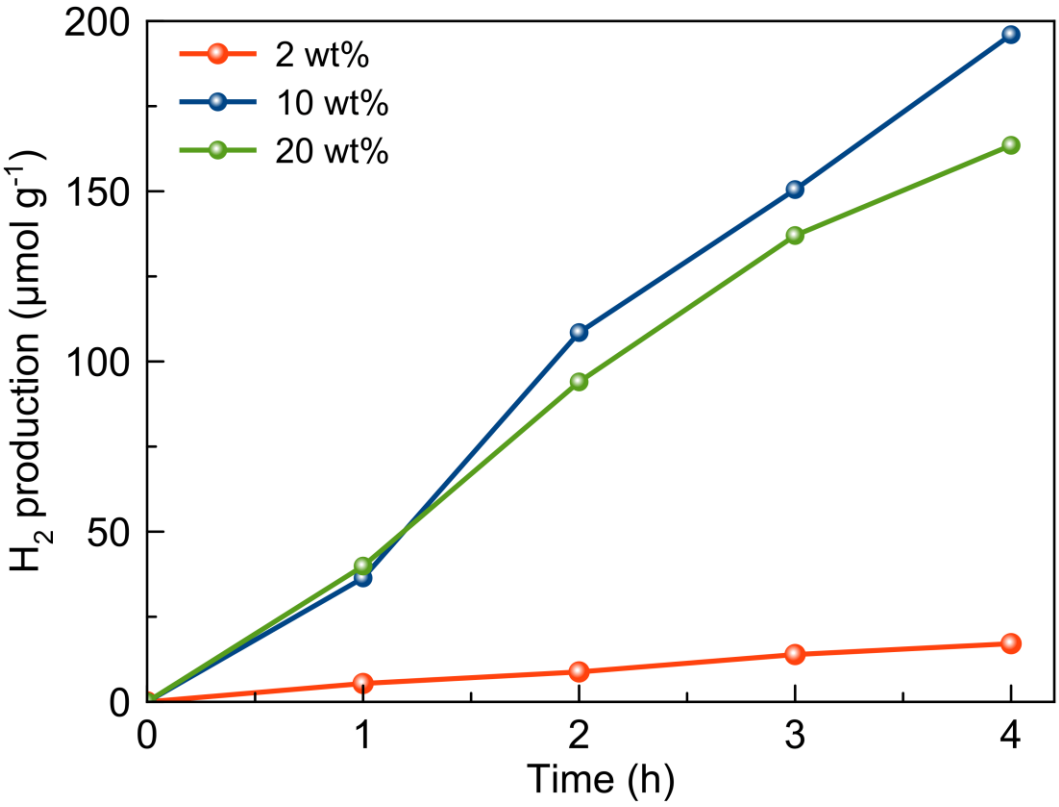

Figure S1. Photocatalytic HER performed using CN_x based materials with varied loading of $\{Mo_3\}$ clusters under 420 nm irradiation. Conditions: [catalyst]: 10 mg, Solvent: 10 ml H_2O:MeOH (9:1, v:v). Note that the hydrogen production rates in these preliminary measurements were lower than in the rest of the study due to a difference in geometry of the reaction cell which resulted in different absorbed photon flux.

FTIR analysis:

FT-IR spectra of CN_x, $Na_2[Mo_3S_{13}]$ and $\{Mo_3\}@CN_x$ nanocomposite are displayed in Figure 1b. In the FT-IR spectrum of CN_x and $\{Mo_3\}@CN_x$ hybrid the peaks at around 1639 cm^{1-} can be ascribed to C−N stretching vibration modes and the peaks at 1245, 1329 and 1416 cm^{1-} are attributed to the aromatic C−N stretching. The sharp peak at 806 cm^{1-} is related to the out-of-plane bending vibration of heterocyclic C−N. The broad peak at around 2900−3400 cm^{1-} can be related to the stretching modes of the N−H bond and the hydroxyl group of the adsorbed water. For the pure $Na_2[Mo_3S_{13}]$, the spectrum displays a sharp peak at 1138 cm^{1-} which can be assigned to the SO_4^{2-} group in the compound which probably is produced during the cation exchange process. However, no distinct sign of $[Mo_3S_{13}]^{2-}$ cluster is obvious in the FT-IR spectrum of $\{Mo_3\}@CN_x$ composite, which can be because of the little amount of $\{Mo_3\}$ in the hybrid and also existence of CN_x.

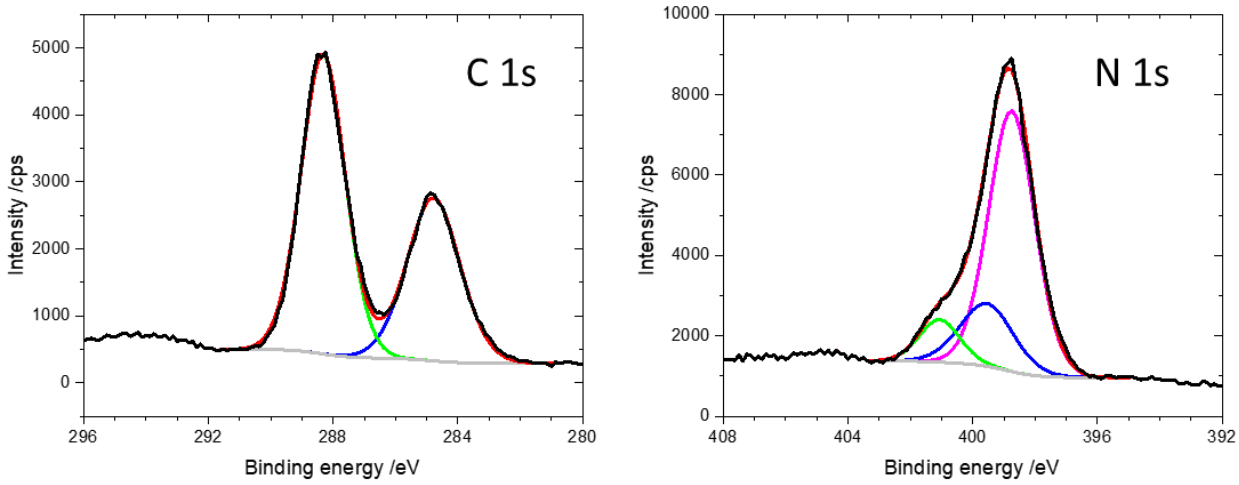

Figure S2. XPS C 1s and N 1s spectra of CN_x-{Mo_3}

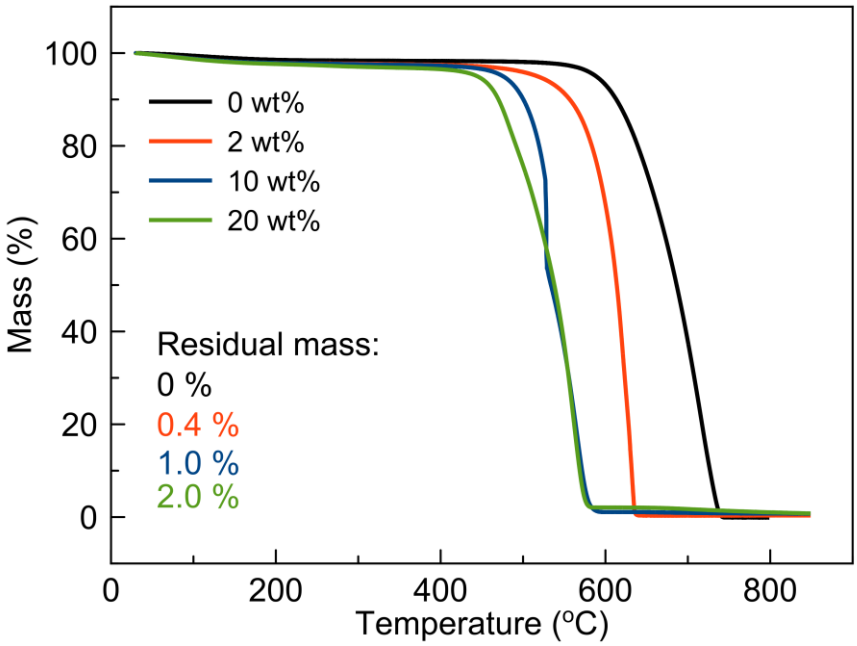

Figure S3. Thermogravimetric analysis of the CN_x materials with different {Mo_3} cluster loadings in air.

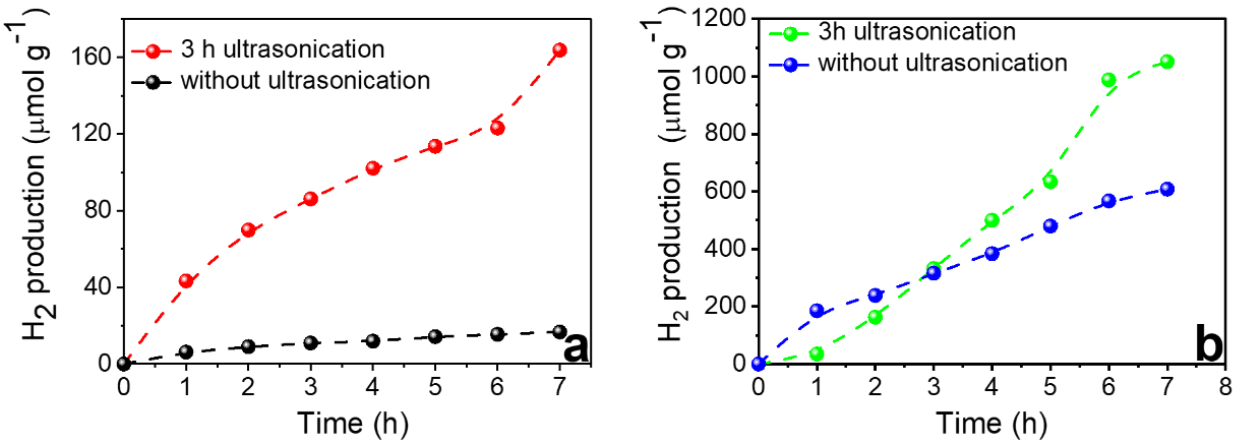

Figure S4. Effect of sonication on photocatalytic HER for (**a**) CN_x and (**b**) CN_x-{Mo_3} under 420 nm irradiation. Conditions: [catalyst] : 10 mg, Solvent: 10 ml H_2O:MeOH (9:1, v:v), in absence of any additional electron donors.

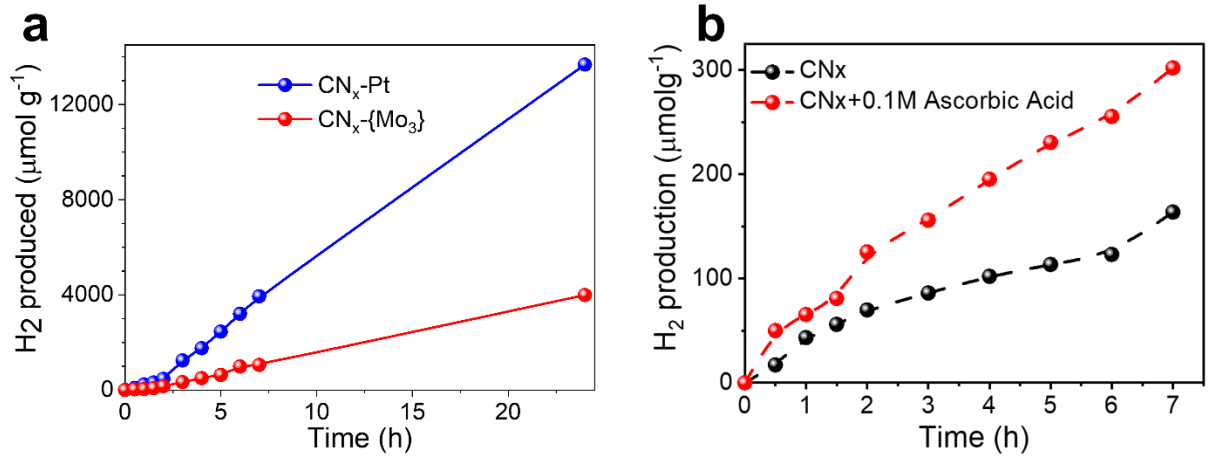

Figure S5. (**a**) H_2 evolution during long-term (24 hours) irradiation. (**b**) Effect of electron donor addition (0.1M ascorbic acid) on photocatalytic HER in presence of CN_x under 420 nm irradiation. Conditions: [catalyst] : 10 mg, Solvent: 10 ml H_2O:MeOH (9:1, v:v).

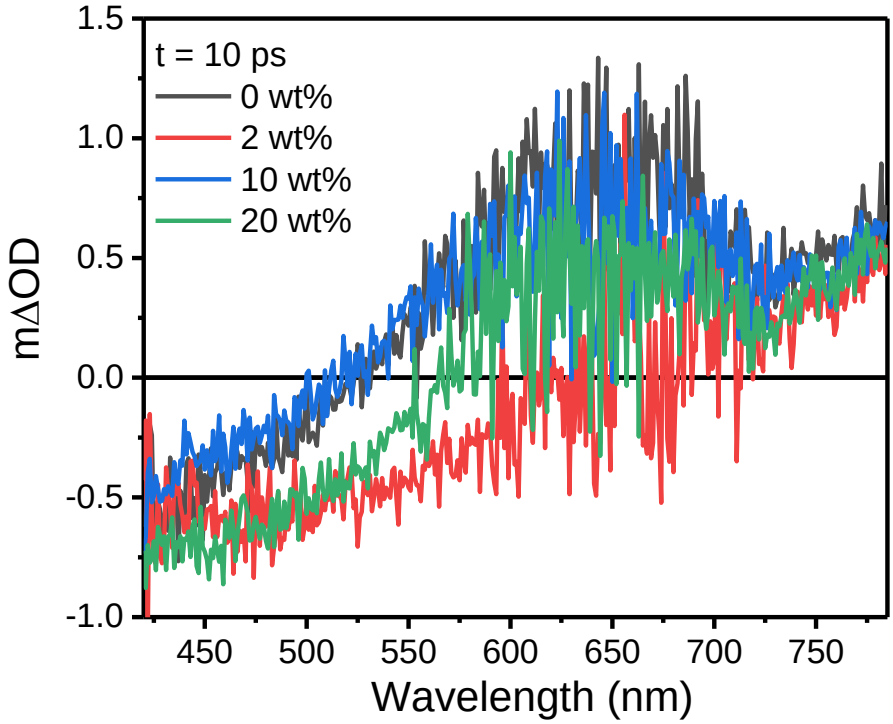

Figure S6. fs-TAS spectra of CN_x-{Mo_3} dispersions in H_2O upon excitation at 325 nm at 10 ps delay times. The figure displays the raw data.

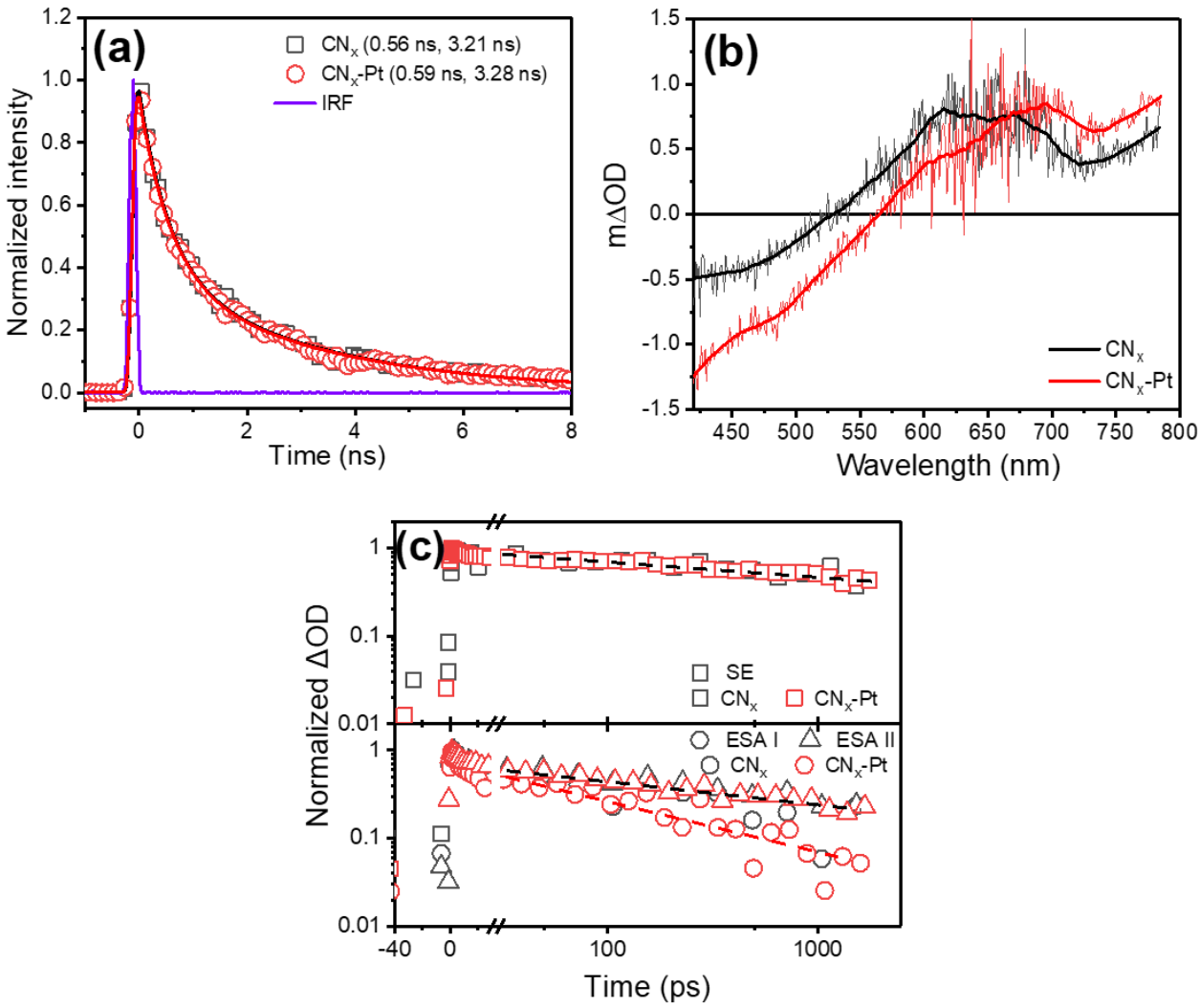

Figure S7. (a) Time-resolved photoluminescence decay curves of Pt functionalized CN_x samples after 385 nm photoexcitation. The samples were prepared by drop casting. (b) fs-TAS spectra at 10 ps delay of CN_x-Pt dispersions in H_2O upon excitation at 325 nm and corresponding (c) fs-TAS decay kinetics obtained by spectrally integrating the transient absorption data in different probe wavelength ranges. A quantitative analysis of the transient absorption data indicates, that the kinetics can be described by a power law model. The exponent of the power law is smaller than unity (~0.43), suggesting that trapping/detrapping plays a significant role in excited state dynamics of the CN_x-Pt samples. This is consistent with the comparably slow time scale for the recombination process.

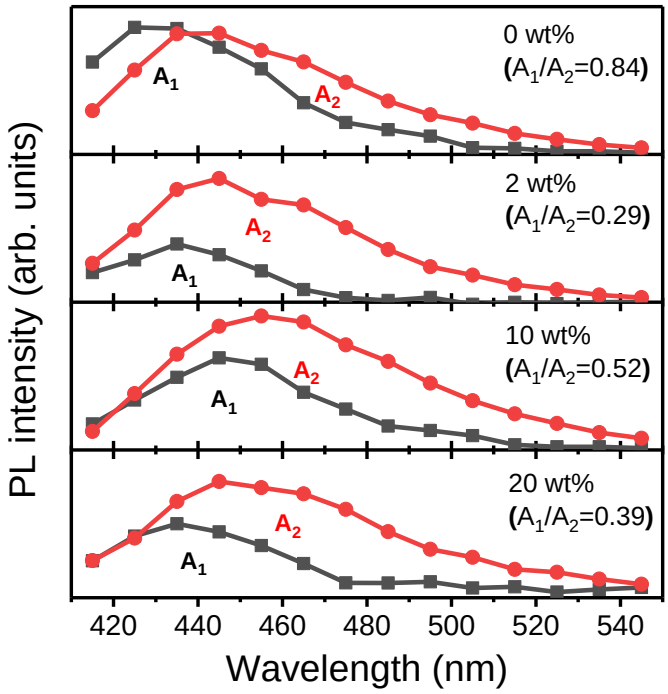

Figure S8. Species-associated emission spectra of CN_x-{Mo_3} with respective lifetimes (black lines present emission from the short-lived photoluminescence (τ< 1ns), while the red spectra reflect the spectra distribution of the long-lived emission with lifetimes ranging from 3.0 to 5.5 ns). The lifetimes are obtained by a global fit of the two-dimensional streak camera data with a biexponential model. The experimental response function of the streak camera measurements is 0.06 ns wide.

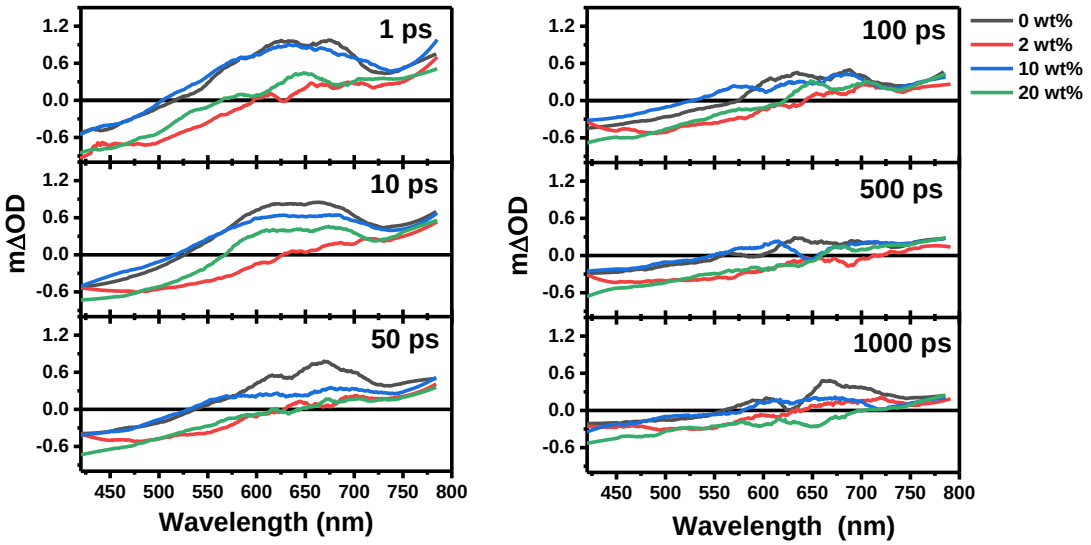

Figure S9. fs-TAS smoothed spectra of CN_x-{Mo_3} dispersions in H_2O. The spectra were recorded upon 325 nm excitation at different delay times.

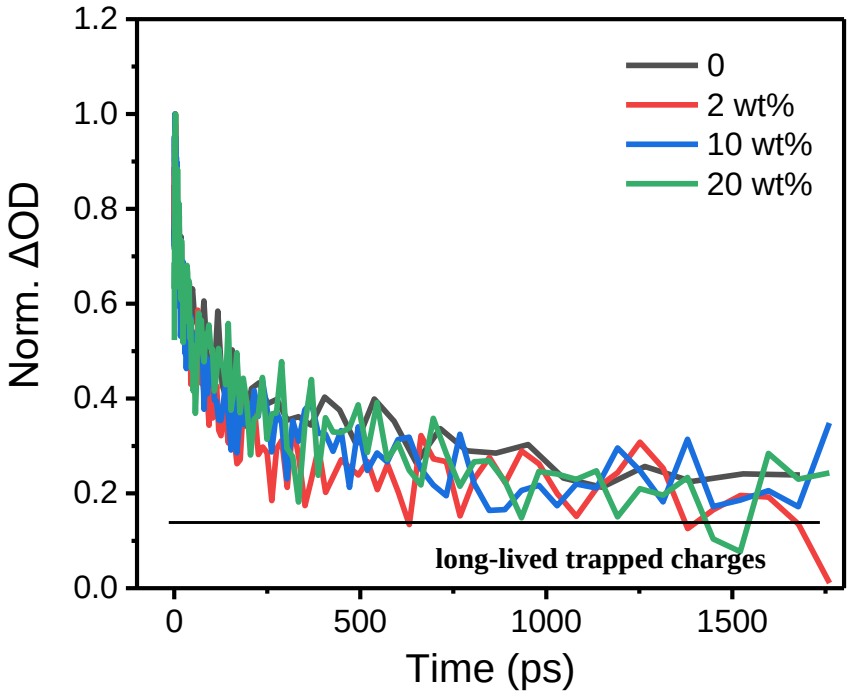

Figure S10. fs-TAS decay of CN_x-{Mo_3} dispersions in H_2O integrated within NIR regions upon 325 nm excitation.

Theoretical calculations:

Density Functional Theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP) version 5.4.4 using the projector-augmented wave (PAW) method to represent the basis set.[1–5] For accuracy of the electronic properties, the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional was employed.[6, 7] The screening parameter m in HSE was set at 0.2 $Å^{-1}$ and the exchange parameter a was 0.25. Grimme's D3 dispersion correction was used to describe long range dispersive interactions.[8, 9] The wavefunction was optimized to an accuracy of 10^{-6} eV while geometries were relaxed until the forces reached below $5 \cdot 10^{-2}$ eV $Å^{-1}$. Gaussian finite-temperature smearing was employed with a smearing width of 0.01 eV. A plane wave energy cut-off of 400 eV for both {Mo_3} and CN_x. To offset the spurious interactions between the periodic images, vacuum was introduced along the z-direction (~20 Å) for CN_x and {Mo_3} was placed to the center of cubic vacuum box (40 Å) with dipole corrections. Integration in the reciprocal space was performed on a 5 x 5 x 1 Monkhorst–Pack ***k***-grid mesh. For implicit solvation effects in water, the GLSSA13 solvent model implemented in the VASPsol extension was invoked,[10-12] using a dielectric constant of bulk water at room temperature of 78.4.

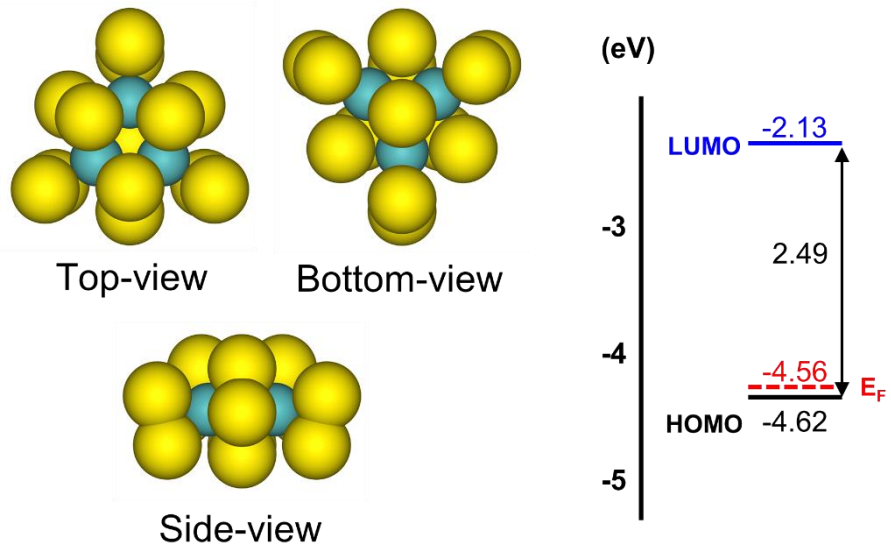

Figure S11. Scheme of the structure {Mo_3} employed in DFT calculation and HOMO-LUMO energy.

References

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