Supporting Information

A Photo-Switchable Molecular Capsule: Sequential Photoinduced Processes

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Experimental Procedures

Synthesis

(DAE) and {PMo₉} were prepared according to literature methods.^{1, 2} Solution-state characterization was conducted in anhydrous solvents due to the hydrolytic instability of the products.

Synthesis of $(TBA)_6[(PMo_9O_{31})_2(DAE)_3] \cdot C_4H_8O_2 - (TBA)_6(1(O_A)_3)$: $(TBA)_3[PMO_9O_{31}(py)_3]$ (200 mg, 82 µmol) and DAE (68 mg, 120 µmol) were dissolved in 15 mL of acetonitrile and stirred for 5 minutes. After stirring, an excess of ethyl acetate/dioxane was added to the reaction mixture to yield a colorless precipitate. The precipitate was filtered using a membrane filter and dried under a high vacuum. Crystals suitable for single-crystal X-ray diffraction were obtained after two days by vapor diffusion of dioxane into an acetonitrile solution of $(TBA)_6(1(O_A)_3)$. Negative Ion-MS (ESI-): m/z 1691.9955 (calculated for 1691.9968 $[(TBA)_3(PMo_9O_{31})_2(C_{25}H_{16}N_2S_2F_6)_3]^{3-}$. ¹H NMR (600 MHz, acetonitrile- d_3) δ 8.79 (d, J = 5.8 Hz, 12H), 7.92 (s, 6H), 7.61 (d, J = 5.9 Hz, 12H), 3.16 - 3.10 (m, 48H), 1.62 (m J = 7.7 Hz, 48H), 1.38 (q, J = 7.4 Hz, 48H), 0.97 (t, J = 7.3 Hz, 72H). ¹⁹F NMR (377 MHz, acetonitrile- d_3) δ -109.25, -109.96, -111.32, -112.02, -132.47. ³¹P NMR (162 MHz, acetonitrile- d_3) δ -0.03. ¹H NMR (600 MHz, dichloromethane- d_2) δ 8.96 - 8.87 (d, 12H), 7.77 (s, 6H), 7.60 - 7.52 (d, 12H), 3.45 - 3.29 (m, 48H), 1.94 (s, 18H), 1.81 - 1.69 (m, 48H), 1.54 (m, 48H), 1.05 (m, J = 7.3 Hz, 72H). Elemental Analysis (%) calculated, (found): C 35.68(34.64), N 2.85(2.89), H 4.65(4.45). FT-IR (v, cm⁻¹): 707, 748, 841, 870, 927, 1011, 1051, 1113, 1191, 1272, 1340, 1379, 1461, 1544, 1610, 1733, 2099, 2235, 2781, 2926, 3283. The methyl resonance of DAE is obscured by residual solvent in acetonitrile- d_3 .

Synthesis of TBA₆[(PMo₉O₃₁)₂(DAE)₃] - (1(C)₃)): The fully ring-closed species was produced in-situ by following the experimental procedure described in the (QYDS) experimental section. ¹H NMR (600 MHz, dichloromethane- d_2) δ 8.98 – 8.88 (m, 12H), 7.56 – 7.45 (m, 12H), 6.96 – 6.87 (m, 6H), 3.44 – 3.27 (m, 48H), 2.32 (d, *J* = 2.2 Hz, 9H), 2.23 (s, 9H), 1.79 – 1.68 (m, 48H), 1.53 (m, 48H), 1.03 (t, *J* = 7.3 Hz, 72H). Attempts to isolate a crystalline sample of this compound have thus far been unsuccessful.

Synthesis of TPP₆[(PMo₉O₃₁)₂(DAE)₃]·4CH₃CN (TPP)₆(1(O_A)₃): A 0.2 mM acetonitrile solution of TPPBr was carefully layered with a solution of (TBA)₆(1(O_A)₃) to yield colorless crystals suitable for single-crystal X-ray diffraction within one day. Negative lon-MS (ESI-): m/z 1788.8402 (calculated - 1788.8425 for [(TPP)₃(PMo₉O₃₁)₂(C₂₅H₁₆N₂S₂F₆)₃]³⁻. ¹H NMR (600 MHz, acetonitrile- d_3) δ 8.76 (d, J = 5.9 Hz, 12H), 7.95 – 7.87 (m, 30H), 7.76 – 7.72 (m, 49H), 7.68 (dddd, J = 13.0, 6.6, 2.0, 1.2 Hz, 49H), 7.57 (d, J = 5.9 Hz, 12H), 1.91 (s, 18H). ¹⁹F NMR (376 MHz, acetonitrile- d_3) δ -109.25, -109.94, -111.28, -111.91, -132.41.³¹P NMR (162 MHz, acetonitrile- d_3) δ 23.60, -0.04. FT-IR (v, cm⁻¹): 684, 715, 743, 835, 872, 928, 1010, 1051, 1106, 1189,1271, 1337, 1436, 1560, 1609, 1702, 1890, 2103, 2205,2781, 3058, 3392. Elemental Analysis (%) calculated, (found): C 41.63(43.30), N 2.14(1.93), H 2.77(2.68). Elemental analysis was perfomed on a vaccuum dried sample due to inconsistent analyses when using air dried samples.

X-ray Diffraction

Low-temperature (173 K) X-ray intensity data were collected using a Rigaku XtaLAB Synergy diffractometer) fitted with a Hypix6000HE hybrid photon counting detector and MoK α (I = 0.71073 Å) or CuK α (I = 1.54184 Å) radiation. Data were processed, using the proprietary diffractometer software package CrysAlisPro v1.171.39.46. The structure was solved by conventional methods and refined on F2 using full-matrix least-squares using the OLEX2 (1.3.0) software suite.³ Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in calculated positions and refined using a riding model. Significant isolated residual electron density that could not be modeled was accounted for by using SQUEEZE (1848 e-) and assigned as 84 acetonitrile molecules per unit cell (Z =4).⁴

Steady-State Spectroscopy

Absorbance spectra were collected on an Agilent Technologies Cary 60 UV-Vis spectrophotometer using Agilent Technologies standard quartz cuvettes of either 1 cm or 0.1 cm pathlength. Baseline corrections were applied over the entire collected wavelength range for each solvent. Transmittance spectra were collected using an Agilent Technologies Cary 60 UV-Vis spectrophotometer fitted with a solid-state sample holder. Samples were prepared as transparent discs in a KBr matrix.

Nuclear Magnetic Resonance

¹H DOSYand 2D Correlation (COSY) and Nuclear Overhauser Effect (NOESY) NMR spectra were recorded, at 298 K, on a Bruker Avance III NMR spectrometer equipped with a 14.1 T magnet and 5 mm TCl cryoprobe, operating at 600 MHz. ¹H NMR diffusion ordered spectroscopy (DOSY) ¹⁹F{¹H} and ³¹P{¹H} NMR spectra were recorded, at 298 K, in acetonitrile- d_3 or dichloromethane- d_2 , on a Bruker Avance III NMR nanobay spectrometer equipped with a 9.4 T magnet and 5 mm BBFO probe, operating at 400 MHz (¹H), 376.5 MHz (¹⁹F), 162 MHz (³¹P). Chemical shifts (δ) are reported in ppm and were referenced to the residual solvent signals (¹H) or external standards (¹⁹F and ³¹P). Bruker software, TopSpin 3.6.1, Dynamics Center 2.6.2 nad MestReNova 14.2 were used for data acquisition and processing. The temperature was set and controlled at 298 K with an airflow of 400 L h⁻¹. The 1H DOSY NMR data were measured with a longitudinal eddy current delay sequence with bipolar gradients and two spoil gradients. The diffusion time (Δ) was 100 ms and the gradient pulse length (δ) was optimized on a per-sample basis to be between 1.4-1.8 ms. Gradient pulses were smoothed square chirp shape. Experiments were performed as pseudo-2D with a linear variation of the gradient from 2 to 98% of maximum intensity in 16 steps. The data were processed and the peak areas, I, were used to fit the Stejskal-Tanner formula, **equ (1)**, as single-component fits, to determine the diffusion coefficient, D.⁵

$$\frac{I}{I(0)} = e^{-D\gamma^2 \delta^2 \sigma^2 g^2 \Delta'}$$
(1)

The Stokes-Einstein equation equ (2) applies to the diffusion of spherical particles through a liquid with a low Reynolds number (laminar, or non-turbulent, flow). Solving the equation for r, assuming the solution viscosity to be that of the neat protonated solvent at 25 °C^{6, 7} gives an indicative hydrodynamic radius, assuming the particle to be spherical.

$$D = \frac{k_B T}{6\pi\eta r_H}$$
(2)

Time-Resolved Spectroscopy

A third harmonic pulse (355 nm) of a Nd:YAG laser with ca. 1mJ output energy and 5 ns pulse width was used as excitation light and a pulsed Xe lamp was utilized as probe light. Transient absorption spectra were obtained from the transient absorption decays recorded at various wavelengths by sampling the absorbance changes for different given delay times. In parallel, our femtosecond time-resolved absorption set up (pump-probe configuration)⁸ is based on Ti:sapphire laser system (Coherent Mira-900-D oscillator and Libra-S regenerative amplifier) delivering 800 nm, 1 mJ, and 90 fs pulses with a repetition rate of 1 kHz. The pump pulses adjusted tuned at either 300 or 330 nm were generated by frequency quadrupling the output of a Quantronix Palitra OPA pumped at 800 nm and the energy at the sample was approximately 2 μ J ($0.2 mJ cm^{-2}$). The probe pulses were obtained by focusing 1 μ J, 800 nm pulses into a 1 mm CaF₂ thick plate to generate a white light continuum. The pump-probe polarization configuration was set at the magic angle (54.7°). Transient absorbance was obtained by comparing signal and reference spectra with and without pump pulses for different delay-times. The delay-time between the pump and probe was varied up to 1.5 ns using an optical delay line. Sample solutions (~ $10^{-5} mol dm^{-3}$, OD \mathbb{R} 0.2-0.5 at the pump wavelength) were circulated in a cell equipped with a 200 μ m thick CaF₂ entrance window and having 2 mm optical path. During measurements, the sample solution was circulated and irradiated by a CW Xe lamp visible light to prevent the accumulation of closed form. The classical characteristic times deduced from kinetics are obtained by

fitting the data with the result of a multiexponential function convolved with a Gaussian pulse mimicking the pump-probe cross-correlation function (FWHM at 180 fs). Our nanosecond transient absorption spectroscopy setup has been described elsewhere.⁹

Electrochemistry and UV-Vis-NIR Spectroelectrochemistry

Cyclic voltammograms (CV) were recorded in a standard three-electrode electrochemical cell using an Au mini-grid as the working electrode, Pt mini-grid as the counter electrode, and Ag/AgCl as the reference electrode. 0.1 M (TBA)PF₆ was used as a supporting electrolyte in acetonitrile + 1,4-dioxane (1 / 1) or neat acetonitrile. The cell was connected to an Autolab PGSTAT30 potentiostat (Eco Chemie, Holland) driven by GSE software running on a personal computer. All potentials are vs. Ag/AgCl used as an internal reference and are uncorrected from the ohmic drop. In situ UV-Vis-NIR spectroelectrochemical measurements were performed with an optically transparent thin-layer electrochemical (OTTLE) cell equipped with an Au minigrid working electrode, Pt minigrid as the counter electrode, and Ag/AgCl as the reference electrode, and CaF₂ optical windows.¹⁰ The optical path length was 0.02 cm. UV-Vis-NIR spectroelectrochemical analyses have been carried out with a Zeiss MCS 601 UV-Vis-NIR diode array spectrometer. Spectrophotometric analyses of the films have been conducted using 0.1 M (TBA)PF₆ as the supporting electrolyte in acetonitrile + 1,4-dioxane (1 / 1) or in neat acetonitrile. The photochemical reactor is a quartz cell where the sample solution is continuously and uniformly stirred and maintained at a constant temperature. The spectrophotometric cuvette has an optical path length of 1 cm and a total volume of 1 × 1 × 4 cm³. Open to closed conversion was completed using λ = 300 nm illumination from a 300 W Arc Xenon lamp in acetonitrile + 1,4-dioxane (1 / 1), while the closed to open process utilized a long pass filter λ > 400 nm in the same setup.

Quantum-Yield Determination

For reaction quantum yield measurements, an improved version of the Quantum Yield Determination Setup (QYDS) was used.¹¹ (See Figure S16) The principle of the QYDS is the precise determination of the ratio between the amount of created reaction product (number of molecules) compared to the number of absorbed photons. The absorbed illumination power is measured photometrically using a calibrated solar cell. For the calibration of the solar cell, a comparison to a thermal power meter (Coherent Inc.; PowerMax USB - PS19Q) that is NIST traceable is performed at higher illumination power. In this way, even an optical power of 200 μ W can be measured with a precision of better than 3%. As an illumination source, high-power LEDs are used, that ensure constant irradiation flux for long periods. The optical power at the sample can be set in coarse steps with neutral density filters and with fine control achieved by the LED current. In this study, a (7.5 μ M) solution of (1(O_A)₃), $\lambda_{max} - 315$ nm, $\varepsilon - 1.59 \times 10^5$ L M⁻¹ cm⁻¹) in DCM was illuminated with a DOWA 325 nm LED with an optical power of 0.213 mW to induce complete conversion to (1(C)₃) over 22 minutes.

Computational Methods

All geometry optimizations were carried out with Turbomole 7.4.1¹² with the efficient PBEh-3c¹³ hybrid-DFT model, which considers London-dispersion effects and has its own atomic-orbital (AO) basis set. Effective core potentials of the def2-ecp¹⁴ type were applied to mimic the core electrons of molybdenum. The Conductor-Like Screening Model¹⁵ (COSMO) was used for implicit solvation. The self-consistent-field (SCF) convergence criterion was set to 10⁻⁷ E_h, and the geometry convergence criterion for total energy changes between two optimization cycles to 10⁻⁶ E_h. Turbomole's default grid "m4" was applied for the numerical integration of the exchange-correlation potential. The resolution of the identity approximation to Coulomb integrals ¹⁶ (RIJ) was used with an appropriate auxiliary basis ¹⁴ Subsequent UV/Vis absorption behavior of both systems was explored with Grimme's simplified Tamm-Dancoff-Approximation DFT (sTDA-DFT) model¹⁷ as implemented in ORCA 5.0.1.¹⁸, ¹⁹ This model requires a converged ground-state DFT calculation and then allows the fast calculation of excitation energies and oscillator strengths within a pre-defined energy window, in this case between 0 and 5 eV. To allow for the description of charge-transfer (CT) excitations, the range-separated hybrid CAM-B3LYP²⁰ was chosen in conjunction with the double- \mathbb{Z} def2-SVPD²¹ AO basis set, which was designed for linear response properties. Again, def2-ecp was applied to molybdenum. ORCA's default grid "defgrid2" was applied in all cases, alongside an SCF convergence criterion of 10⁻⁸ E_h, the Conductor-Like Polarizable Continuum Solvation Model²² (CPCM), and the RIJ combined the chain-of-sphere approximation²³ (RIJCOSX) to accelerate the ground-state calculation of Coloumb and exchange integrals.

Electrospray ionization mass spectrometry (ESI-MS)

High-resolution electrospray ionization mass spectra (ESI-MS) in the negative ion mode were collected on an Orbitrap Elite ETD linear ion trap mass spectrometer (Thermo Scientific). Samples of $(1(O_A)_3)$ as both the tetrabutylammonium and tetraphenylphosphonium salts were dissolved in anhydrous acetonitrile and diluted to ca. 100 μ M. These solutions were separately introduced into the mass spectrometer *via* direct infusion to a heated electrospray ionization (HESI) source at an injection rate of 5 μ L min⁻¹. The source was optimized to yield a stable current of ca. 0.5 μ A with the following typical conditions being used: spray voltage (-1.5 kV), capillary temperature (150 °C), sheath gas flow (10 a.u.), aux gas flow (0 a.u.), sweep gas flow (0 a.u.), S-Lens RF (30%).



Figure S1. ¹H NMR of the aromatic region of $(1(O_A)_3)$ immediately following dissolution in anhydrous acetonitrile- d_3 and after 1 day, 2 days, and 21 days in a sealed amber NMR tube.





Figure S2. ³¹P NMR of **(1(O_A)₃)** immediately following dissolution in anhydrous acetonitrile-*d*₃ and after 1 day, 2 days, and 21 days in a sealed amber NMR tube.

Figure S3. Solution-state UV-Vis Spectroscopy of $(1(O_A)_3)$ at t - 0, 24, 48hrs. For this study, 0.18 mM stock solution of $(1(O_A)_3)$ was prepared in anhydrous acetonitrile and was stored in the dark. The stock solution was diluted to 5.32 μ M to obtain the required UV-Vis spectrum.



Figure S4. Solution-state UV-Vis Spectroscopy of {PMo₉} over 60 minutes.



Figure S5. Solution-state UV-Vis spectroscopy of $\{PMo_9\}$ under UV illumination over 34 minutes (λ_{ex} - 325 nm).



Figure S6. Solid-state transmittance Spectroscopy and optical photographs of $(1(O_A)_3)$ and $(1(O_A)_x(C)z)$.

| CCDC Number | 2173175 (1TPP) |
|---------------------------------|--|
| Empirical Formula | C265 H237 F18 Mo18 N29 O62 P8 S6 |
| Formula Weight (g/mol) | 7329.31 |
| Data Collection Temperature (K) | 123 |
| Wavelength | 1.54184 |
| Crystal System | Monoclinic |
| Space Group | C2/c |
| Unit cell dimensions | a = 28.6129(2); b = 15.7456(1); c = 64.1580; β = 94.437(1) |
| Volume | 28813.3(3) |
| Z | 4 |
| Density (calculated) | 1.689 |
| Absorption coefficient | 7.779 |
| F(000) | 14640 |
| Crystal dimensions | 0.164 x 1.44 x 0.052 |
| Theta range for data collection | 3.443 – 77.788 |
| Reflections collected | 30099 |
| Independent reflections | 28006 |
| Completeness to theta = 77.788 | 0.979 |
| Data / restraints / parameters | 30099 / 1664 /60 |
| Goodness-of-fit F ² | 1.190 |
| Final R indices [I>2sigma(I)] | 0.0761 |
| R indices (all data) | 0.0794 |
| Largest diff. peak and hole | 1.384; -1.352 |

Table S1. Crystallographic data for (1)



| Atoms | Distances/Angles |
|-----------|------------------|
| | |
| C9-C19 | 3.43 (2) Å |
| N1-N2 | 14.917(10) Å |
| N1-Mo4 | 2.313(8) Å |
| N1-C9 | 6.675(15) Å |
| O28—H35 | 2.446 Å |
| O24—H5 | 2.568 Å |
| O31 –H11 | 2.624 Å |
| C9-C8-C21 | 123.1 |
| N1-Mo4-O7 | 170.4 |

Table S2. Important intramolecular distances and angles for $(TPP)_6(1)$.



Figure S7. ¹H spectra showing the evolution of the methyl protons following illumination of **(1(O_A)₃)** (325 nm, 0.21 mW) at (t = 0s; 50s; 106s; 171s; 538s and 1302s) during a typical QYDS experiment to yield **(1(C)₃)**.





Figure S8. Full Orbitrap ESI-MS in the negative ion mode of anhydrous samples of $(TBA)_6(1)$ and $(TPP)_6(1)$.

Figure S9. Expansion of Figure S6 to show the high-resolution isotopic envelope of $(1(O_A)_3)$ as the trianion $\{TBA_3[(PMo_9O_{31})_2(DAE)_3]\}^3$.



Figure S10. Expansion of Figure S6 to show the high-resolution isotopic envelope of $(1(O_A)_3)$ as the trianion $\{TPP_3[(PMo_9O_{31})_2(DAE)_3]\}^3$.



Figure S11. ¹H NMR of (1(O_A)₃) recorded at 298K in acetonitrile-*d*₃.





Figure S13. ¹H 2D NOESY spectra of (1(O_A)₃) recorded at 298K in acetonitrile-d₃.

Figure S14. ¹H 2D COSY spectra of (1(O_A)₃) and recorded at 298K in acetonitrile-d₃.



Figure S15. ¹H 2D DOSY spectrum (1(O_A)₃) recorded at 298K dichloromethane-d₂.



Figure S16. ¹H 2D DOSY spectrum of (1(O_A)₃) recorded at 298K in acetonitrile-d₃.

| acetonitrile -d ₃ | D (m²/s) | r (nm) | dichloromethane-d ₂ | D (m²/s) | r (nm) |
|------------------------------|-----------|--------|--------------------------------|-----------|--------|
| 1 (Ha*) | 4.52 e-10 | 1.31 | 1 (Ha*) | 3.87 e-10 | 1.36 |
| 3 (Hb*) | 4.51 e-10 | 1.31 | 3 (Hb*) | 3.86 e-10 | 1.40 |
| 2 (Hc*) | 4.61 e-10 | 1.29 | 2 (Hc*) | 3.77 e-10 | 1.36 |

Table S3. Diffusion coefficients of $(1(O_A)_3)$ in acetonitrile- d_3 and dichloromethane- d_2 and the calculated hydrodynamic radius.



Figure S17. ¹H 2D DOSY spectrum of $(1(C)_3)$ recorded at 298K in dichloromethane- d_2 .



Figure S18. Quantum Yield Determination Setup.



Figure S19. Femtosecond transient absorption data for **(DAE)** in dry acetonitrile for (λ_{ex} 330 nm) displayed in three separated temporal windows [0.95-1.2 ps] (top), [1.3-8 ps] (middle) and [15-2000 ps] (bottom). The absorption spectra for the PPS solution is appended (gray dashed line) for comparison.



Figure S20. Femtosecond absorption data for **(L1)** in dry acetonitrile for a laser excitation of 300 nm and temporal window [50-2000 ps]. In the lower panel, stationary absorption and emission (300 nm excitation) spectra are presented.



Figure S21. Global fit of transient absorption data for (1(O_A)₃) using a triple exponential model for the temporal window [0.7-1000ps]. The 5 selected wavelengths were 400, 495, 545, 590 and 700 nm.



Figure S22. Nanosecond transient absorption data for $(1(O_A)_3)$ in dry acetonitrile for $(\lambda_{ex} 330 \text{ nm})$. The absorption spectra for the PPS solution is appended (gray dashed line) for comparison.



Figure S23.Qualitative Reconstruction of the transient trace of **(1)** at 2000 ps (Figure 5) making a linear combination with a CF spectra, the transient trace of L1 (2000 ps-Figure S18); the spectroelectrochemical traces for POM- and POM+ spectra (fgure 6).

| Compound | E _{ox} (V) | E _{red} (V) |
|---|---------------------|--|
| DAE ^a | 1.49 ^{irr} | -1.30 ^{irr} |
| | | -1.99 ^{irr} |
| | | 5 4 5 4 5 0 0 0 4 * |
| TBA ₃ [PMo ₉ O ₃₁ (py) ₃] ^a – {PMo ₉ } | - | $E_{pc} = -1.15 \text{ V} \text{ and } E_{pa} = +0.02 \text{ V} *$ |
| | | -1.87 ^{irr} |
| | | |
| | | |
| | | |
| | | |
| | | |
| TBA ₆ [(PMo ₉ O ₃₁) ₂ (DAE) ₃] – (1(O _A) ₃) ^a | 1.26 ^{irr} | -0.69 ^{irr} |
| | | -1.15 ^{irr} |
| | | -1.35 ^{irr} (closed) |
| | | -1.52 ^{irr} (closed) |
| | | -1.95 ^{irr} |
| | | |
| | | |

Table S4. Redox properties of **DAE**, {**PMo**₉} and (**1**(**O**_A)₃) *versus* Ag/AgCl in CH₃CN + 1,4-dioxane (1 / 1) + 0.1 M N(Bu)₄PF₆ or in CH₃CN + 0.1 M N(Bu)₄PF₆. Working electrode Glassy carbon. Irr = irreversible.* Slow electron transfer.^a Measured in CH₃CN + 1,4-dioxane (1 / 1) + 0.1 M N(Bu)₄PF₆.^b Measured in CH₃CN + 0.1 M N(Bu)₄PF₆.



Figure S24. UV-Vis-NIR spectroelectrochemistry of **(DAE).** A) Irradiation with UV-Visible-NIR light until reaching maximum absorbance in the visible range. B) Evolution of the UV-Vis-NIR spectra recorded during oxidation. Inset: CV at scan rate of 20 mV.s-1 recorded during the spectroelectrochemistry measurement. Optical path length = 0.02 cm. Note that the start of the recording for the spectroelectrochemistry measurements (blue curve) is done when the steady-state between closed to open form is reached under UV-visible illumination.



Figure S25. Differential UV-Vis-NIR spectroelectrochemistry upon electrochemical oxidation and reduction of **(DAE).** A) Irradiation with UV-Visible-NIR light until reaching maximum absorbance in the visible range. B) Evolution of the UV-Vis-NIR spectra recorded during the CV measurement. Inset: CV at scan rate of 20 mV.s⁻¹ recorded during the spectroelectrochemistry measurement. Optical path length = 0.02 cm. *Note that the start of the recording (red curve) is done when the steady-state between closed to open*



Figure S26. UV-Vis-NIR spectroelectrochemistry of **{PMo₉}.** A) and B) Evolution of the UV-Vis-NIR spectra recorded during first reduction. Inset of A) CV at scan rate of 20 mV.s⁻¹ recorded during the spectroelectrochemistry measurement. Note that the start of the recording corresponds to the red curve. Optical path length = 0.02 cm.



Figure S27. Differential UV-Vis-NIR spectroelectrochemistry upon electrochemical reduction of **{PMo**₉**}**. Evolution of the UV-Vis-NIR spectra recorded during first reduction. Inset CV at scan rate of 20 mV.s⁻¹ recorded during the spectroelectrochemistry measurement. Note that the start of the recording corresponds to the red curve. Optical path length = 0.02 cm.



Figure S28. UV-Vis-NIR spectroelectrochemistry of $\{PMo_9\}$ upon first and second electrochemical reduction. A) and B) Evolution of the UV-Vis-NIR spectra recorded during reduction. Inset of A) CV at scan rate of 20 mV.s-1 recorded during the spectroelectrochemistry measurement. Note that the start of the recording corresponds to the red curve. Optical path length = 0.02 cm.





Figure S29. Differential UV-Vis-NIR spectroelectrochemistry upon electrochemical reduction of **{PMo**₉**}**. Evolution of the UV-Vis-NIR spectra recorded during first reduction. Inset CV at scan rate of 20 mV.s⁻¹ recorded during the spectroelectrochemistry measurement. Note that the start of the recording corresponds to the red curve. Optical path length = 0.02 cm.

Figure S30. UV-Vis-NIR spectroelectrochemistry of (1(O_A)_x(C)_z); x + z = 3) upon electrochemical oxidation. A) Evolution of the UV-Vis-NIR spectra recorded during oxidation. B) CV at a scan rate of 20 mV.s⁻¹ recorded during the spectroelectrochemistry measurement. Note that the start of the recording (red curve) is done when the steady state between closed to open form is reached under UV-visible illumination.



Figure S31. Differential UV-Vis-NIR spectroelectrochemistry upon electrochemical oxidation of (1(O_A)_x(C)_z); x + z = 3). The baseline has been measured in the presence of the (TBA)₆(1(O_A)₃). A) Evolution of the UV-Vis-NIR spectra recorded during the CV measurement. Optical path length = 0.02 cm. B) CV at a scan rate of 20 mV.s⁻¹ recorded during the spectroelectrochemistry measurement.



Figure S32. UV-Vis-NIR spectroelectrochemistry of of $(1(O_A)_x(C)_z)$; x + z = 3) upon electrochemical oxidation and reduction. A) Evolution of the UV-Vis-NIR spectra recorded during the experiment. B) CV at a scan rate of 20 mV.s⁻¹ recorded during the spectroelectrochemistry measurement. Note that the start of the recording (red curve) is done when the steady state between closed to open form is reached under UV-visible illumination.



Figure S33. Differential UV-Vis-NIR spectroelectrochemistry upon electrochemical oxidation and reduction of (1(O_A)_x(C)_z); x + z = 3). Baseline has been measured in the presence of the (TBA)₆(1(O_A)₃). A) Evolution of the UV-Vis-NIR spectra recorded during the CV measurement. Optical path length = 0.02 cm. B) CV at scan rate of 20 mV.s⁻¹ recorded during the spectroelectrochemistry measurement.



Figure S34. CV of the $(1(O_A)_x(C)_z)$ (c = 1.72.10⁻⁴ M, 20°C) upon in 0.1 M n-Bu₄NPF₆ in acetonitrile / 1,4-dioxane (1 / 1) solution at scan rate of 20 mVs⁻¹recorded upon UV-visible (red curve), only visible illumination (green curve) or without illumination (black, red curve) on glassy carbon electrode.



Figure S35. CV of the **(1(O_A)_x(C)_z)** (c = 1.72.10⁻⁴ M, 20°C) upon in 0.1 M n-Bu₄NPF₆ in acetonitrile / 1,4-dioxane (1 / 1) solution at scan rate of 20 mV.s⁻¹recorded upon UV-visible (red curve), only visible illumination (blue curve), only UV illumination (green curve) or without illumination (black or red curve) on glassy carbon electrode.

| | ΔE/eV | ΔE/nm | f osc | Dominant orbital contribution | Comments |
|---|-------|-------|--------------|-------------------------------|--|
| 1 | 4.430 | 279.9 | 0.138946 | $HOMO \rightarrow LUMO+7$ | CT from ligand to POMs and other ligands |
| 2 | 4.574 | 271.1 | 0.167108 | HOMO-2 \rightarrow LUMO+6 | same as above |
| 3 | 4.667 | 265.7 | 1.198484 | $HOMO \rightarrow LUMO+7$ | same as above |
| 4 | 4.860 | 255.1 | 0.518569 | HOMO-1 \rightarrow LUMO+6 | same as above |
| 5 | 4.941 | 251.0 | 0.177399 | $HOMO \rightarrow LUMO+9$ | same as above |

Table S5. First five excitation energies (ΔE in eV and nm) for (1(O_A)₃), including calculated oscillator strength (f_{osc} in length
form), most dominant orbital contribution, and description of the nature of the transition. All findings are based on sTDA-
CAMB3LYP/def2-SVPD calculations.

| | ΔE/eV | ΔE/nm | f osc | Dominant orbital contribution | Comments |
|----|-------|-------|--------------|-------------------------------|--|
| 1 | 2.254 | 550.1 | 0.667750 | $HOMO \rightarrow LUMO$ | local, closed ligand |
| 2 | 3.394 | 365.3 | 0.073798 | HOMO-5 \rightarrow LUMO | local, closed ligand |
| 3 | 3.792 | 326.9 | 0.683857 | $HOMO \rightarrow LUMO+8$ | CT from closed ligand into POM units and other |
| | | | | | ligands |
| 4 | 4.120 | 300.9 | 0.000009 | HOMO-1 \rightarrow LUMO | CT from open to closed ligands |
| 5 | 4.131 | 300.1 | 0.000017 | $HOMO-2 \rightarrow LUMO$ | CT from open to closed ligands |
| 6 | 4.161 | 298.0 | 0.002262 | $HOMO \rightarrow LUMO+2$ | CT from closed ligand to POMs |
| 7 | 4.174 | 297.0 | 0.016724 | $HOMO \rightarrow LUMO+1$ | CT from closed ligand to POMs |
| 8 | 4.362 | 284.2 | 0.004542 | $HOMO \rightarrow LUMO+3$ | CT from closed ligand to POMs |
| 9 | 4.380 | 283.1 | 0.003122 | $HOMO \rightarrow LUMO+4$ | CT from closed ligand to POMs |
| 10 | 4.405 | 281.4 | 0.000058 | $HOMO \rightarrow LUMO+5$ | CT from closed ligand to POMs |
| 11 | 4.410 | 281.1 | 0.001542 | $HOMO \rightarrow LUMO+4$ | CT from closed ligand to POMs |

Table S6. First eleven excitation energies (ΔE in eV and nm) for $(1(O_A)_2(C)_1)$, including calculated oscillator strength (f_{osc} in length form), most dominant orbital contribution and description of the nature of the transition. All findings are based on sTDA-CAMB3LYP/def2-SVPD calculations.



Figure S36. CAMB3LYP/def2-SVPD orbitals (plotted with standard settings in VESTA) relevant for the excitations in (1(O_A)₃) listed in Table S5.



Figure S37. CAMB3LYP/def2-SVPD orbitals (plotted with standard settings in VESTA) relevant for the excitations in $(1(O_A)_2(C)_1)$ listed in Table S6.

References

- 1.C. Li, N. Mizuno, K. Yamaguchi and K. Suzuki, J. Am. Chem. Soc., 2019, 141, 7687-7692.
- 2.M. Han, Y. Luo, B. Damaschke, L. Gómez, X. Ribas, A. Jose, P. Peretzki, M. Seibt and G. H. Clever, Angew. Chem., Int. Ed., 2016, 55, 445-449.
- 3.O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, Chem. Commun., 2009, 42, 339-341.
- 4.P. van der Sluis and A. L. Spek, Acta Crystallogr., Sect. A, 1990, 46, 194-201.
- 5.D. Sinnaeve, Concepts Magn. Reson. A: Bridg. Educ. Res., 2012, 40A, 39-65.
- 6.D. Li, G. Kagan, R. Hopson and P. G. Williard, J. Am. Chem. Soc., 2009, 131, 5627-5634.
- 7.Y.-T. Chan, X. Li, J. Yu, G. A. Carri, C. N. Moorefield, G. R. Newkome and C. Wesdemiotis, J. Am. Chem. Soc., 2011, 133, 11967-11976.
- 8.G. Buntinx, R. Naskrecki and O. Poizat, J PHYS CHEM, 1996, 100, 19380-19388.
- 9.G. Buntinx, O. Poizat and N. Leygue, J PHYS CHEM, 1995, 99, 2343-2352.
- 10.M. Krejčik, M. Daněk and F. Hartl, J ELECTROANAL CHEM, 1991, 317, 179-187.
- 11.U. Megerle, R. Lechner, B. König and E. Riedle, *Photochem. Photobiol. Sci.*, 2010, **9**, 1400-1406.
- 12.F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka and F. Weigend, Wiley Interdiscip. Rev. Comput. Mol. Sci, 2014, 4, 91-100.
- 13.S. Grimme, J. G. Brandenburg, C. Bannwarth and A. Hansen, J. Chem. Phys., 2015, 143, 054107.
- 14.F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys, 2005, 7, 3297-3305.
- 15.A. Klamt and G. Schüürmann, J. Chem. Soc., Perkin Trans. 2, 1993, DOI: 10.1039/P29930000799, 799-805.
- 16.K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, Chem. Phys. Lett., 1995, 240, 283-290.
- 17.S. Grimme, J. Chem. Phys., 2013, 138, 244104.
- 18.F. Neese, Wiley Interdiscip. Rev. Comput. Mol. Sci, 2012, 2, 73-78.
- 19.F. Neese, Wiley Interdiscip. Rev. Comput. Mol. Sci, 2018, 8, e1327.
- 20.T. Yanai, D. P. Tew and N. C. Handy, Chem. Phys. Lett., 2004, 393, 51-57.
- 21.D. Rappoport and F. Furche, J. Chem. Phys., 2010, 133, 134105.
- 22.V. Barone and M. Cossi, J. Phys. Chem. A, 1998, 102, 1995-2001.
- 23.R. Izsák and F. Neese, J. Chem. Phys., 2011, 135, 144105.