

Supporting Information

Hierarchical Self-Assembly of Electron-Transferring Hybrid Nanostructures: CdS-Polymer-Porphyrin Nanoparticles in Aqueous Solution

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Chemicals

Cadmium nitrate tetrahydrate (99.999% trace metals basis), sodium sulfide nonahydrate ($\geq 98.0\%$), silver nitrate ($\geq 99.0\%$), poly(acrylic acid) (Average $M_W = 100\,000\text{ g mol}^{-1}$) were purchased from Sigma Aldrich. 5,10,15,20-Tetrakis(4-trimethylammonium-phenyl) porphyrin tetrachloride (H_2TAPP) was purchased from Fluka.

In all experiments, deionized water was used, which was filtered through a $0.450\ \mu\text{m}$ hydrophilic Millipore filter purchased from Merck.

Preparation

The preparation of CdS nanoparticles was achieved by mixing $\text{Cd}(\text{NO}_3)_2$ $3.5 \times 10^{-4}\text{ mol L}^{-1}$ and poly(acrylic acid) ($3.5 \times 10^{-4}\text{ mol L}^{-1}$ monomer concentration) in water. The poly(acrylic acids) used have an average $M_W = 2000\text{ g mol}^{-1}$, $M_W = 5100\text{ g mol}^{-1}$, $M_W = 10000\text{ g mol}^{-1}$, $M_W = 450000\text{ g mol}^{-1}$. To this solution, Na_2S ($4.27 \times 10^{-4}\text{ mol L}^{-1}$) was added and after 15 minutes of vigorously stirring the pH was adjusted to 10.5 with 1 M NaOH. Three different charge ratios l were obtained by adding porphyrin stock solutions: for $l = 0.125$ $c(\text{TAPP}/\text{ZnTAPP}) = 1.16 \times 10^{-5}\text{ mol L}^{-1}$, $l = 0.250$ $c(\text{TAPP}/\text{ZnTAPP}) = 2.32 \times 10^{-5}\text{ mol L}^{-1}$ and $l = 0.500$ $c(\text{TAPP}/\text{ZnTAPP}) = 4.64 \times 10^{-5}\text{ mol L}^{-1}$. The charge ratio l is defined as molar concentration of the cationic charges divided by the molar concentration of the anionic charges

$$l = \frac{c(\text{NMe}_3^+)}{c(\text{COO}^-)}$$

In the case of TAPP, the solution turned slightly green after several minutes indicating a metalation of the porphyrin with Cd^{2+} , which could be determined in UV-vis. After addition of

the porphyrin, the samples were ultrasonicated for 30 minutes at 35°C, leading to purely green solutions.

The preparation of 1%, 5% and 10% silver(I)-loaded CdS nanoparticles was achieved by mixing Cd(NO₃)₂ 3.46x10⁻⁴ mol L⁻¹ (1% Ag); 3.33x10⁻⁴ mol L⁻¹ (5% Ag); 3.20x10⁻⁴ mol L⁻¹ (10% Ag) with silver nitrate (1% Ag: 3.46x10⁻⁶ mol L⁻¹, 5% Ag: 1.67x10⁻⁵ mol L⁻¹, 10% Ag: 3.20x10⁻⁵ mol L⁻¹) and poly(acrylic acid) (3.5x10⁻⁴ mol L⁻¹ monomer concentration) in water. To this solution, Na₂S (4.27x10⁻⁴ mol L⁻¹) was added and after 15 minutes of vigorously stirring, the pH was adjusted to 10.5 with 1 M NaOH. After 15 minutes, TAPP (5.1x10⁻⁶ mol L⁻¹) was added, leading to a green colored solution, which was set under ultrasound to dissolve the remaining larger PAA precipitates. This solution was additionally filtered through a 0.450 μm cellulose acetate filter, providing monodisperse solutions.

Characterization techniques

For the light scattering experiment, a CGS 3 goniometer (ALV Langen, Germany) with a 22 mW laser providing a wavelength of $\lambda = 632.8$ nm and a ALV 5000 correlator with 320 channels were used. During the measurement, the angles between 30° to 150° were covered in 10° steps. Data analysis of dynamic light scattering was taken out via transformation of the autocorrelation function of the scattered light into the autocorrelation function of the electric field using the Siegert equation. The inverse Laplace transformation was carried out with the program CONTIN. The characteristic τ were transferred into the apparent diffusion coefficients using the equation. The apparent diffusion coefficients were extrapolated against $q^2 \rightarrow 0$. The extrapolated diffusion coefficient translates to the hydrodynamic radius with the Stokes Einstein equation.

UV/vis measurements were carried out with a Shimadzu UV-spectrometer (UV-1800). Quartz cuvettes with a path-length of 1 cm and 1 mm, purchased from Hellma/Mülheim, were used. CdS crystal sizes were determined from the slope at the absorption edge via “Henglein equation”.^{35,36}

Fluorescence measurements were performed with a Horiba Jobin Yvon fluorescence spectrometer using a slit width of 2 nm and an integration time of 0.1 s.

Transmission electron microscopy (TEM) images were obtained with a Zeiss EM 912 microscope, operated at 80 kV at magnifications from 20 000 to 250 000. The specimens were prepared by depositing 5 μL of the sample solution onto carbon-coated copper grids, 300 mesh, and air-dry the grids. The sizes of the particles were determined using the freely available software ImageJ.

Steady-state photoluminescence excitation and emission spectra were recorded on a FluoTime300 spectrometer from PicoQuant equipped with a 300 W ozone-free Xe lamp (250-900 nm), a 10 W Xe flash-lamp (250-900 nm, pulse width < 10 μ s) with repetition rates of 0.1 – 300 Hz, an excitation monochromator (Czerny-Turner 2.7 nm/mm dispersion, 1200 grooves/mm, blazed at 300 nm), diode lasers (pulse width < 80 ps) operated by a computer-controlled laser driver PDL-820 (repetition rate up to 80 MHz, burst mode for slow and weak decays), two emission monochromators (Czerny-Turner, selectable gratings blazed at 500 nm with 2.7 nm/mm dispersion and 1200 grooves/mm, or blazed at 1250 nm with 5.4 nm/mm dispersion and 600 grooves/mm), Glan-Thompson polarizers for excitation (Xe-lamps) and emission, a Peltier-thermostatized sample holder from Quantum Northwest (-40°C – 105°C), and two detectors, namely a PMA Hybrid 40 (transit time spread FWHM < 120 ps, 300 – 720 nm) and a R5509-42 NIR-photomultiplier tube (transit time spread FWHM 1.5 ns, 300-1400 nm) with external cooling (-80°C) from Hamamatsu. Steady-state and fluorescence lifetimes were recorded in TCSPC mode by a PicoHarp 300 (minimum base resolution 4 ps). Emission and excitation spectra were corrected for source intensity (lamp and grating) by standard correction curves. Lifetime analysis was performed using the commercial FluoFit software. The quality of the fit was assessed by minimizing the reduced chi squared function (χ^2) and visual inspection of the weighted residuals and their autocorrelation. Photoluminescence quantum yields were measured with a Hamamatsu Photonics absolute PL quantum yield measurement system (C9920-02) equipped with a L9799-01 CW xenon light source (150 W), monochromator, C7473 photonic multi-channel analyzer, integrating sphere and employing U6039-05 PLQY measurement software (Hamamatsu Photonics, Ltd., Shizuoka, Japan). All solvents used were of spectrometric grade.

The Femtosecond Transient Absorption spectra of the assemblies were recorded using a transient absorption pump / probe detection systems (Helios and Eos, Ultrafast Systems). The laser pulses were generated by a Ti:sapphire regenerative amplifier fs laser system (CPA-2110, Clark MXR) operating at 1 kHz (output 775 nm, pulse width 150 fs). The 570 nm excitation wavelength was generated with a femtosecond non-collinear optical parametric amplifier (NOPA, Clark MXR). The individual solutions were transferred into a 2 mm quartz cuvette, and purged with nitrogen.

Photocatalysis.

Photocatalytic reduction of methylviologen dication: The photocatalytic reduction of the methyl viologen dication MV^{2+} to the methyl viologen radical cation was also carried out with the 500 W tungsten lamp and the samples were placed at one-meter distance. The concentration of MV^{2+} was set to 4.8×10^{-5} mol L⁻¹ and the concentration of the sacrificial donor (triethanolamine, TEA) was set to 3.3×10^{-3} mol L⁻¹ in 3 mL.

Photocatalytic degradation of crocin and alizarin yellow. The photocatalytic model reaction with crocin was performed in aqueous medium using 3 mL of initial nanoparticle stock solution ($pH = 10.5$). The concentration of crocin was kept at $1.0 \times 10^{-4} \text{ mol L}^{-1}$. The degradation of Alizarin Yellow (AY) was carried out at $pH = 12$, reducing the overlap of AY and TAPP in the UV/vis spectrum. The concentration of AY was kept at $1 \times 10^{-5} \text{ mol L}^{-1}$. The irradiation was taken out with a solar light simulator and the sample was placed in 30 cm distance.

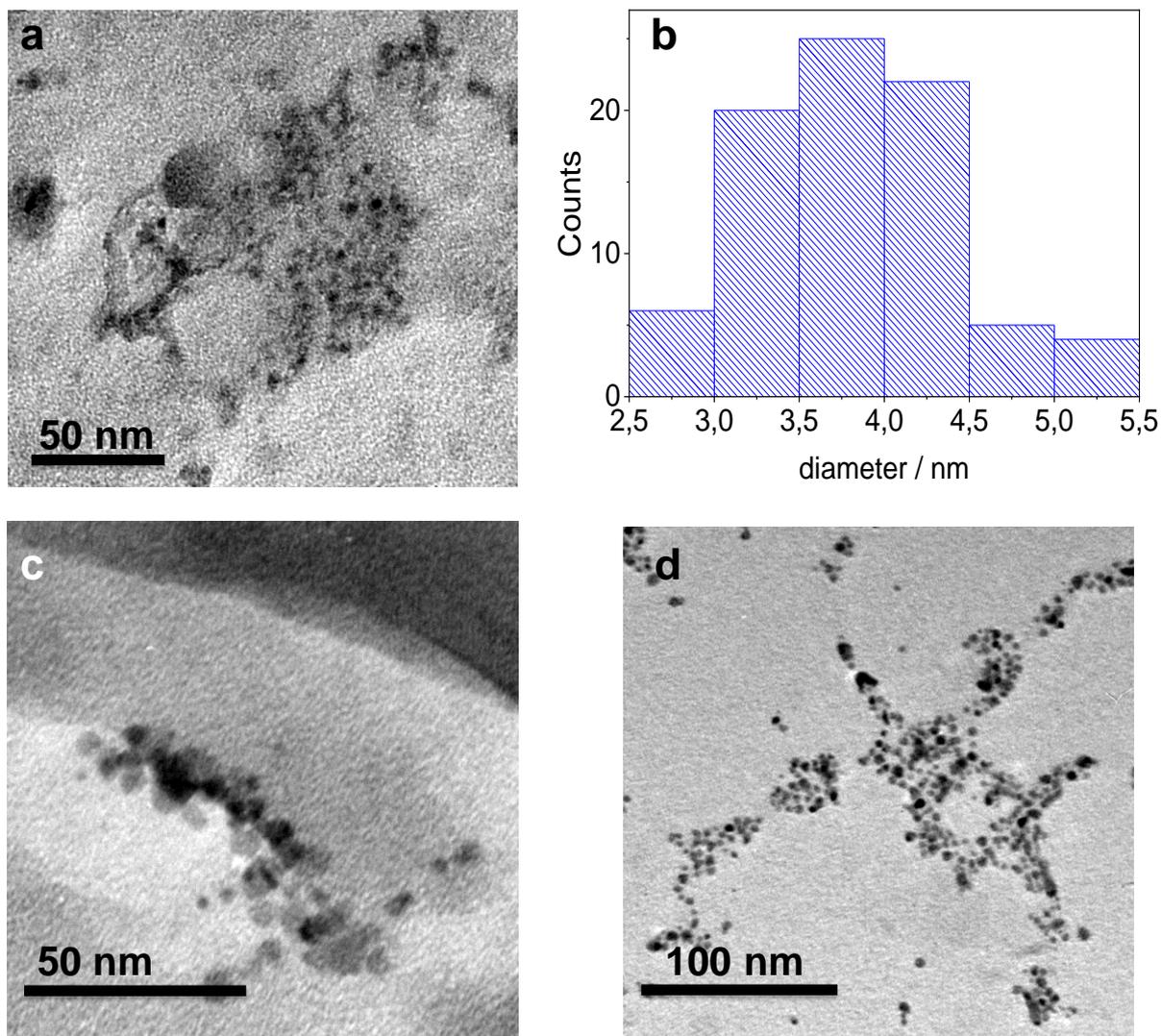


Figure S1. TEM of a) CdS nanoparticles grown in PAA100k with b) size distribution depicted as histogram of over 100 particles, c) 1% Ag and d) 10% Ag/CdS nanocrystals grown in PAA100k.

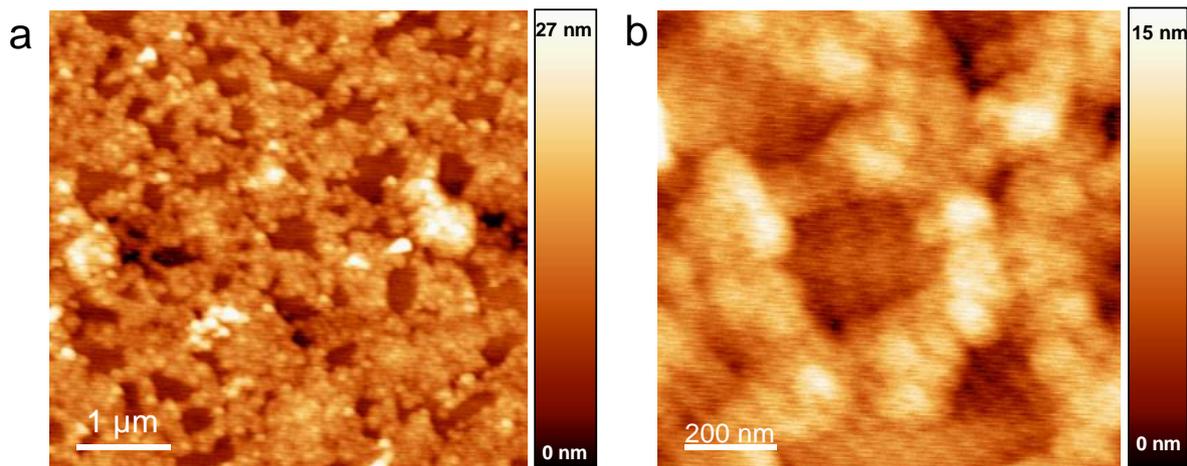


Figure S2. a) AFM image of CdS nanoparticles grown in PAA5.1k and assembled with TAPP at a loading ratio $l = 0.5$ on a mica grid. b) Magnified image of CdS nanoparticles grown in PAA5.1k and assembled with TAPP at a loading ratio $l = 0.5$ with visible smaller structures of $d_{\text{average}} = 100$ nm.

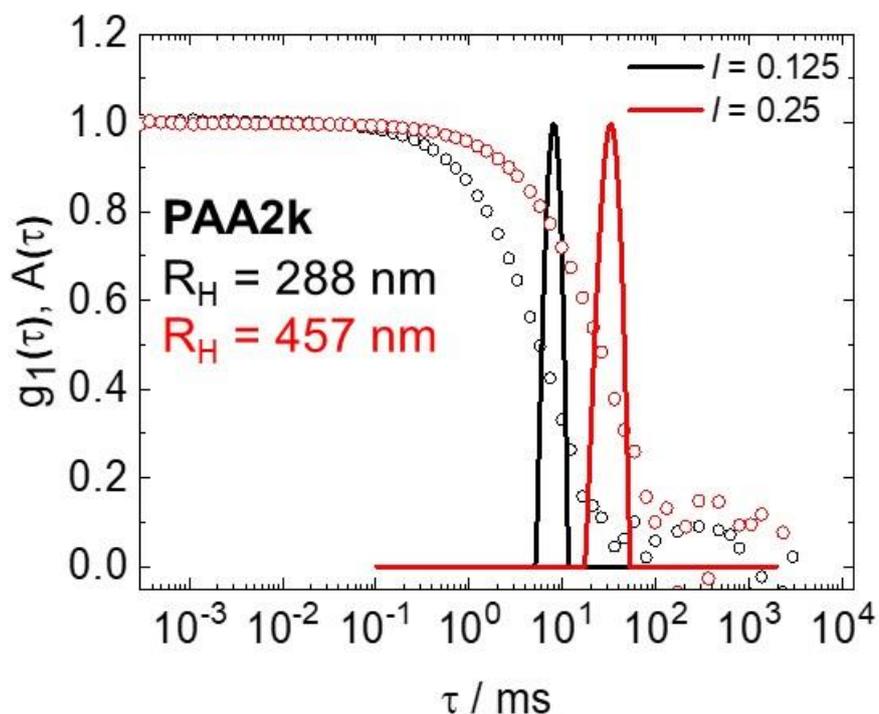


Figure S3. Dynamic light scattering of CdS-PAA-TAPP assemblies with varying PAA molecular masses. Electric field autocorrelation function $g_1(\tau)$ (circles) and distribution of relaxation times $A(\tau)$ (lines) of CdS-PAA2k-TAPP loading ratios of 0.125 (black), 0.25 (red) at a scattering angle $\theta = 90^\circ$. The R_H values depicted in the graph were obtained by extrapolation of the measured angles to $q = 0$. (PAA2k with $l = 0.5$ precipitates and cannot be measured with DLS).

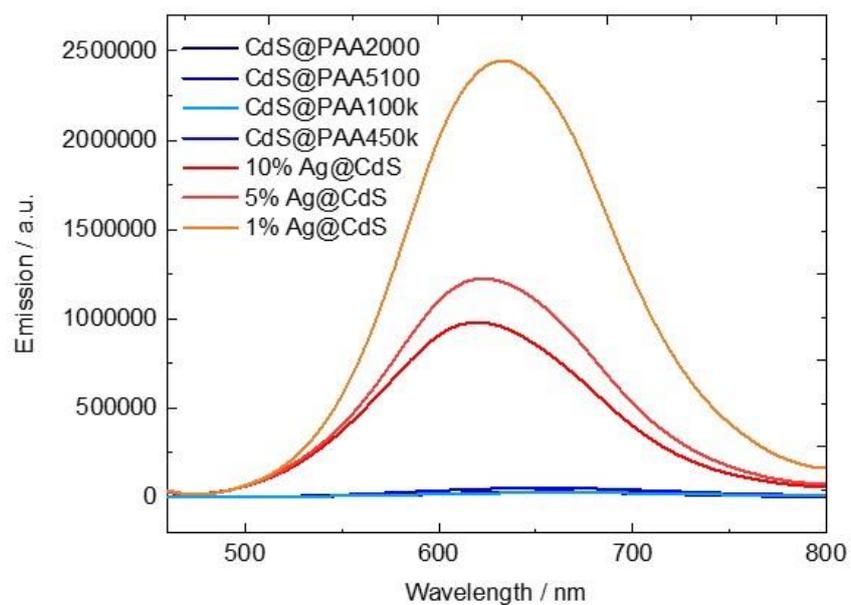


Figure S4. Direct comparison of steady-state photoluminescence intensity of pure CdS (bluish colors) and silver(I)-loaded CdS (reddish colors). Excited at $\lambda = 425$ nm.

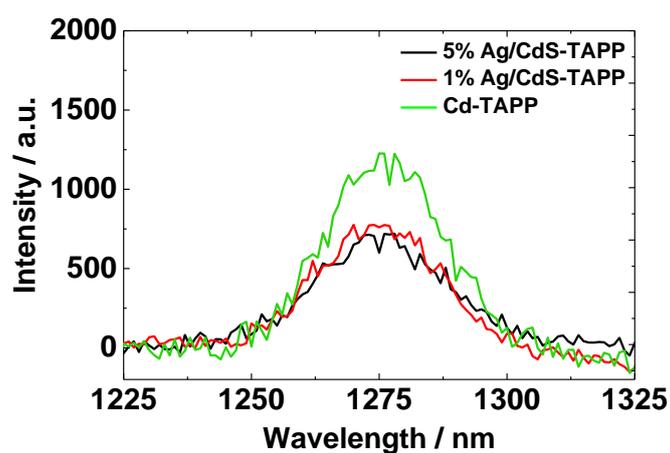


Figure S5: Singlet oxygen phosphorescence spectra for 5% Ag/CdS-TAPP (black), 1% Ag/CdS-TAPP (red), Cd-TAPP (green). Excited at $\lambda = 425$ nm.

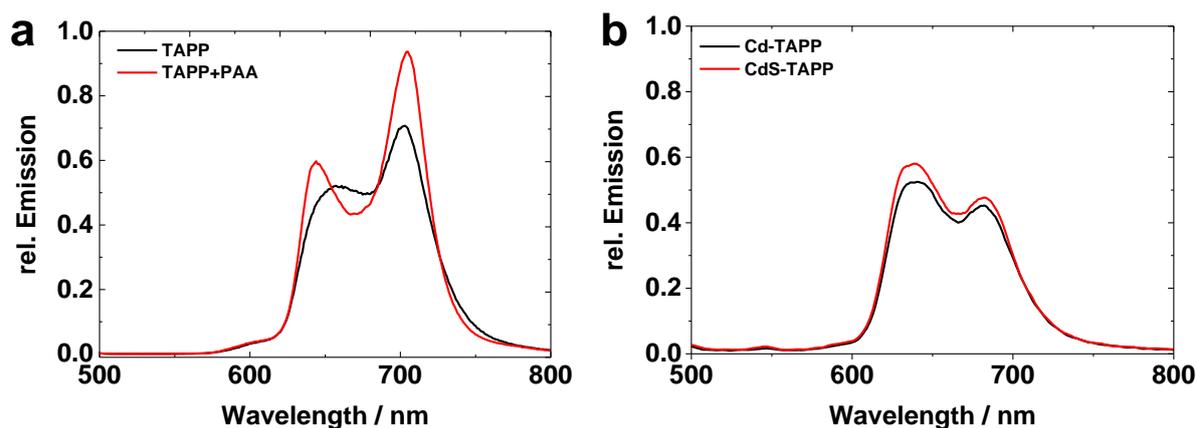


Figure S6: Steady-state photoluminescence spectra of a) TAPP (black curve) and TAPP+PAA (red curve) excited at $\lambda = 425$ nm; b) steady-state photoluminescence spectra of Cd-TAPP and CdS-TAPP excited at 450 nm. In combination with the reduction of Q-bands this result gives a strong indication that the TAPP is metallated with Cd(II) instead of undergoing simple self-assembly with the polymer.

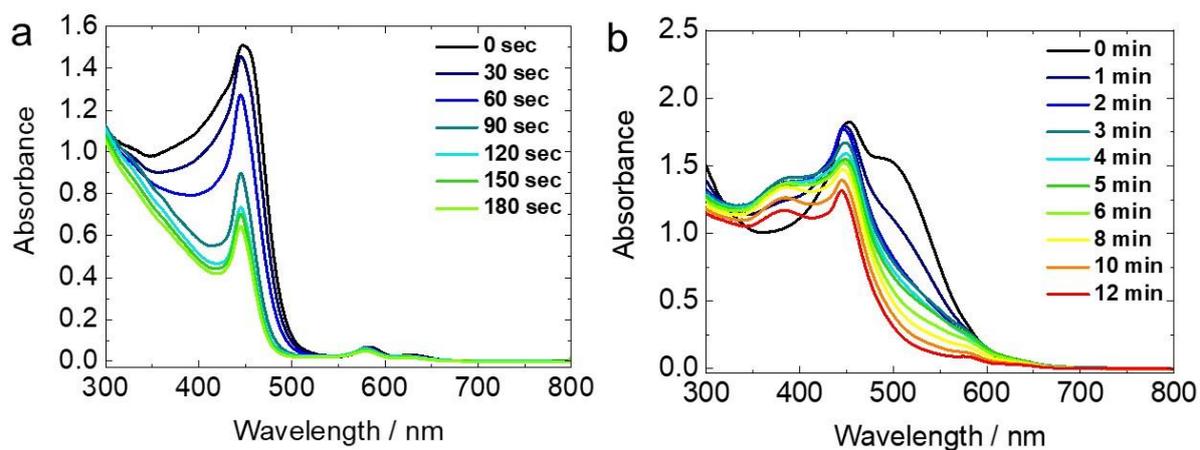


Figure S7. UV/vis absorption spectra measured along the degradation process of crocin and alizarin yellow, recorded after defined time intervals during irradiation. a) Degradation of crocin in the presence of CdS-PAA100k-TAPP with $I = 0.06$. b) Degradation of alizarin yellow in the presence of CdS-PAA100k-TAPP with $I = 0.06$.

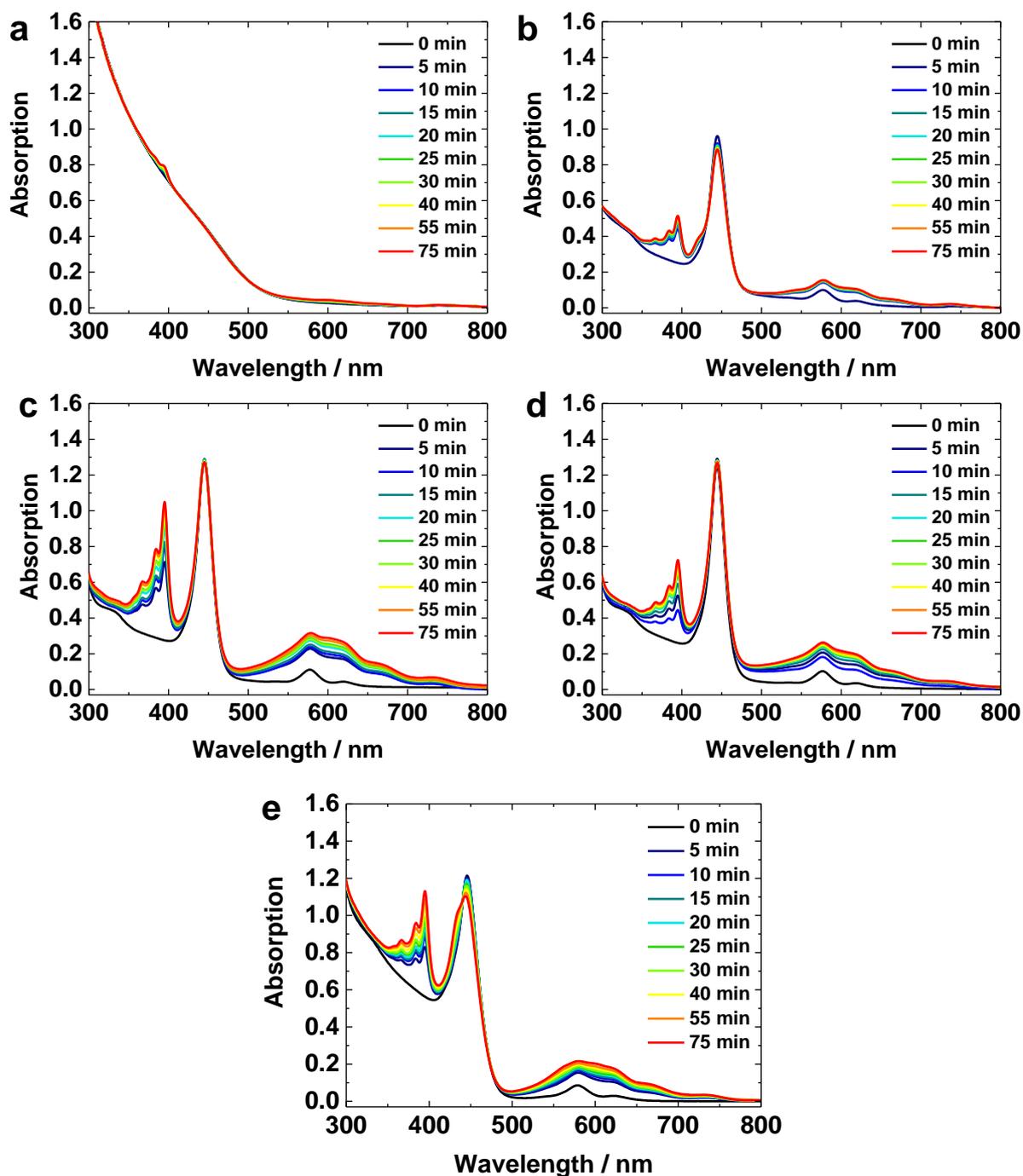


Figure S8: UV/vis absorption spectra measured to monitor the methylviologen radical cation formation with using a) CdS, b) Cd-TAPP, c) 5% Ag/CdS+TAPP, d) 10% Ag/CdS+TAPP, e) CdS-TAPP (recorded after defined intervals during the irradiation process).