

Supporting Information

Influence of Complex-Formation Equilibria on the Temporal Persistence of Cysteinate-Functionalized CdSe Nanocrystals in Water

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S1. Experimental Details

Materials. All materials were used without further purification. L-cysteine (Cys) and sodium sulfite were obtained from Sigma Aldrich. Selenium powder and cadmium sulfate octahydrate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) were purchased from Alfa Aesar. Sodium hydroxide (NaOH) and 2-propanol were obtained from J.T. Baker. Deionized water (DI) was obtained using a Barnstead International EASYPure II water purifier.

Synthesis of MC₄₂₂. MC₄₂₂ was prepared by adaptation of an all-aqueous route reported in the literature.¹⁻³ A solution of NaSeSO₃ was made by mixing selenium powder (0.167 g) and NaSO₃ (0.797 g) in deionized water (DI) (42 mL) in a round-bottom flask. The flask was covered with foil to prevent photooxidation, heated to a gentle boil and left to reflux overnight. A cadmium precursor solution was made in DI (78 mL) through the addition of Cys (0.180 g) and $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (0.115 g). Solid NaOH was added to the solution until a pH of at least 12.5 was obtained. The entire cadmium precursor solution was magnetically stirred while an aliquot of the NaSeSO₃ solution (4 mL) was added. The reaction solution was allowed to age for at least 7 days in the dark under ambient laboratory conditions prior to further analysis. The

concentrations of the reactants in the final reaction solution were as follows: $[\text{Cd}^{2+}] = 5.5 \text{ mM}$, $[\text{Se}^{2-}] = 2.5 \text{ mM}$ and $[\text{Cys}] = 18 \text{ mM}$.

Analysis by X-Ray Powder Diffraction (XRD). The MC_{422} sample was prepared by combining an aliquot (15 mL) from the MC_{422} reaction solution with 2-propanol (30 mL) in a centrifuge tube. The solution was shaken and then centrifuged (1509 g) for 10 minutes. The supernatant was discarded and the solid pellet was allowed to dry for 3 days. The pellet was ground to a fine power using a mortar and pestle and distributed evenly in a well. XRD data were generated in the θ -2 θ geometry on a Rigaku Ultima IV X-ray diffractometer operating with Cu K α radiation ($\lambda = 0.154 \text{ nm}$) scanning from 20° to 65° at 1° per minute. The resulting spectrum was processed by Savitzky-Golay smoothing.

Analysis by UV-Visible Absorption Spectroscopy. The MC_{422} sample was prepared by mixing an aliquot (500 μL) from the MC_{422} reaction mixture with 2-propanol (500 μL) in a microcentrifuge tube. After centrifugation (5585 g) for 30 seconds, the supernatant was discarded and an aliquot of a 100 mM NaOH (500 μL) was added to resuspend the extracted MC_{422} pellet. An aliquot of this suspension (200 μL) was combined with an aliquot (2.8 mL) containing the evaluated solution (Table S1) in a plastic cuvette (1 cm path length) sealed with Parafilm. Samples were prepared and analyzed in the dark to minimize photooxidation. Control samples were prepared directly from the various solutions described in Table S1. Spectra for these controls were obtained in tandem with those of MC_{422} . Absorption spectra were obtained using an 8453 ultraviolet-visible spectrophotometer from Agilent Technologies. Spectra were baseline corrected through the subtraction of the average absorbance value calculated between 800-900 nm.

Preparation of Solutions. The solutions used to test the temporal persistence of MC₄₂₂ in the presence of Cys and Cd²⁺ were prepared as described in Table S1 below. The solutions containing both Cys and Cd²⁺ were prepared in a specific manner to enable complete dissolution of the constituents. The appropriate amount of 3CdSO₄•8H₂O was combined with DI in a volumetric flask. The contents were then mixed until all solid had dissolved. At this point, the appropriate mass of Cys was added to the flask, which generated a white precipitate. The addition of an aliquot of concentrated NaOH to the flask dissolved the precipitate and DI was added to the mark. If the pH was raised prior to the combination of the solid Cys and CdSO₄, a white solid formed that remained insoluble under the solution conditions. The concentration of NaOH added to the solution was determined by the amount of Cys present, as it was desired to maintain a pH above ~12.5, well above the pK_a values of Cys.

Under certain molar ratios of Cys:Cd²⁺ (*R*) in the control solutions, a spectrum began to evolve with features similar to those observed in the literature for CdS NCs, despite the lack of an alternative source of sulfide other than from Cys.⁴⁻⁶ In a recent work, Döllefeld et al. reported the spontaneous growth of CdS NCs in an aqueous alkaline solution with 1-thioglycerol as the only sulfide source.⁴ The growth of the spectrum was observed only for the control solutions containing *R*= 6.5, 13 or 26. A representative spectral overlay can be seen in Figure S7. No further analysis was conducted to confirm the identity of the species giving rise to the spectra as it was beyond the scope of this report.

Perturbing the Equilibria. In order to test the equilibria described in this report, an aliquot containing MC₄₂₂ was taken directly from the reaction solution and exposed either to excess Cys or to a Cd²⁺-Cys solution with *R*=2. Changes in the absorption spectrum were then monitored as a function of time to determine whether decay pathways reflected those predicted by the

proposed equilibria (Scheme 2). A “bulk mixture” was generated by combining an aliquot from the original MC₄₂₂ reaction solution (1.067 mL) with 100 mM NaOH (14.933 mL). The mixture was prepared without performing the 2-propanol extraction procedure. The resulting solution was then used to prepare the five samples described below. Five aliquots from the bulk mixture (2.950 mL) were placed into five separate plastic cuvettes and sealed with Parafilm. Absorption spectra were then obtained during a 24 hour period. After the 24 hour period, the samples were treated as described below, and spectra were obtained at random intervals for an additional 50 hours.

Samples:

1. *Spiked with R=2*: An aliquot (50 μ L) of a solution containing 3CdSO₄•8H₂O (102.6 mM), Cys (616.2 mM) and NaOH (1.3 M) was added to the cuvette and a spectrum was obtained immediately.
2. *Spiked with 81 mM Cys*: An aliquot (50 μ L) of NaOH (11.1 M) and solid Cys (27.5 mg) were sequentially added to the cuvette. The sample was mixed until the Cys had dissolved and a spectrum was obtained immediately.
3. *Control 1*: This sample is from the bulk mixture that was sealed and remained undisturbed while spectra were acquired for the entire 74 hour analysis.
4. *Control 2*: This sample is a control solution for the “Spiked with R=2” sample described above. An aliquot (50 μ L) of NaOH (25 mM) was added to the cuvette and a spectrum was obtained immediately.
5. *Control 3*: This sample is a control solution for the “Spiked with 81 mM Cys” sample described above. An aliquot (50 μ L) of NaOH (11.1 M) was added to the cuvette, and a spectrum was obtained immediately.

Table S1. Composition of the solutions used to evaluate the persistence of MC₄₂₂ in the presence of Cys and Cd²⁺.

<i>Solution Description</i>	<i>Solution #</i>	<i>[Cys] (mM)</i>	<i>[Cd²⁺] (mM)</i>	<i>[NaOH] (mM)</i>
Base	-	0	0	100
1 mM Cys	-	1.0	0	100
9 mM Cys	-	9.0	0	100
18 mM Cys	-	18	0	100
81 mM Cys	-	81	0	200
144 mM Cys	-	144	0	350
<i>R</i> *=2	1	18	9.0	100
<i>R</i> =2	2	11	5.5	100
<i>R</i> =3.3	3	18	5.5	100
<i>R</i> =6.5	4	18	2.75	100
<i>R</i> =6.5	5	36	5.5	100
<i>R</i> =13	6	18	1.38	100
<i>R</i> =13	7	72	5.5	200
<i>R</i> =26	8	18	0.69	100
<i>R</i> =26	9	144	5.5	350

**R* = molar ratio of Cys:Cd²⁺

S2. Supporting Figures

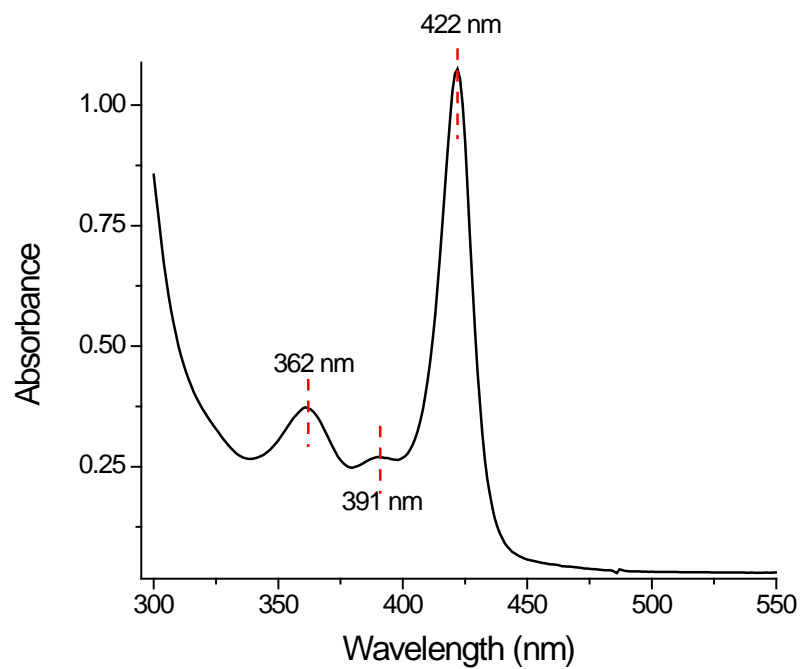


Figure S1. Typical absorption spectrum of extracted MC₄₂₂ suspended in an alkaline solution prior to degradation. Distinct spectral features, including λ_{max} , are indicated on the spectrum.

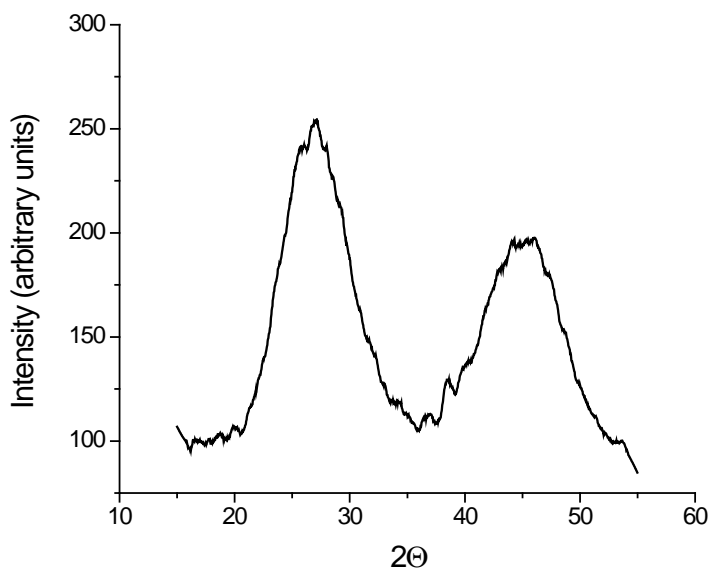


Figure S2. X-ray powder diffraction spectrum for as-synthesized MC₄₂₂.

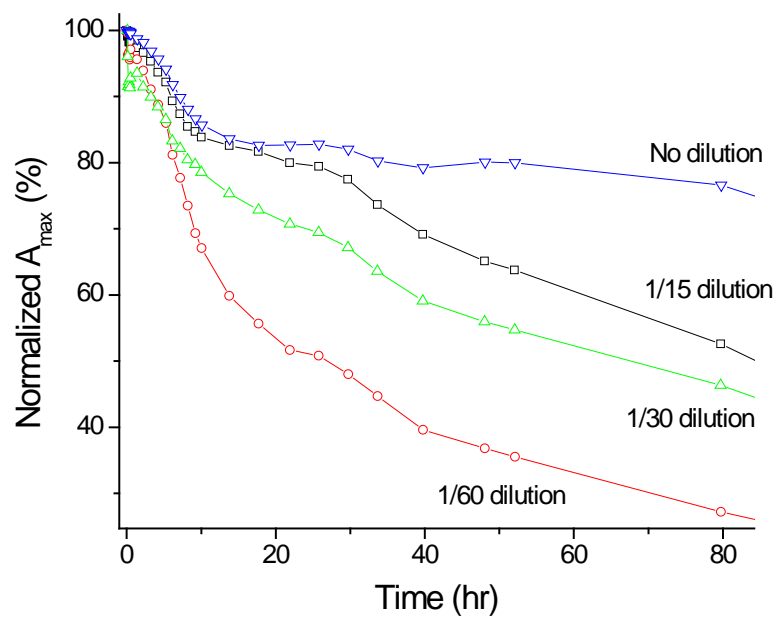


Figure S3. Influence of the concentration of MC₄₂₂ on the rate at which A_{\max} decreased after dilution into 100 mM NaOH. Normalized A_{\max} values reported as a percentage relative to the first data point.

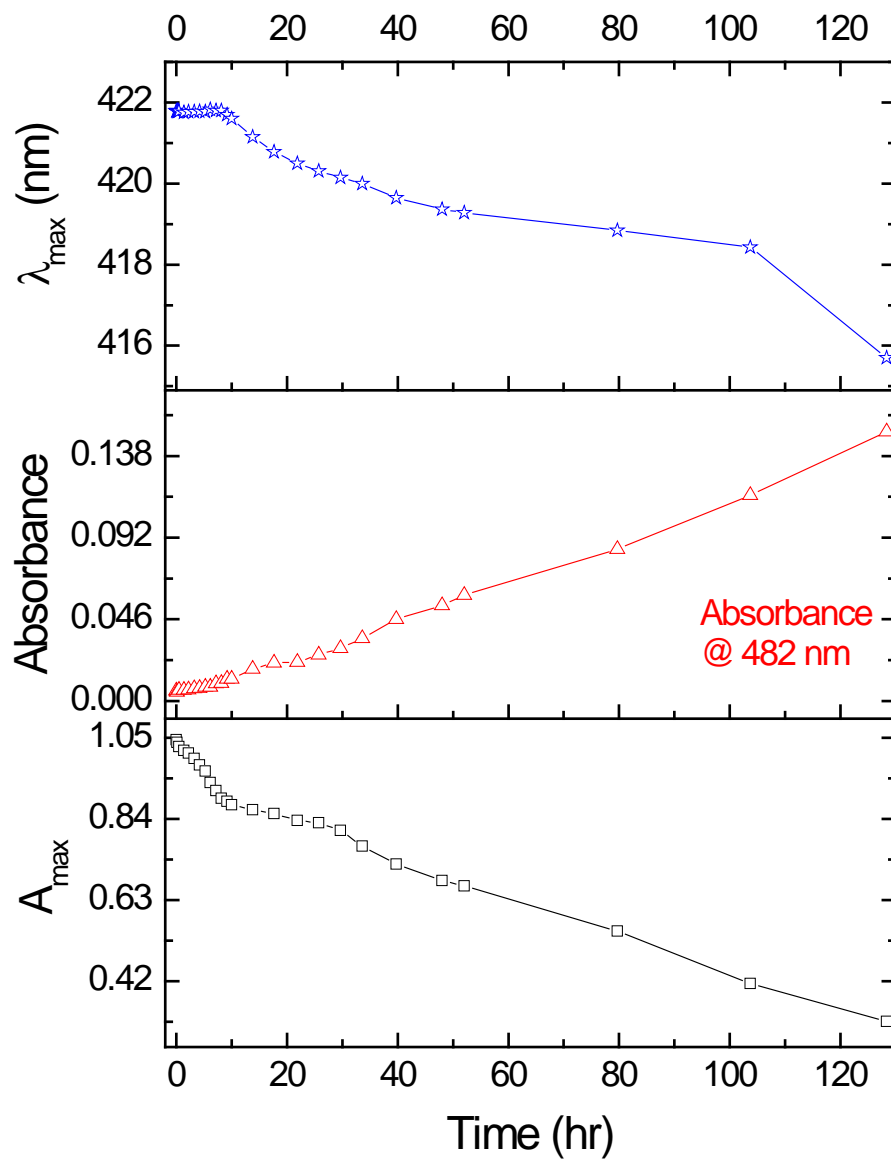


Figure S4. A_{max} (bottom), absorbance at 482 nm (middle) and λ_{max} (top) as a function of time after dilution of MC₄₂₂ into 100 mM NaOH.

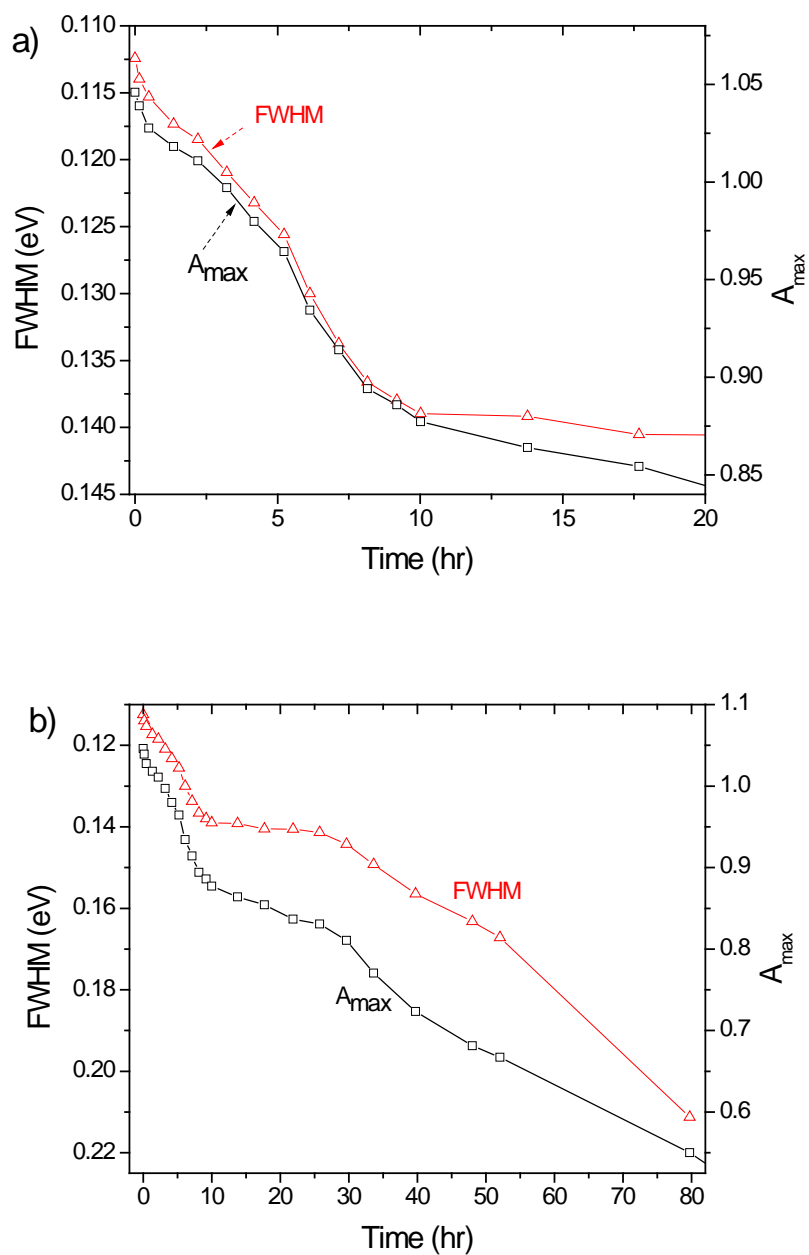


Figure S5. A_{\max} (black trace) and FWHM (red trace) as a function of time after dilution of MC₄₂₂ into 100 mM NaOH. The plots show data from the first 20 hours after dilution (a) and all data prior to flocculation (b).

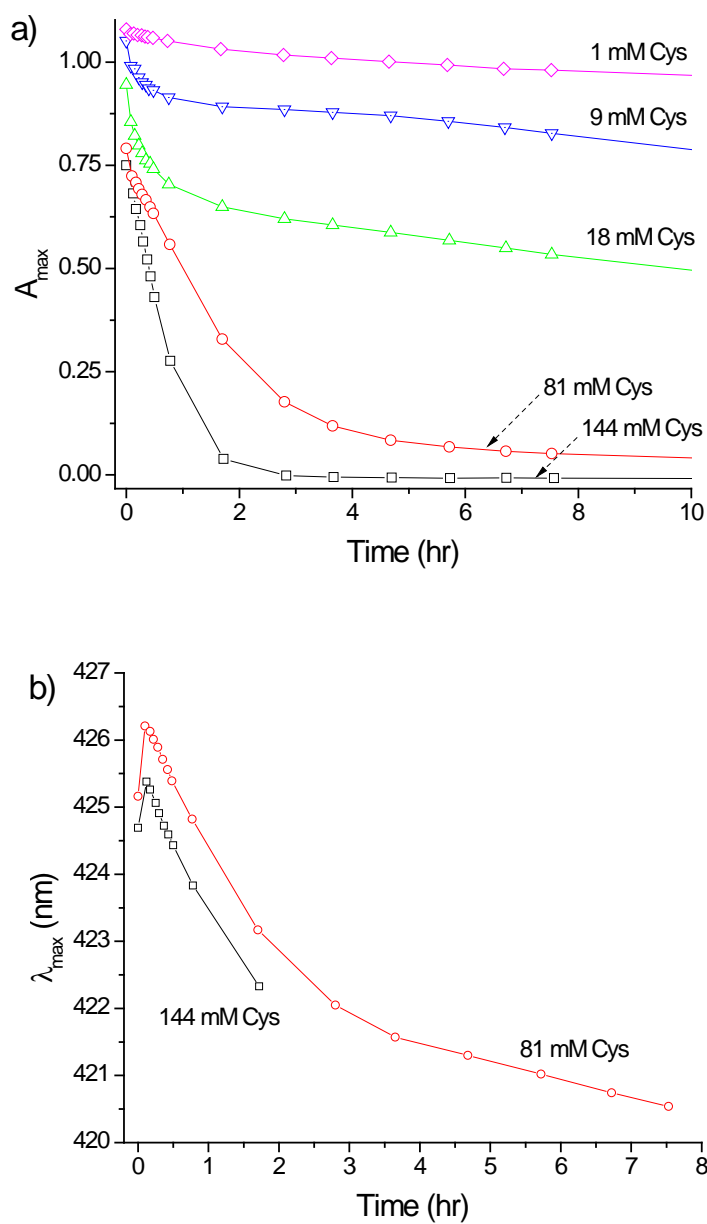


Figure S6. A_{\max} (a) and λ_{\max} (b) as a function of time after dilution of MC₄₂₂ into basic ($\text{pH} \geq 12.5$) solutions containing various concentrations of Cys.

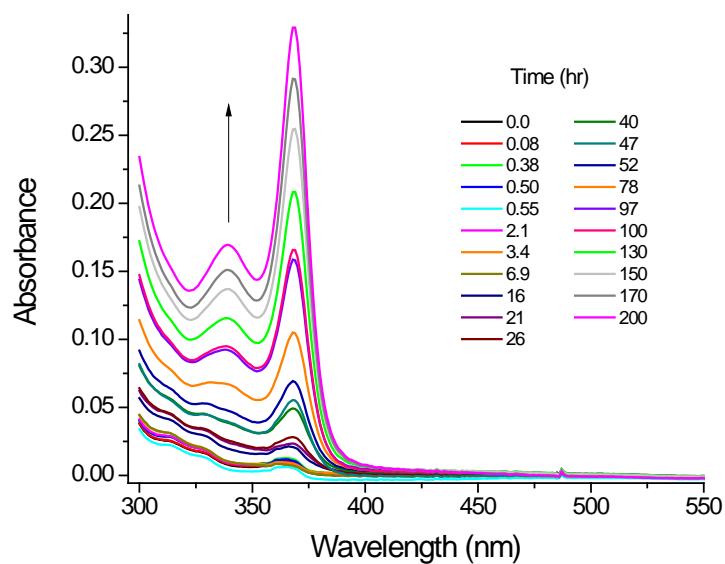


Figure S7. Temporal evolution of the absorption spectrum of a control sample consisting of an aqueous solution of Cys (36 mM), CdSO₄ (5.5 mM), and NaOH (100 mM). The arrow indicates the direction of the change of absorbance.

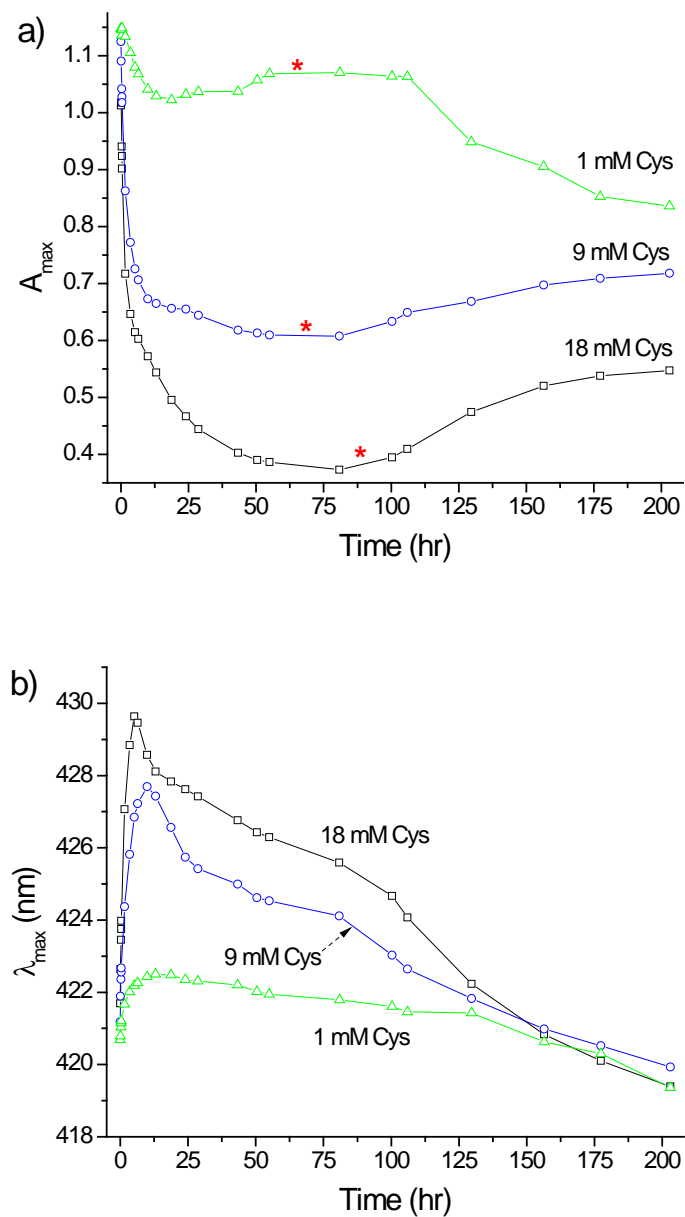


Figure S8. A_{\max} (a) and λ_{\max} (b) as a function of time after dilution of MC₄₂₂ into aqueous solutions containing 100 mM NaOH and various concentrations of Cys. The red asterisks (a) indicate the time at which the red-shifted absorption bands were first observed for each sample.

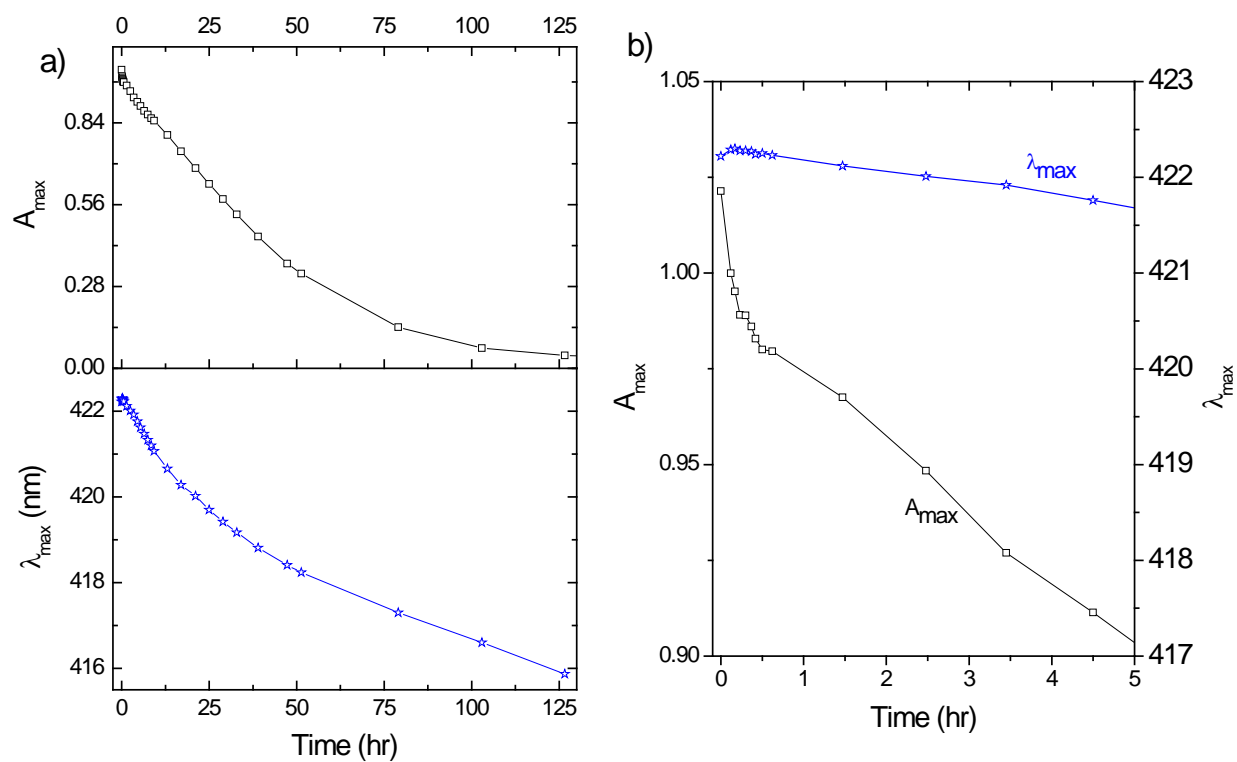


Figure S9. a) A_{\max} (top) and λ_{\max} (bottom) as a function of time after dilution of MC_{422} into solution 1 ($R=2$). b) Overlay highlighting the initial changes prior to 5 hours.

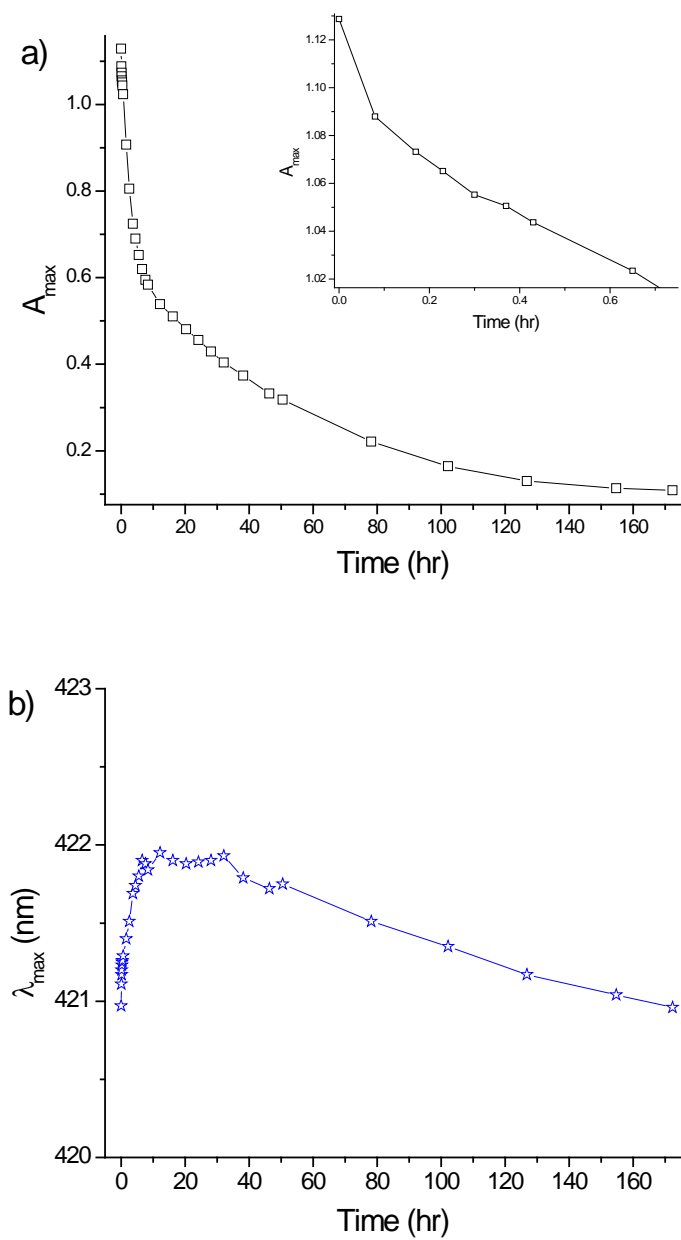


Figure S10. A_{\max} (a) and λ_{\max} (b) as a function of time after dilution of MC_{422} into solution 9 ($R=26$). Inset (a) highlights the initial decay kinetics.

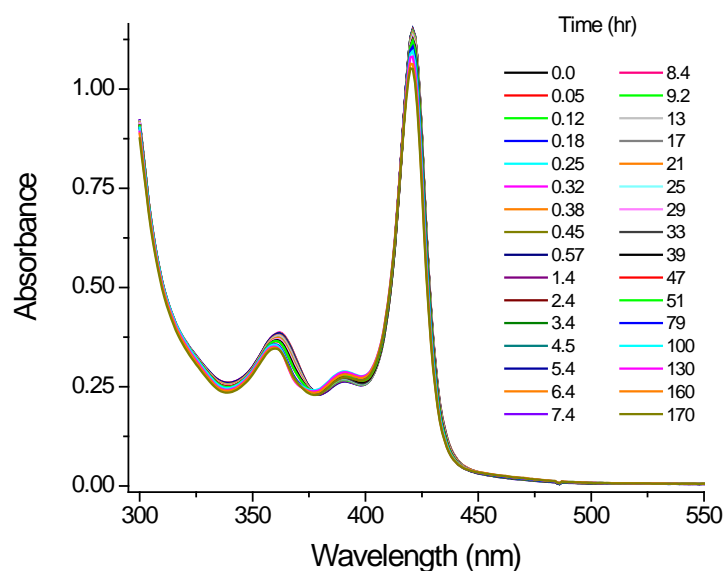


Figure S11. Temporal evolution of the absorption spectrum of MC₄₂₂ after dilution into solution 8 ($R=26$, $[\text{Cd}^{2+}] = 0.69 \text{ mM}$, $[\text{Cys}] = 18 \text{ mM}$).

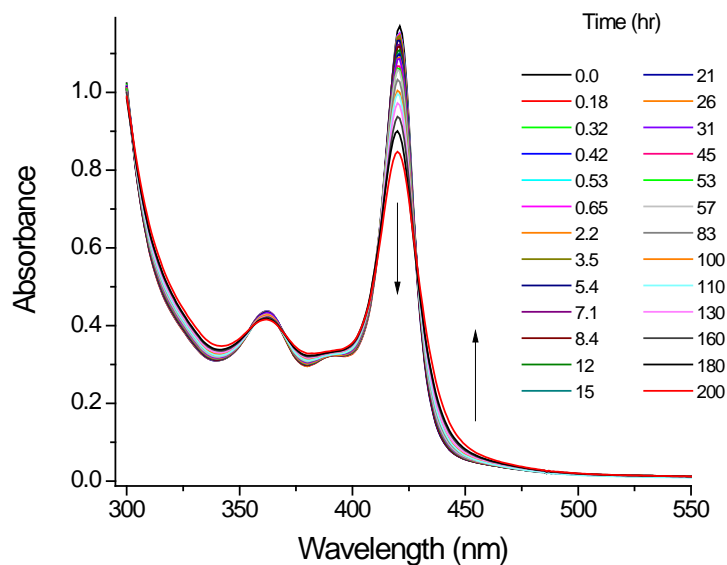


Figure S12. Temporal evolution of the absorption spectrum for an unextracted aliquot containing MC₄₂₂ taken directly from the reaction mixture, suspended in an alkaline solution. Arrows indicate the directions of the changes of absorbance.

References

1. Park, Y.-S.; Dmytruk, A.; Dmitruk, I.; Kasuya, A.; Okamoto, Y.; Kaji, N.; Tokeshi, M.; Baba, Y. Aqueous Phase Synthesized CdSe Nanoparticles with Well-Defined Numbers of Constituent Atoms. *J. Phys. Chem. C* **2010**, *114*, 18834-18840.
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