

Carbon dots for photocatalytic H₂ production in aqueous media with molecular Co catalysts

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1. General information

All the reagents and the solvents were purchased from usual commercial sources and used without further purification, unless otherwise stated. The purification of carbon dots was carried out in dialysis bag Ready Lyzer 20, MWCO 1kDa, SERVA. For the characterization of the synthesized Co catalysts ^1H NMR spectroscopy and MALDI-TOF mass spectrometry were performed. The ^1H NMR spectra of the compounds were recorded on Bruker AMX-500 MHz and Bruker DPX-300 MHz spectrometers. The solution of the sample was in deuterated solvent by using the solvent peak as the internal standard. X-Ray powder diffraction (XRD) Bruker Model D8 equipped with twin-twin technology, Geometry 2theta/theta. A transmission electron microscopy (TEM) system (Model JEM-2100F electron microscope (JEOL, Japan)) was used for morphology characterization of C-Dots. A dilute carbon dot stock solution was deposited onto the grid for subsequent HRTEM imaging, using an 80 kV accelerating voltage. High-resolution mass spectra were recorded on a Bruker ultrafleXtreme MALDI-TOF/TOF spectrometer.

2. Photophysical Measurements

The UV-Vis absorption spectra of all compounds in solution were obtained using a Shimadzu UV-1700 spectrophotometer in quartz cuvettes of 1 cm path-length. The emission spectra of all derivatives in solution were measured on a JASCO FP-6500 fluorescence spectrophotometer equipped with a red-sensitive WRE-343 photomultiplier tube (wavelength range: 200-850 nm).

3. Electrochemical Measurements

Cyclic and square wave voltammetry experiments were carried out in deionized water at room temperature using an AutoLab PGSTAT20 potentiostat in the presence of 0.1 M sodium sulfate (Na_2SO_4) solution at pH=5 as the supporting electrolyte. A three-electrode cell setup was used with platinum as the working electrode (3 mm diameter), Ag/AgCl as the reference electrode and a platinum wire as the counter electrode. Oxygen was removed by purging the aqueous solution with nitrogen. The

working electrode was polished before use with 0.05 μm alumina suspension and deionized water.

4. Synthetic procedures

I. Preparation of carbon dots

Citric acid 5 g was placed in a glass flask, then it was added in the oven and heated at 180 °C for 48 h. A yellow-brown sticky solid was obtained and was dissolved in 10 ml deionized water, purified in a 1kDa dialysis bag for 48 h. The product was cooled to room temperature naturally. Finally, the product **CDot** was freeze-dried overnight to obtain a light brown solid in ca. 35% yield.

II. Preparation of N-doped carbon dots

Citric acid 1.05 g and ethylenediamine 340 μl were dissolved in 10 ml deionized water in a Teflon-lined autoclave that was sealed and heated at 180 °C for 8 h and the reactor was left to obtain room temperature naturally. The resulted **NCDot** were purified in a 1kDa dialysis bag for 48 h, the freeze-dried overnight to obtain a dark brown foam like solid in ca. 40% yield.

III. Preparation of Cobalt catalysts CatCo(III)1, CatCo(III)2, CatCo(III)3

Cobalt based molecular catalysts were synthesized as described in the literature.¹⁻³

5. Light-driven hydrogen production experiments

The photocatalytic reactions were performed in 3 ml aqueous solution of TCEP/AA (1:1) 0.1 M each at pH 5.0. The TCEP and AA are both serving as reversible sacrificial electron donors. A 10 ml flask was used with a rubber septum where the mixture was purged with nitrogen for 15 min in order to remove oxygen. The reaction mixture was continuously stirred with irradiated with a 100 W UV led (375 nm) and a 100 W white led emitting lamp. At certain time intervals 100 μl was removed from the headspace of the flask and was analyzed by Shimadzu GC 2010 plus chromatograph with a TCD detector and a molecular sieve 5 Å column (30 m - 0.53 mm) in order to measure the amount of H₂ that was produced. The H₂ amount produced was quantified using a

calibration curve and in all cases, the reported H₂ production and the Turn Over Number (TON) is the average of three independent experiments.

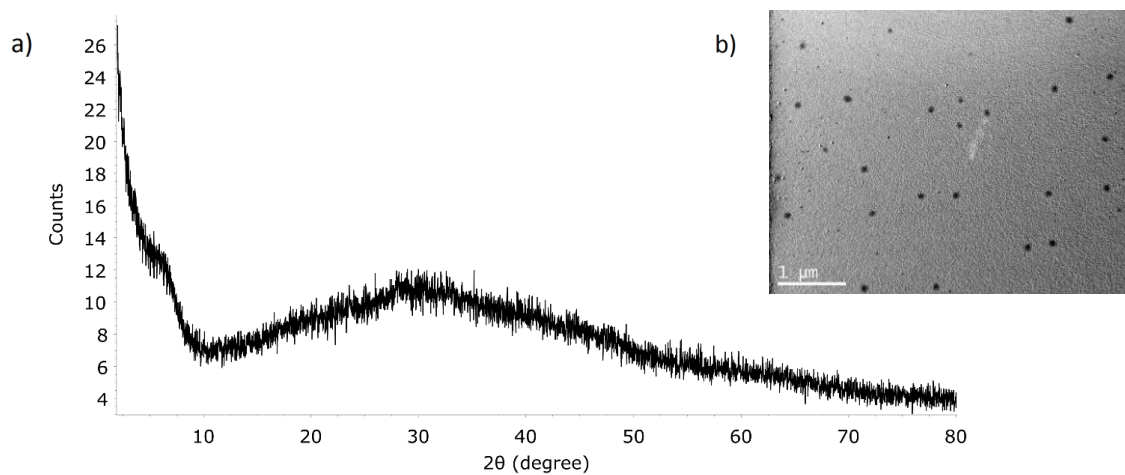


Figure S1. a) XRD pattern and b) TEM image of **CDot**.

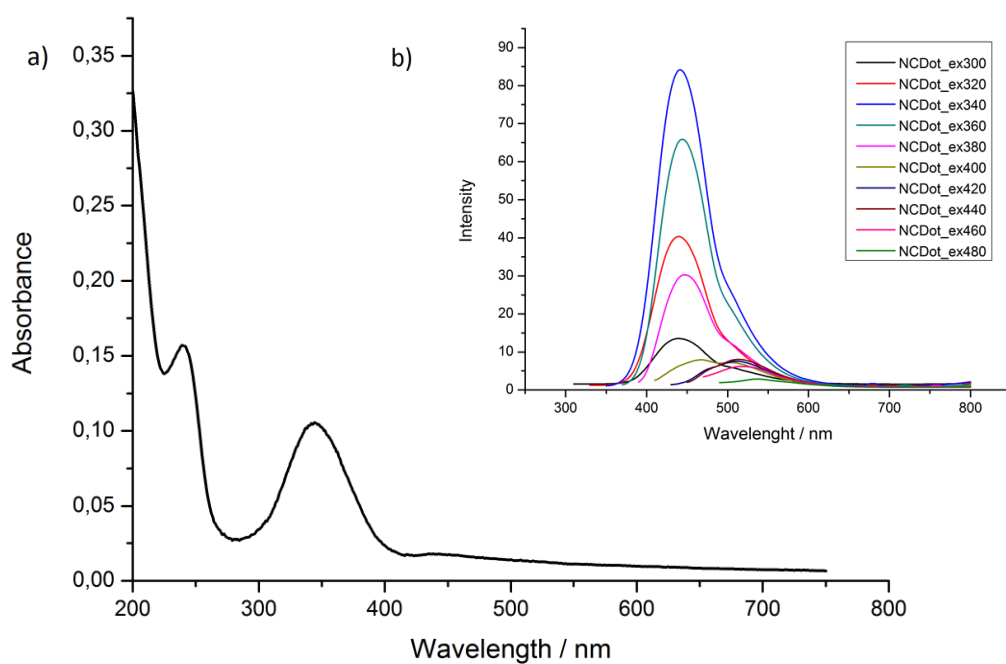


Figure S2. a) UV-Vis absorption spectra and b) Fluorescence spectra of **NCDotMix**.

Table S1. Oxidation and reduction potentials of carbon dots vs Ag/AgCl.

| Carbon Dots | $E_{1/2}$ Ox (V) | $E_{1/2}$ Red ¹ (V) | $E_{1/2}$ Red ² (V) |
|-------------|------------------|--------------------------------|--------------------------------|
| NCDot | +0.82 | -1.06 | - |
| NCDotMix | +0.82 | -1.25 | - |
| CDot | +0.99 | -0.98 | -1.22 |

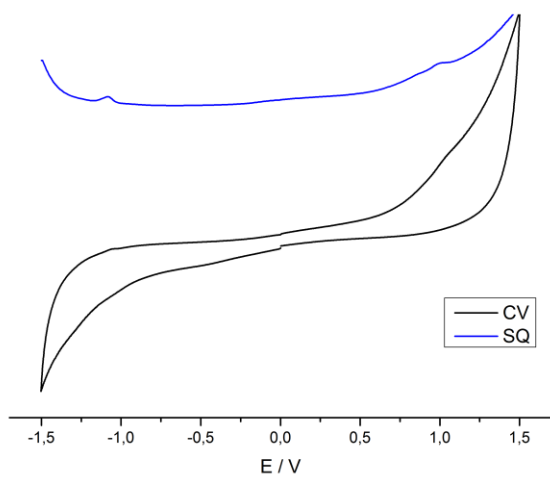


Figure S3. Cyclic voltammetry of **CDot** in Na₂SO₄ 0.1M pH=5 at room temperature.

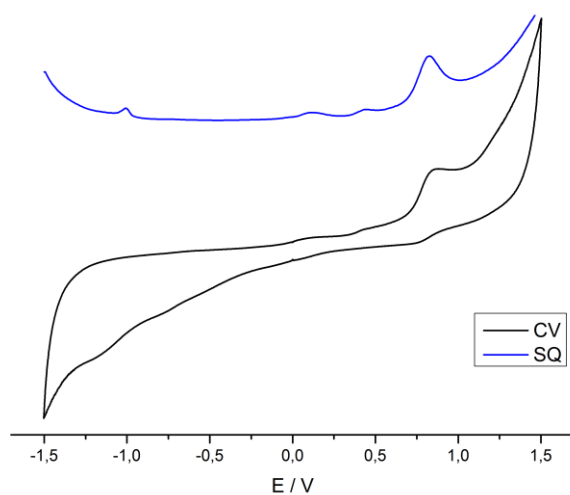


Figure S4. Cyclic voltammetry of **NCDot** in Na₂SO₄ 0.1M pH=5 at room temperature.

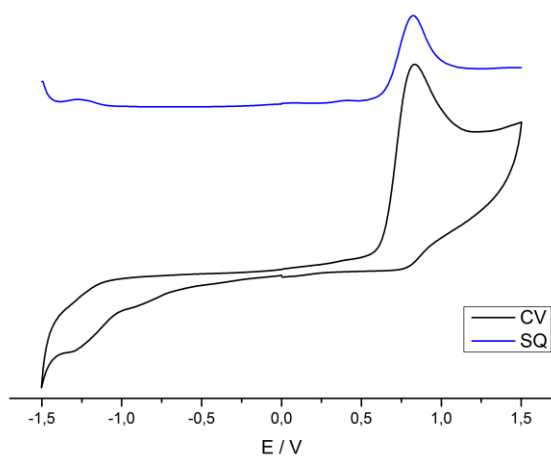


Figure S5. Cyclic voltammetry of **NCDotMix** in Na_2SO_4 0.1M pH=5 at room temperature.

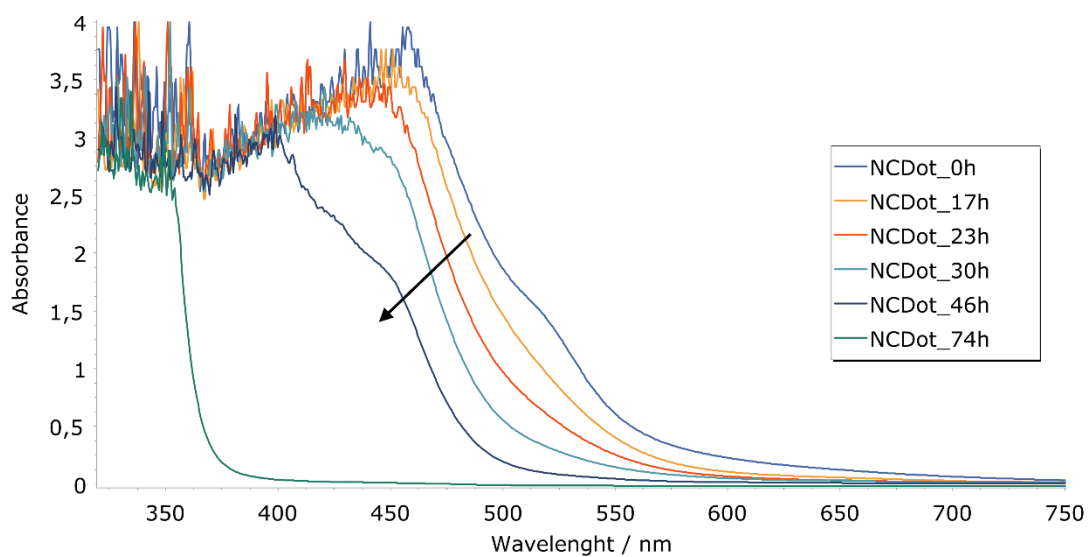


Figure S6. UV-Vis spectra of 10 mg **NCDot** in TCEP/AA (1:1) 0.1 M each pH=5, during UV led irradiation over time.

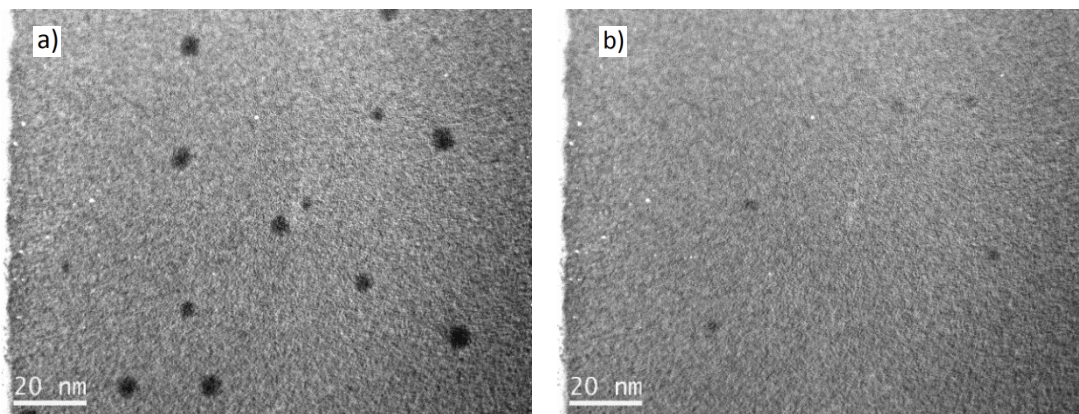


Figure S7. TEM image of **NCDot** a) after 50 h of UV irradiation b) after 70 h of UV irradiation.

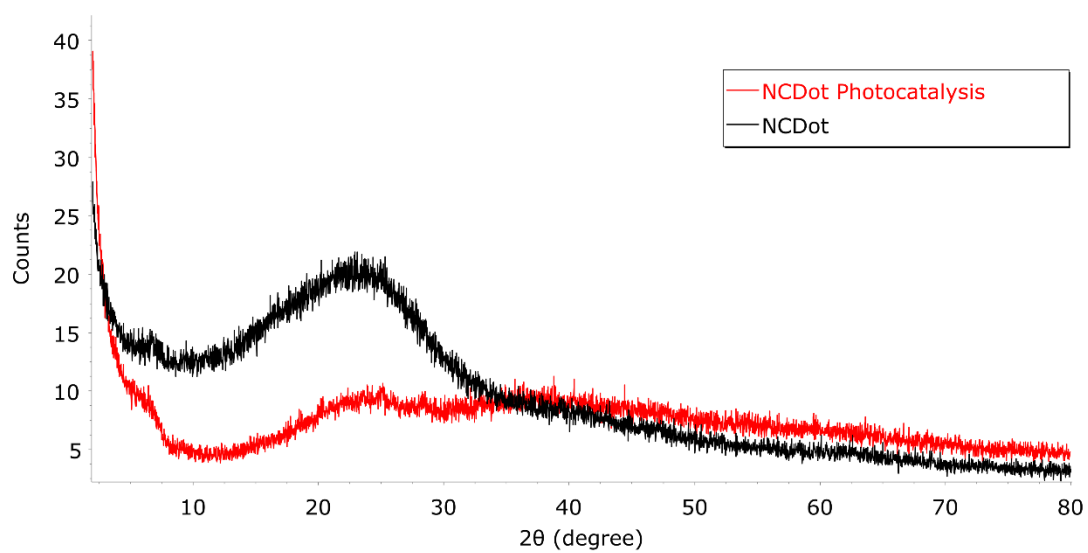


Figure S8. XRD pattern of **NCDot** before (black) and after photocatalytic experiment (red).

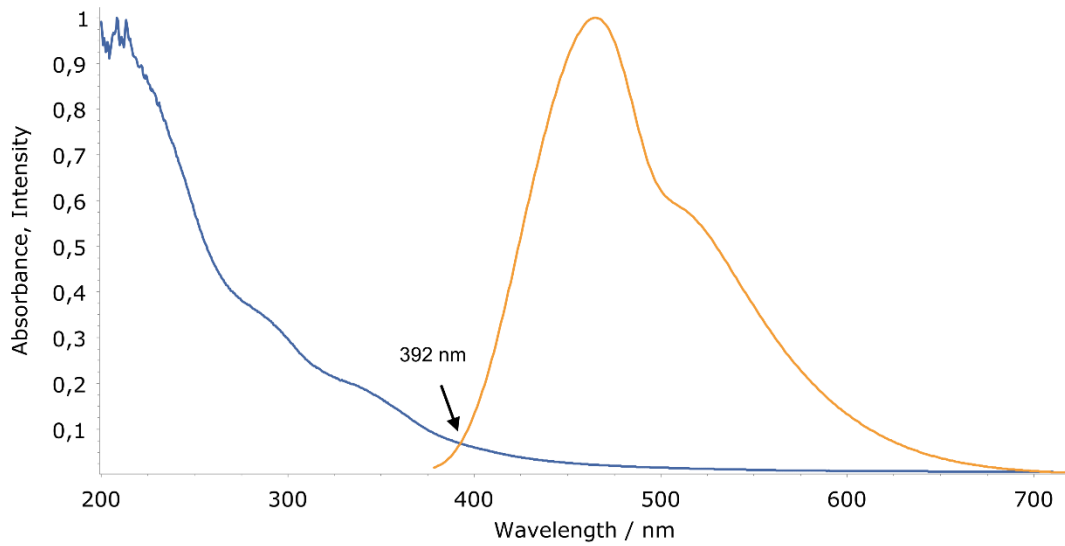


Figure S9. The normalized absorption and photoluminescence spectra of **CDot** in water. The intersection between the absorbance and photoluminescence spectra is at $\lambda=392\text{nm}$.

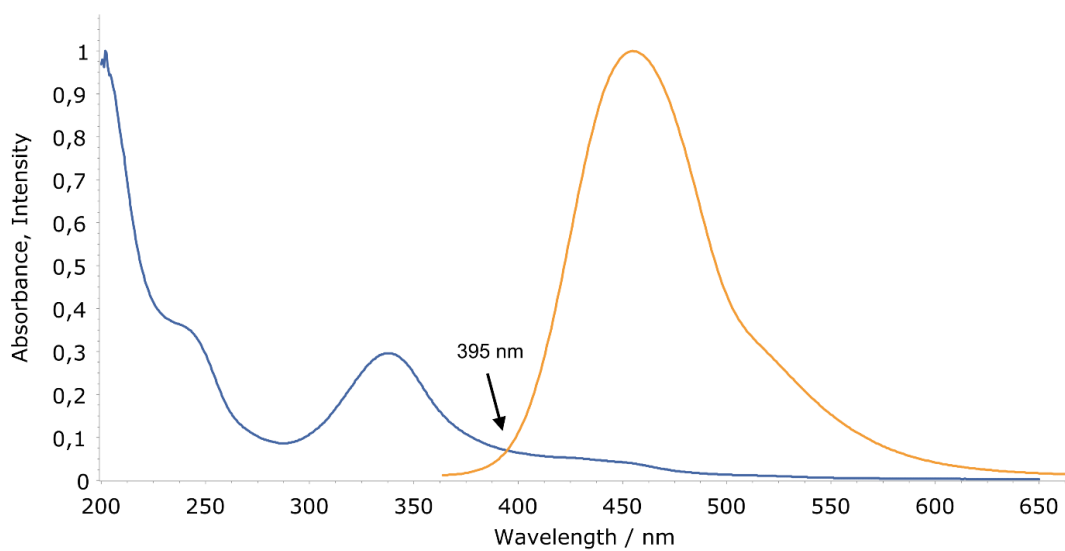


Figure S10. The normalized absorption and photoluminescence spectra of **NCDot** in water. The intersection between the absorbance and photoluminescence spectra is at $\lambda=395\text{ nm}$.

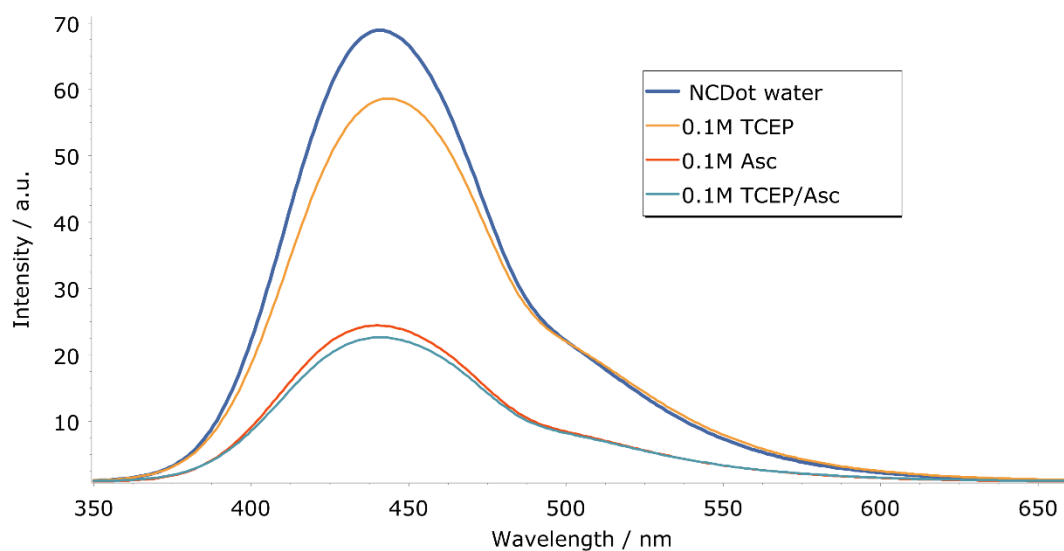


Figure S11. Emission spectra in water recorded with different SEDs.

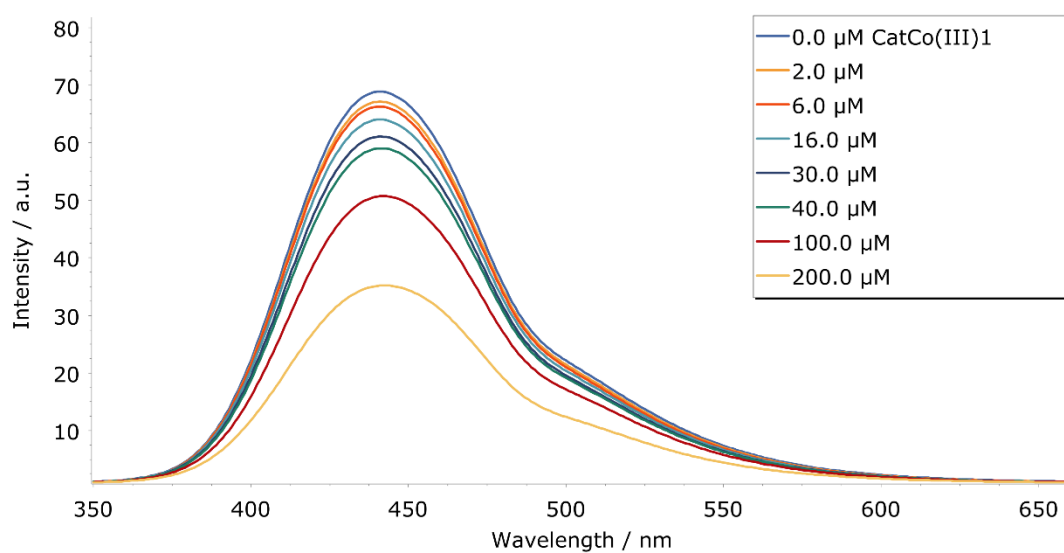


Figure S12. Emission spectra in water recorded at increasing the concentration of the CatCo(III)1.

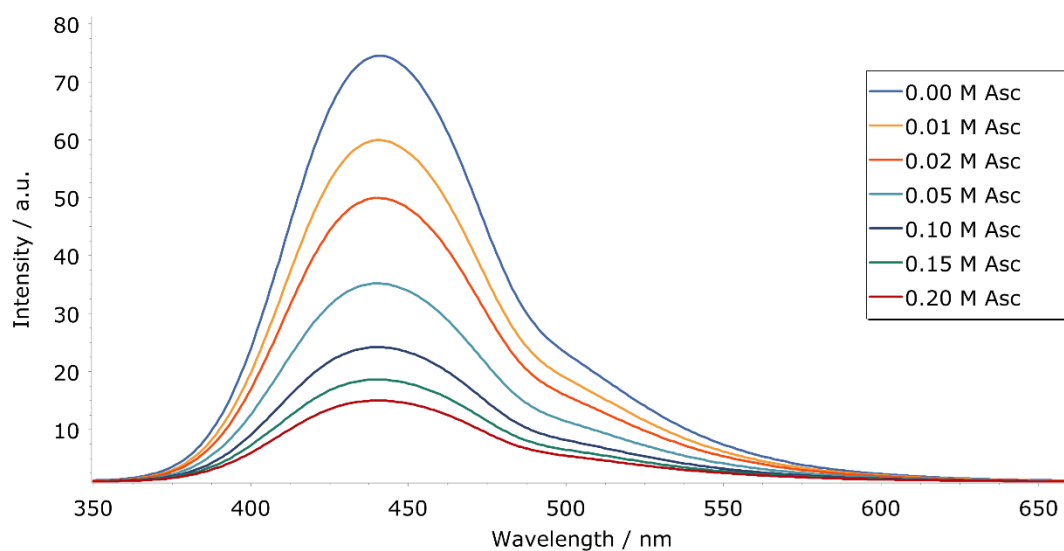


Figure S13. Emission spectra in water recorded at increasing the concentration of Ascorbic Acid.

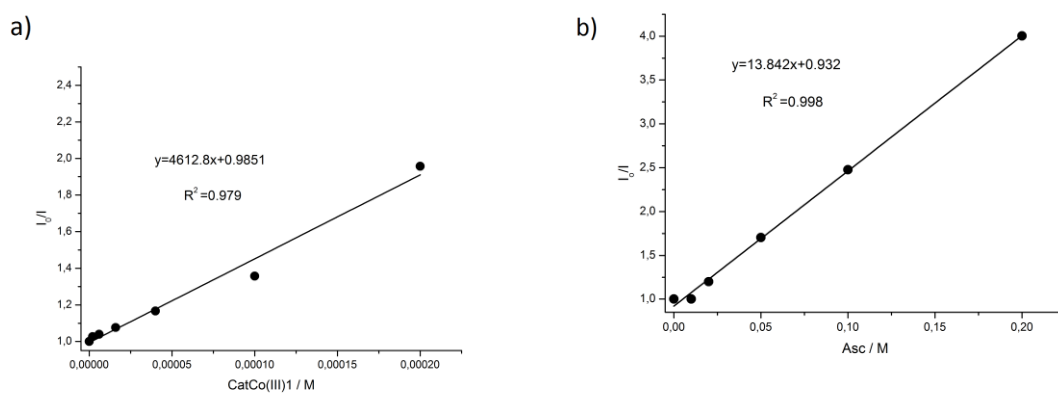


Figure S14. Stern-Volmer plots of NCDot emission quenching with a) CatCo(III)1 b) Ascorbic Acid (Asc).

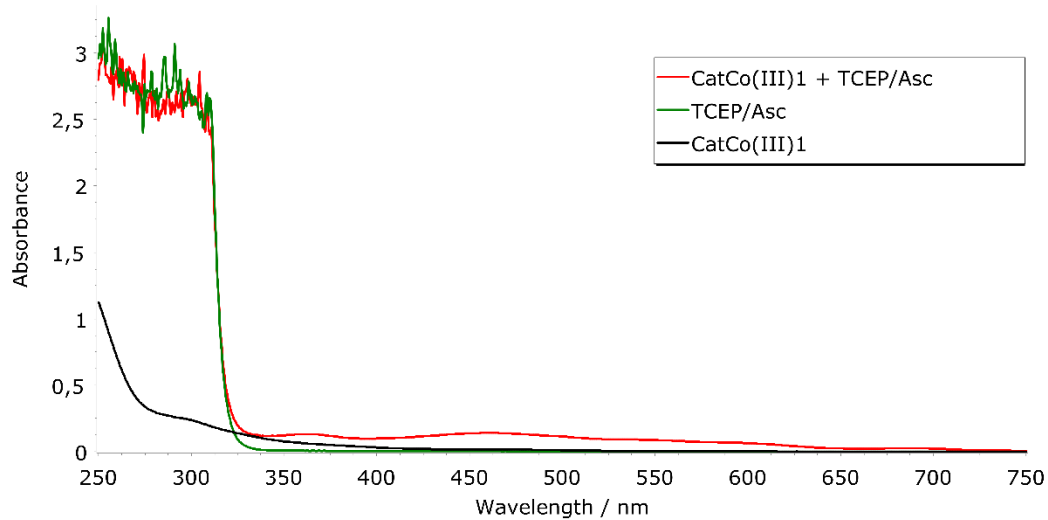


Figure S15. UV-Vis spectra in water of **CatCo(III)1** + TCEP/Asc (1:1) 0.1 M each (red line), TCEP/Asc (1:1) 0.1 M each (green line), **CatCo(III)1** (black line).

6. References

1. D. Skrzypek, I. Madejska and J. Haddas, *Solid State Sciences*, 2007, **9**, 295-302.
2. D. Dolui, S. Das, J. Bharti, S. Kumar, P. Kumar and A. Dutta, *Cell Reports Physical Science*, 2020, **1**, 100007.
3. K. M. Long and D. H. Busch, *Journal of Coordination Chemistry*, 1974, **4**, 113-123.