SUPPLEMENTAL INFORMATION

for

Fine-Tuning the Assemblies of Carbon Nanodots and Porphyrins

By

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Experimental Details

Physical Measurements

Steady state absorption and fluorescence spectroscopy measurements were performed with a Lambda 2 from Perkin Elmer and a Fluoromax-3 from Horiba, respectively, keeping a strict argon atmosphere in contact with the solutions. Electrochemical characterization was accomplished with a home- made three-electrode setup connected to a µAutolabIII/FRA2 potentiostat from Metrohm-Autolab. A 3 mm glassy carbon disk served as a working electrode and a platinum wire was used as a counter electrode. All potentials were measured against a Ag/AgCl reference electrode.

Ultrafast transient absorption (TA) experiments were conducted using an amplified Ti:sapphire fs laser system (Clark MXR CPA2101 and 2110, FWHM = 150 fs, λexc = 420 nm, 200 nJ per pulse) with TA pump / probe Helios detection systems from Ultrafast Systems. White light was generated focusing a fraction of the fundamental 775 nm output onto a 2 mm sapphire disk. A magic angle configuration was employed to avoid rotational dynamics. Excitation pulses of 420 nm wavelength were generated by a NOPA with subsequent frequency doubling. Bandpass filters with ± 5 or ± 10 nm were used to ensure low spectral width and to exclude 775 and 387 nm photons. All measurements were conducted in a 2 mm quartz cuvettes under argon atmosphere. Obtained data were treated by global analyses using the R- package TIMP and GloTarAn. For details please see references 21-23 in the manuscript.

DLS measurements were carried out using an ALV 5000 correlator with 320 channels, a CGS 3 goniometer (ALV Langen, Germany) and a HeNe laser with a wavelength of λ = 632.8 nm with 22 mW output power. A range of scattering angles of $30° < \vartheta < 150°$ was covered in 5° steps. Data collection periods were 30 min to 2 h per scattering angle with 1 to 4 runs each. Data analysis was carried out by converting the measured intensity autocorrelation function into the scattered electric field autocorrelation function using the Siegert relation. The electric field autocorrelation functions were further analyzed by regularized inverse La Place transformation using the program CONTIN by S. Provencher to obtain the intensity weighted distribution of relaxation times. From this, the apparent diffusion coefficients were calculated using the relation $D_{app} = q^{-2} \cdot \tau^{-1}$ for the mean τ of each process. To determine the hydrodynamic radius R_H, the apparent diffusion coefficient D_{app} is extrapolated to zero scattering angle and then converted into R_H through the Stokes-Einstein relationship. In addition, volume-weighted size distributions were calculated from the electric field autocorrelation functions through the corresponding regularized inverse La Place transformation.

Sample Preparation for DLS: The pCND sample was diluted 1:100, treated in an ultrasonic bath for 15 min and filtered three times through 0.2 µm pore size filters. The **ZnP-am•pCND** sample was filtered twice through 0.2 µm pore size filters under Argon (filters: hydrophilic PTFE 0.2 µm Millipore Millex-LG).

Steady State Spectroscopy

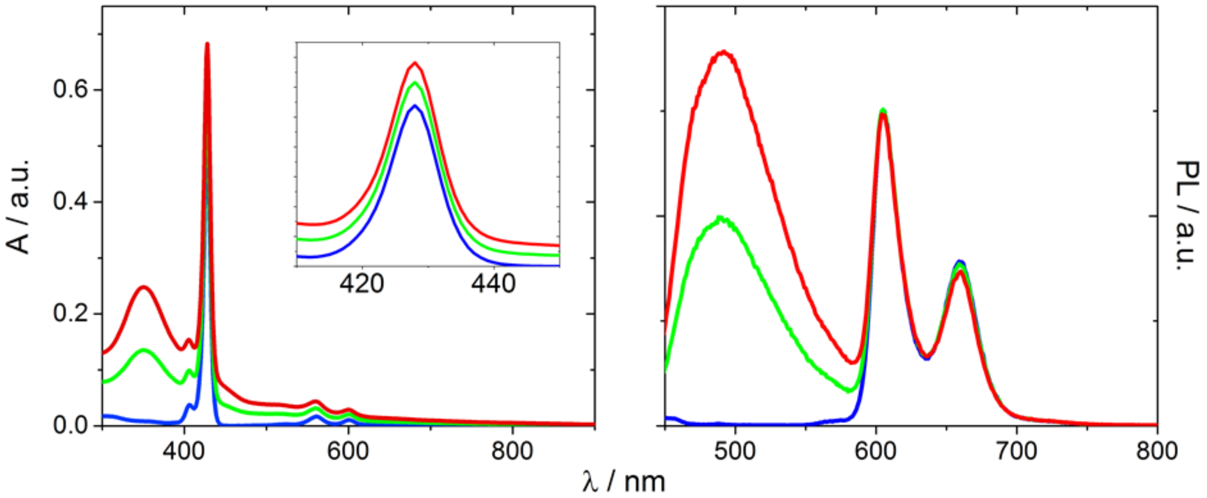


Figure S1. Absorption (left) and fluorescence (right) spectra of **ZnP** (blue, $2x10^{-6}$ M) during the course of a titration with **pCND** (green to red) in anhydrous DMF at room temperature. λ_{ex} = 420 nm. Final spectra correspond to **pCND** concentrations of 10 mg/L.

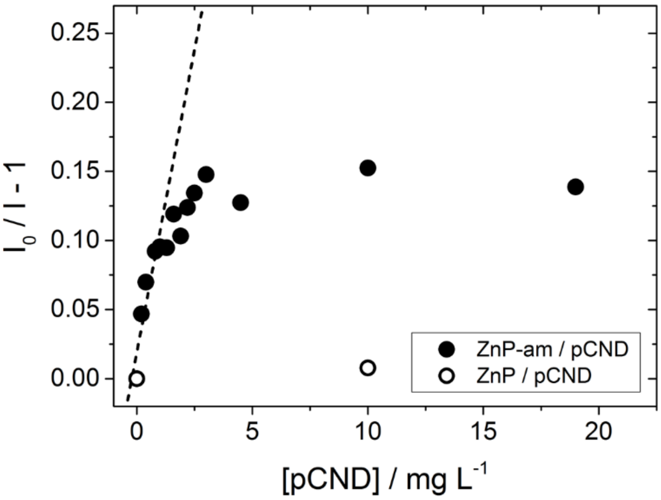


Figure S2. Stern-Volmer plots for the fluorescence quenching of **ZnP-am** and **ZnP** upon the addition of **pCND**s in anhydrous DMF at room temperature.

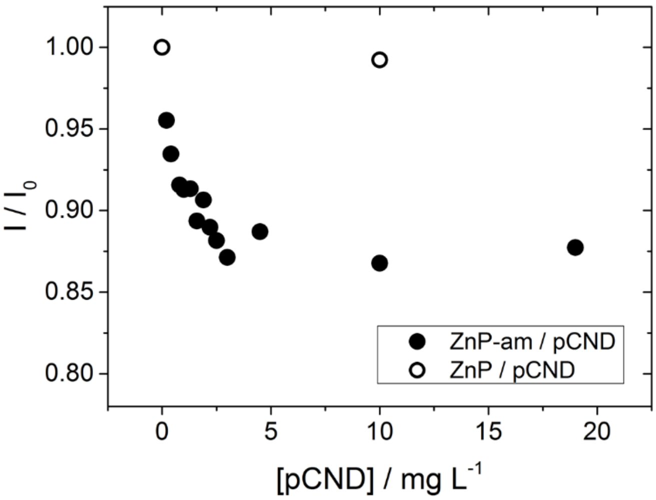
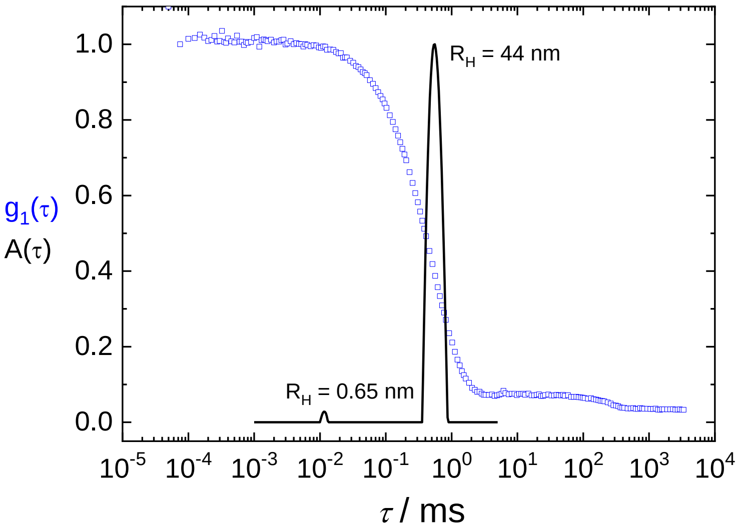


Figure S3. Relative quenching of the fluorescence of of **ZnP-am** and **ZnP** upon the addition of **pCND**s in anhydrous DMF at room temperature.

Dynamic Light Scattering



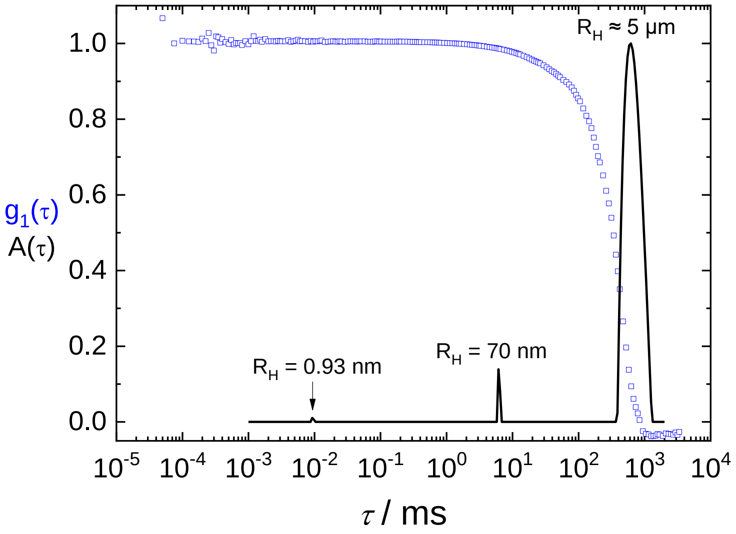


Figure S4. Dynamic Light Scattering: Electric field autocorrelation function $g_1(\tau)$ (blue) and intensity-weighted relaxation time distribution $A(\tau)$ (black) at a scattering angle of $\Theta = 90°$ for **pCND**s in the upper part and for **ZnP-am•pCND**s in the lower part. Resulting hydrodynamic radii R_H (after extrapolation to zero scattering angle) are also indicated.

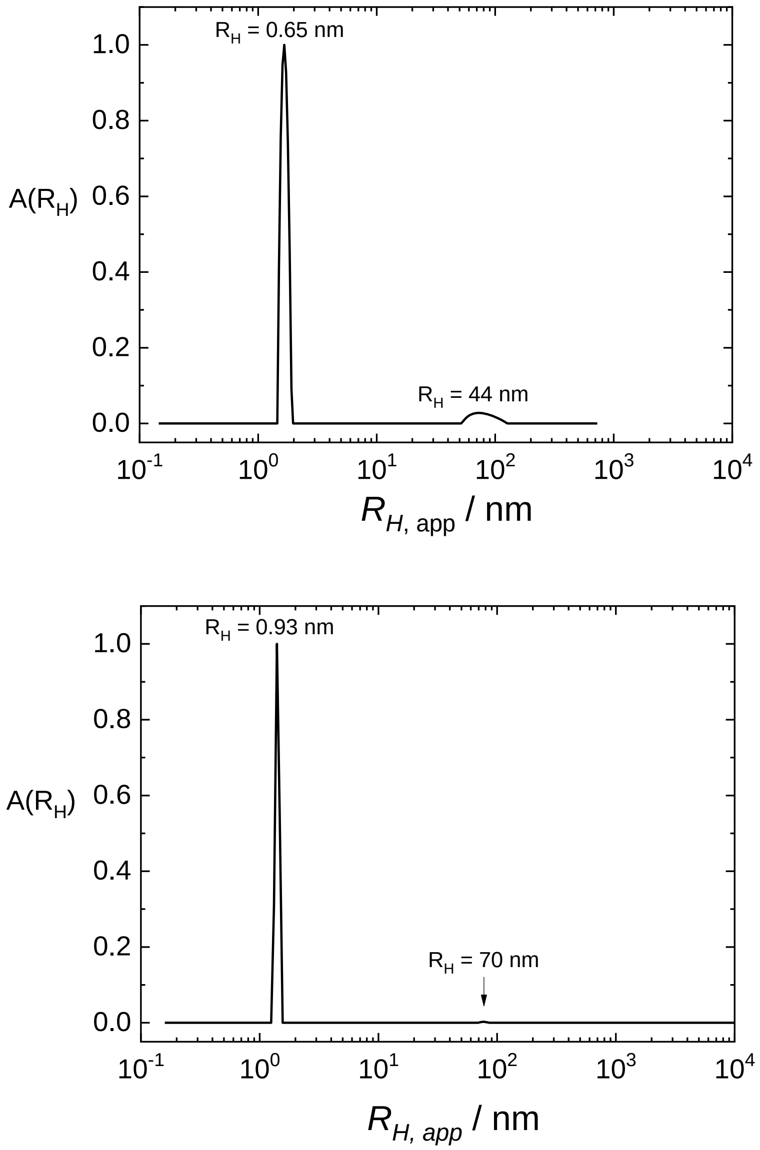


Figure S5. Dynamic Light Scattering: Volume-weighted size distribution A($R_{H,,\mathrm{app}}$) as function of the apparent hydrodynamic radius $R_{H,,\mathrm{app}}$ at a scattering angle of Θ = 90° for **pCND**s in the upper part and for **ZnP-am•pCND**s in the lower part. Resulting hydrodynamic radii $R_{H,}$ (after extrapolation to zero scattering angle) are also indicated.

Table S1: DLS-Results for **pCND** and **ZnP-am•pCND**: Hydrodynamic radius $R_{H,}$ distribution width (standard deviation) σ and relative amount of the species in the intensity and volume distribution. The error for $R_{H,}$ results from the angular extrapolation of the mean apparent diffusion coefficient to zero scattering angle.

sample	**R_H**	**σ**	**Relative weight in intensity distribution**	**Relative weight in volume distribution**
pCND	(0.65 ± 0.42) nm	0.08	0.9 %	92 %
	(44 ± 3) nm	0.32	99.1 %	8 %
ZnP-am•pCND	(0.93 ± 0.34) nm	0.36	0.2 %	99.7 %
	(70 ± 18) nm	0.43	0.13 %	0.3 %
	≈ 5 µm	0.16	99.67 %	-

Electrochemistry

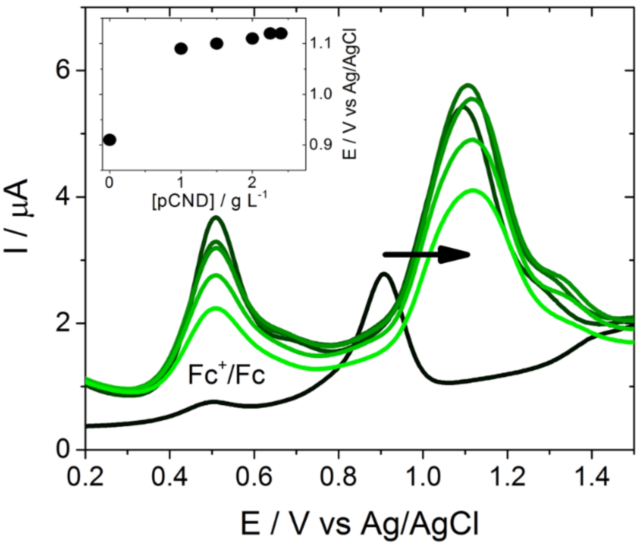


Figure S6. Square-wave voltammograms of **ZnP-am** (10^{-3} M) upon the addition of **pCND**s in anhydrous DMF at room temperature. Inset: peak potential versus **pCND**s concentration.

Transient Absorption Spectroscopy

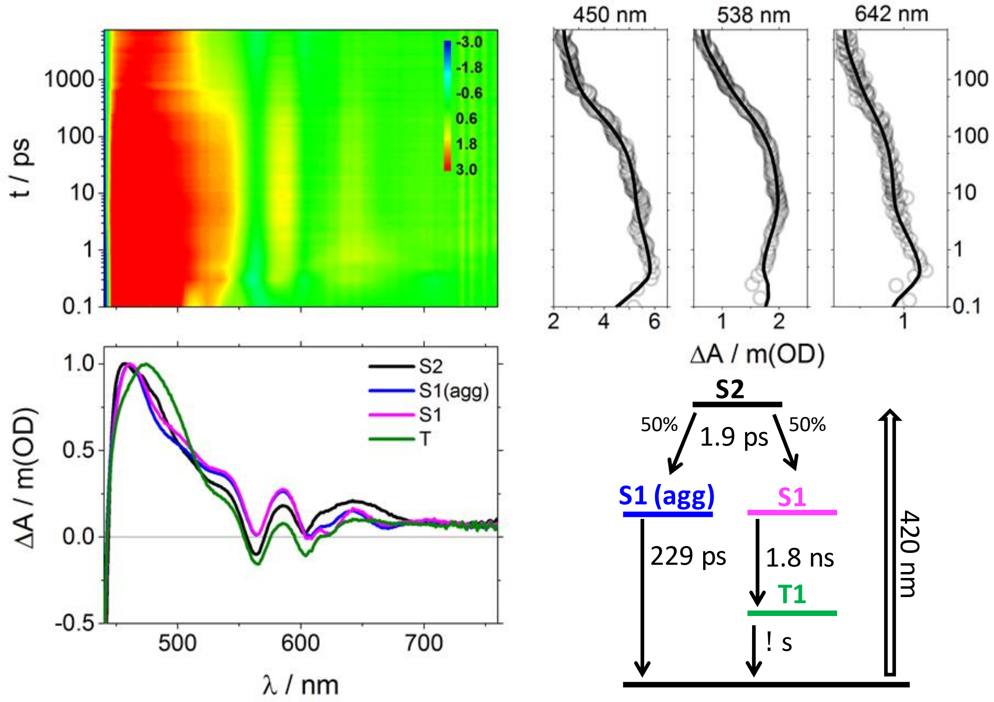


Figure S7. Upper left: Differential absorption 3D map obtained upon femtosecond pump-probe experiments (λ_{ex} = 420 nm) of **ZnP-am** in anhydrous DMF at room temperature. Upper right: Time absorption profiles (open circles) and global analysis fittings (solid lines). Bottom left: Normalized decay associated spectra: S2, black; S1(agg), blue; S1, magenta; T, green. Bottom right: scheme indicating the different lifetimes obtained from global analysis.

Table S2. Lifetimes extracted from global analysis of the data for the different systems studied in this work, in anhydrous DMF at room temperature.

Sample	τ_1 / ps	τ_2 / ps	τ_3 / ps	τ_4 / ps	τ_5 / ps
ZnP-am	1.9	-	229	1800	>15000
ZnP-am•pCND	2.0	27.0	868	1300	>15000

Spectroelectrochemistry

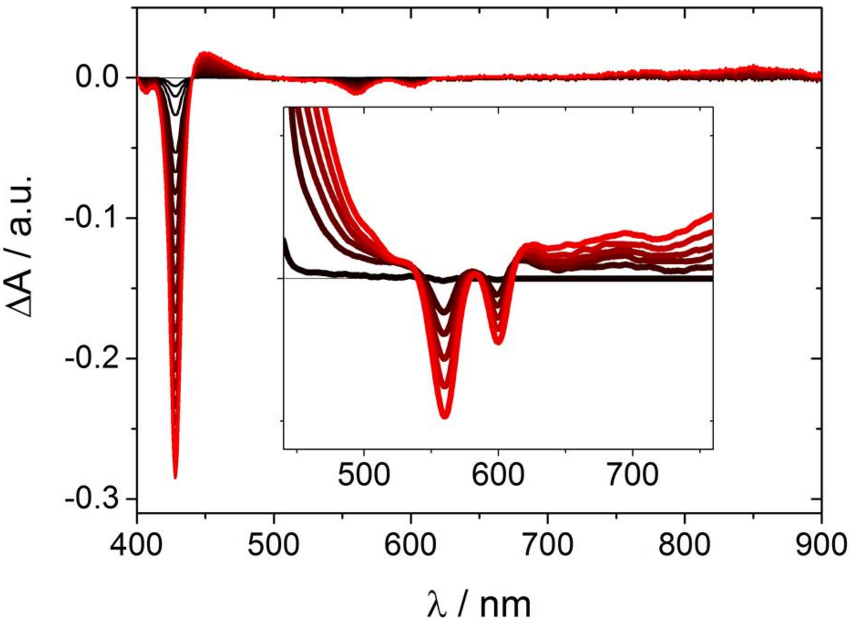


Figure S8. Difference absorption spectra of **ZnP-am** upon oxidation in anhydrous DMF at room temperature (from black to red, 0.8 V to 1.2 V). Supporting electrolyte: $TBAPF_6$ 0.1 M.