

Electronic supplementary information for

Green-light ionization of 3-aminoperylene in SDS micelles — a promising access to hydrated electrons despite a myth debunked

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1 Experimental details

1.1 General

We synthesized 3-aminoperylene **PerNH₂** according to the procedure described in the literature,^[1] via nitration of perylene followed by reduction of the obtained 3-nitroperylene by hydrazine with palladium on carbon as catalyst, and stored it under argon at $-20\text{ }^{\circ}\text{C}$ in the dark. IR $\tilde{\nu}$ in cm^{-1} : 1617 (m), 1566 (m), 1520 (m), 1498 (m), 1453 (m), 1386 (m), 1327 (m), 1266 (m), 1187 (m), 1015 (w), 892 (m), 825 (s), 804 (vs), 756 (vs). ¹³C-NMR δ (DMSO *d*6) in ppm: 146.0, 135.1, 132.8, 131.8, 131.0, 129.4, 128.2, 127.6, 127.4, 127.0, 125.1, 124.9, 123.3, 123.2, 123.1, 121.4, 119.9, 118.5, 117.6, 109.3. The ¹H-NMR data and the UV-VIS absorption maxima in cyclohexane, acetonitrile and dimethylformamide were identical to the published values.^[2,3]

The chemicals for this synthesis (Roth: perylene, $\geq 99\%$; acetic anhydride, $\geq 99\%$; sulfuric acid, 98 % nitric acid, $\geq 65\%$ p.a.; Sigma-Aldrich: hydrazine monohydrate, 98 % and palladium 10 wt. % on activated carbon) as well as all chemicals for the photochemical experiments (sodium dodecyl sulfate, different manufacturers, $\geq 99.5\%$ or better; sodium ascorbate, $\geq 99\%$, Roth; 6-*O*-palmitoyl-L-ascorbic acid, $\geq 99\%$, Sigma-Aldrich; sodium hydrogen phosphate dihydrate, $\geq 99\%$, Fluka; sodium dihydrogen phosphate dihydrate, $> 98\%$, VEB Laborchemie Apolda; sodium hydroxide, $> 98\%$, Sigma-Aldrich; fluorescein sodium, BioReagent, Fluka; *N,N*-dimethyl-3-nitro-aniline, 98 %, Alfa Aesar) were obtained in the highest available purity and used as received. The solvent for all photochemical experiments was ultrapure Millipore Milli-Q water (specific resistance, 18.2 M Ω cm). The solutions were deoxygenated with argon or N₂O, both of purity 5.0 and obtained from AirLiquide. Measurements at pH 8 were carried out in 6.7 mM dihydrogen phosphate / hydrogen phosphate buffer whereas for the experiments in more basic medium the pH was adjusted with sodium hydroxide.

1.2 Cyclic voltammetry

Cyclic voltammetry was carried out with an AUT 72615 Metrohm potentiostat (software Nova 1.10). A 2 mm polished platinum disc and a platinum wire served as working and

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counter electrodes. The reference was ferrocene/ferrocenium. The solvent acetonitrile was dried over 3 Å molecular sieve. The solutions contained 0.1 M tetraethylammonium tetrafluoroborate as conductive salt and 1 mM **PerNH₂**; they were degassed with nitrogen before the measurements.

1.3 Photophysical experiments

Steady-state absorption and fluorescence spectra were recorded using a Shimadzu UV-2102 and a Perkin-Elmer LS 50B spectrometer. *N, N*-dimethyl-3-nitro-aniline was employed as reference^[4] to correct for the wavelength-dependent sensitivity of the fluorescence spectrometer, and the fluorescence quantum yields were determined against fluorescein as standard.^[5]

1.4 Quantum-mechanical computations

The transitions in Figure 4a of the main article were calculated by time-dependent DFT with the Gaussian 09 package,^[6] using the B3LYP functional,^[7] the 6-311++G(2d,2p) basis set, and as solvation model IEFPCM^[8] with the solvent methanol. Methanol has almost the same polarity as experienced by the first excited singlet state of **PerNH₂** in an SDS micelle (see, Figure 2b of the main article). Besides, recalculations in the solvent dimethyl sulfoxide — to take into account a possible displacement of the radical cation towards the more polar Stern layer of the micelle — gave practically no difference for these two transitions.

1.5 Laser flash photolysis

The home-made laser-flash photolysis setup has been described elsewhere.^[9] Briefly, excitation is performed by a frequency-doubled (532 nm) or frequency-tripled (355 nm) Nd:YAG laser (pulse width, *ca* 5 ns) with (variable) very high intensities. Collimated beams and optically thin solutions ensure homogeneous excitation of the observed volume, and a motor-driven syringe pump that is activated between flashes serves to avoid a depletion of the reactants or accumulation of products in the course of a measurement. Absorption or luminescence are detected at right angles to the excitation beam with a time-resolution down to 1 ns. Optical path lengths, 2 mm (excitation) and 4 mm (detection).

Supplementary References

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