Electronic Supplementary Information

Efficiency and Stability of Spectral Sensitization of Boron-Doped-Diamond Electrode through Covalent Anchoring of a Donor-Acceptor Organic Chromophore (P1)

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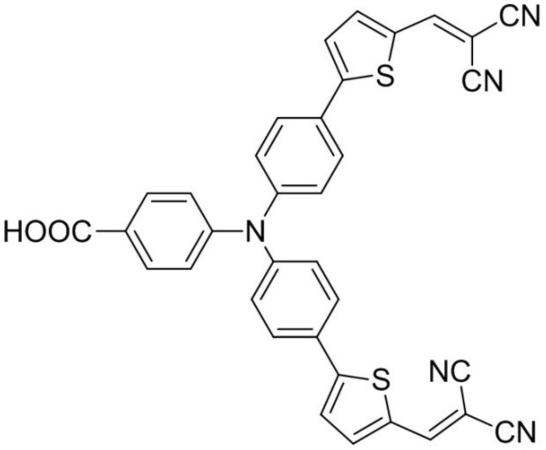

Scheme S1: Molecular formula of P1 dye

Table S2a: Results of the XPS surface analysis (concentrations in atom %). A pronounced drop of the B-content is obvious in the series BDD > BDD+**1** > BDD+**1** (deprotected) > **P1**@BDD. The BDD+**1** sample shows the F/N ratio = 2.8 (calc. 3). For **P1**@BDD, the S/N ratio = 0.7 (calc. 0.33).

	C 1s	**B 1s**	**O 1s**	**N1s**	**S 2p**	**Cl 2p**	**F 1s**	**Si 2s**	**other**[*]
BDD	94.8	2.5	2.3	-	-	-	-	0.4	-
BDD + **1**	84.8	1.6	8.1	0.4	0.2	0.3	1.1	3.3	0.2
BDD + **1** (deprotected)	80.1	1.1	11.5	1.5	0.4	1.0	0.7	1.3	2.4[**]
P1@BDD (linker **1**)	80.1	0.7	10.0	3.9	2.9	0.3	0.4	0.9	0.8
P1@BDD (linker **2**)	85.8	1.7	7.7	1.0	0.8	-	0.8	0.7	1.5

[*] Other impurities (Ca, Na, P)

[**] The main impurity in the BDD+**1** (deprotected) sample is Na (1.8 %) originating presumably from the reactants used in the deprotection steps (see Experimental Section in the main text).

Table S2b: Results of the XPS surface analysis (binding energies in eV). Very weak peaks are not evaluated.

	C 1s	**B 1s**	**O 1s**	**N1s**	**S 2p**	**Cl 2p**	**F 1s**	**Si 2s**
BDD	284.4	187.6	532.4	-	-	-	-	-
BDD + **1**	284.4	186.8	532.0	-	-	199.2	688.4	153.2
BDD + **1** (deprotected)	284.4	186.4	532.4	402.8	168.4	197.6	685.2	153.6
P1@BDD (linker **1**)	284.4	187.0	532.0	399.9 402.0	164.4	-	-	153.3
P1@BDD (linker **2**)	284.4	186.4	532.0	400.3 402.6	168.8	-	688.0	153.5

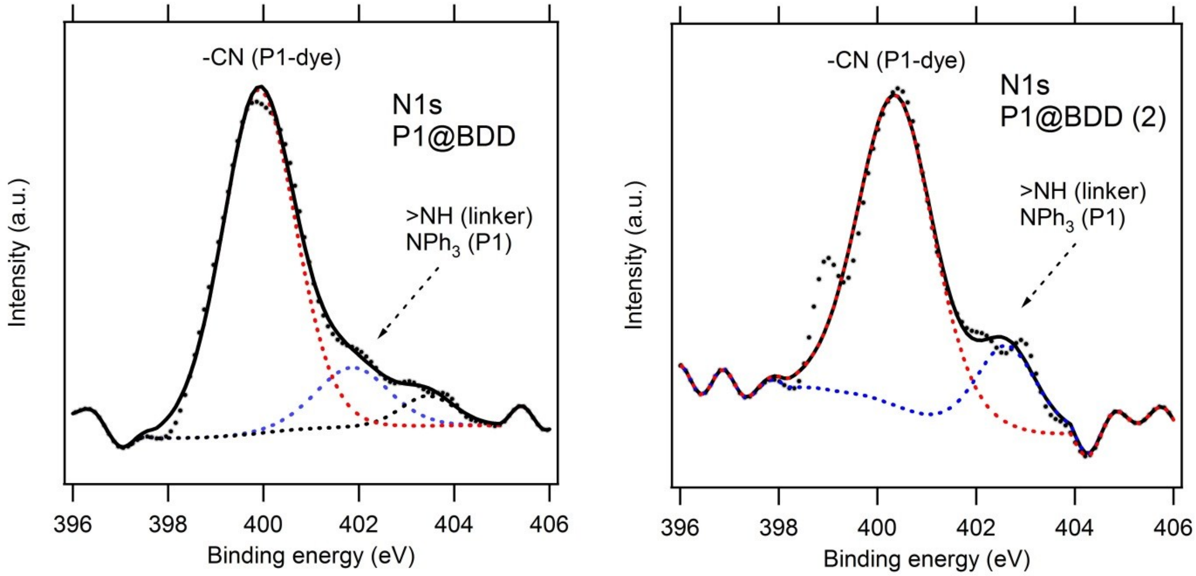

Figure S3: Detail of the N1s photoelectron spectra with deconvoluted components. Left chart: the optimized sample P1@BDD (linker **1**). Right chart: P1@BDD (2) (linker **2**). Tentative assignment of photoemission lines to >NH groups from the linker, triphenylamino group from the **P1** dye and the cyano-group from the **P1**-dye is provided.

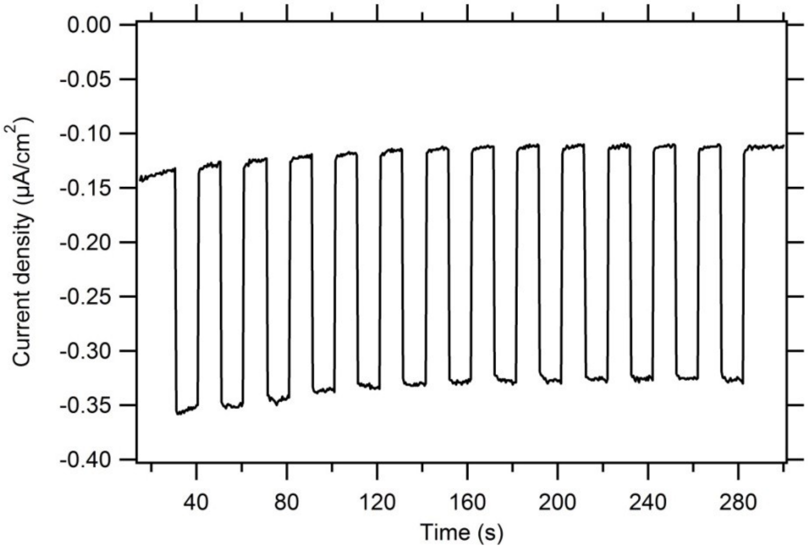

Figure S4: Chronoamperometric plot for a BDD electrode sensitized with P1 (anchored via linker **2**). Electrolyte solution 0.1 M Na_2SO_4 containing 5 mM dimethylviologen, applied bias voltage -0.3 V vs. Ag/AgCl. Chopped white light illumination (100 mW/cm^2; simulated AM1.5G solar spectrum, 10 s dark/light interval).

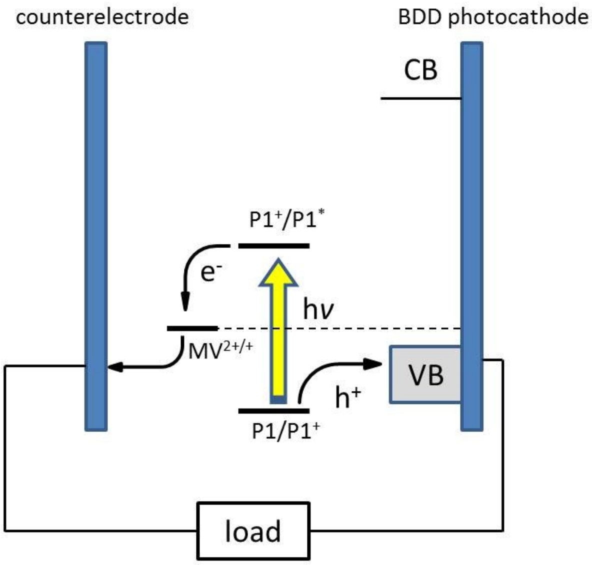

Figure S5: Scheme of photocurrent generation in an electrochemical cell with boron-doped diamond photocathode sensitized with P1.

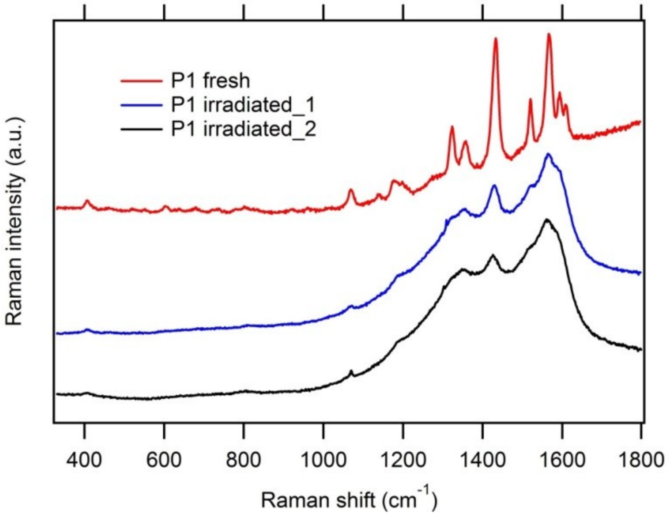

Figure S6: Raman spectra (at 488 nm excitation) of pure solid **P1** dye (red curve) and the same **P1** sample which passed long-term irradiation by the 488 nm laser (blue curve). Black curve is for the same sample after subsequent irradiation.

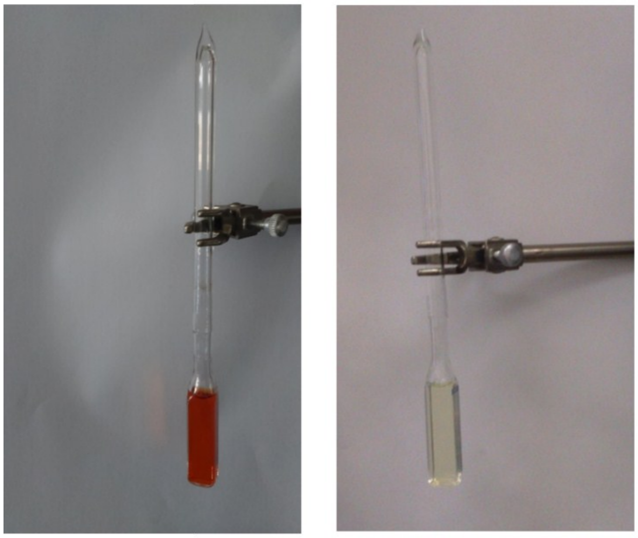

Figure S7: Solution of the P1 dye in absolute ethanol (concentration 10^{-4} mol/L) in vacuum-sealed quartz optical cell (1 cm); before irradiation (left image) and after 24 hours of irradiation at 1 sun intensity (right image). The yellowish coloration of the solution after photochemical treatment (right image) comes from the tail of the UV band (see Fig. 7 in the main text). There are no traces of P1 in the illuminated solution detectable by HPLC (cf. Figure S8).

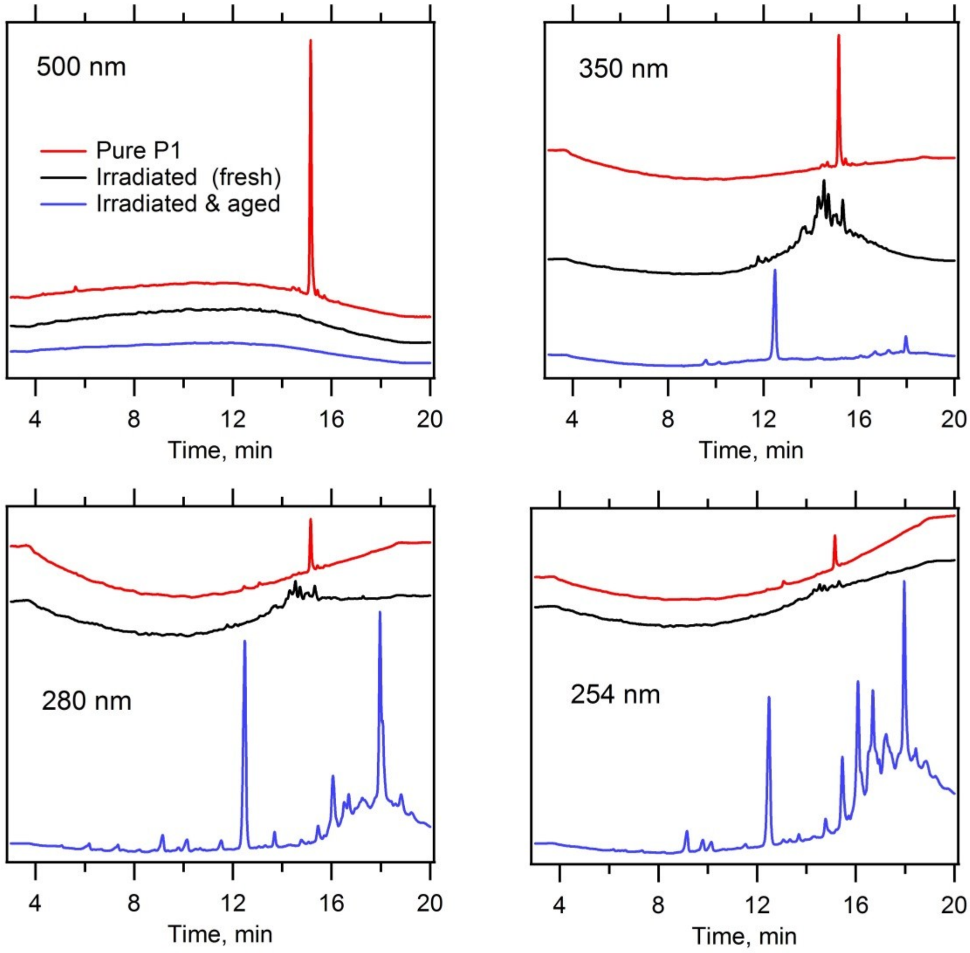

Figure S8: HPLC chromatograms of the 10^{-5} mol/L solution of the **P1** dye in absolute ethanol measured shortly (≈ several hrs) after irradiation for 1 day at 1 sun intensity in a closed quartz cell (black curves). Blue curves are for the irradiated solution, which was stored for 2 months in air at room temperature. Reference chromatograms for freshly made solution of **P1** are shown by red curves. Spectrophotometric detection was carried out at four different wavelengths (500 nm, 350 nm, 280 nm and 254 nm) as it is labeled on each chart.

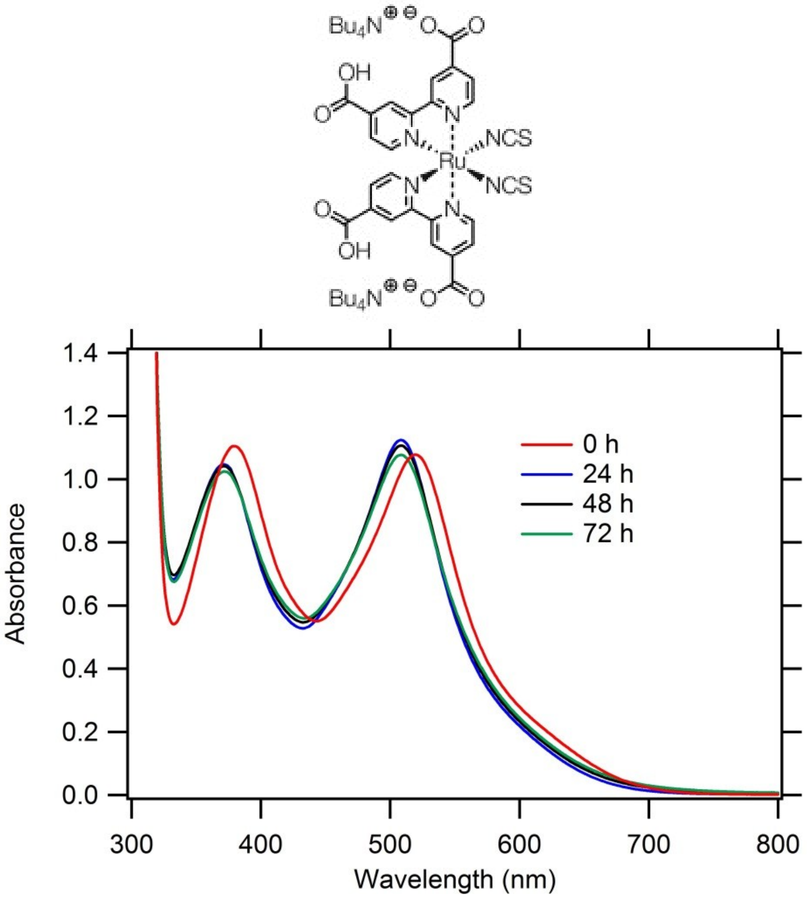

Figure S9: UV-Vis spectrum of the solution of **N719** dye (see the chemical formula on top of the chart) in absolute ethanol. Optical length 1 cm. The spectrum of a fresh solution (red curve) and that after illumination with a white light of 1 sun intensity for 24 hours (blue curve), 48 hours (black curve) and 72 hours (green curve).