Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2023

SUPPORTING INFORMATION

Photochemical transformation of a perylenediimide derivative beneficial for in situ formation of molecular photocatalyst of hydrogen evolution reaction

Estera Hoffman,[1] Karol Kozakiewicz,[1,2] Małgorzata Rybczyńska,[1,2] Michał Mońka,[1] Daria Grzywacz,[1,2] Beata Liberek,[2] Piotr Bojarski,[1] Illia E. Serdiuk[1]*

[1] Faculty of Mathematics, Physics and Informatics, University of Gdańsk, Wita Stwosza 57, 80-308 Gdańsk, Poland

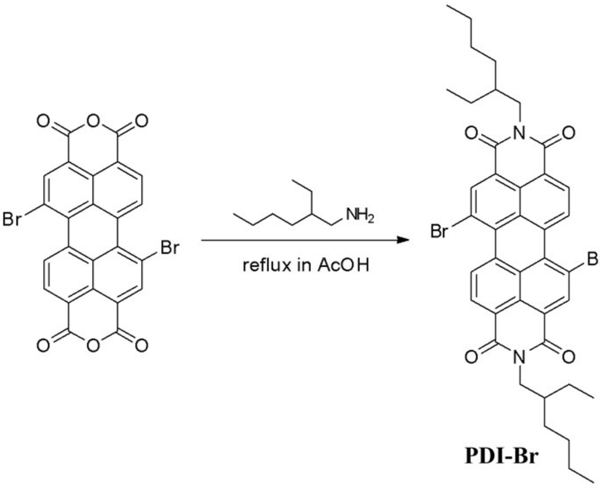
[2] Faculty of Chemistry, University of Gdańsk, Wita Stwosza 63, 80-308 Gdańsk, Poland

*Corresponding author, e-mail: illia.serdiuk@ug.edu.pl, phone + 48 58 523 22 44

Contents

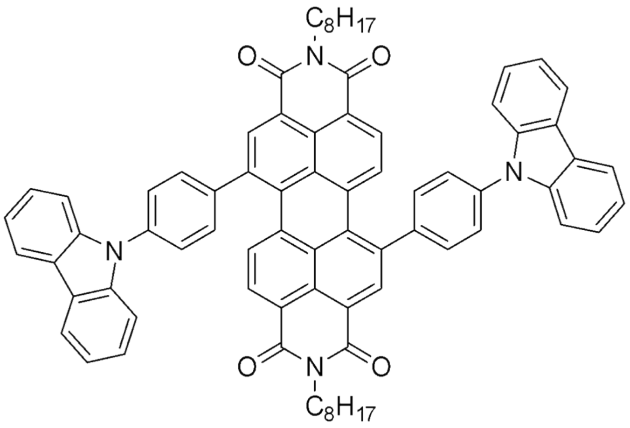
Synthesis and analysis

1,7-Dibromo-*N*,*N'*-bis(2-ethylhexyl)perylene3,4:9,10-tetracarboxylic acid diimide (**Br-PDI**)



1,7-Dibromo-perylene-3,4,9,10-tetracarboxylic dianhydride (1.1 g, 2 mmol) and 2-ethylhexylamine (5 cm^3, 3.95 g, 30.6 mmol) in glacial acetic acid (50 cm^3) were heated under the reflux for 24 h. Then, it was evaporated and the oily residue was added to the mixture of methanol and water (2:1 v:v). Crude product was filtered off under the reduced pressure, dried, and purified on column chromatography (chloroform : hexane : methanol, 100:100:1), Fraction containing purified product was evaporated to dryness yielding **Br-PDI** (1.1 g, 71%, orange-red powder); 1H NMR CDCl3 (500 MHz, CHLOROFORM-d) d 9.47 (d, J = 8.24 Hz, 2 H, H_{Ar}), 8.91 (s, 2 H, H_{Ar}), 8.68 (d, J = 7.94 Hz, 2 H, H_{Ar}), 4.18 (dd, J = 12.81 Hz, 7.94 Hz, 2 H, NCH), 4.12 (dd, J = 12.81 Hz, 7.02 Hz, 2 H, NCH'), 1.95 (hep, J = 6.41 Hz, 2 H, CH), 1.44-1.30 (m, 16 H, 8 x CH_2), 0.95 (t, J = 7.32 Hz, 6 H, 2 x CH_3), 0.90 (t, J = 7.02 Hz, 6 H, 2 x CH_3); MALDITOF-MS: m/z 771.174 (M-H)+

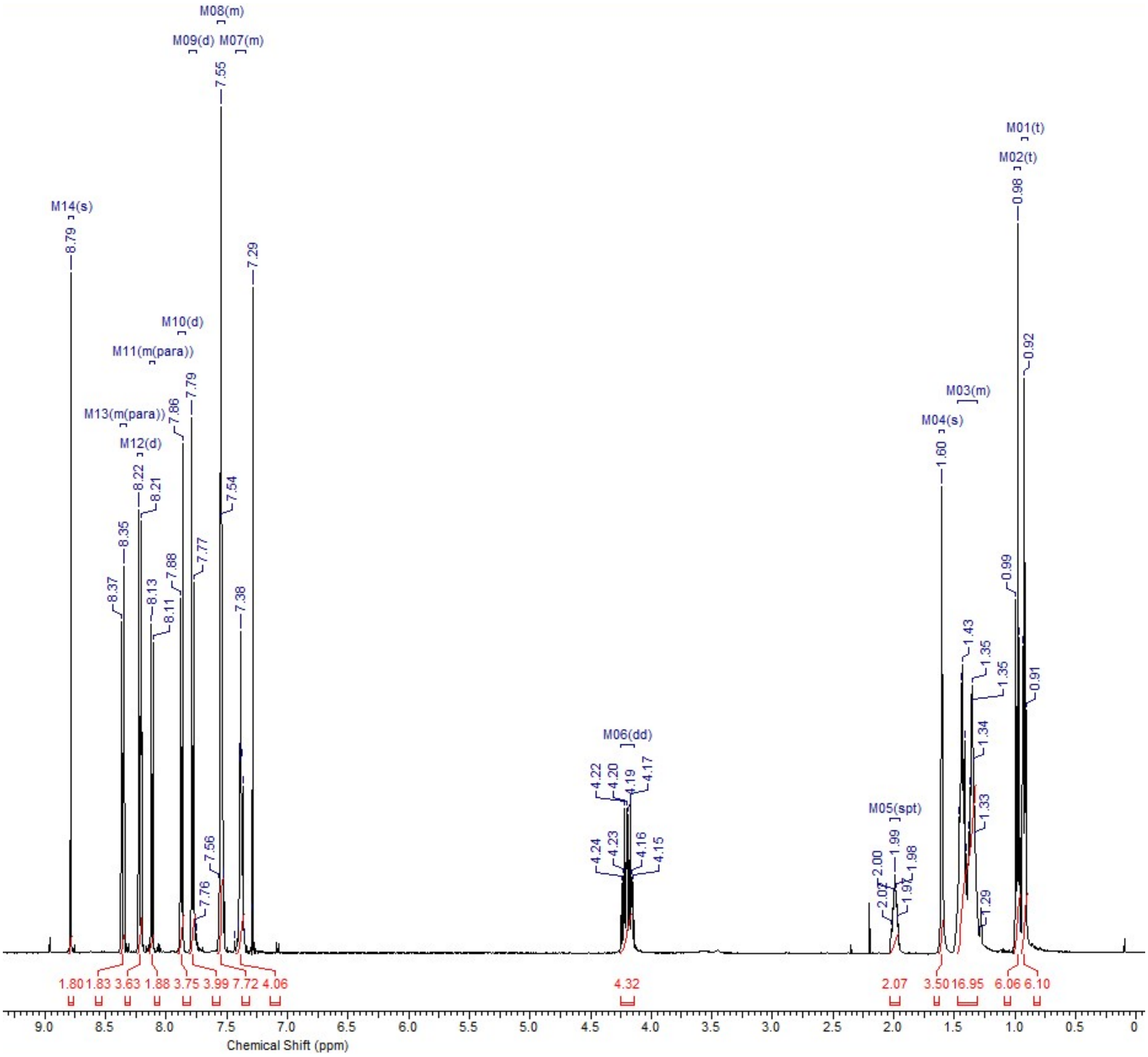
1,7-Bis[4-(Carbazol-9-yl)phenyl]-*N*,*N*-bis(2-ethylhexyl)perylene-3,4:9,10-tetracarboxylic acid diimide (A4)



Cbz-PDI

Br-PDI (77.2 mg, 0.1 mmol), 4-[(carbazol-9-yl)phenyl]boronic acid (229 mg, 0.8 mmol), K_2CO_3 (276 mg, 2 mmol) and $Pd(PPh_3)_4$ (25 mg) were added to a round bottom flask equipped with a magnetic stir-bar and a silicone septum. The mixture of dioxane and water (25 cm^3, 4:1 v:v) was added. After replacing the air in the flask with argon, the mixture was stirred under heating at 50 °C for 12 h. After the reaction was completed, solvent was evaporated. Water (30 mL) was added to dry residue, extracted with DCM, and purified on column chromatography (toluene : ethyl acetate 10:1). Fraction containing purified product was evaporated to dryness yielding **Cbz-PDI** (101 mg, 92%, dark violet powder); ($CDCl_3$): d 8.76 (s, 2 H, H_{Ar}), 8.33 (d, J = 8.24 Hz, 2 H, H_{Ar}), 8.19 (d, J = 7.69 Hz, 4 H, H_{Ar}), 8.09 (d, J = 7.96 Hz, 2 H, H_{Ar}), 7.84 (t, J = 8.24 Hz, 4 H, H_{Ar}), 7.75 (d, J = 8.51 Hz, 4 H, H_{Ar}), 7.52 (m, 8 H, H_{Ar}), 7.35 (m, J = 7.96 Hz, J = 7.68 Hz, 4 H, H_{Ar}), 4.19 (dd, J = 13.18 Hz, 7.69 Hz, 2 H, NCH), 4.14 (dd, J = 13.18 Hz, 6.59 Hz, 2 H, NCH'), 1.96 (hep, J = 6.31 Hz, 2 H, CH), 1.44-1.37 (m, 8 H, 4 x CH_2), 1.36-1.29 (m, 8 H, 4 x CH_2), 0.95 (t, J = 7.41 Hz, 6 H, 2 x CH_3), 0.89 (t, J = 7.14/6.87 Hz, 6 H, 2 x CH_3); MALDITOF-MS: m/z 1098.543 (M+H).

^{1}H-NMR spectrum of **Cbz-PDI** in $CDCl_3$



LCMS analysis

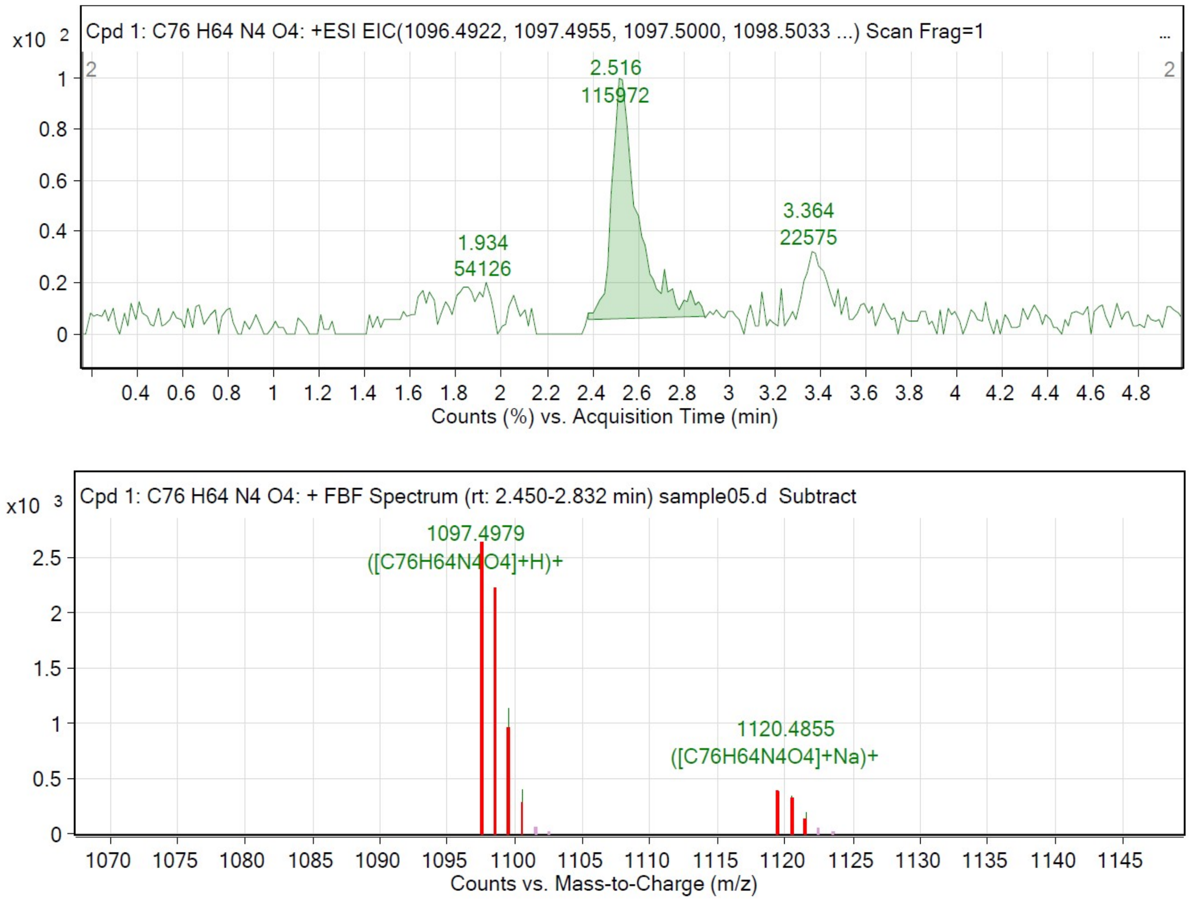


Figure S1. Chromatogram and mass spectrum of **Cbz-PDI**

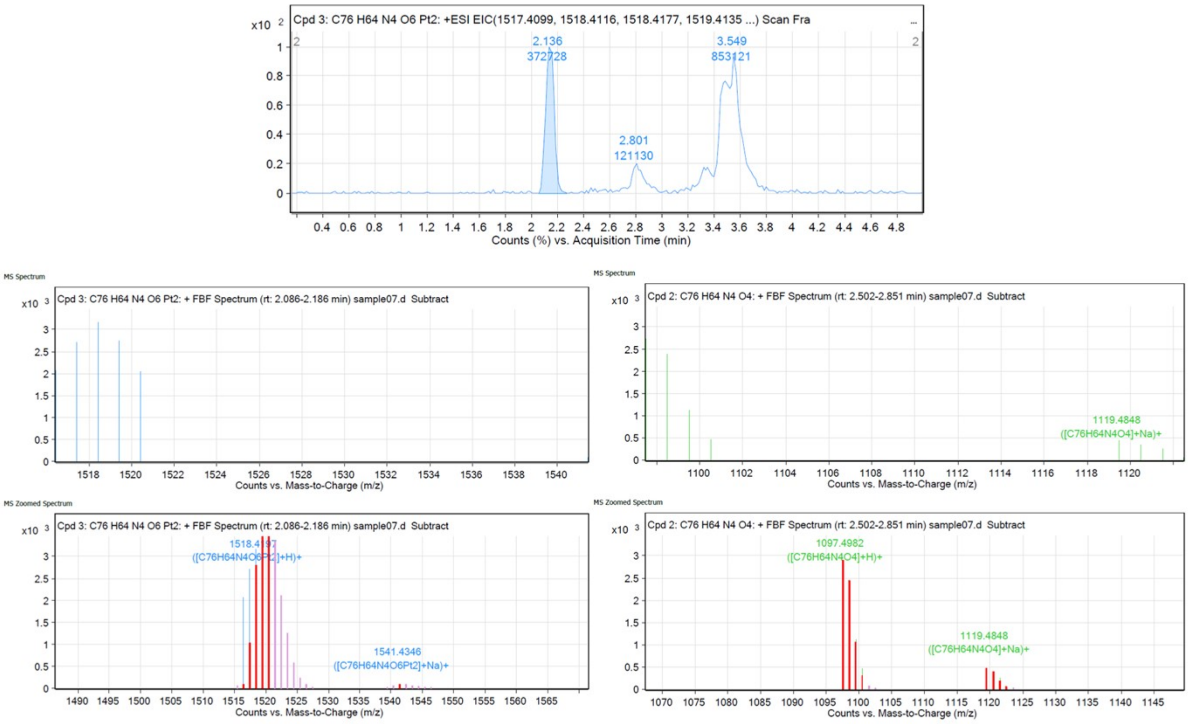
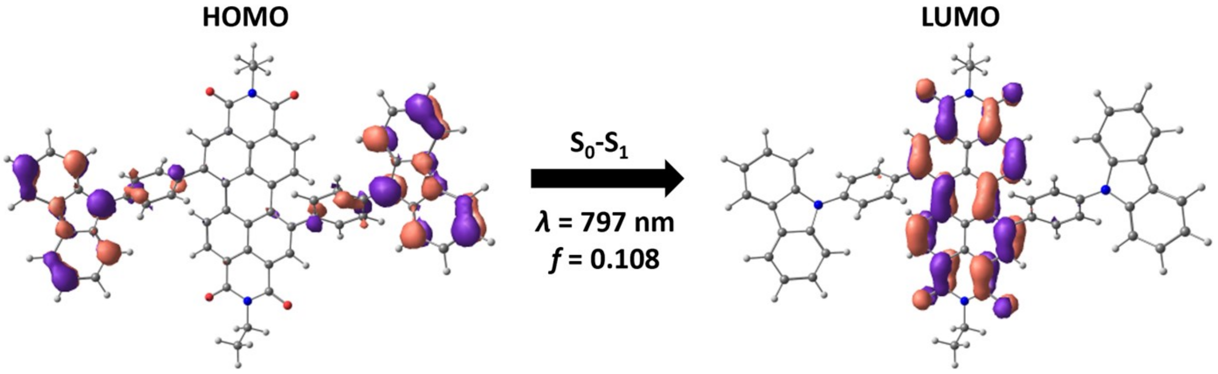
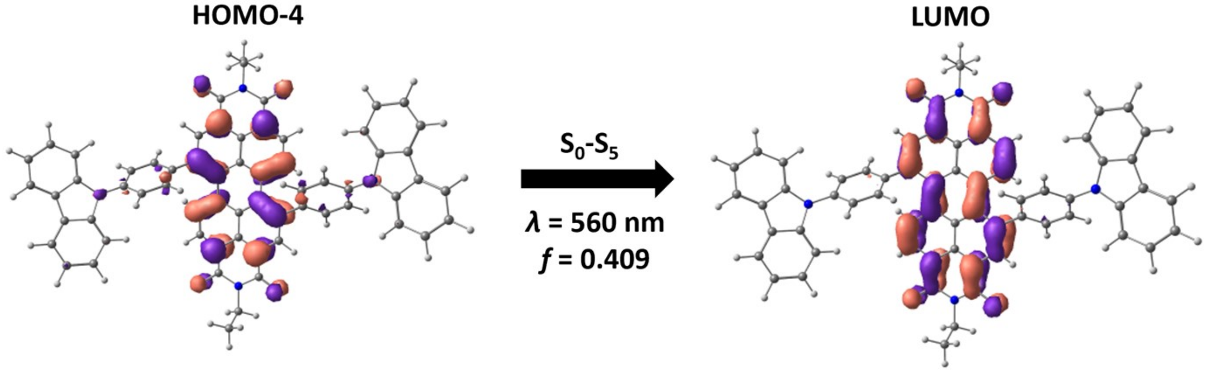


Figure S2. LCMS chromatogram and mass spectrum of the activated **Cbz-PDI** mixture and detection of **Cbz-PDCA-Pt$_2$**.

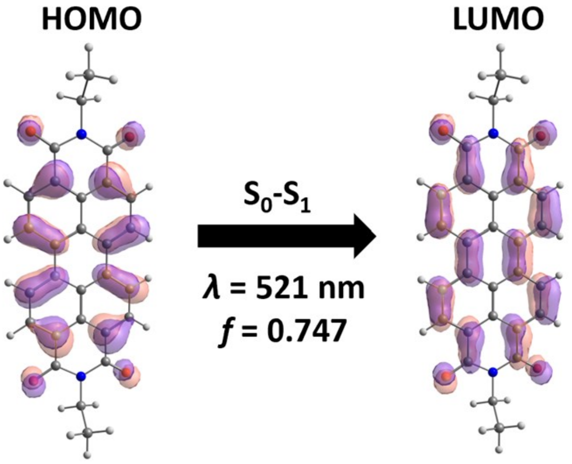
Calculation results

Cbz-PDI

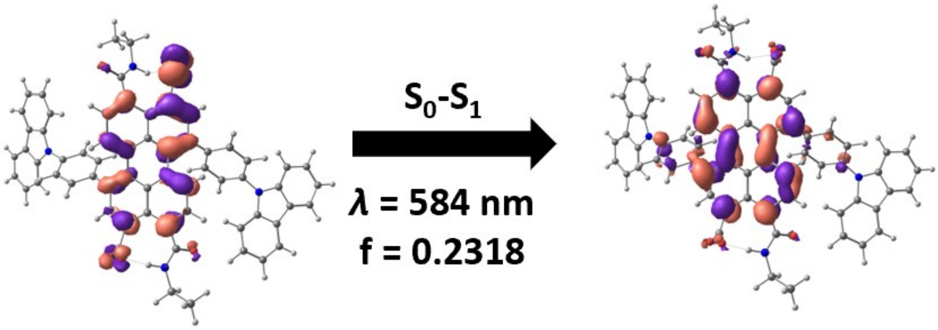




PDI



Cbz-PDCA



Cbz-PDCA-Pt$_2$

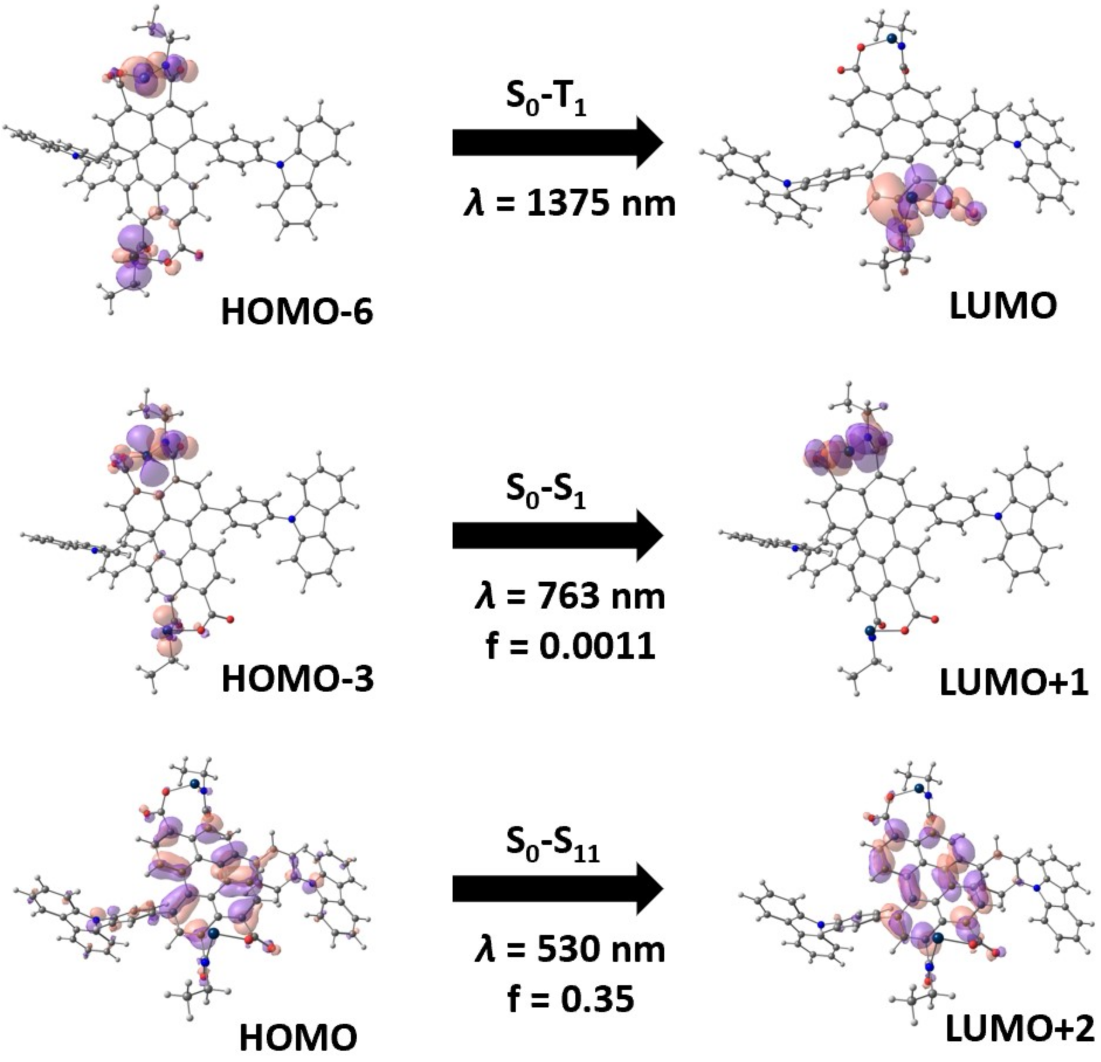


Figure S3. Molecular orbitals of **Cbz-PDI** and **PDI** for the electronic transitions responsible for absorption in the visible region.

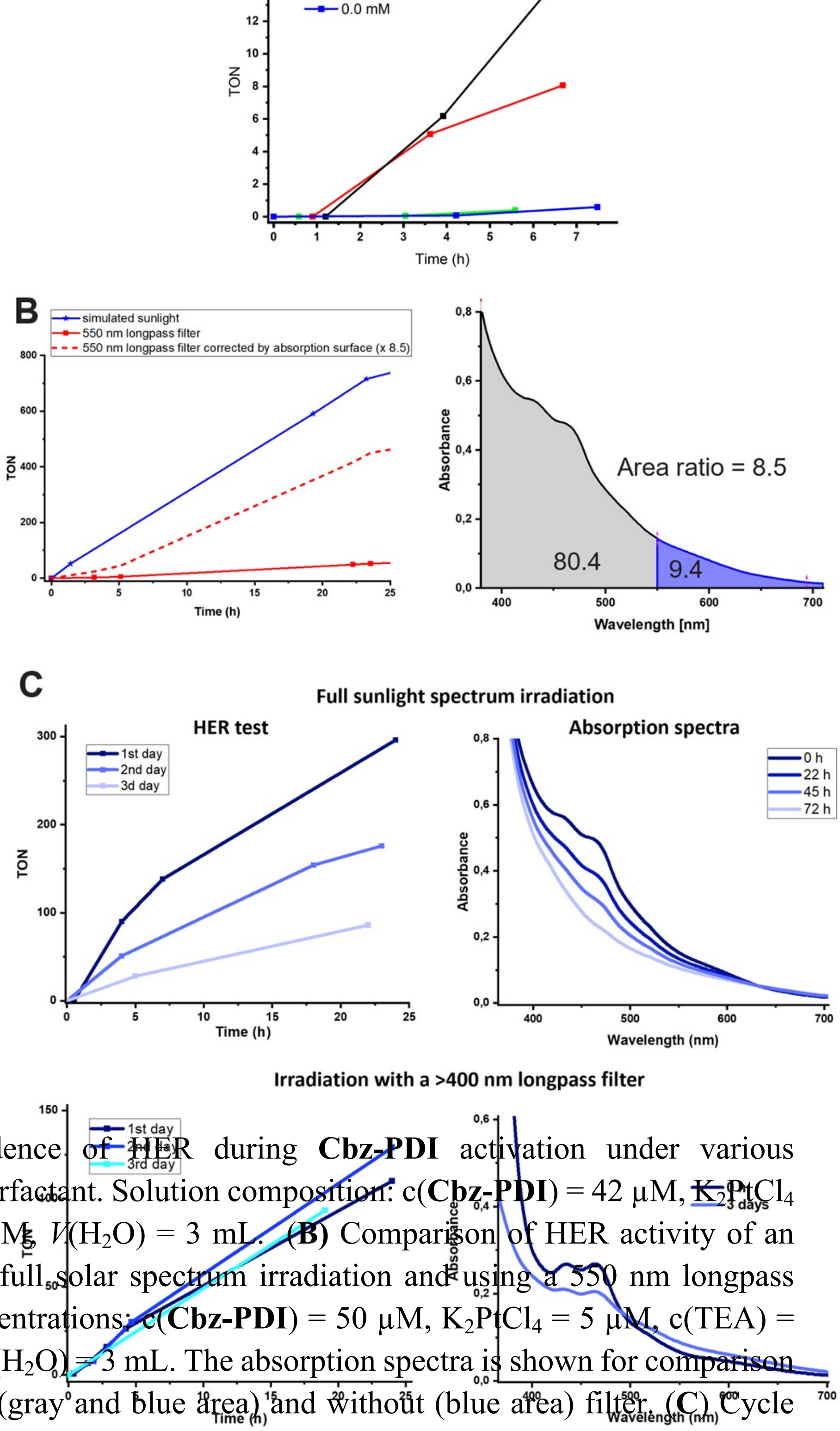


Figure S4. A) Dependence of HER during **Cbz-PDI** activation under various concentrations of SDS surfactant. Solution composition: c(**Cbz-PDI**) = 42 µM, K_2PtCl_4 = 42 µM, c(TEA) = 0.3 M, $V(H_2O)$ = 3 mL. **(B)** Comparison of HER activity of an activated mixture under full solar spectrum irradiation and using a 550 nm longpass optical filter; initial concentrations: c(**Cbz-PDI**) = 50 µM, K_2PtCl_4 = 5 µM, c(TEA) = 0.3 M, c(AA) = 0.7 M, $V(H_2O)$ = 3 mL. The absorption spectra is shown for comparison of absorbance area with (gray and blue area) and without (blue area) filter. **(C)** Cycle tests of HER performance at 1 SUN (full sunlight spectrum), >400 nm light, and respective changes in absorption spectra; initial concentrations: c(**Cbz-PDI**) = 50 µM, K_2PtCl_4 = 5 µM, c(TEA) = 0.3 M, c(AA) = 0.7 M, $V(H_2O)$ = 21 mL.

Photoluminescence measurements

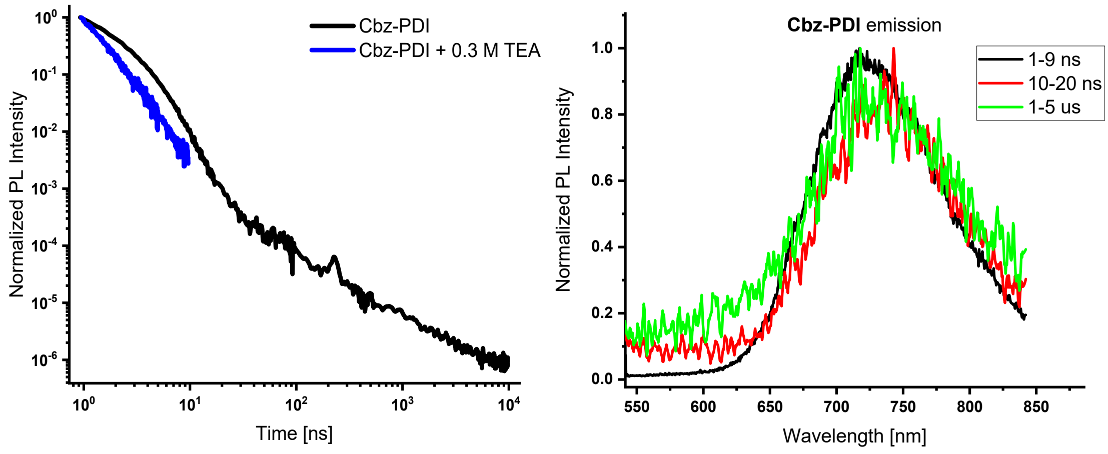


Figure S5. Emission decays in the absence and in the presence of TEA (0.1 mM) (left side) and evolution of emission spectra in time (right side) for **Cbz-PDI** in the SDS (2.1 mM) water solution.

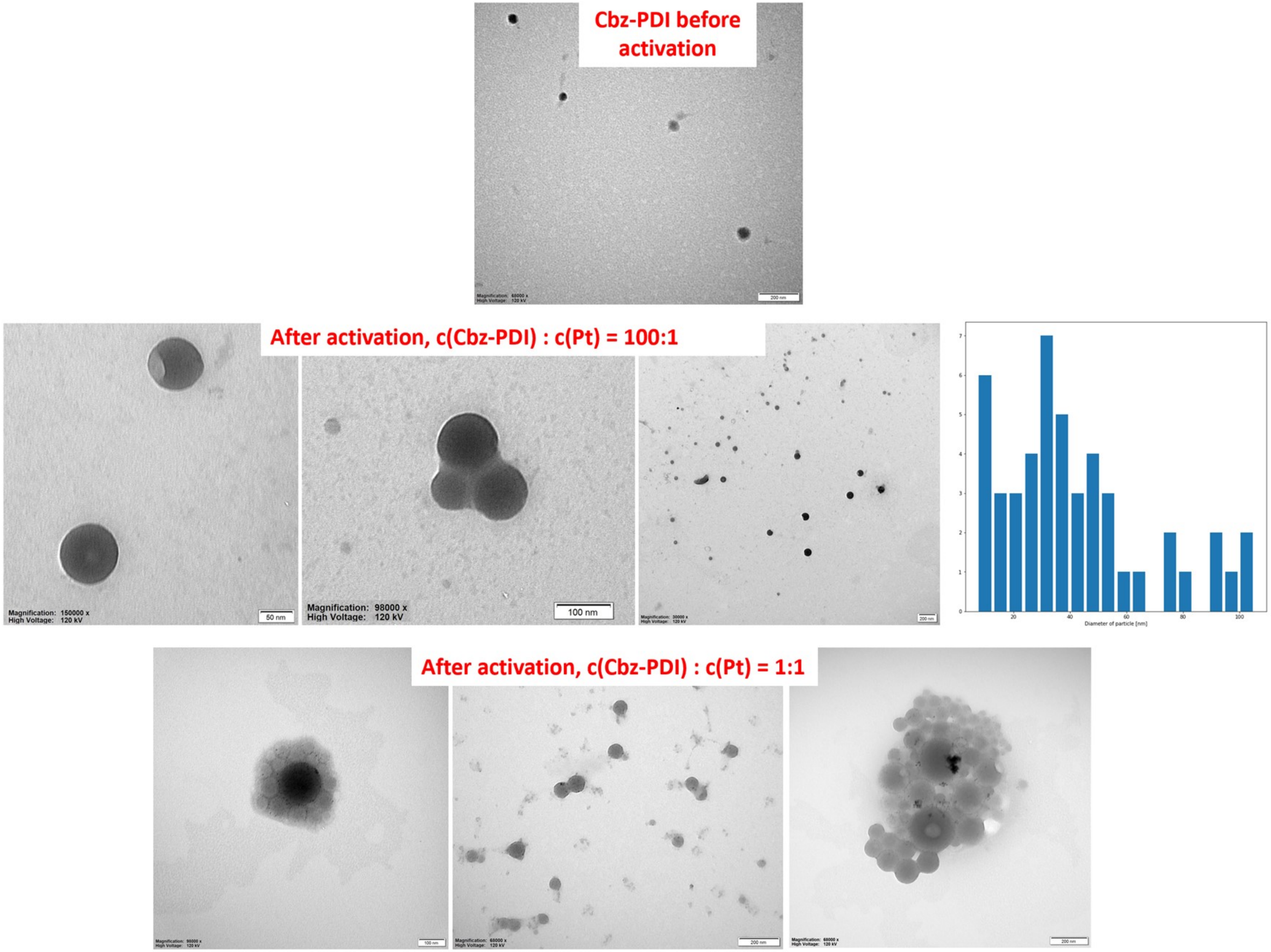
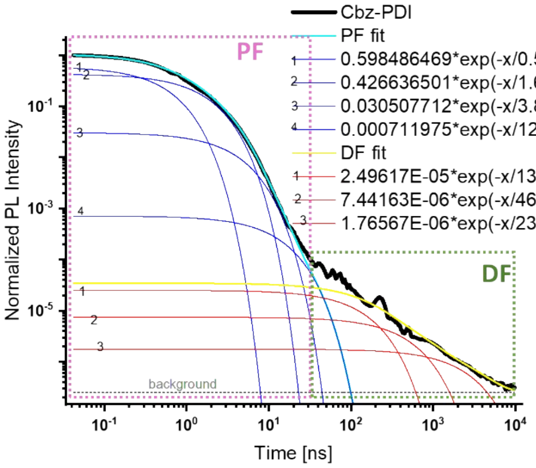
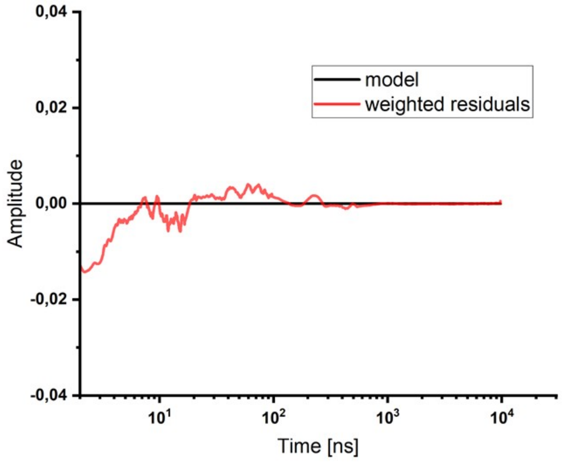


Figure S6. TEM images of SDS water solutions of **Cbz-PDI** and its mixtures with K_2PtCl_4 after activation.

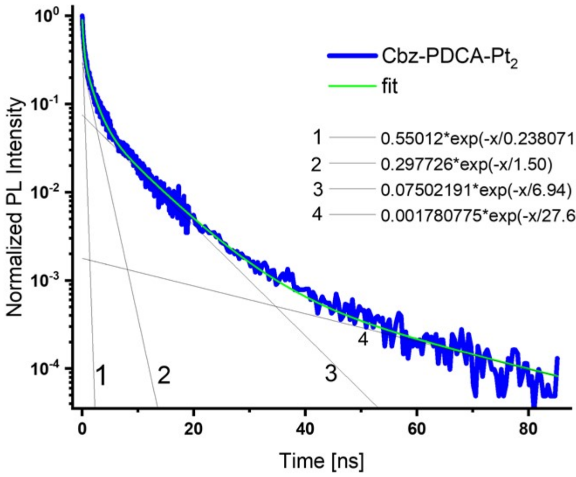
Additional data on the emission decay of water-SDS systems and the details of fitting

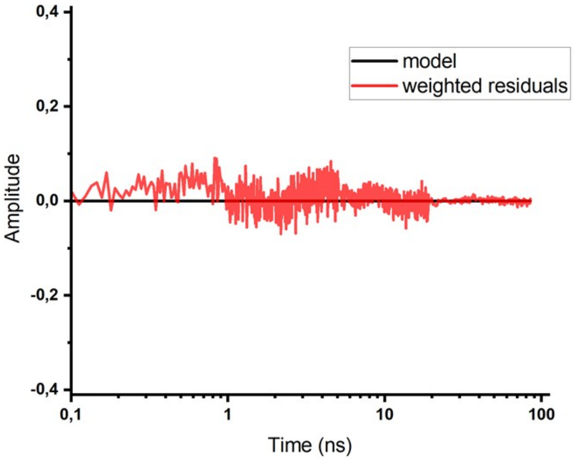
Cbz-PDI





Cbz-PDCA-Pt$_2$





Cbz-PDCA-Pt$_2$ + TEA