

Supplementary Information for

Ultra-fast and Slow Charge Recombination Dynamics of Diketopyrrolopyrrole-NiO Dye Sensitized Solar Cells

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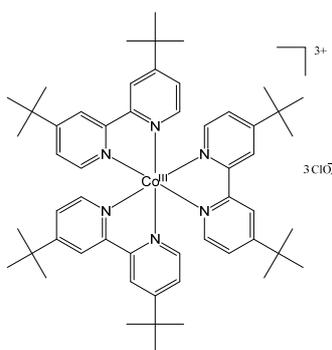


Figure S1. Structure of the $[\text{Co}(\text{dtb})_3]^{3+}$ complex used as redox mediator (prepared with PF_6^- as counter ion).

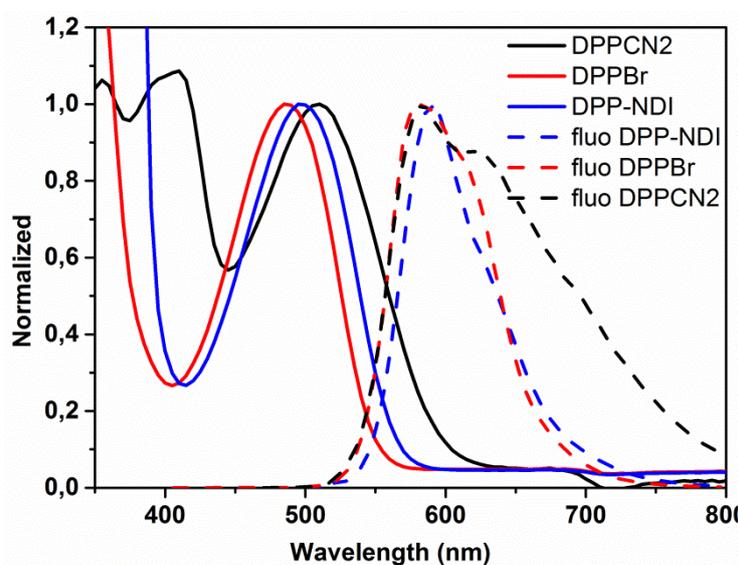


Figure S2. Normalized UV-vis absorption (solid lines) and emission spectra (dashed lines) of diketopyrrolopyrroles (DPPs) in dichloromethane DCM at 298K.

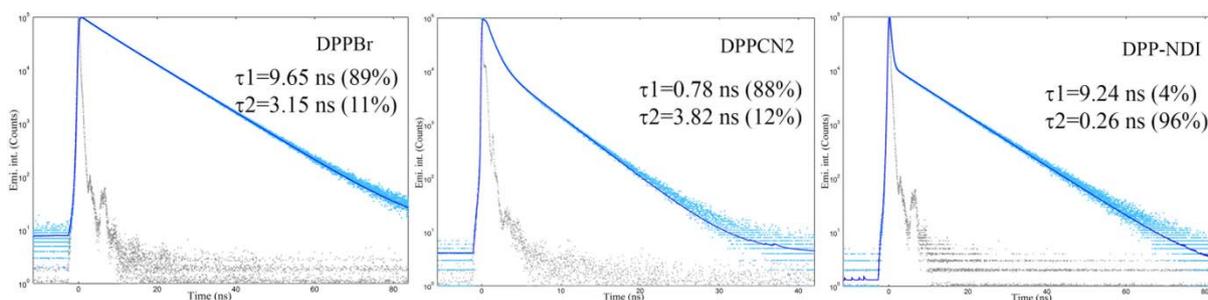


Figure S3. Time-Correlated Single Photon Counting (TCSPC) data and emission lifetime results of DPP sensitizers in DCM (Absorbance=0.1, excitation at 470 nm).

For DPP-NDI the 4% of long-lived fluorescence is most certainly a DPP-derivative without NDI (9 ns fluorescence lifetime, similar to DPPBr). This is too little to distinguish in both the NMR (Figure S15-S17) and in the transient absorption data, as it will also recombine rapidly relative to DPP-NDI.

For the other compounds we assign the impurity to a DPP derivative that has a 3-4 ns fluorescence lifetime. It's NMR is very similar to that of DPPBr and DPPCN2 (Figure S15-S17). The impurity is not likely to affect the results of the transient absorption studies significantly: the behavior in solution and on NiO of the DPPBr and DPPCN2 is similar but yet quite distinct; see e.g. the traces in Figure S5, and the different DAS in Figures S7-S8. Also, the small fraction of charge separated species remaining on the ns-us time scale shows a distinctly different wavelength for the ground state bleach for the two dyes (Figure S13, spectra with LiClO₄).

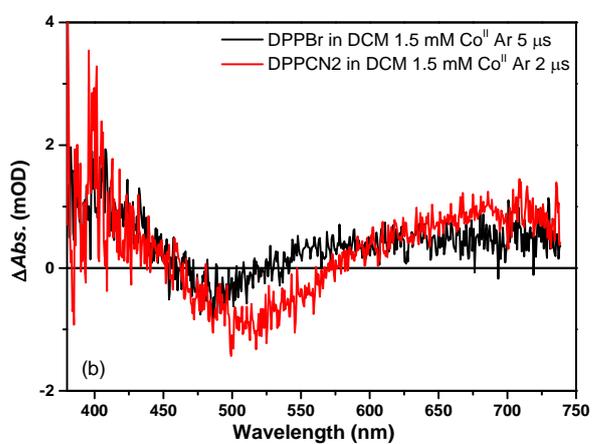
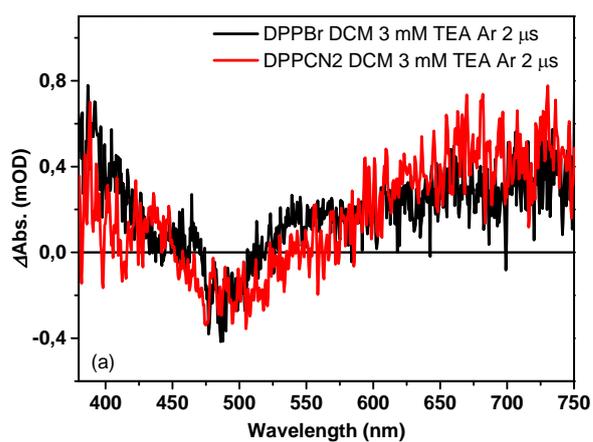


Figure S4. Transient absorption spectra after 10 ns laser flash excitation of DPPBr in DCM with (a) 3 mM triethylamine (TEA) or (b) 1.5 mM $\text{Co}^{\text{II}}(\text{dtb})_3$ as electron donor. The spectra are assigned to the reduced $\text{DPP}^{\bullet-}$ radical anion.

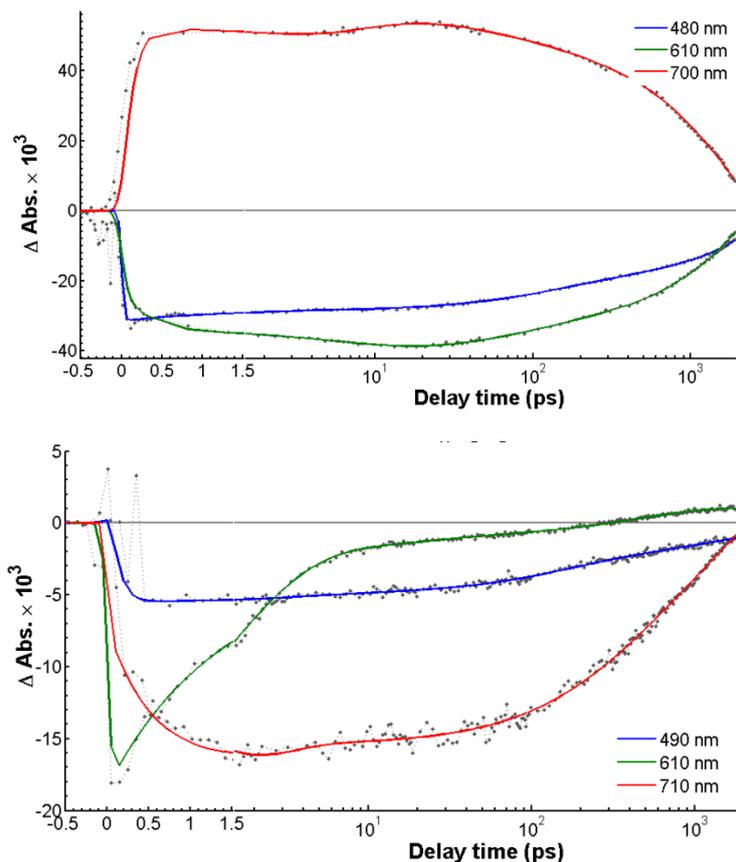


Figure S5. Transient absorption traces for DPPBr (up) and DPPCN2 (bottom) in DCM after excitation at 510 nm.

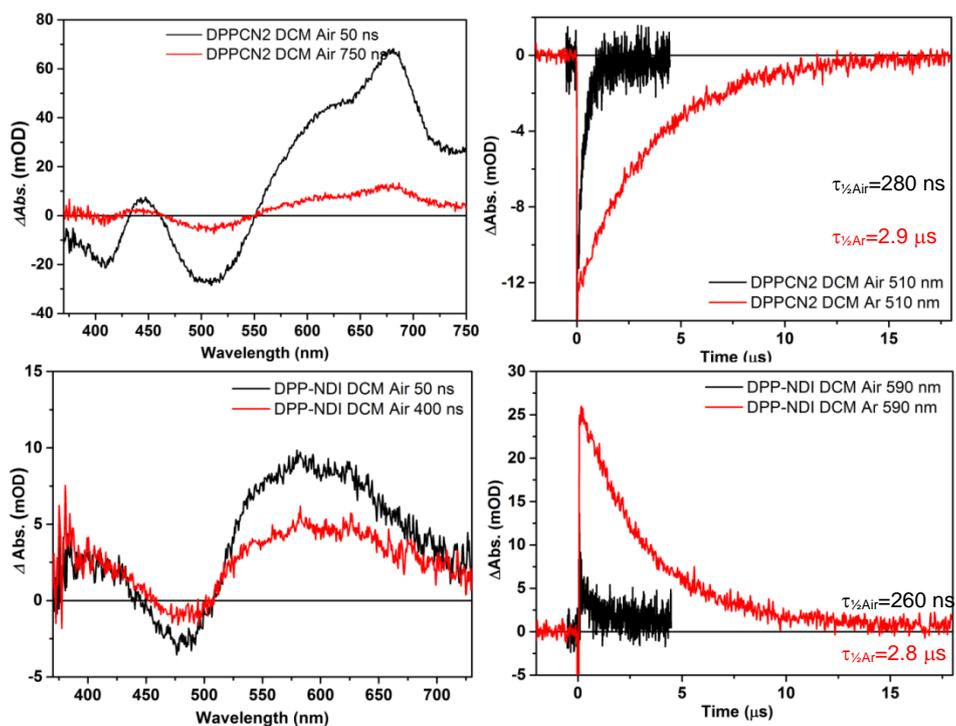


Figure S6. Nanosecond time-resolved transient absorption spectra upon excitation at 532 nm of the DPPCN2 (top) and DPP-NDI (bottom) in air-saturated DCM (left) and representative kinetic traces with either air or argon atmosphere (right).

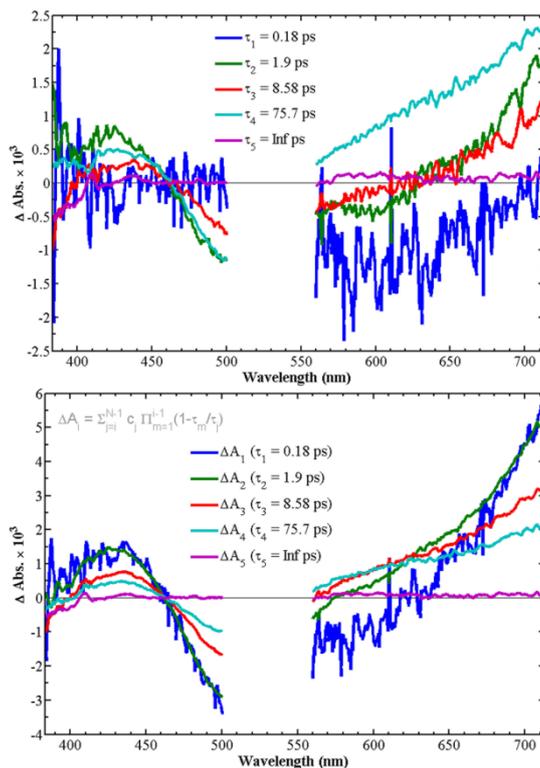


Figure S7. Decay associated spectra (DAS) and Species associated spectra (SAS) from global fit of fs-transient absorption data for NiO/DPPBr excited at 525 nm.

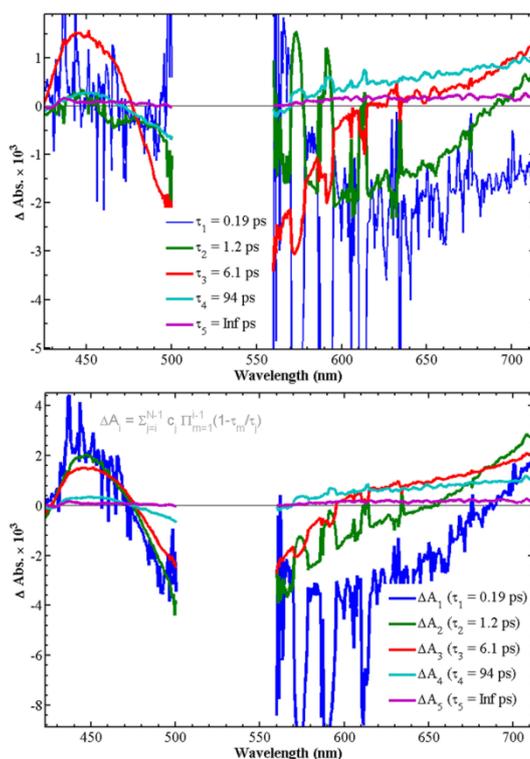


Figure S8. Decay associated spectra and Species associated spectra from global fit of fs-transient absorption data for NiO/DPPCN2 excited at 525 nm. The “noise” arises because the first component is close to the instrument response function. Therefore the amplitude is sensitive to artefacts that are strongly wavelength dependent. Yet, the overall spectral shape is quite clear, as the noise is moderate at most wavelengths.

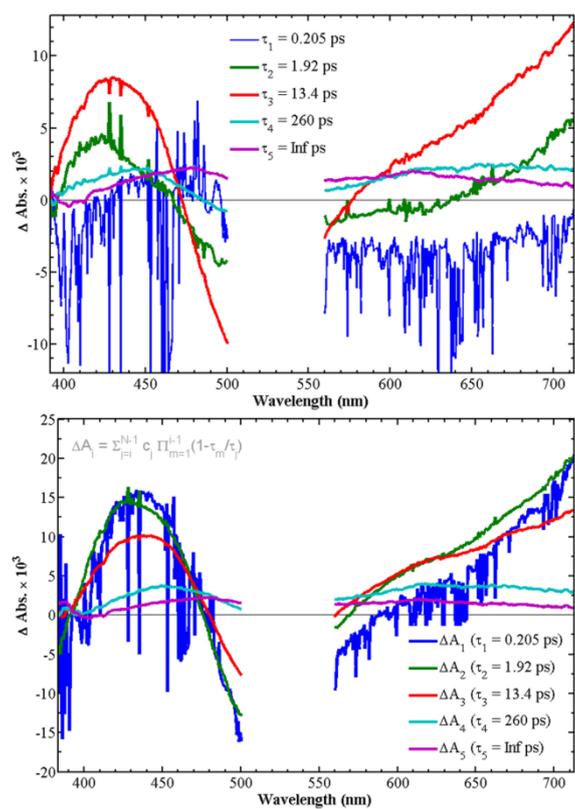


Figure S9. Decay associated spectra and Species associated spectra from global fit of fs-transient absorption data for NiO/DPP-NDI excited at 525 nm.

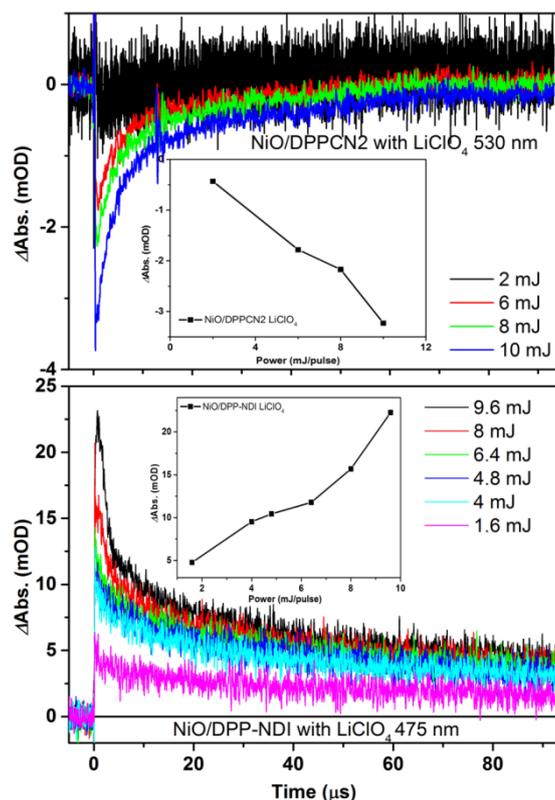


Figure S10. Excitation power dependence of nanosecond transient absorption kinetics for DPPCN2 (top) and DPP-NDI (bottom) sensitizers on NiO, after 10 ns laser excitation at 532 nm. The insets show the peak absorption change as a function of pulse power (approximately linear dependence).

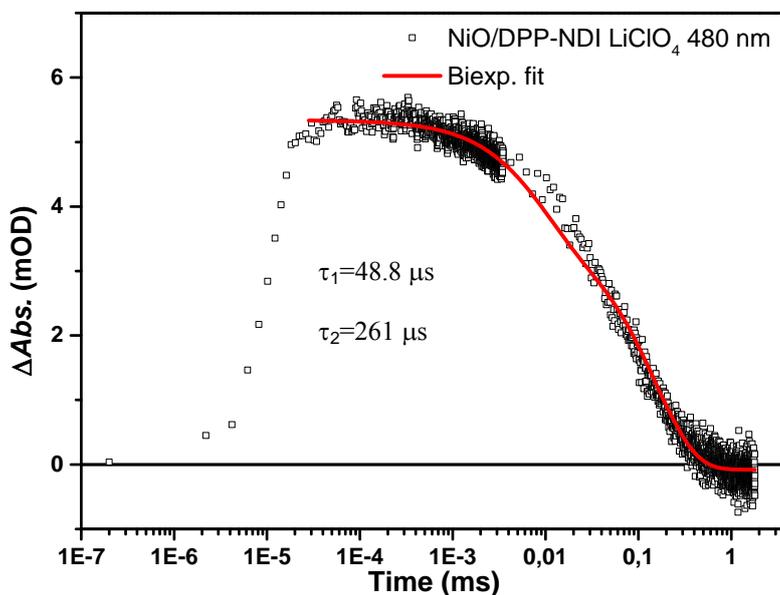


Figure S11. Nano-second transient absorption kinetic for NiO/DPP-NDI, showing the long-lived charge separated state. Excitation at 532 nm, 2 mJ/pulse, a shortpass filter at 500 nm was used before the monochromator to reduce scattered laser light.

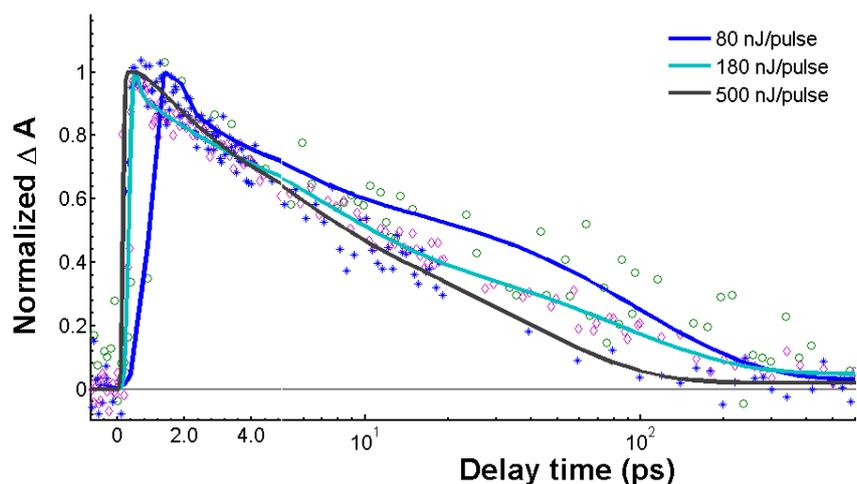


Figure S12. Normalized kinetic traces of NiO/DPPBr with different laser pump power at 440 nm. The apparent slower rise of the signal at 80 nJ pump power is because of low signal to noise and the fact that only few data points were taken around time zero. This does not imply that the injection actually is slower. Instead the experiment was performed to investigate possible effects on the subsequent charge recombination

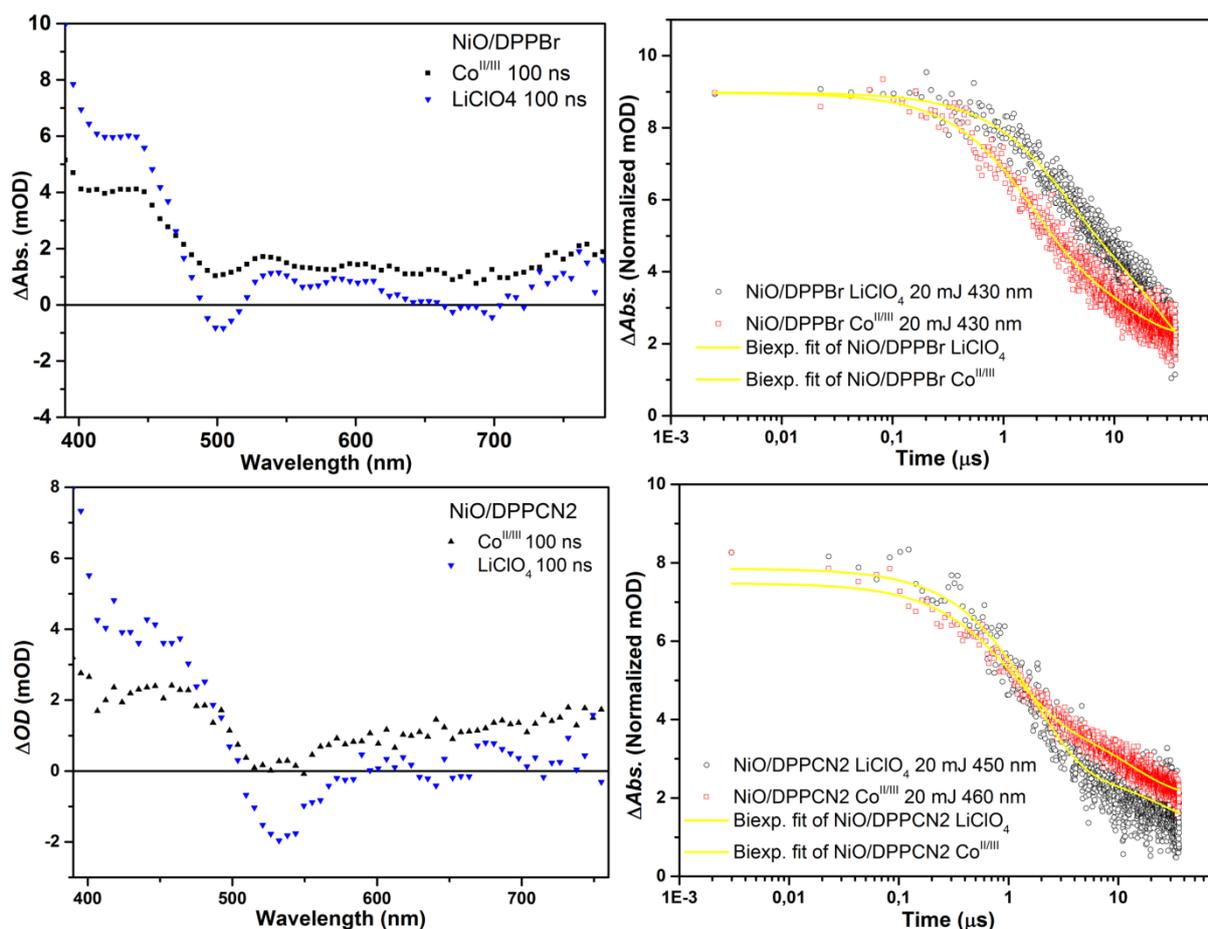


Figure S13. Nanosecond transient absorption spectra (Left) and kinetic traces (Right) of NiO/DPPBr and NiO/DPPCN2 with LiClO₄ or Co^{II/III} electrolyte in propylene carbonate, after excitation at 532 nm. The traces were monitored at 430 nm and 450 or 460 nm for DPPBr and DPPCN2, respectively.

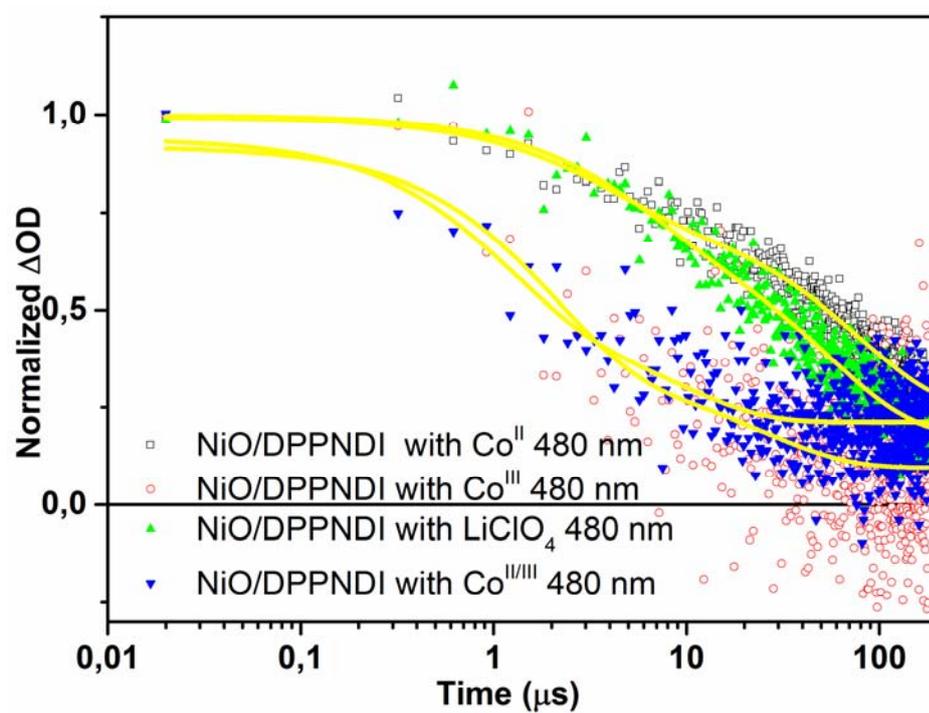


Figure S14. Normalized kinetic traces of NiO/DPP-NDI with and without electrolyte at 480 nm, after excitation at 532 nm. (Open circles and open squares is data with Co^{III} and Co^{II} , green dot and blue triangles is the traces for inert $LiClO_4$ and $Co^{II/III}$)

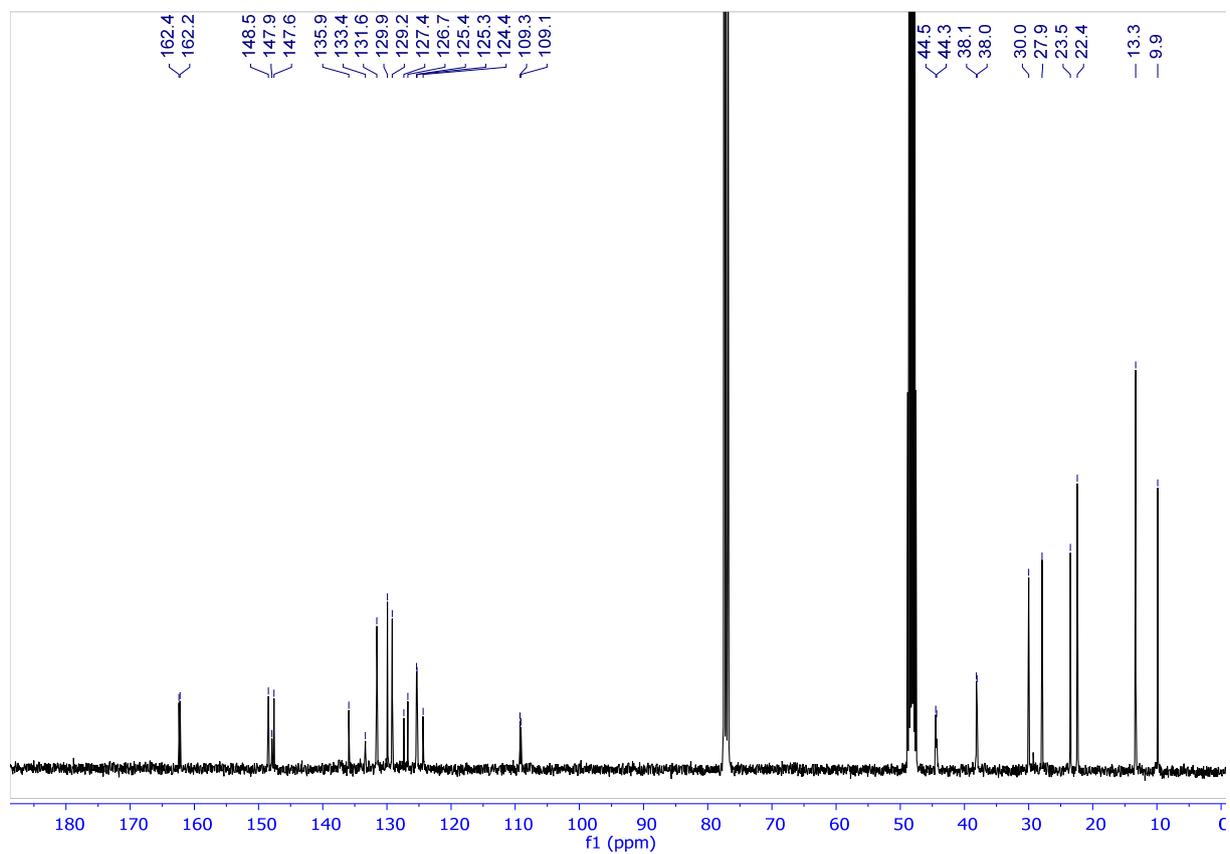
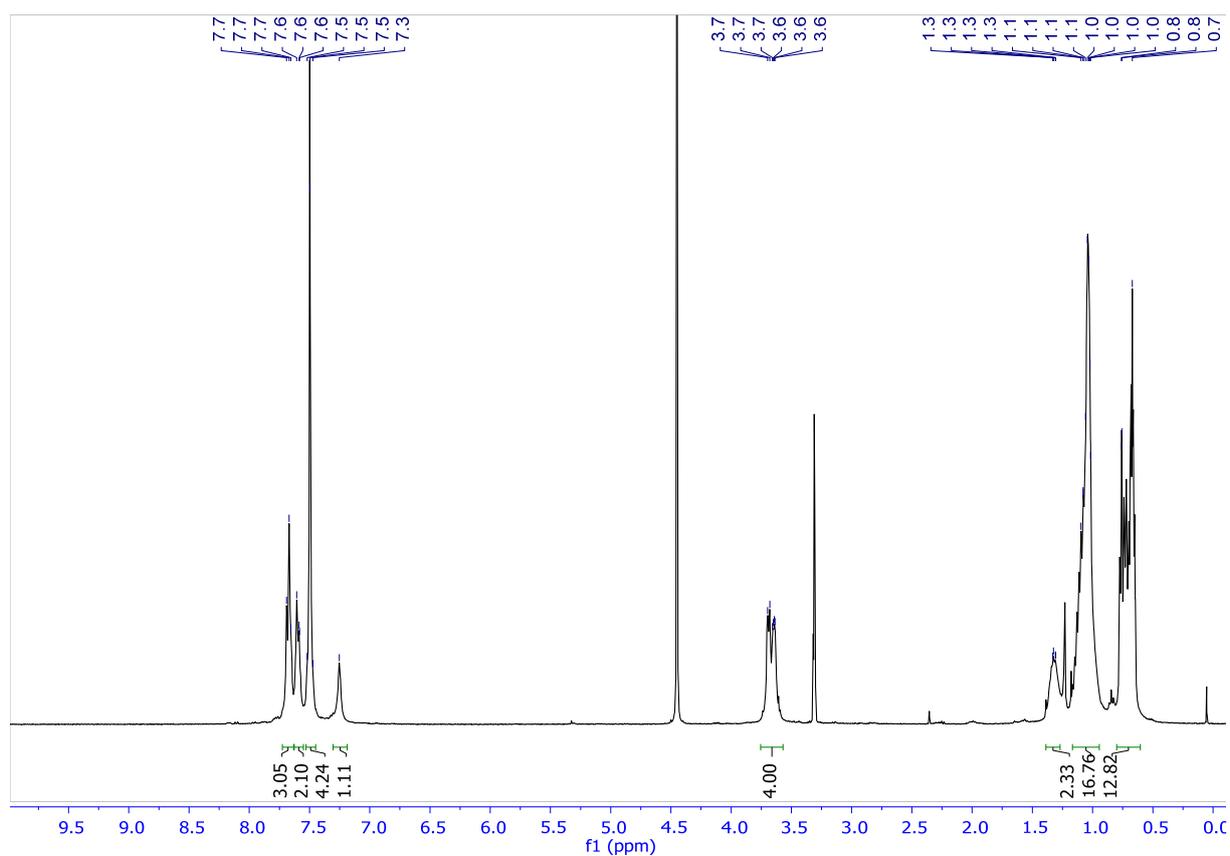


Figure S15: ¹H (top) and ¹³C NMR (bottom) spectra of DPPBr (400 MHz, 125 MHz, CDCl₃/MeOD (1/1), 298 K).

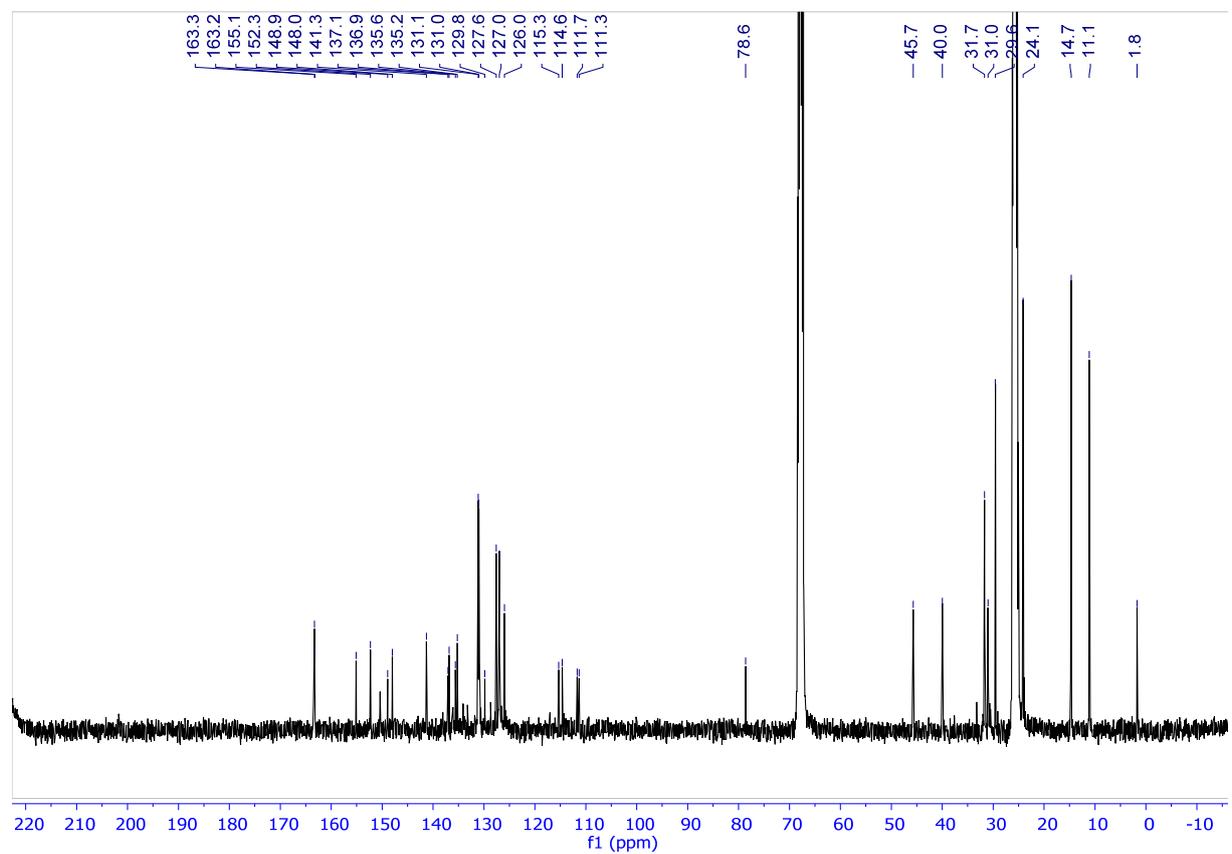
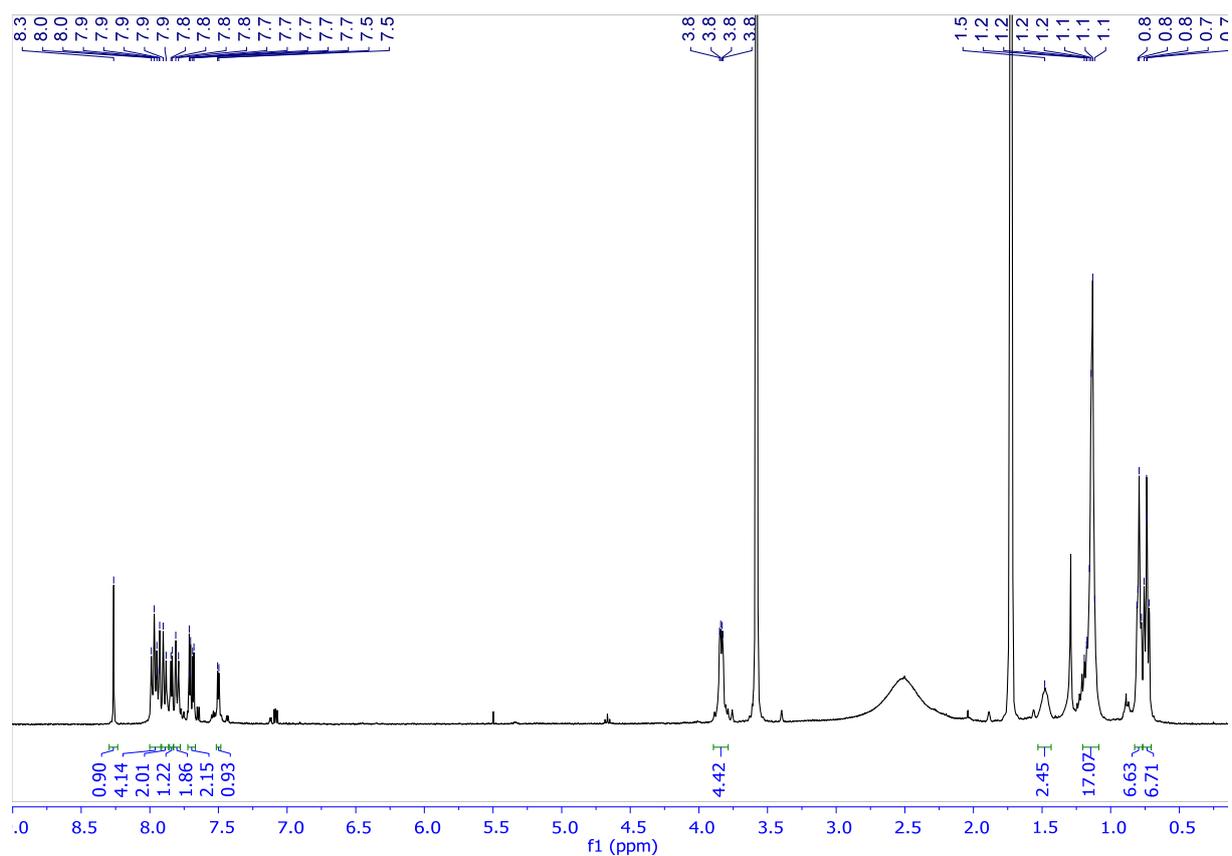


Figure S16: ^1H (top) and ^{13}C NMR (bottom) spectra of DPPCN (400 MHz, 125 MHz, THF- d_8 , 298 K).

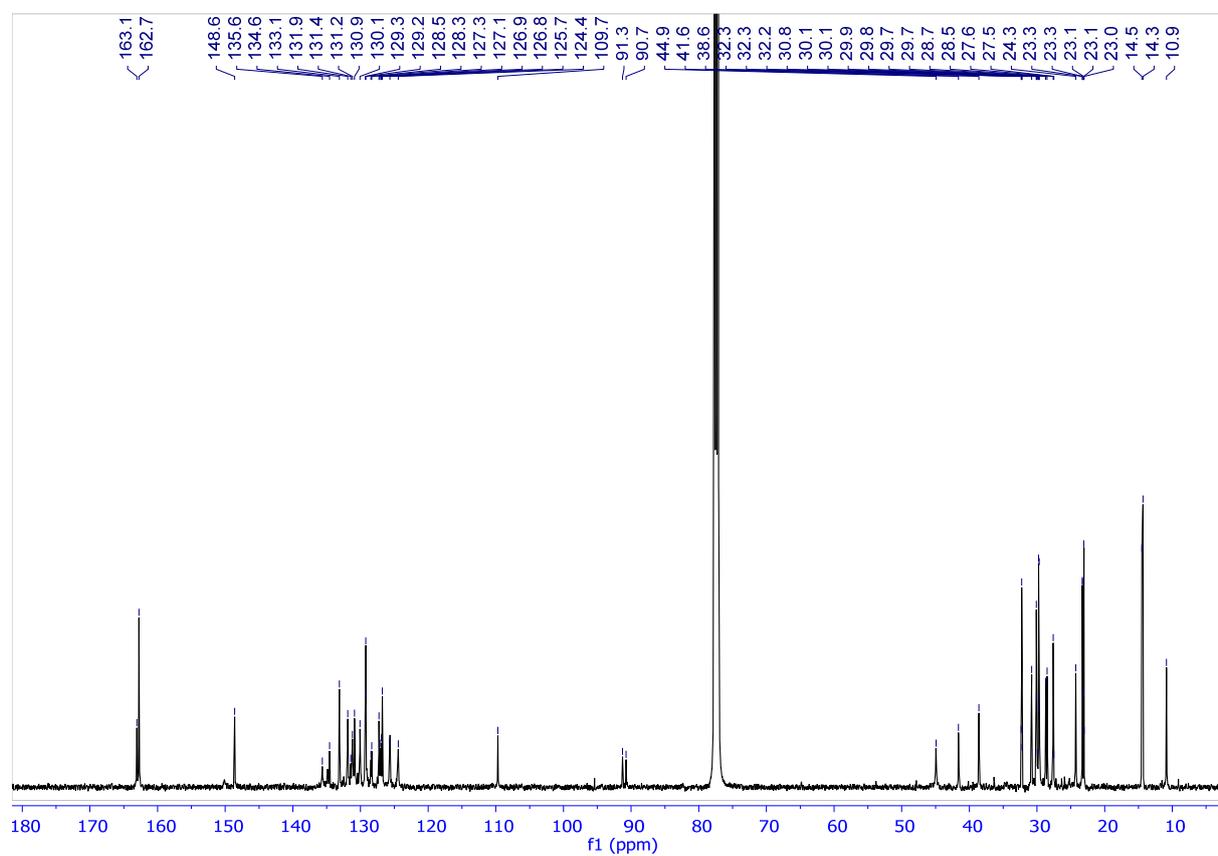
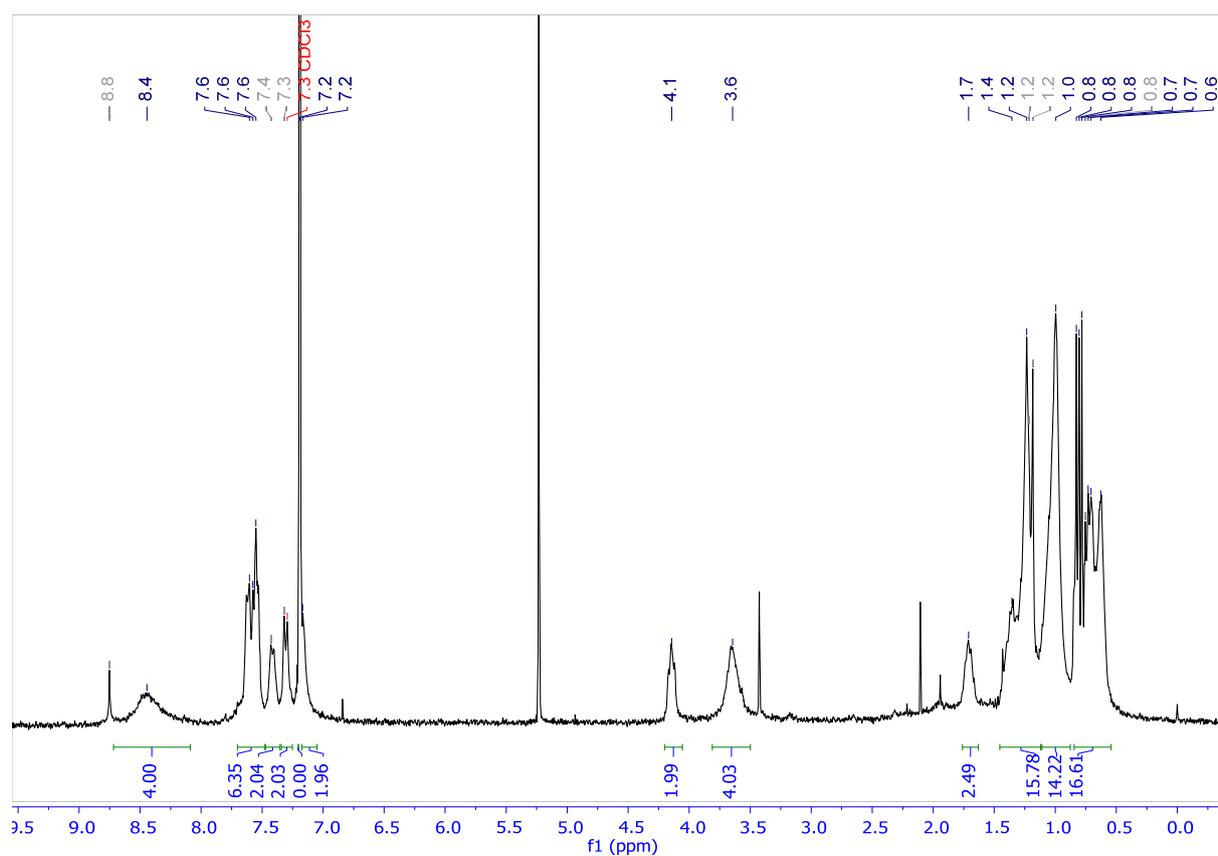


Figure S17: ¹H (top) and ¹³C NMR (bottom) spectra of DPP-NDI (400 MHz, 125 MHz, CDCl₃, 298 K).