Supplementary information

Synthesis and characterization of perylene–bithiophene–triphenylamine triads: Studies on the effect of alkyl-substitution in p-type NiO based photocathodes

Martin Weidelener,[a] Amaresh Mishra,[a]* Andrew Nattestad,[b,d] Satvasheel Powar,[c] Attila J. Mozer,[d] Elena Mena-Osteritz,[a] Yi-Bing Cheng,[b] Udo Bach[b]* and Peter Bäuerle[a]*

[a] Institute for Organic Chemistry II and Advanced Materials, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany.
[b] ARC Centre of Excellence for Electromaterials Science, Department of Materials Engineering, Monash University, Clayton Victoria, Australia.
[c] ARC Centre of Excellence for Electromaterials Science, School of Chemistry, Monash University, Clayton, Victoria, 3800 Australia.
[d] ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, AIIM Facility, Innovation Campus, University of Wollongong, New South Wales, 2522, Australia.

* Email: amaresh.mishra@uni-ulm.de, peter.baeuerle@uni-ulm.de, udo.bach@monash.edu

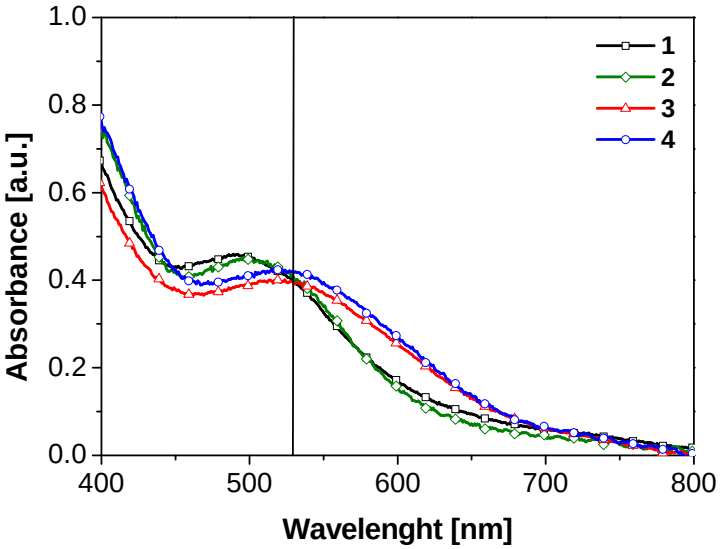

Figure S1. Absorbance of the dyes NiO films used for transient absorption (TA) studies. αd at 532 nm are 0.39 for dye **1-3** and 0.42 for dye **4**.

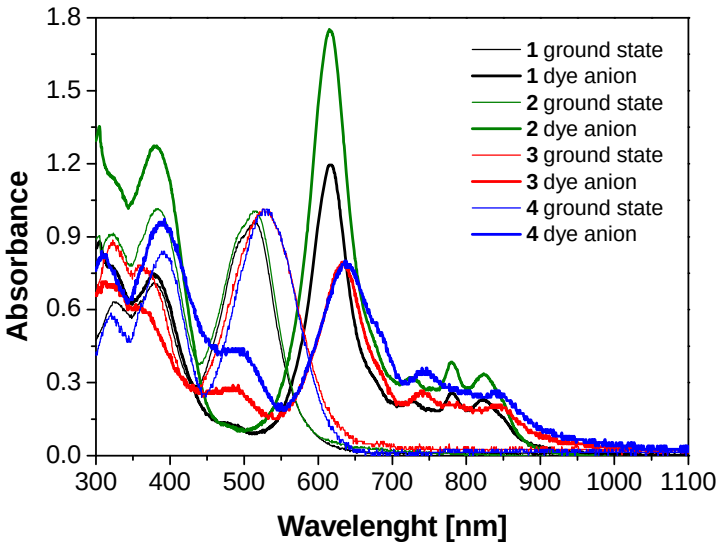

Figure S2. Neutral and anion absorption spectra, normalized to most red-shifted ground state absorption peak (~500-550nm). The anion spectra of **1**, **2** and **4** shown here were recorded at −500 mV whereas for **3** it was at −550 mV.

Dye anion spectra were collected by a spectroelectrochemcial method. Dyes were dissolved in a solution 0.1M TBAPF6 in DMF. This was injected into a OTTLE (Optically Transparent Thin-Layer (spectro)Electrochemical) cell from IDEAS! UvA B.V. The cell contains two platinum grids, the counter electrode and the working electrode which is in the optical path, as well as a silver pseudo reference.

The ground state absorption spectra (open circuit) were recorded as a reference. Subsequently a stepped bias (50mV increments) was applied, with absorption spectra recorded at each step. This was increased until the anion signal was stabilized. Following this, the cell was returned to open circuit for an extended period of time to ensure there were no permanent changes to the dye ground state absorption.

Ground state absorption data from Table 1 was used along with the ratio between the measured spectra (Figure S1) to determine the extinction coefficients of the various anions (Table S1).

Table S1: Comparison of solution dye peak absorption, dye anion peak absorption and absorption at 700nm.

	Peak ground state abs. (from Table 1) ε[L mol^{-1} cm^{-1}]	Anion : ground abs. ratio (approx.)	Peak Anion absorption ε[L mol^{-1} cm^{-1}]	Anion absorption at 700 nm ε[L mol^{-1} cm^{-1}]
1	45000	1.20 : 1	54000 (616 nm)	9711
2	41500	1.75 : 1	72625 (615 nm)	12887
3	43100	0.80 : 1	34480 (638 nm)	10491
4	46000	0.80 : 1	36800 (637 nm)	17787