Electronic Supplementary Information

Using vibrational spectroscopy to probe charge-separated states in p-type dye-sensitized solar cells

Fiona A. Black[a], Charlotte A. Clark [b] , Gareth H. Summers[a,b], Ian P. Clark,[c] Michael Towrie,[c,d] Thomas Penfold,[a] Michael W. George,[b,d,e] Elizabeth A. Gibson[a,b]*

[a] *School of Chemistry, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK*
[b] *School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK.*
[c] *Central Laser Facility, Research Complex at Harwell, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, Oxfordshire, OX11 0QX, UK.*
[d] *Dynamic Structural Science Consortium, Research Complex at Harwell, Didcot, Oxfordshire, OX11 0FA UK.*
[e] *Department of Chemical and Environmental Engineering, University of Nottingham Ningbo China, 199 Taikang East Road, Ningbo 315100, China.*

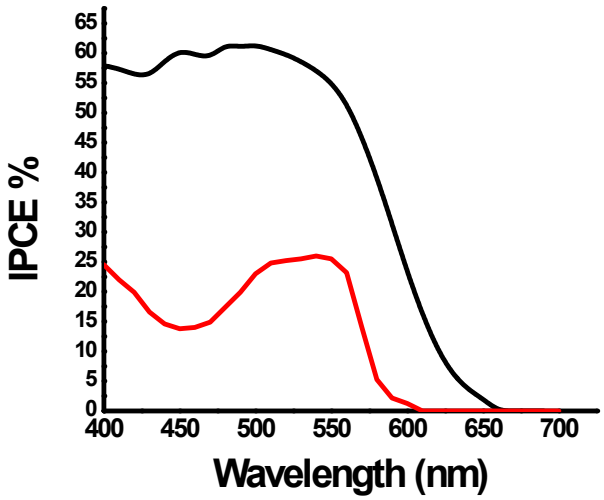

Figure S1. Spectral response of p-DSCs incorporating **1** (black) and **2** (red). The cells were assembled as described in reference [21].

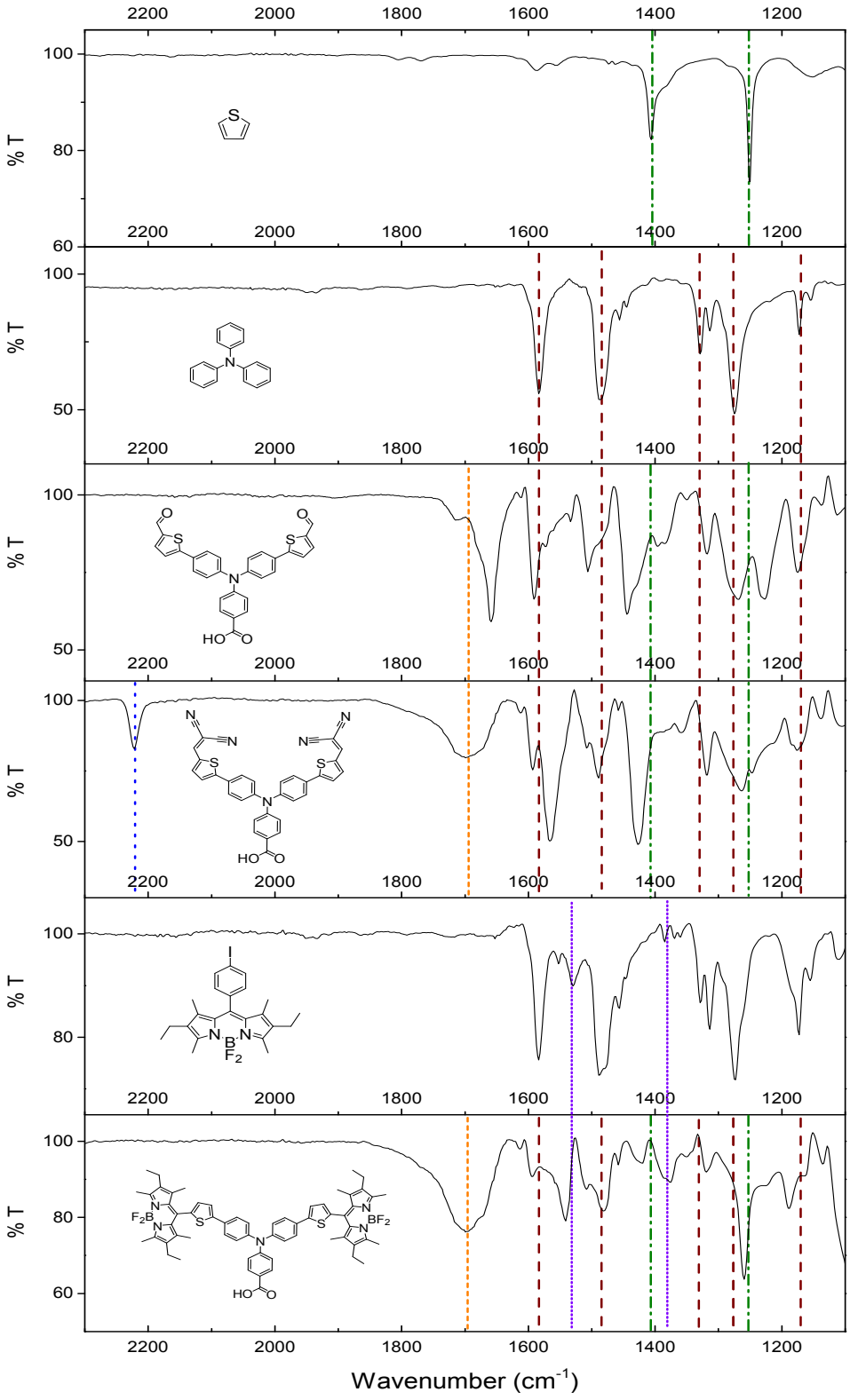

Figure S2. Ground state ATR FTIR spectra of **1**, **2** and their corresponding precursor molecules. The corresponding assignments of the vibrational bands are shown; phenyl bands (dashed lines), carbonyl bands (short

dashed lines), nitrile bands (short dotted line), thiophene bands (dash-dot-dashed lines) and bodipy bands (dotted lines).

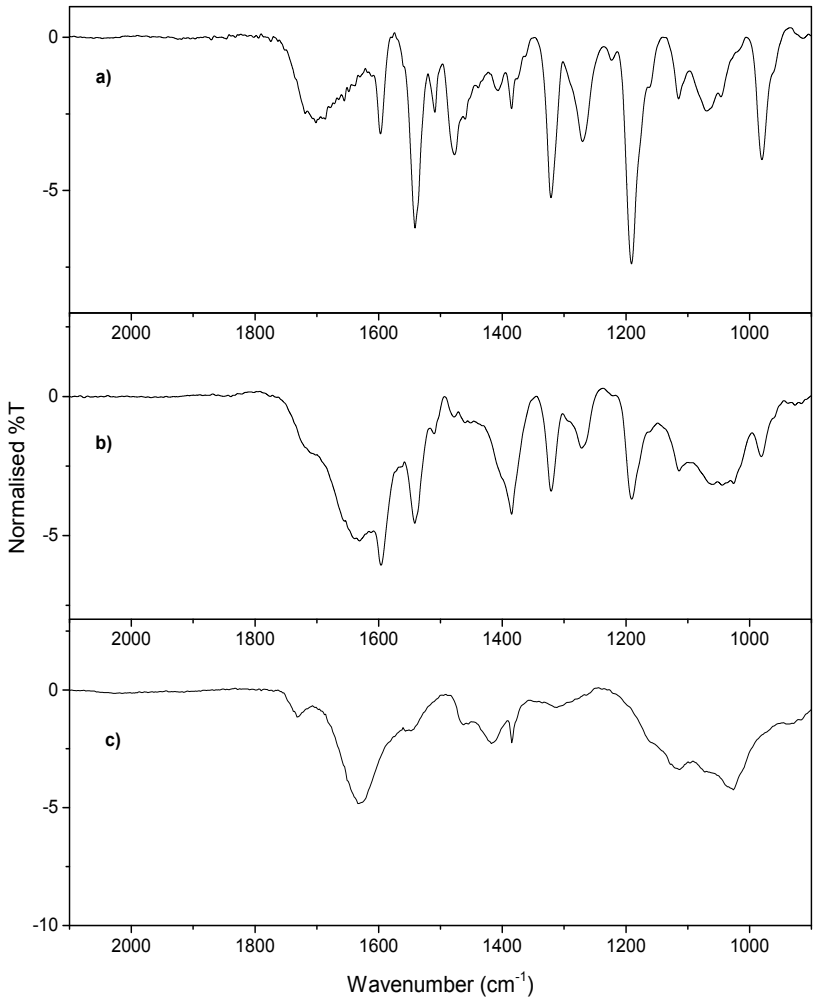

Figure S3. Ground state FTIR spectra of a) **2**, b) **2**|NiO and c) NiO.

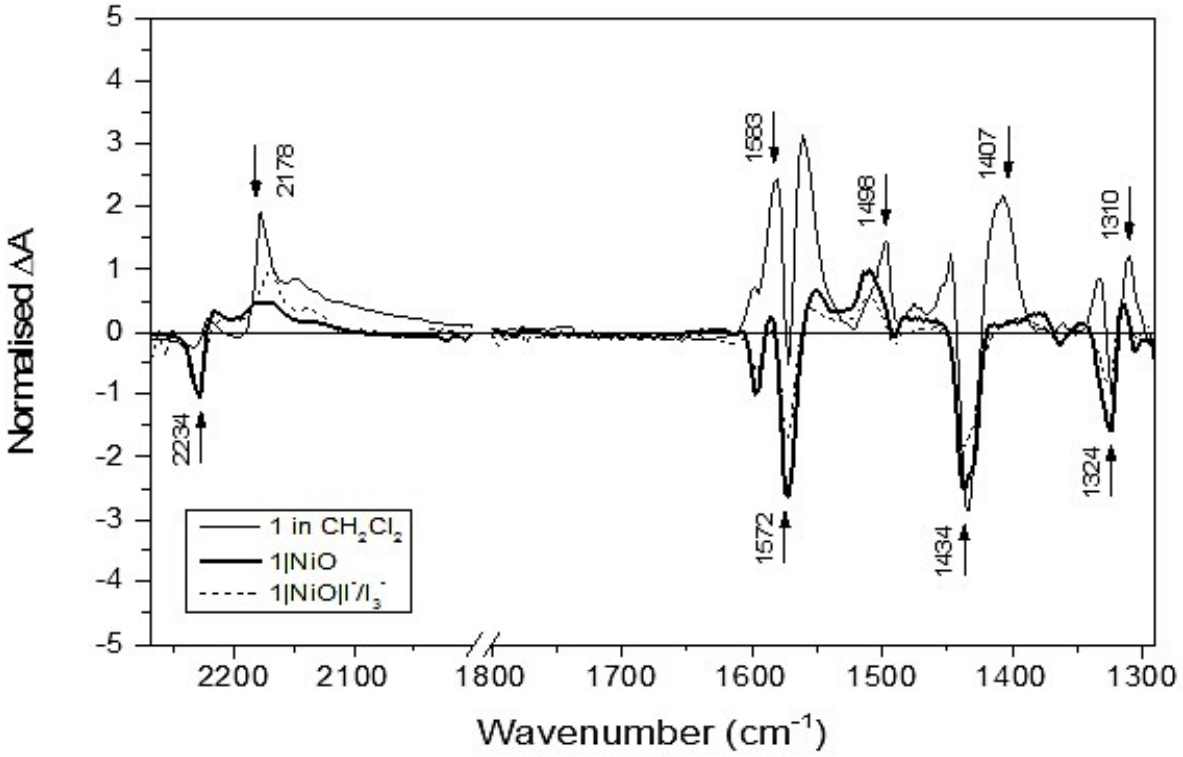

Figure S4. Overlay of the TRIR spectra of **1** in CH_2Cl_2 (thin solid black), **1**|NiO (thick solid black) and **1**|NiO|I^-/I_3^- (dashed black) at a delay time of 15 ps after excitation at 532 nm.

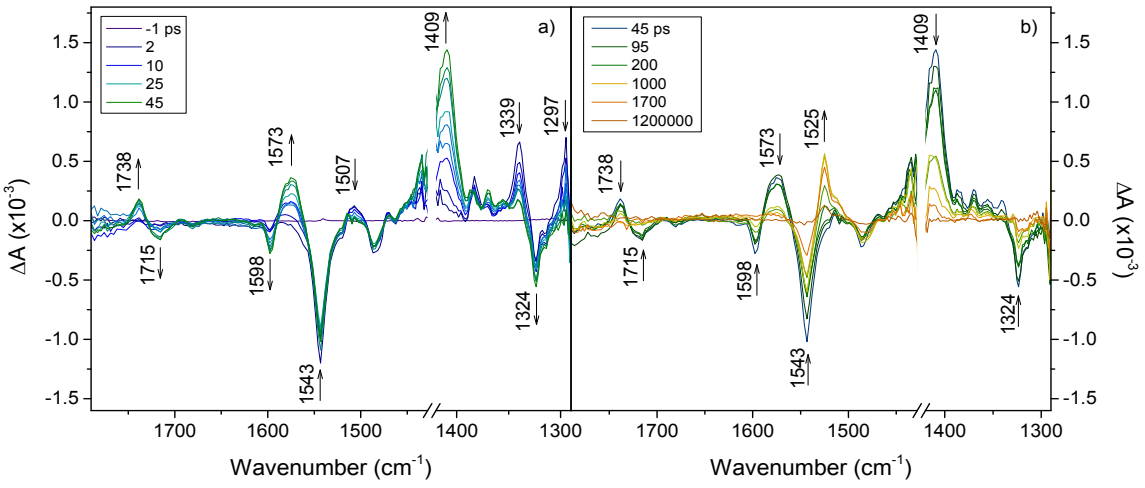

Figure S5 TRIR spectra of **2** in CH_2Cl_2 at early (a) and late (b) times after excitation. Region of the spectra not shown between 1440-20 cm^{-1} due to absorption by the solvent.

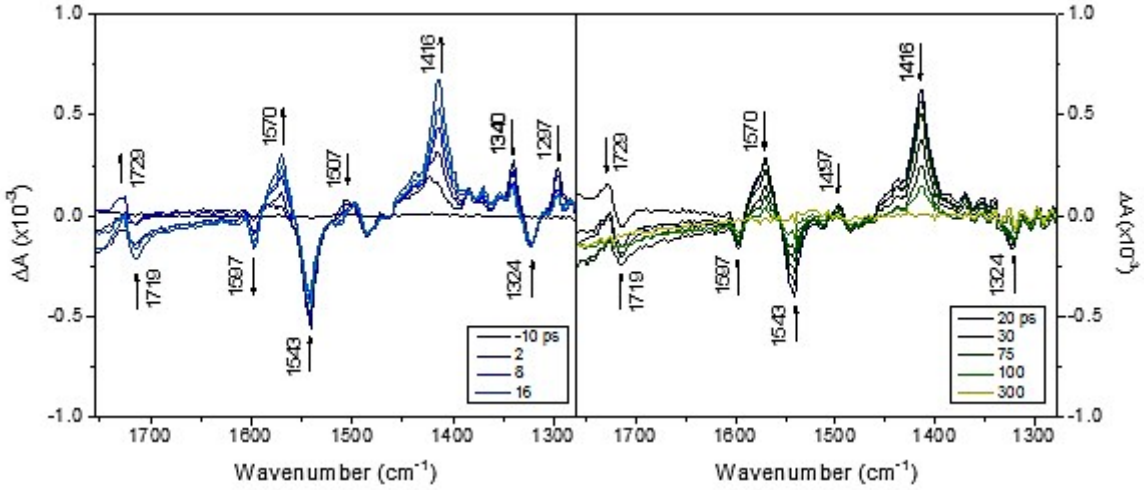

Figure S6 TRIR of **2** in CD_3CN at early (left) and late (right) delay times after excitation at 532 nm.

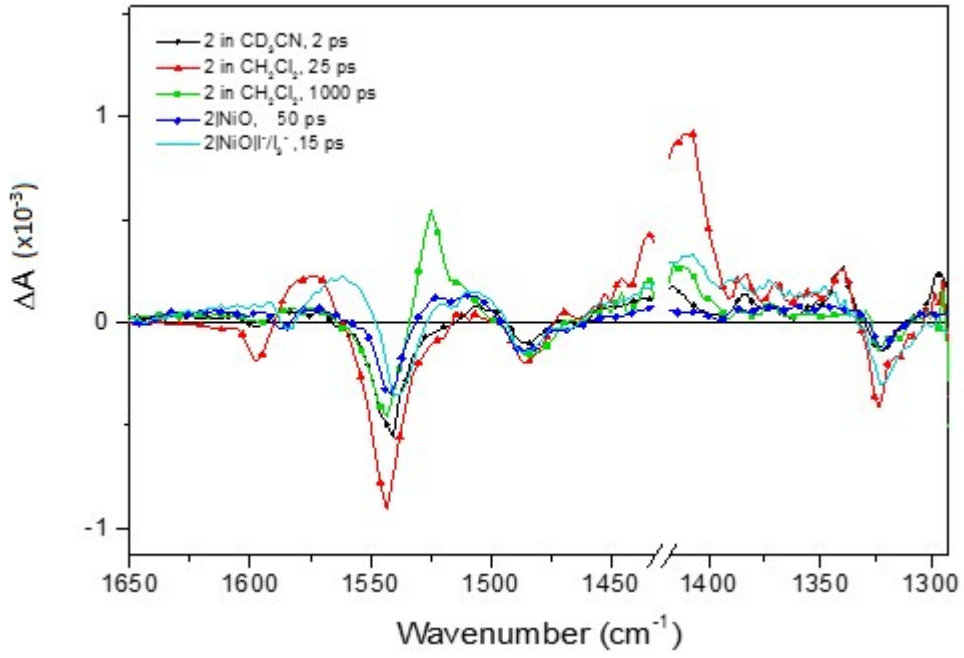

Figure S7. Overlay of the TRIR spectra of **2** in CD_3CN (black), **2** in CH_2Cl_2 after 25 ps (red), **2** in CH_2Cl_2 after 1000 ps (green), **2**|NiO (dark blue) and **2**|NiO|I^-/I_3^- (light blue) after excitation at 532 nm.

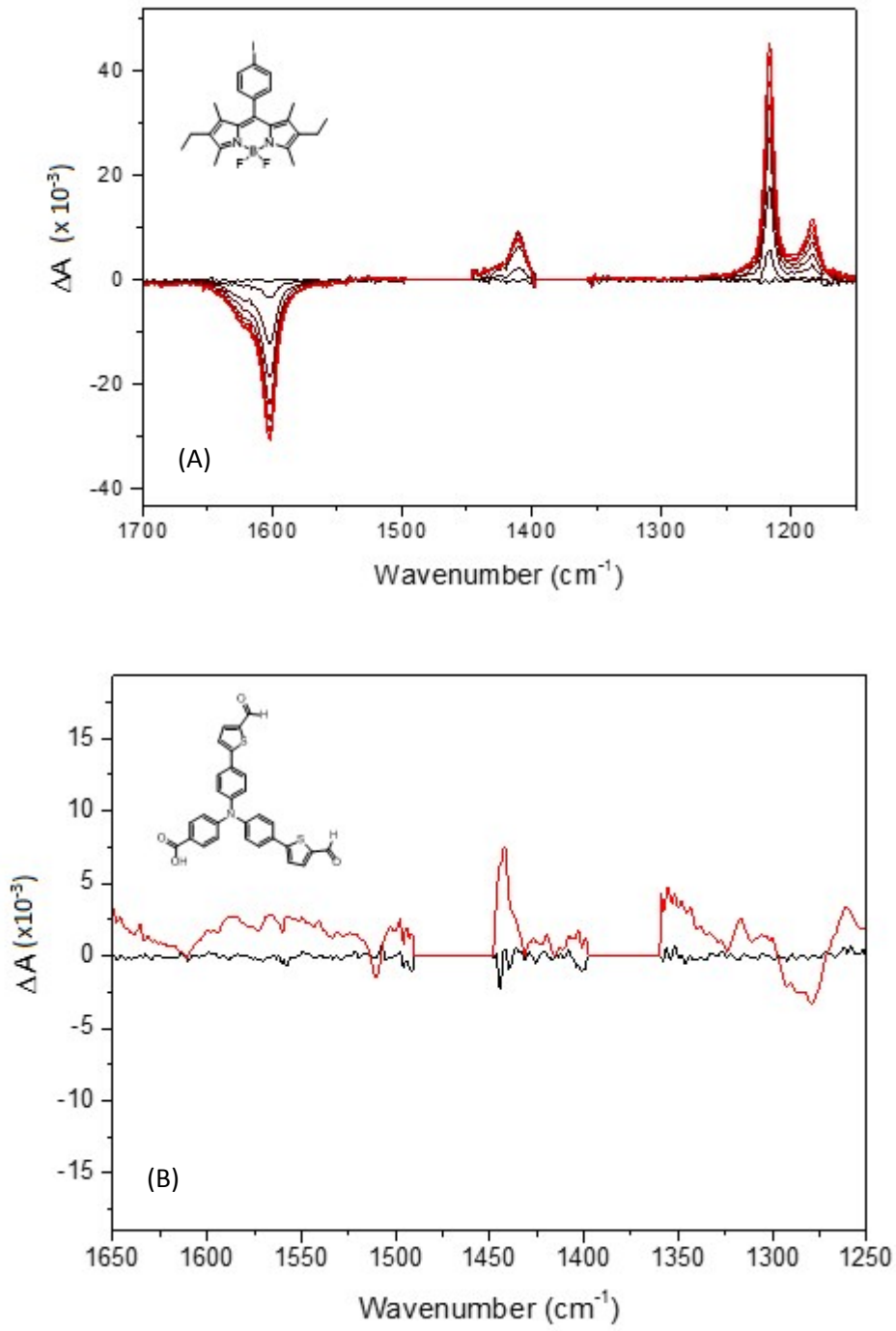

Figure S8 (A) Infrared difference spectra of the electrochemical reduction of a bodipy derivative in an electrolyte solution of $TBAClO_4$ and $CDCl_3$ at -1.08V vs. $Fc^{+/0}$. Solvent signals have been omitted at 1475 and 1375 cm^{-1}. (B) Infrared difference spectra of triphenylamine derivative before (black) and after (red) applying a positive potential of 0.92V vs. $Fc^{+/0}$. Solvent signals have been omitted at 1475 and 1375 cm^{-1}.

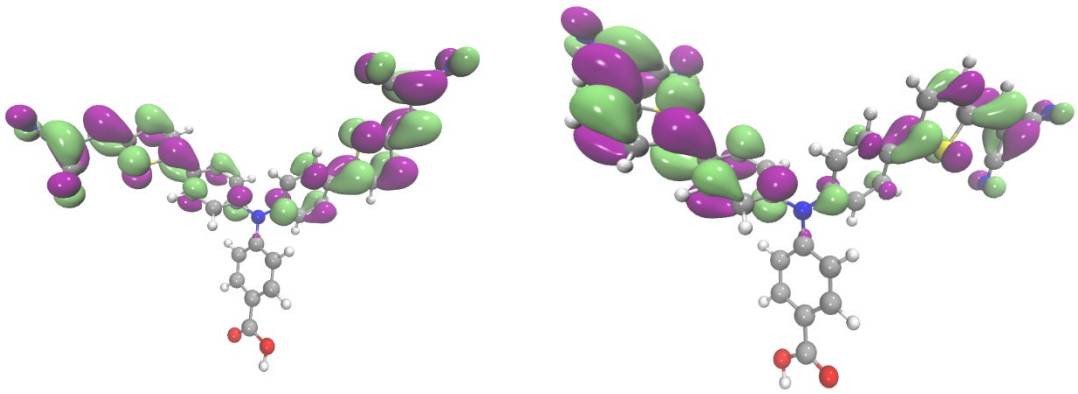

Figure S9. The LUMO and SOMO orbitals of **1** in the ground and excited S_1 state geometries. The structural change in the excited state clearly gives rise to an assymetry in the electronic density on the nitrile acceptor ligands.

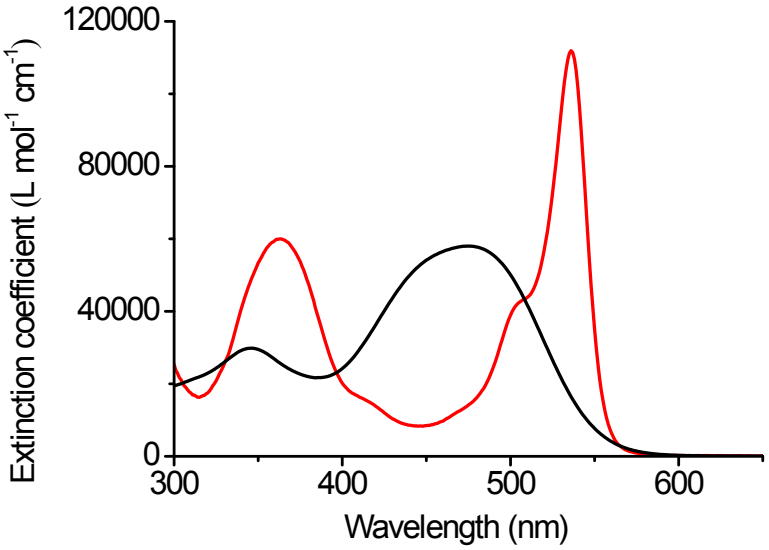

Figure S10. The absorption spectra of **1** (black) and **2** (red) in dichloromethane solution.

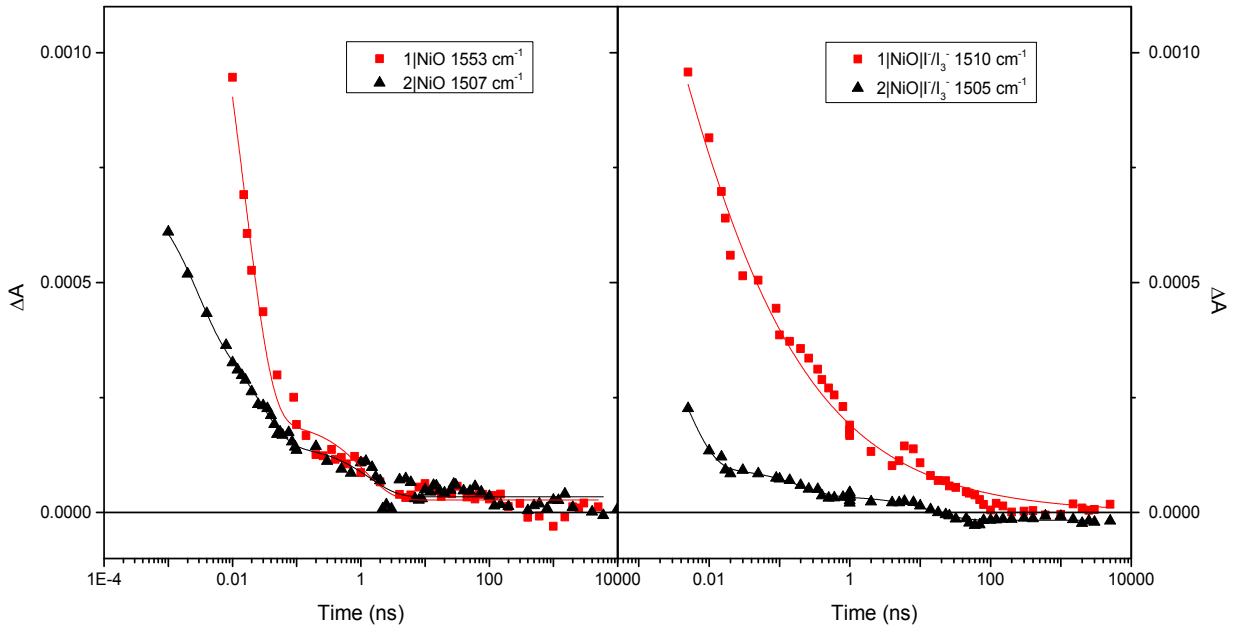

Figure S11. Kinetic traces from TRIR experiments for **1** (black squares) and **2** (red squares), when adsorbed on NiO in the absence (left) and presence of I^-/I_3^- in CD_3CN (right).

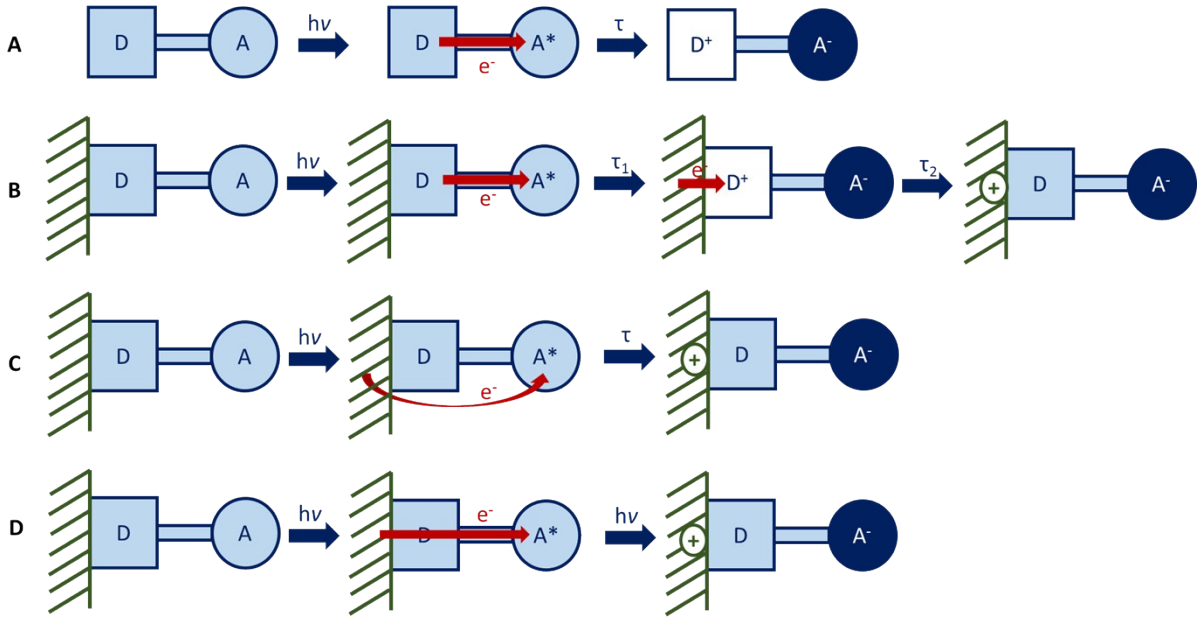

Figure S12. Possible light-induced processes discussed in this manuscript. A. Photoinduced intramolecular charge-transfer in a donor (D) - acceptor (A) dye molecule. B. Photoinduced intramolecular charge-transfer in a dye molecule adsorbed on a NiO surface, followed by electron transfer from NiO to the dye. C. Direct photoinduced charge transfer from NiO to an excited acceptor A* through space. D. Direct photoinduced charge transfer from NiO to an excited acceptor A* mediated through the donor and π-linker.