A Bifurcated Molecular Pentad Capable of Sequential Electronic Energy Transfer and Intramolecular Charge Transfer

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Supporting Information

Experimental part

General methods. ^{1}H and ^{13}C spectra were recorded at rt on 300 and 400 MHz spectrometers using perdeuterated solvents as internal standard. Chemical shifts of ^{1}H- and ^{13}C-NMR spectra are given in ppm relative to residual protiated solvent and relative to the solvent, respectively. ^{11}B-NMR spectra were recorded at rt on a 400 MHz spectrometer using $BF_3.Et_2O$ as reference. FT-IR spectra were recorded using a spectrometer equipped with an ATR “diamond” apparatus. Chromatographic purification was conducted using 40-63 μm silica gel or aluminium oxide 90. Thin layer chromatography (TLC) was performed on standardized silica gel or aluminium oxide plates coated with fluorescent indicator. All mixtures of solvents are given in v/v ratio. The anhydrous reactions were carried out under dry argon using Schlenk tube techniques.

Preparation of compound PEN. To a degassed solution of **ACC** (92 mg, 0.056 mmol) and **DON** (43 mg, 0.056 mmol) in benzene (20 mL) and triethylamine (2 mL) was added $[Pd(PPh_3)_4]$ (10 mg). The resulting mixture was stirred for 19h at 80°C before being cooled to room temperature. After evaporation of the solvent under vacuum, the organic product was extracted with CH_2Cl_2, washed with water and subsequently with brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness under vacuum. The crude product was purified by silica gel chromatography (from 80/20 to 50/50 Petroleum Ether/CH_2Cl_2) to obtain a grey compound (119 mg, 93%), which was recrystallized by evaporation in THF/pentane and washed with pentane to afford the brown compound **PEN** (112 mg, 88%). ^{1}H-NMR (400 MHz, chloroform-d) δ (ppm) 8.80 (d, ^3J = 9.0 Hz, 2 H), 8.60 (d, ^3J = 9.2 Hz, 2 H), 7.96 - 8.29 (m, 18 H), 7.77 (d, ^3J = 7.9 Hz, 2 H), 7.66 - 7.74 (m, 2 H), 7.51 (d, ^3J = 7.9 Hz, 2 H), 7.39 (d, ^3J = 7.1 Hz, 2 H), 7.21 - 7.31 (m, 10 H), 6.99 - 7.17 (m, 24 H), 6.22 (s, 2 H), 3.18 (s, 6 H), 1.80 - 1.97 (m, 8 H), 1.56 (s, 6 H), 1.54 (s, 6 H), 1.11 - 1.31 (m, 24 H), 0.94 - 1.07 (m, 8 H), 0.82 (t, ^3J = 6.5 Hz, 12 H) ; ^{13}C-NMR (101 MHz, d-chloroform) δ (ppm) 158.7, 155.9, 147.4, 141.2, 132.5, 132.3, 132.2, 132.1, 131.6, 131.3, 131.2, 131.0, 130.5, 130.2, 129.7, 129.3, 128.7, 128.6, 128.5, 128.4, 127.9, 127.5, 127.3, 127.2, 126.3, 126.2, 126.0, 125.7, 125.7, 125.3, 125.2, 124.6, 124.4, 124.4, 124.4, 124.2, 123.9, 123.1, 122.4, 122.0, 120.3, 116.5, 82.7, 82.6, 38.0, 31.6, 29.7, 26.9, 24.5, 22.7, 16.6, 15.0, 14.9, 14.6, 14.1. EI-MS, m/z (%) 2281.1 (100.0%), 2262.1 (30), 2243.1 (15%). Anal. Calcd for $C_{156}H_{136}B_2F_2N_6S_4$: C, 82.08; H, 6.01; N, 3.68; found; C, 81.74; H, 5.78; N, 3.51.

Electrochemical Measurements

Electrochemical studies employed cyclic voltammetry with a conventional 3-electrode system using a BAS CV-50W voltammetric analyser equipped with a Pt microdisk (2 mm^2) working electrode and a silver wire counter-electrode. Ferrocene was used as an internal standard and was calibrated against a saturated calomel reference electrode (SCE) separated from the electrolysis cell by a glass frit presoaked with electrolyte solution. Solutions contained the electro-active substrate in deoxygenated and anhydrous dichloromethane containing tetra-n-butylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The quoted half-wave potentials were reproducible to within ≈ 10 mV.

^{1}H- and ^{13}C-NMR Traces

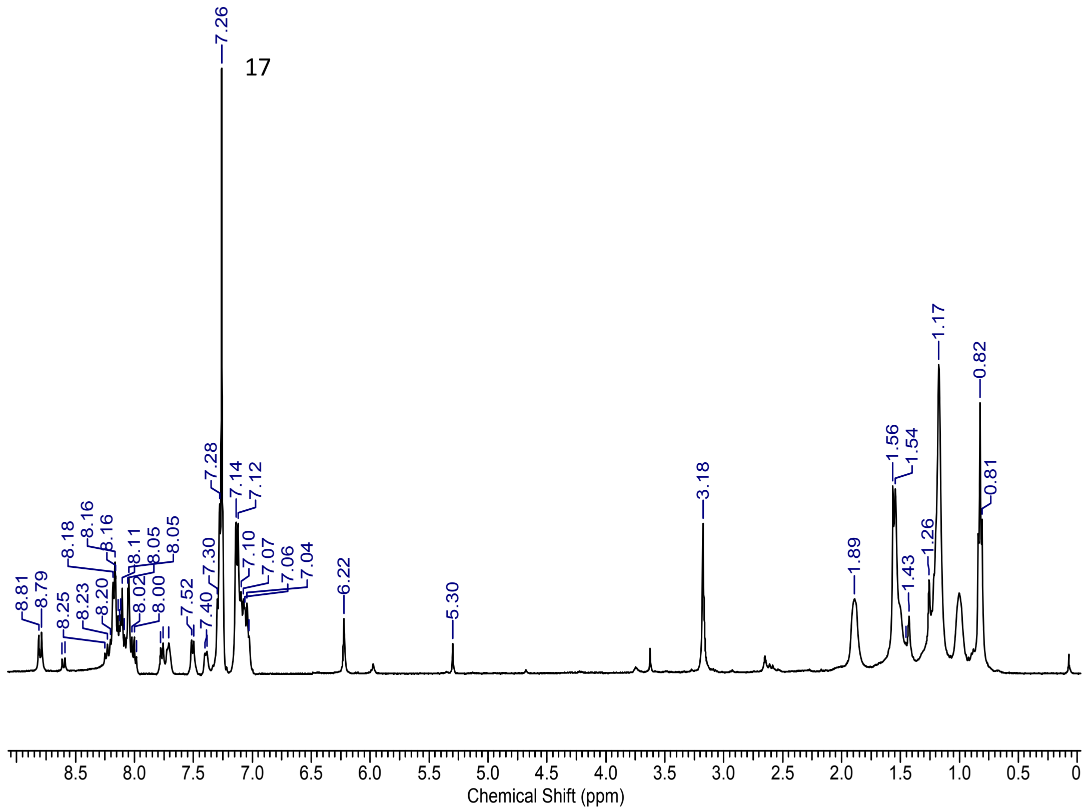

Figure S1. ^{1}H-NMR spectrum recorded for **PEN** in $CDCl_3$ at rt.

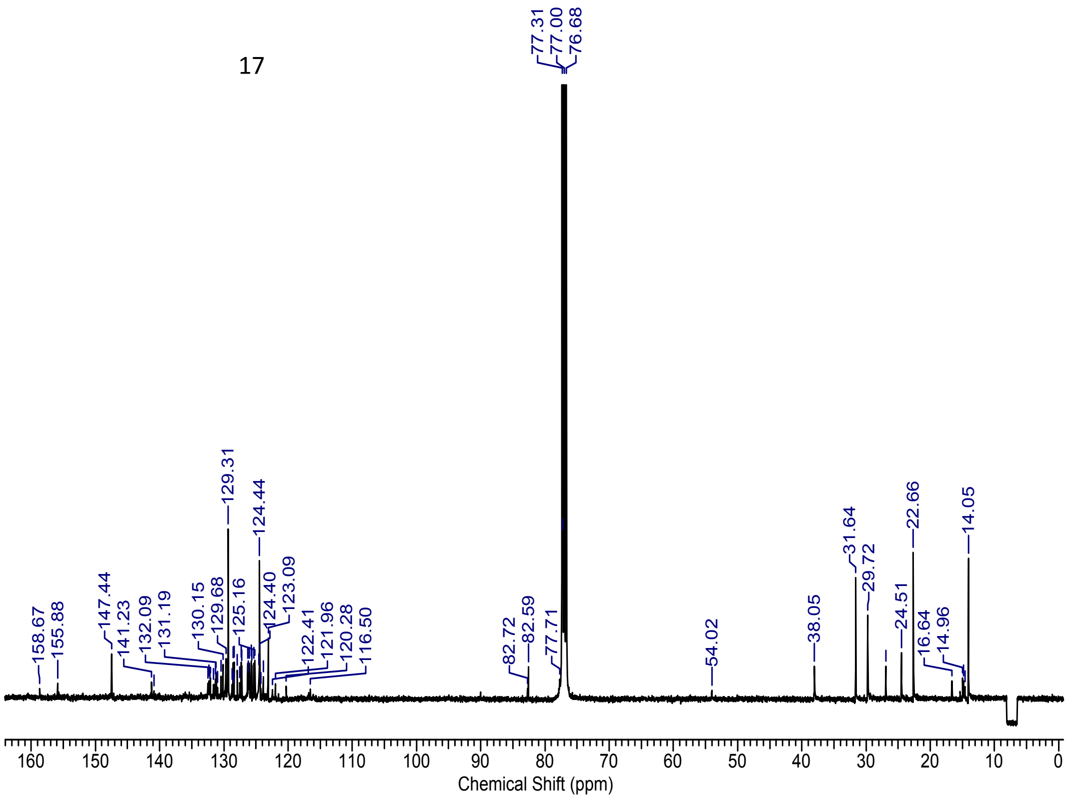

Figure S2. ^{13}C-NMR spectrum recorded for **PEN** in $CDCl_3$ at rt.

Spectroscopic studies

Solvents were purchased from Sigma-Aldrich as spectroscopic grade and were used as received. Absorption spectra were recorded with a Perkin-Elmer Lambda-35 spectrophotometer while emission spectra were recorded with a Hitachi F-4500 spectrofluorometer. In order to minimise experimental error resolution was set to be 0.2 nm. For the absorption measurements slit width was 1nm whereas for emission slit widths were 2.5 nm. The estimated experimental error for absorption and emission measurements is 1-2nm. For the far-red emitting samples, specialised facilities were provided by Edinburgh Photonics (a division of Edinburgh Instruments). Fluorescence quantum yields were determined with a fully-corrected, high radiance integrating sphere. Fluorescence lifetimes were determined by time correlated, single-photon counting methods following excitation with an ultra-short laser diode. Data analysis was carried out using standard procedures and statistical routines. For steady-state irradiation experiments, the solution was deoxygenated by purging with dry N_2 and sealed into a quartz cuvette. The sample in a sealed quartz cuvette was exposed at 30 cm to the white light source (JCC Model IP66, 450W E40) for varying time intervals. Absorption spectra were recorded 30 minutes over two days. The sample was stored overnight in the dark at 4 ^{0}C in order to imitate natural conditions and check whether any ‘dark’ reaction takes place. The light intensity at the front surface of the cuvette was determined with a PM100 power meter fitted with a Si-photodiode sensor head. For some experiments, the course of reaction was followed by NMR spectroscopy with the deaerated sample being illuminated in a quartz NMR sample tube. An example of such an experimental record is provided as Figure S3.

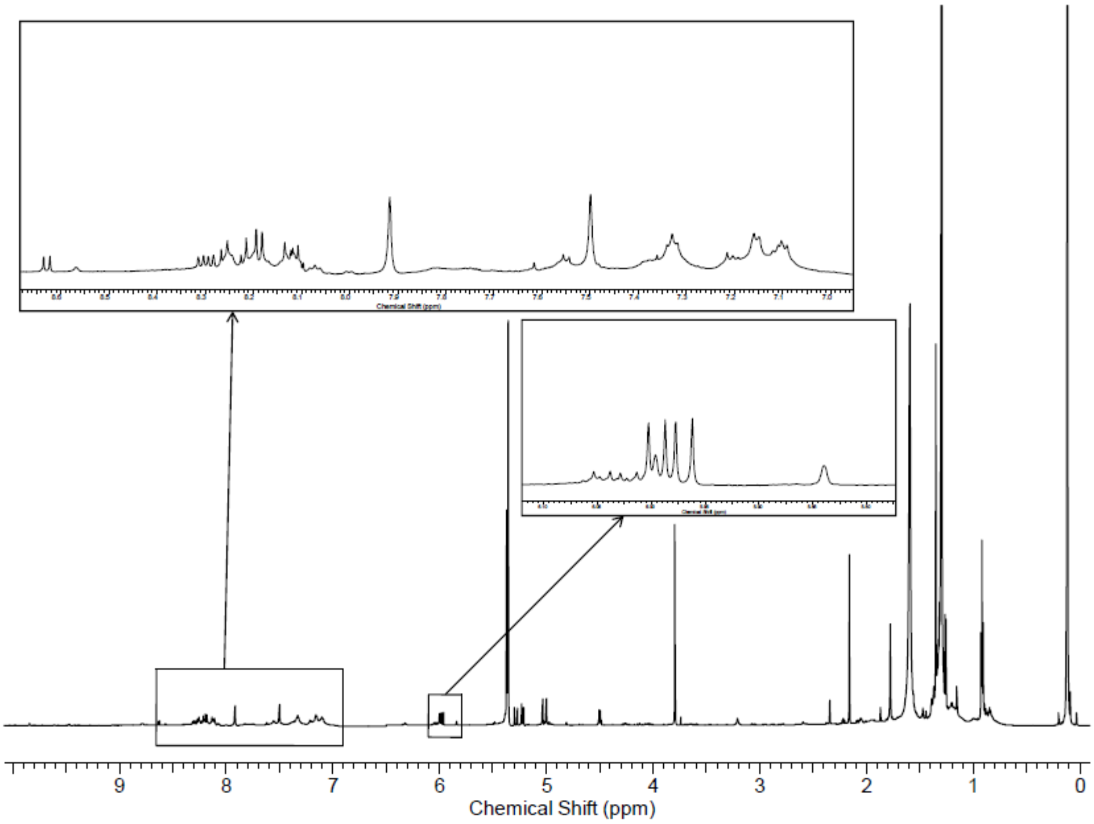

Figure S3. Example of a 700 MHz proton NMR spectrum recorded for PEN (about 10^{-4} M) in CD_2Cl_2 after exposure to white light at rt.

Quantum chemical calculations were made with TURBOMOLE[S1] running on a multiple processor work-station. Calculations were made at both ground- (DFT/B3LYP/aug-cc-pVTZ) and excited-state (TD-DFT/CAM-B3LYP) levels with the target compound embedded in a solvent continuum using the CPCM model.[S2]

S1. R. Ahricha, M. Bär, M. Häser, H. Horn and Cölmel, *Chem. Phys. Lett.*, 1989, **162**, 165-174.

S2. Y. Takane and K. N. Houk, *J. Chem. Theory Comput.*, 2005, **1**, 70-77.

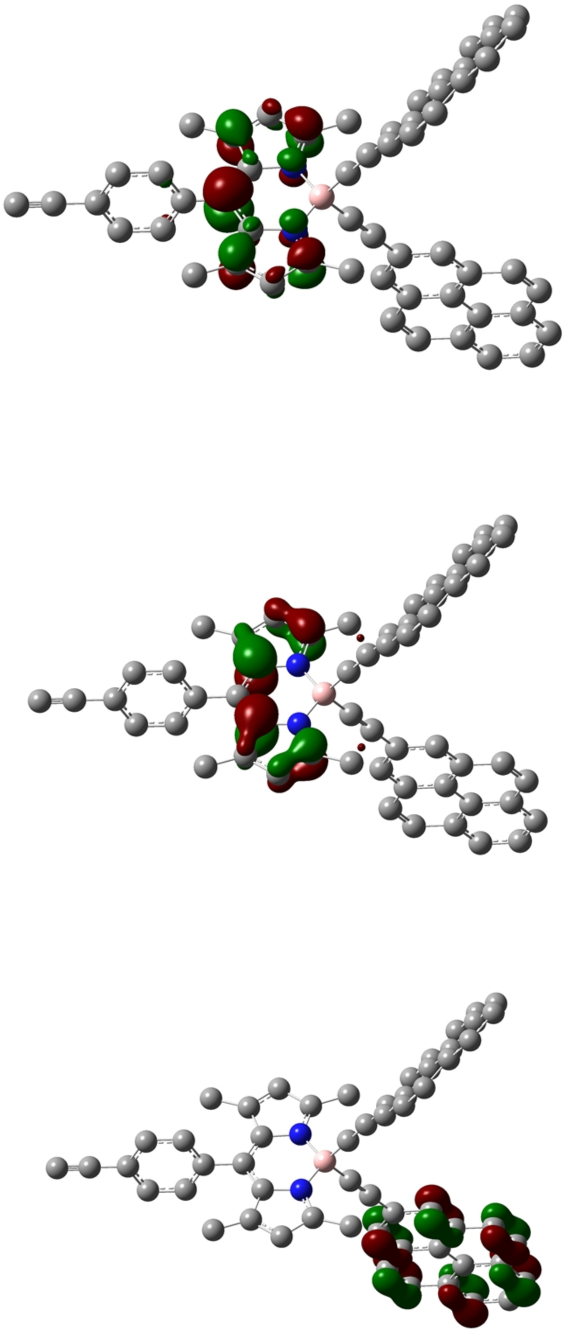

Figure S4. Kohn-Sham (iso-density = 0.02) representations of the LUMO (uppermost panel), HOMO (central panel) and HOMO(-1) (lower panel) computed for **DON** in a solvent reservoir. NB The hydrogen atoms have been omitted for clarity.

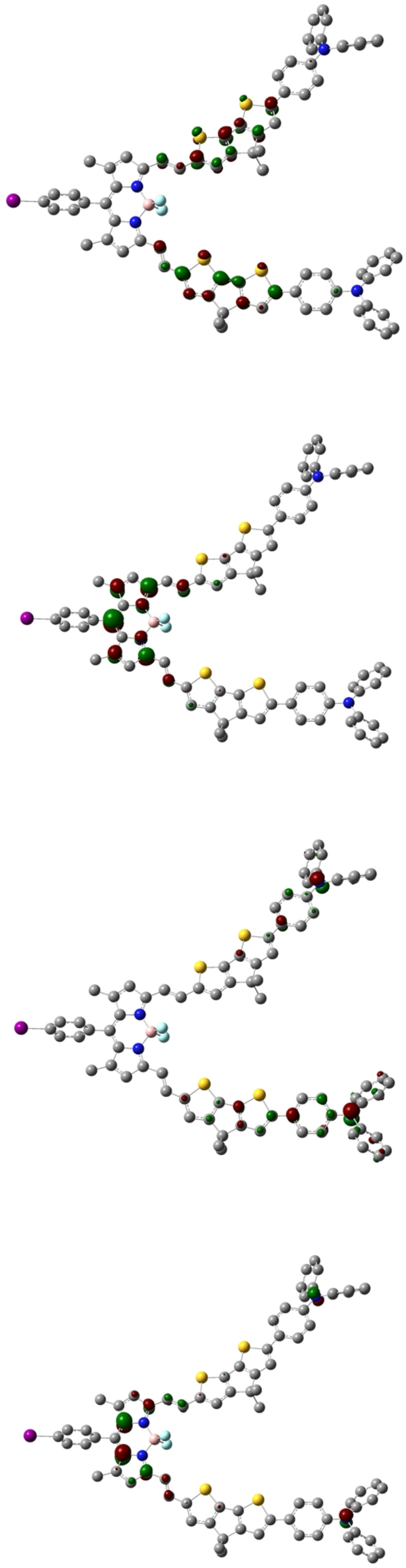

Figure S5. Kohn-Sham (iso-density = 0.02) representations of the LUMO(1) (uppermost panel), LUMO (upper central), HOMO (lower central) and HOMO(-1) (lower panel) computed for **ACC** in a solvent reservoir. NB The hydrogen atoms have been omitted for clarity.

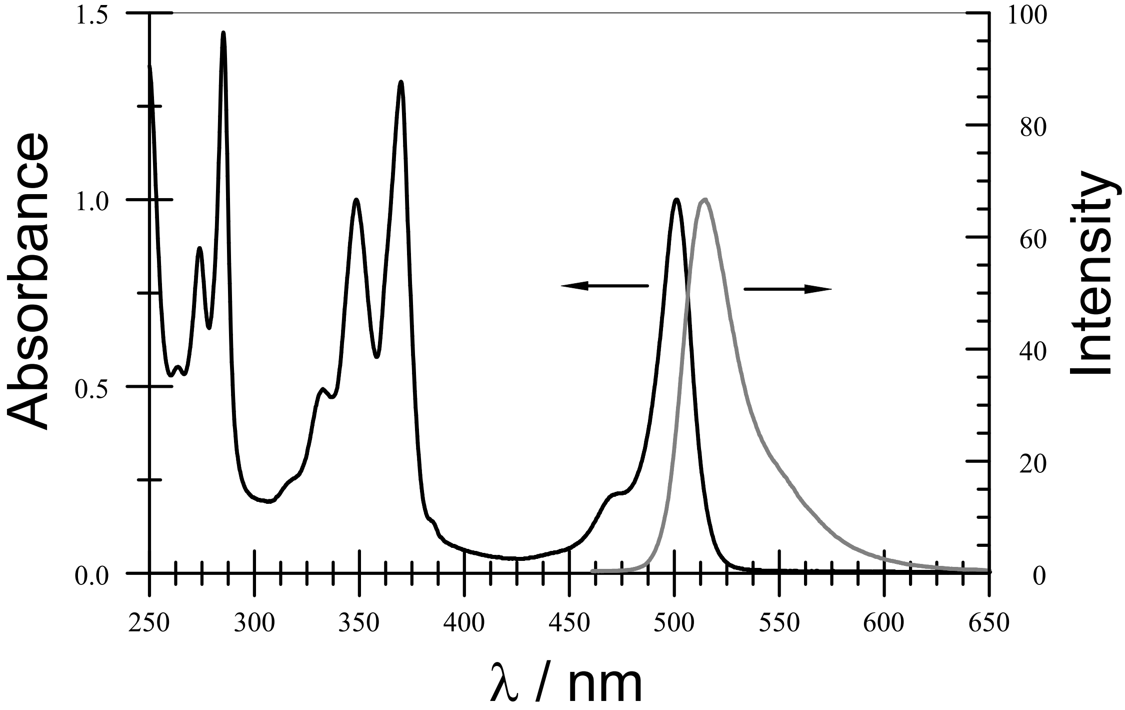

Figure S6. Absorption (black curve) and fluorescence (grey curve) spectra recorded for **DON** in CH_2Cl_2 solution.

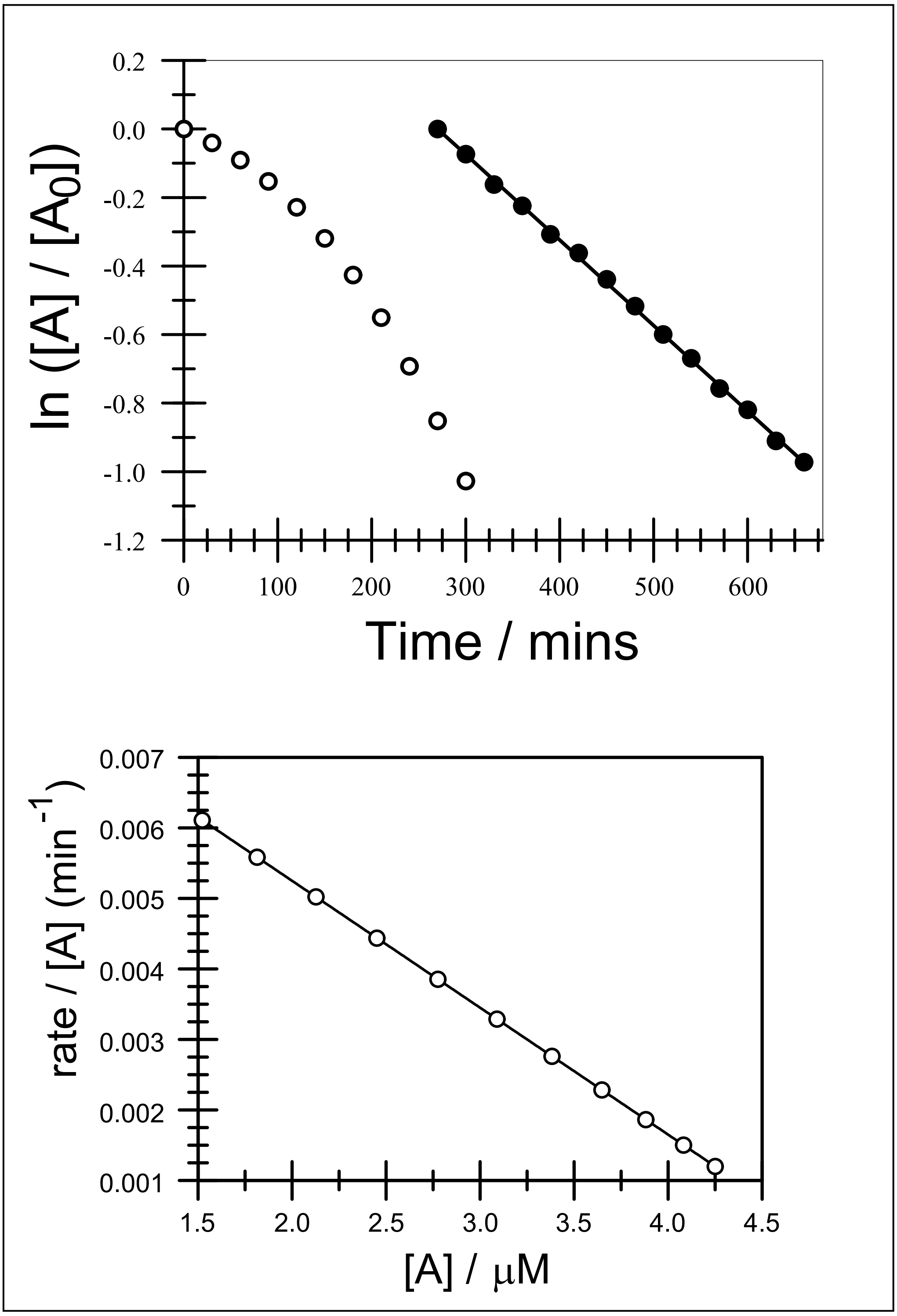

Figure S7. Examples of kinetic plots constructed for photobleaching of **ACC** in deaerated CH_2Cl_2 at rt. The upper panel shows a fit to conventional first-order kinetics for bleaching of the 813-nm band (open circles) and the primary product (closed circles). The lower panel shows a fit to an auto-catalytic process for bleaching of the 813-nm band. Global fitting routines were used in all cases. Here, [A] refers to molar concentration of a particular species and [A_0] is the initial concentration of that same species. The equation used to fit the auto-catalytic reaction is shown below as Equation S1.

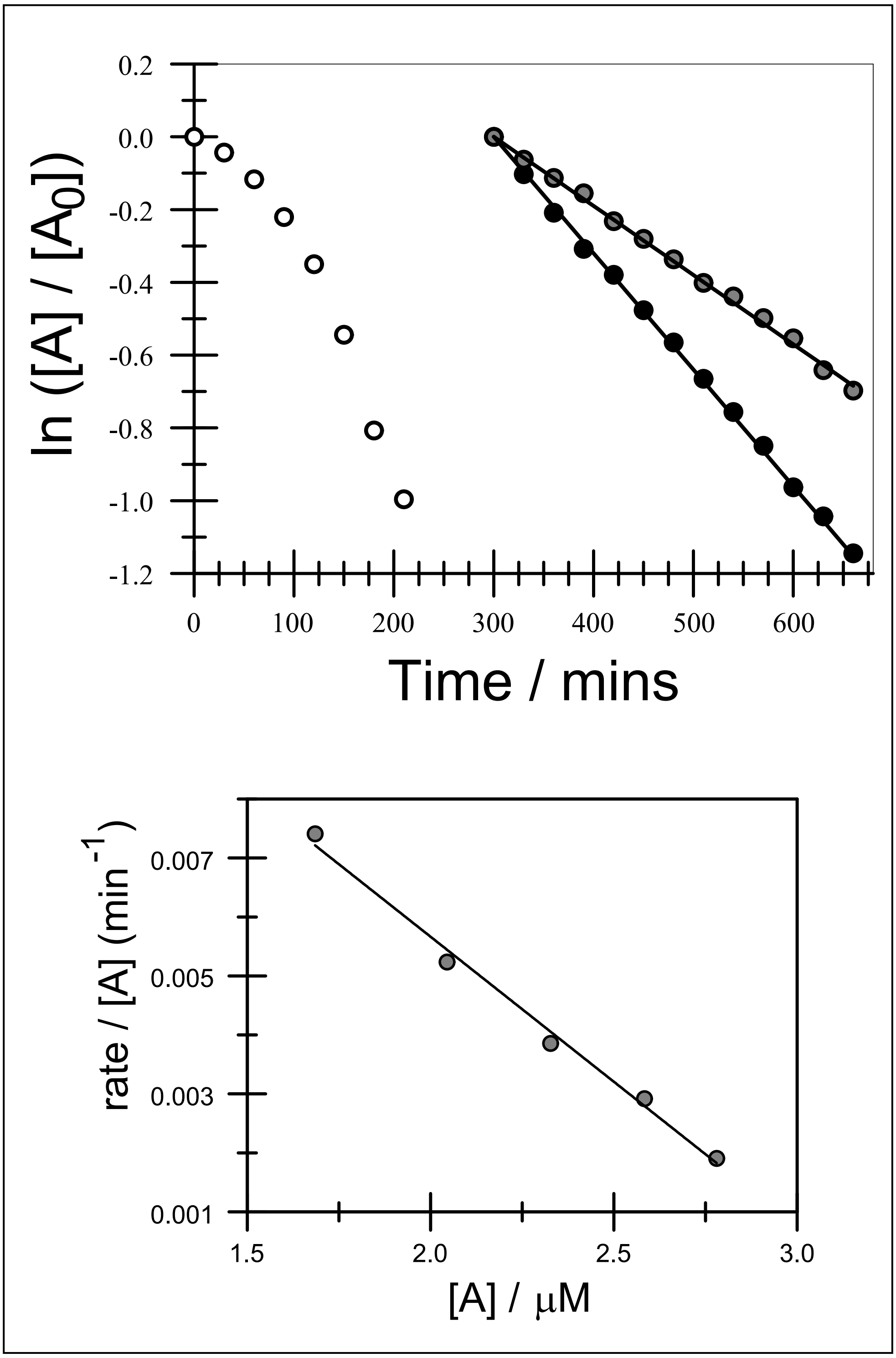

Figure S8. Examples of kinetic plots for photobleaching of **PEN** in deaerated CH_2Cl_2 at rt. The upper panel shows a fit to first-order kinetics for bleaching of the 811-nm band (open circles) and the primary products associated with Bod (grey closed circles) and ExBod (black closed circles) chromophores. The lower panel shows a fit to an auto-catalytic process for bleaching of the 811-nm band. Global fitting routines were used in all cases. Here, [A] refers to molar concentration of a particular species and $[A_0]$ is the initial concentration of that same species. The equation used to fit the auto-catalytic reaction is shown below as Equation S1.

The equation used to model the auto-catalytic bleaching process is given below (Equation S1) :

$$\frac{rate}{[A]} = \left(k_0 + k_C\left[A_0\right]\right) - k_C\left[A\right] \tag{S1}$$

Here, rate refers to the rate of photo-bleaching at a certain wavelength in units of μM min^{-1}. The actual rate at time t was determined as the tangent to a plot of three consecutive time intervals. The terms k_0 and k_C refer, respectively, to the first-order rate constant for bleaching that would be expected in the absence of the auto-catalytic step and to the rate constant for the auto-catalytic process. The concentration of chromophore is designated [A] and has units of μM. For further details see :

F. Mata-Perez and J. F. Perez-Benito, *J. Chem. Educ.*, 1987, **64**, 925-927.

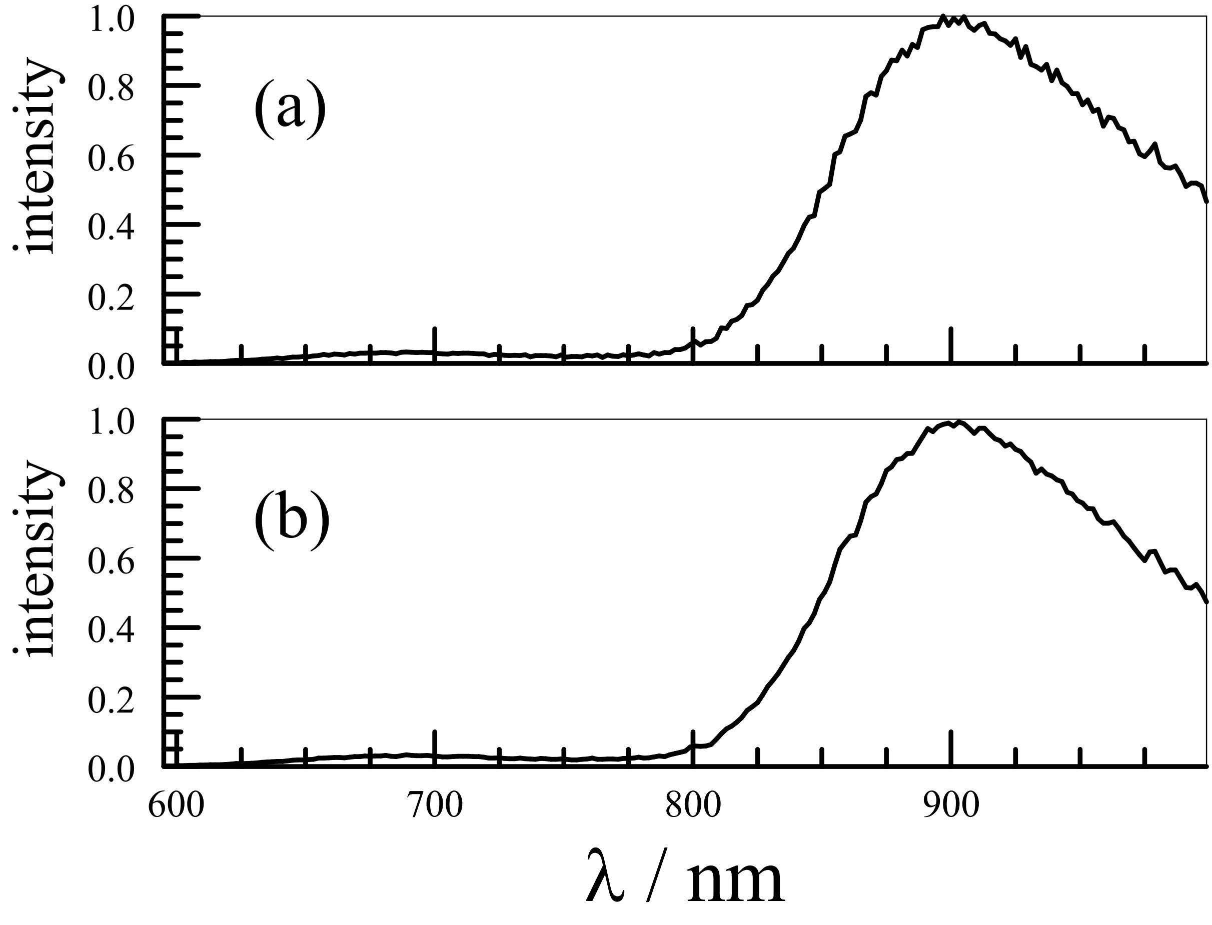

Figure S9. Fluorescence spectra recorded for PEN in CH_2Cl_2 solution following excitation into (a) ExBOD (at 645 nm) and (b) PYR (at 370 nm). The spectra were normalized at the emission peak. No emission is evident that could be attributed to either PYR of DON on excitation at 370 nm.

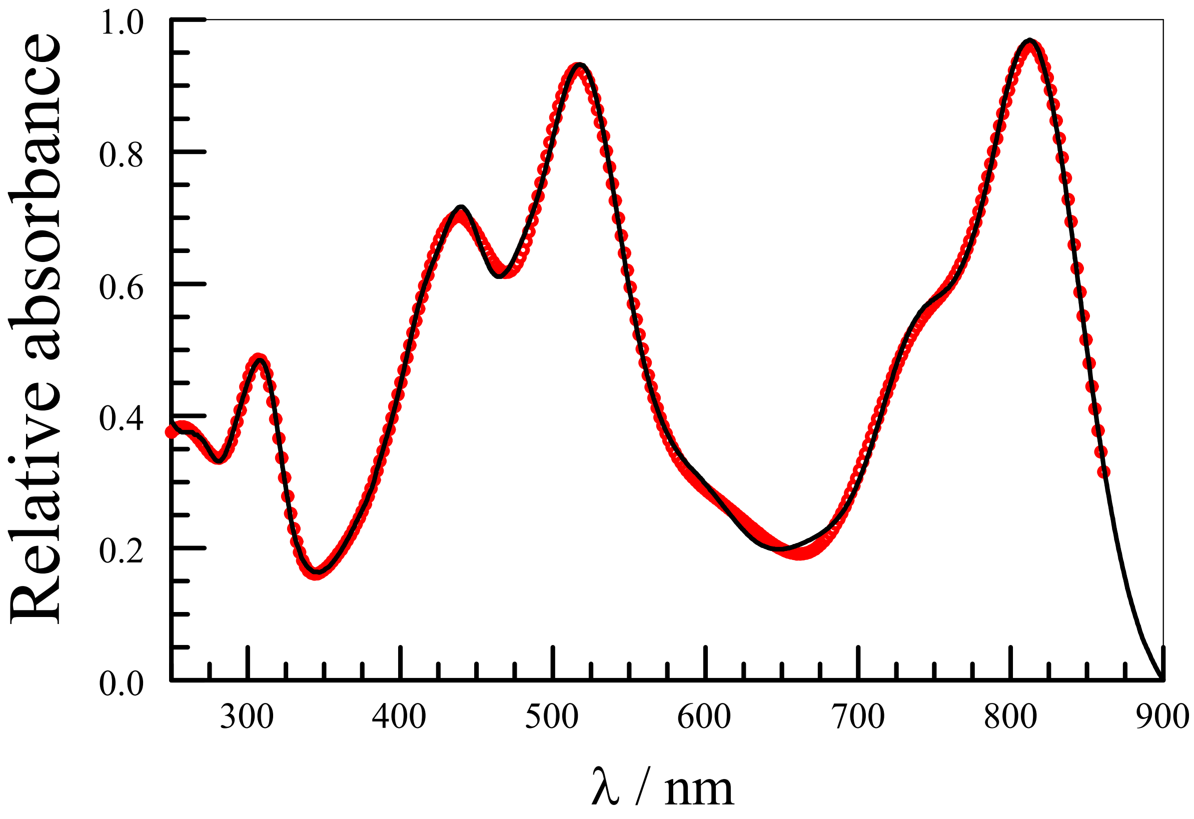

Figure S10. Comparison of absorption (black curve) and excitation (red circles) spectra recorded for ACC in CH_2Cl_2 solution. The emission wavelength was 920 nm.

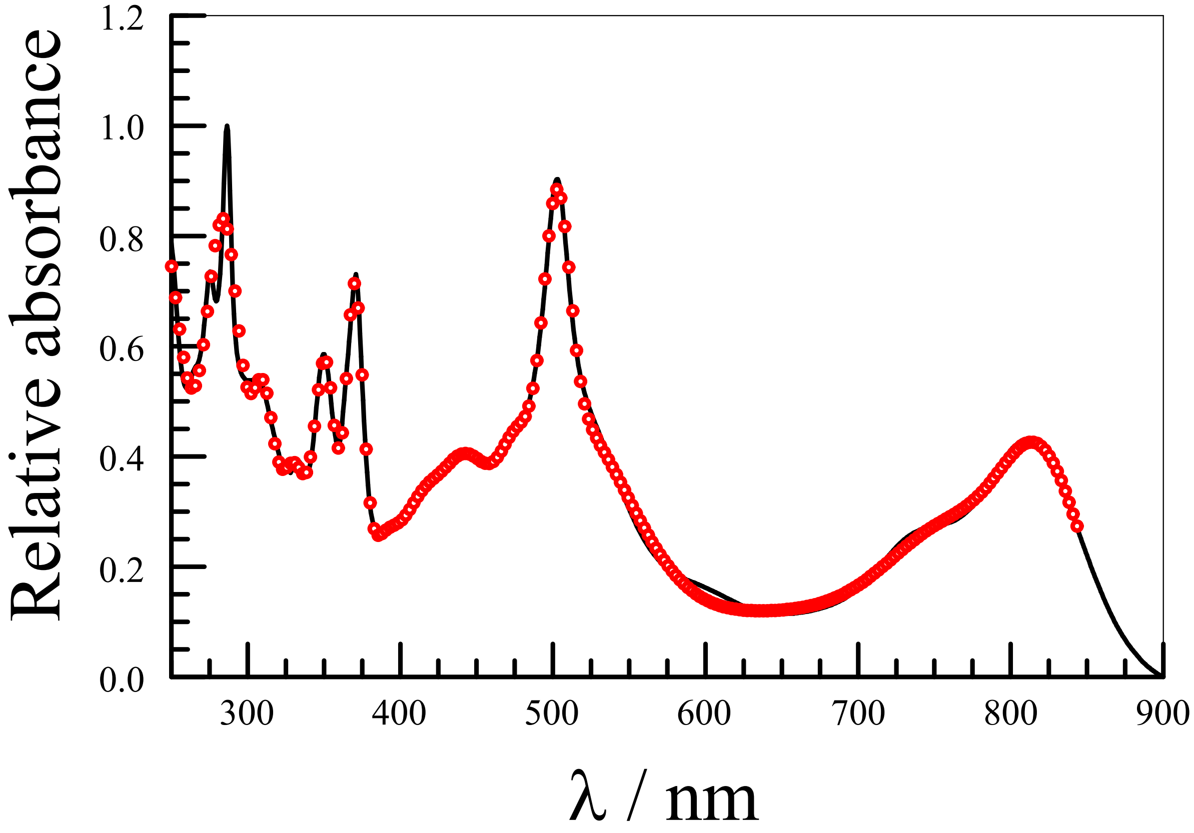

Figure S11. Comparison of absorption (black curve) and excitation (red circles) spectra recorded for PEN in CH2Cl2 solution. The fluorescence wavelength was 920 nm.

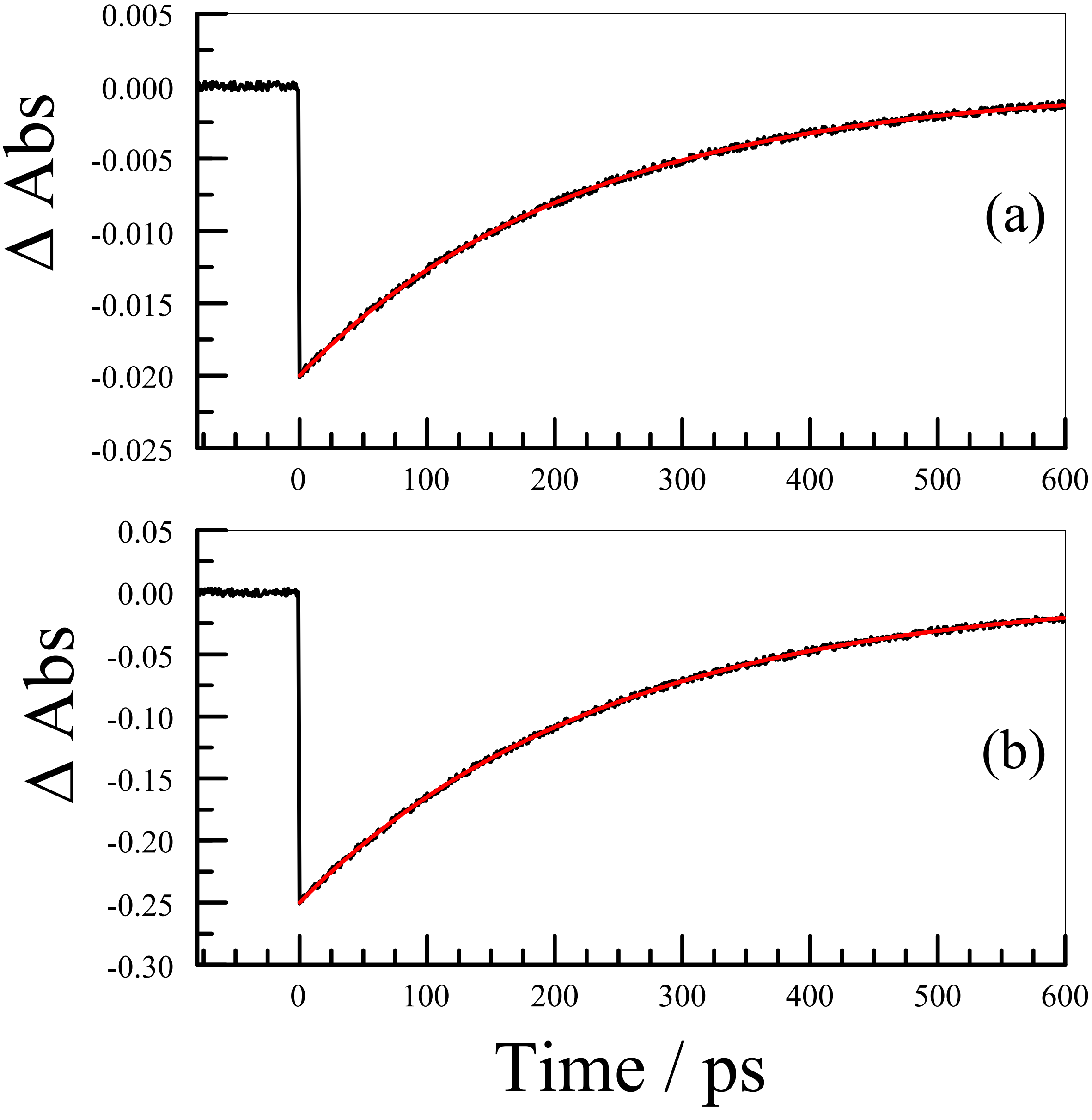

Figure S12. Decay curves observed following laser excitation of (a) ACC and (b) PEN in deoxygenated CH2Cl2 solution at 420 nm. Decay curves were recorded at 810 nm. The red curve corresponds to a non-linear least-squares fit to the experimental data (black curve), with lifetimes of (a) 220 ps and (b) 240 ps.