

# Supplementary Information

## S1 Structural analysis

Elemental analysis for  $C_{35}H_{36}BN_5O_6S_2 \cdot H_2O$ :

- Calculated: C, 58,74; H, 5,35; N, 9,79; S, 8,96.
- Measured: C, 58,38; H, 5,63; N, 9,46; S, 9,25.

NMR analysis:

- $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  8.38 (AA' part of an AA'BB' system, 2H), 7.70 (AA' part of an AA'BB' system, 4H), 7.53 (BB' part of an AA'BB' system, 2H), 7.30 (BB' part of an AA'BB' system, 4H), 5.99 (s, 2H), 4.97 (s, 2H), 3.05 (bs, 4H), 2.60 (s, 6H), 2.43 (s, 6H), 1.34 (s, 6H) ppm
- $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  156.5 (s), 143.8 (s), 142,33 (s), 141,71 (s), 138,19 (s), 136,4 (s), 129,9 (d), 129.8 (s) 129.6 (d), 127.1 (d), 124.3 d), 121.69 (d)43.0 (t), 21.5 q), 15.1 (q), 15.0 (q), 14.7 (q)
- $^{19}F$  ( $CDCl_3$ , 376 MHz): no signal (starting compound X showed a signal at -146.28 ppm)

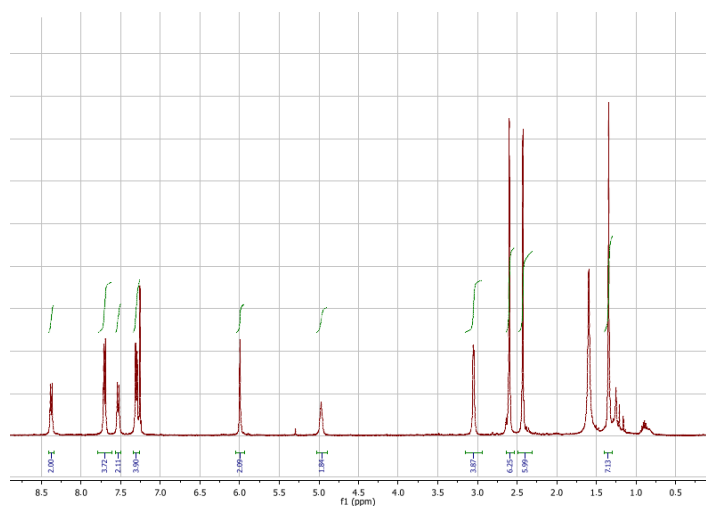


Figure S1:  $^{13}C$  NMR spectrum of compound **1**.

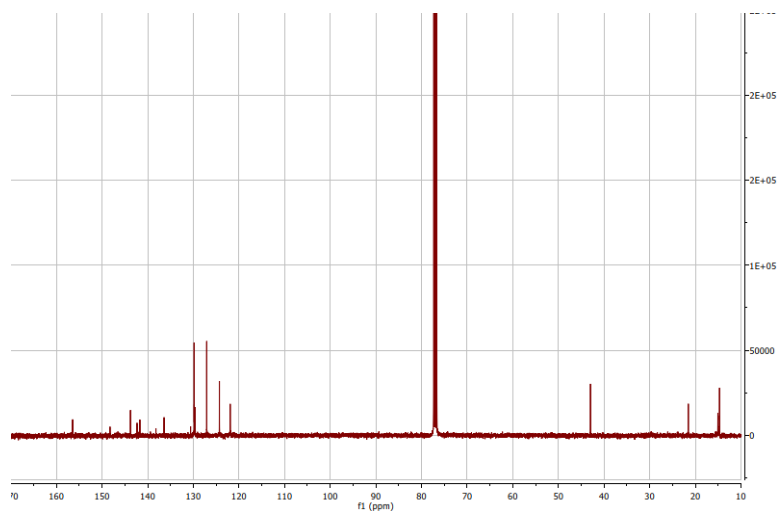


Figure S2:  $^{13}C$  NMR spectrum of compound **1**.

## S2 Linear spectroscopy

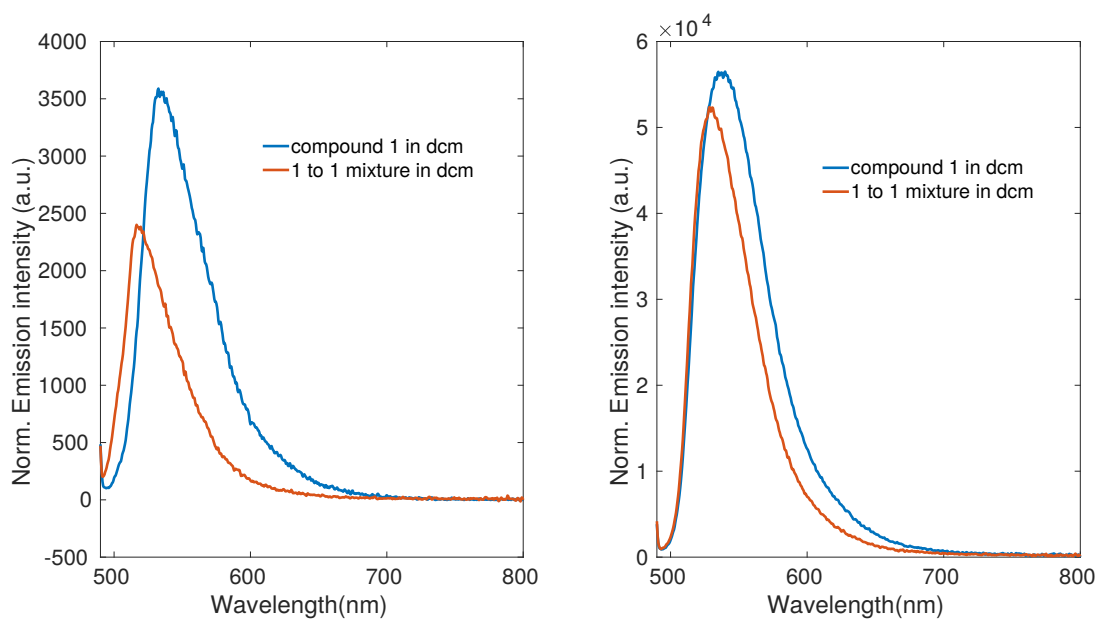


Figure S3: Fluorescence emission spectra, normalized to the optical absorbance at the excitation wavelength (480 nm), of the *N*-Bodipy compound **1** (blue line) and of a 1 to 1 mixture of a parent *N*-BODIPY lacking of diamino-tosyl substituents - but with meso nitrophenyl appendant- and the free tosyl amine group (orange line), in dichloromethane (left) and toluene (right).

## S3 Transient Absorption Spectroscopy

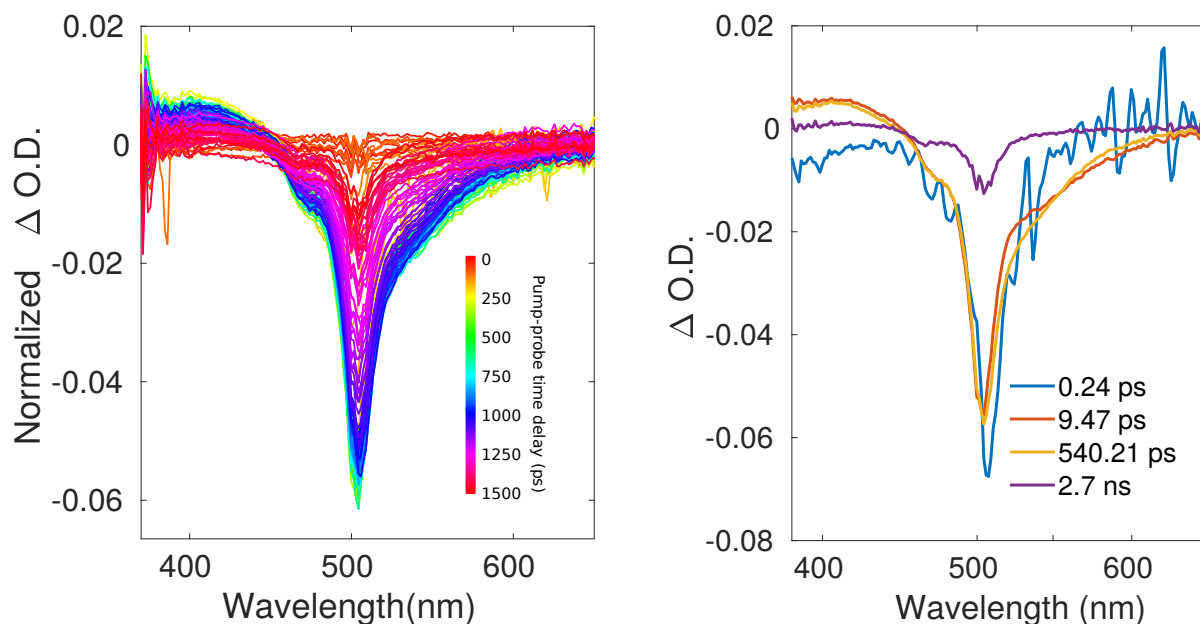


Figure S4: Experimental transient spectra (left) and EADS (right) of compound **1** dissolved in hexane and excited at 350 nm.

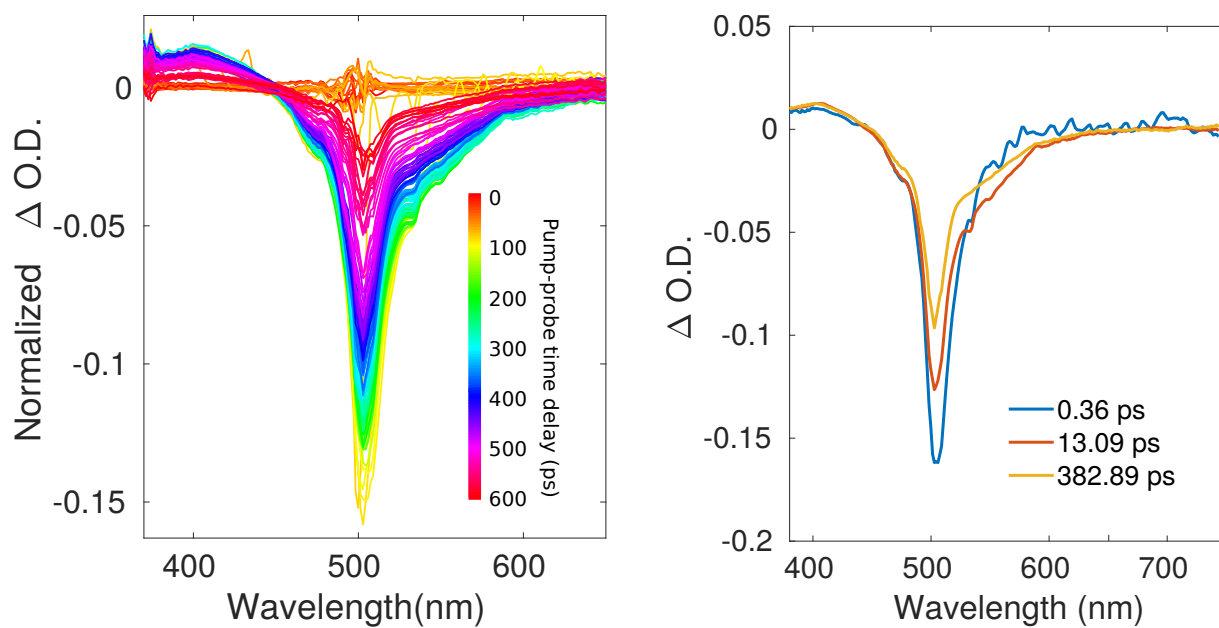


Figure S5: *Experimental transient spectra (left) and EADS (right) of compound **1** dissolved in hexane and excited at 500 nm.*

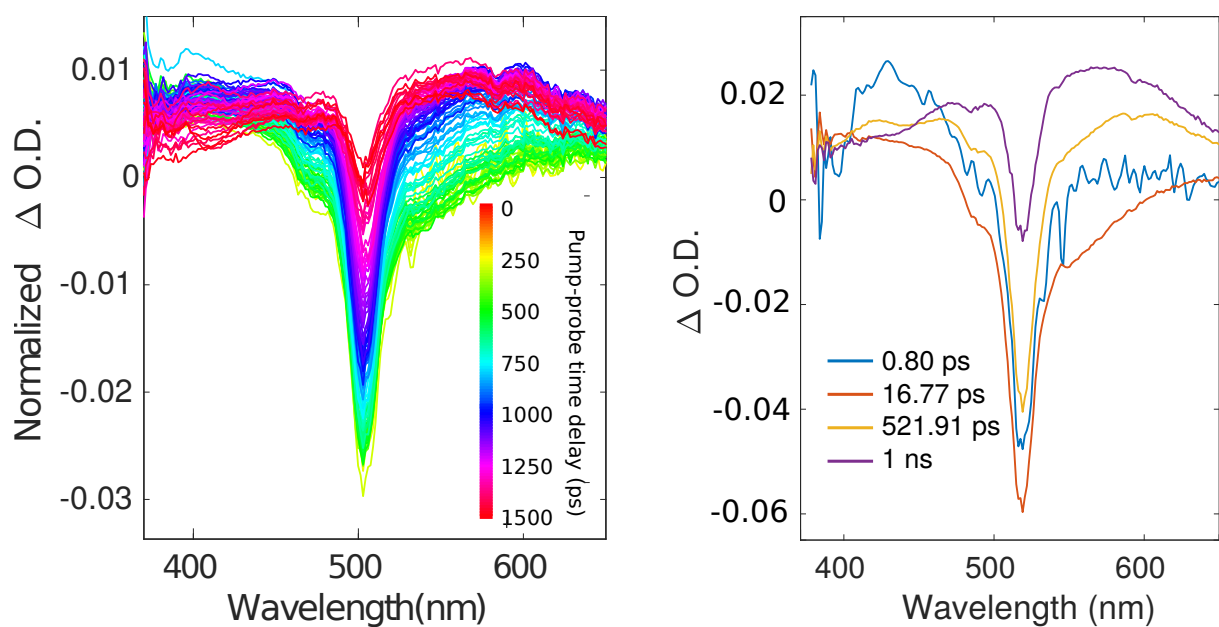


Figure S6: *Experimental transient spectra (left) and EADS (right) of compound **1** dissolved in toluene and excited at 350 nm.*

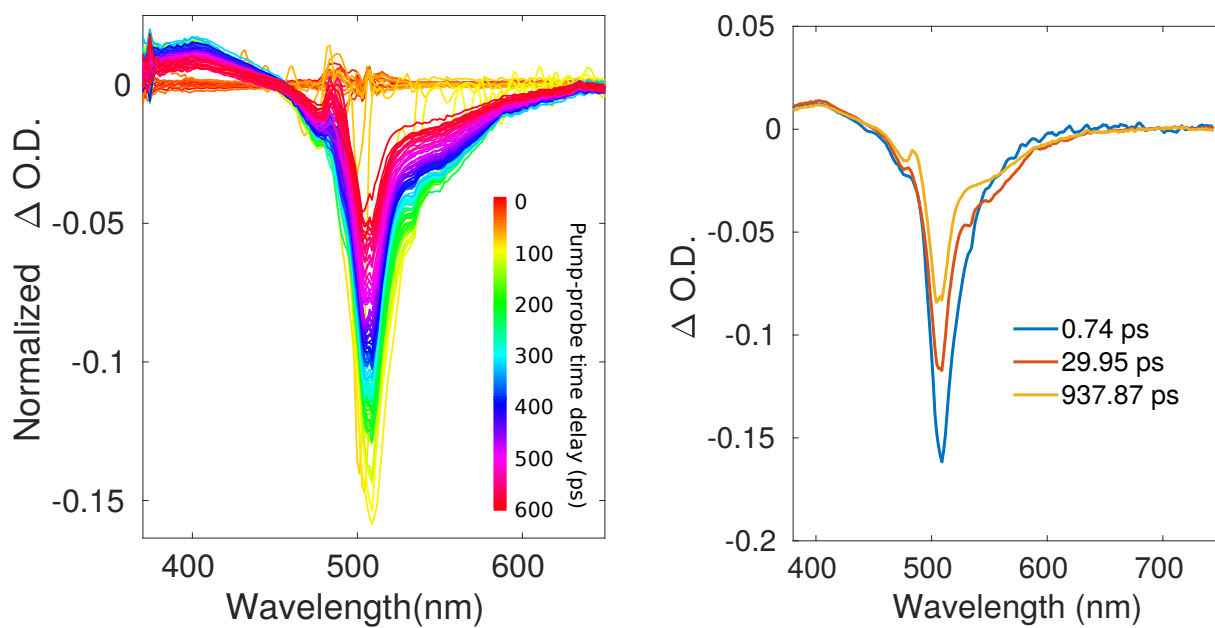


Figure S7: *Experimental transient spectra (left) and EADS (right) of compound 1 dissolved in toluene and excited at 500 nm.*

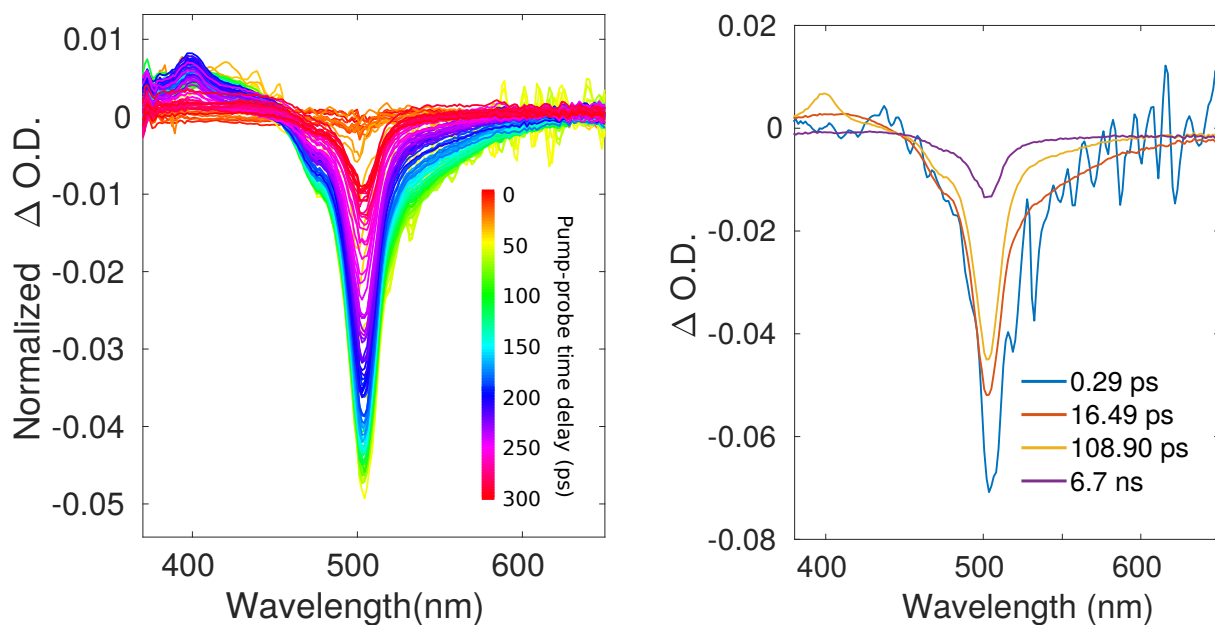


Figure S8: *Experimental transient spectra (left) and EADS (right) of compound 1 dissolved in dichloromethane and excited at 350 nm.*

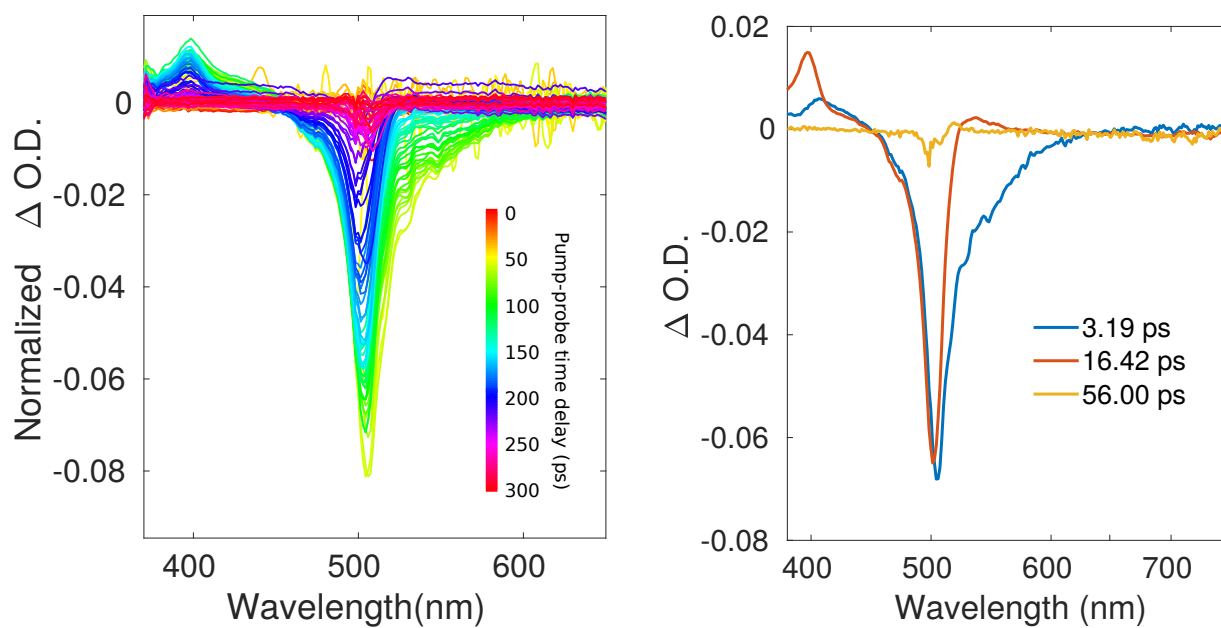


Figure S9: *Experimental transient spectra (left) and EADS (right) of compound 1 dissolved in dichloromethane and excited at 500 nm.*

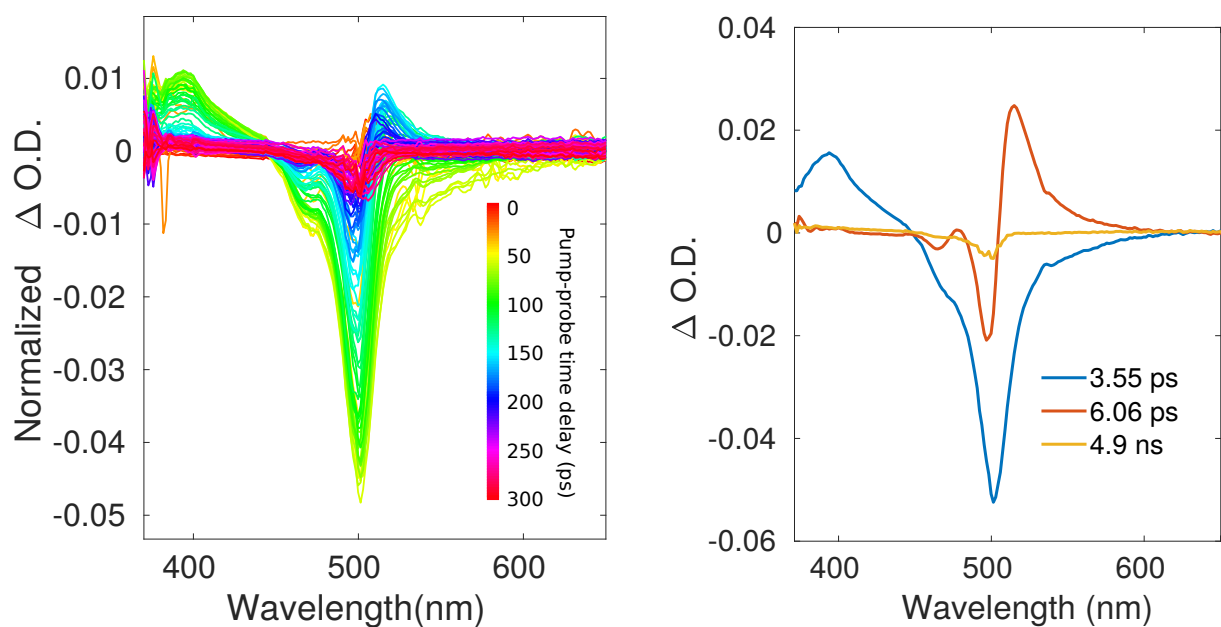


Figure S10: *Experimental transient spectra (left) and EADS (right) of compound 1 dissolved in acetonitrile and excited at 350 nm.*

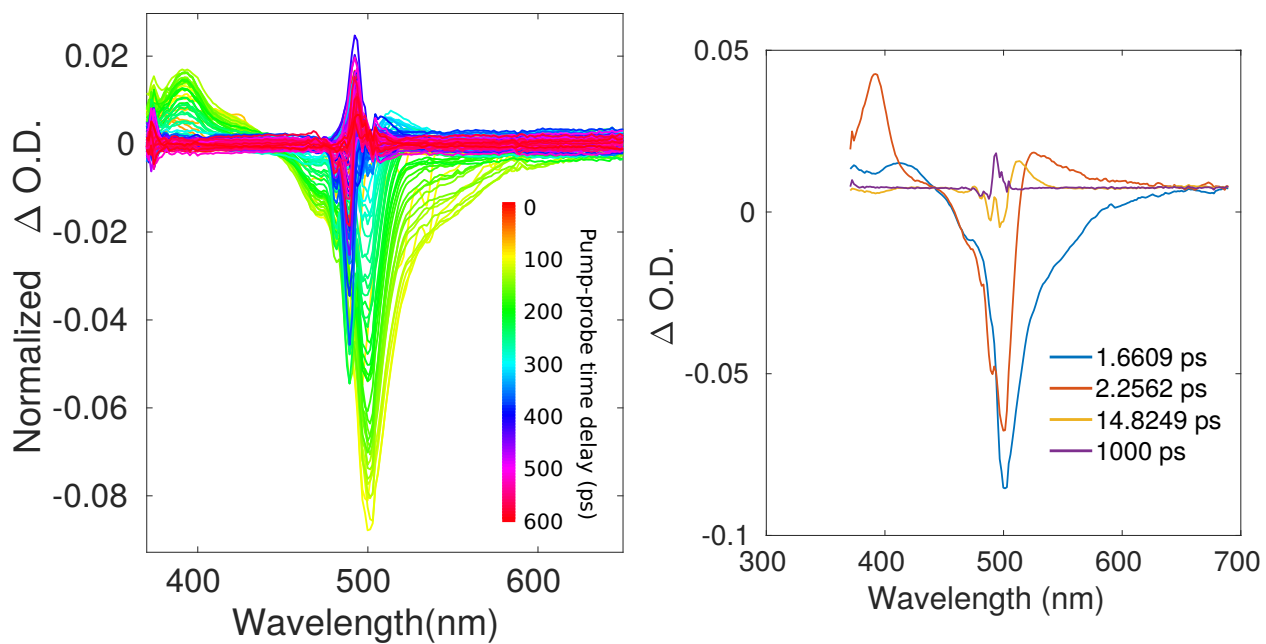


Figure S11: *Experimental transient spectra (left) and EADS (right) of compound 1 dissolved in acetonitrile and excited at 500 nm.*

Solvent	Polarity Index	$\tau_1(ps)$	$\tau_2(ps)$	$\tau_3(ps)$	$\tau_4(ps)$
<i>Hexane</i>	0.1	0.24	9.5	540	2690
<i>Toluene</i>	2.4	0.10	21.7	1723	1729
<i>Dichloromethane</i>	3.1	0.29	16.5	108.9	6678
<i>Acetonitrile</i>	5.8	3.6	6.1	4948	--

Table S1: Summary of the time constants obtained by global fit of the transient spectra (350 nm pump wavelength) performed by Glotaran software.

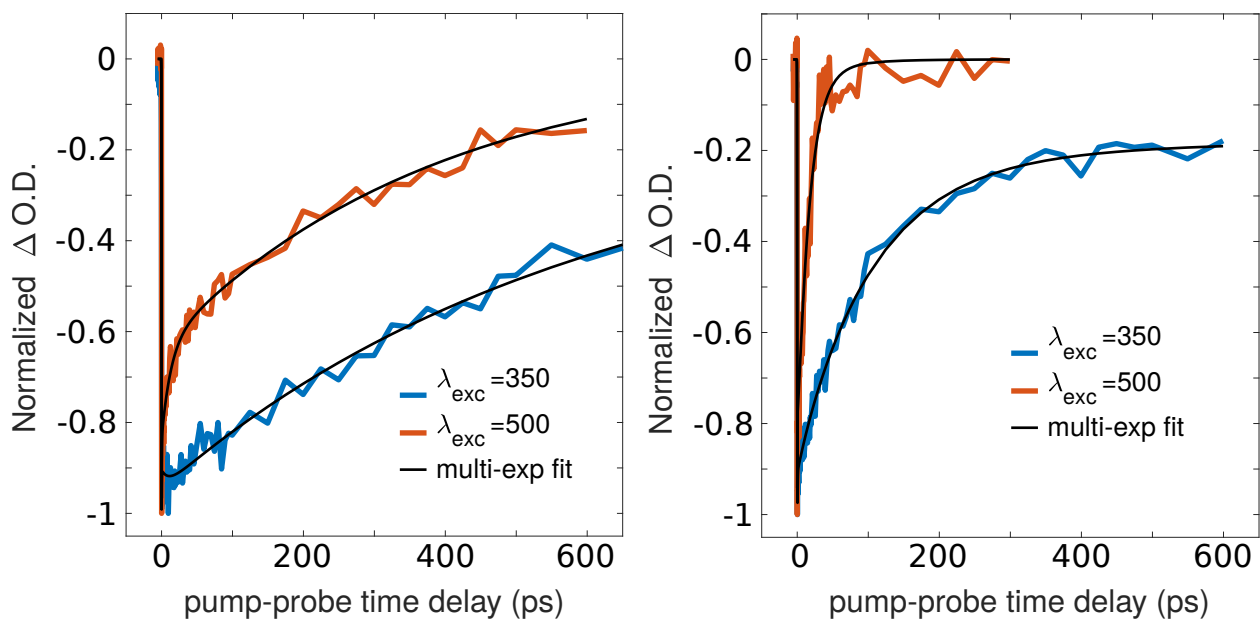


Figure S12: Single wavelength kinetics recorded on the maximum of the bleaching signal (504 nm) upon excitation at 350 nm and 500 nm of compound **1** in hexane (left) and dichloromethane (right)

## S4 Computed electronic states couplings

	CT1	LE3 <sub>(np)</sub>	LE5 <sub>(np)</sub>
LE1	103.3	<0.01	2.2
LE2	21.5	<0.01	11.0
LE3 <sub>(np)</sub>	<0.01	--	--
LE4	<0.01	<0.01	<0.01
LE5 <sub>(np)</sub>	346.8	--	--

Table S2: Calculated couplings between the electronic states. All values in  $cm^{-1}$ . The subscript(np) indicates states localized on the nitrophenyl moiety.