

Supporting Information for “Solvent-Dependent Dual Fluorescence of the Push-Pull System 2-Diethylamino-7-Nitrofluorene”

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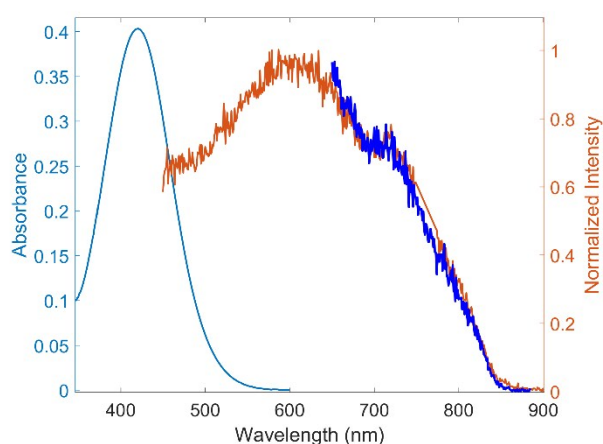
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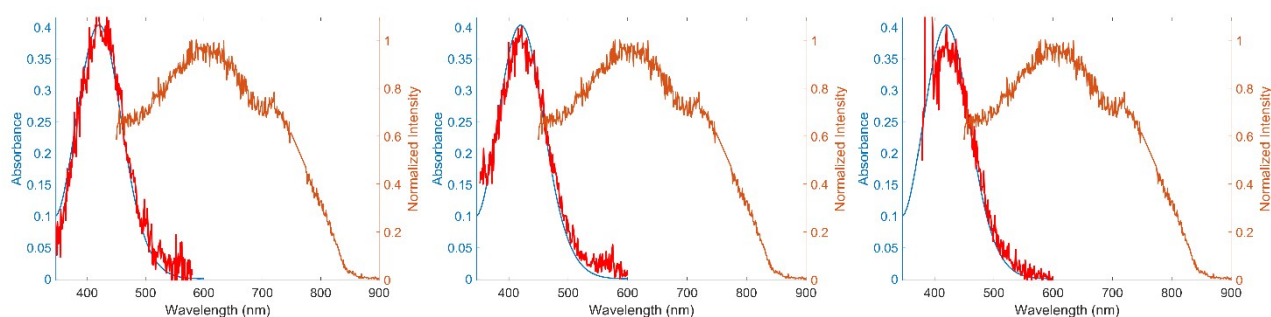
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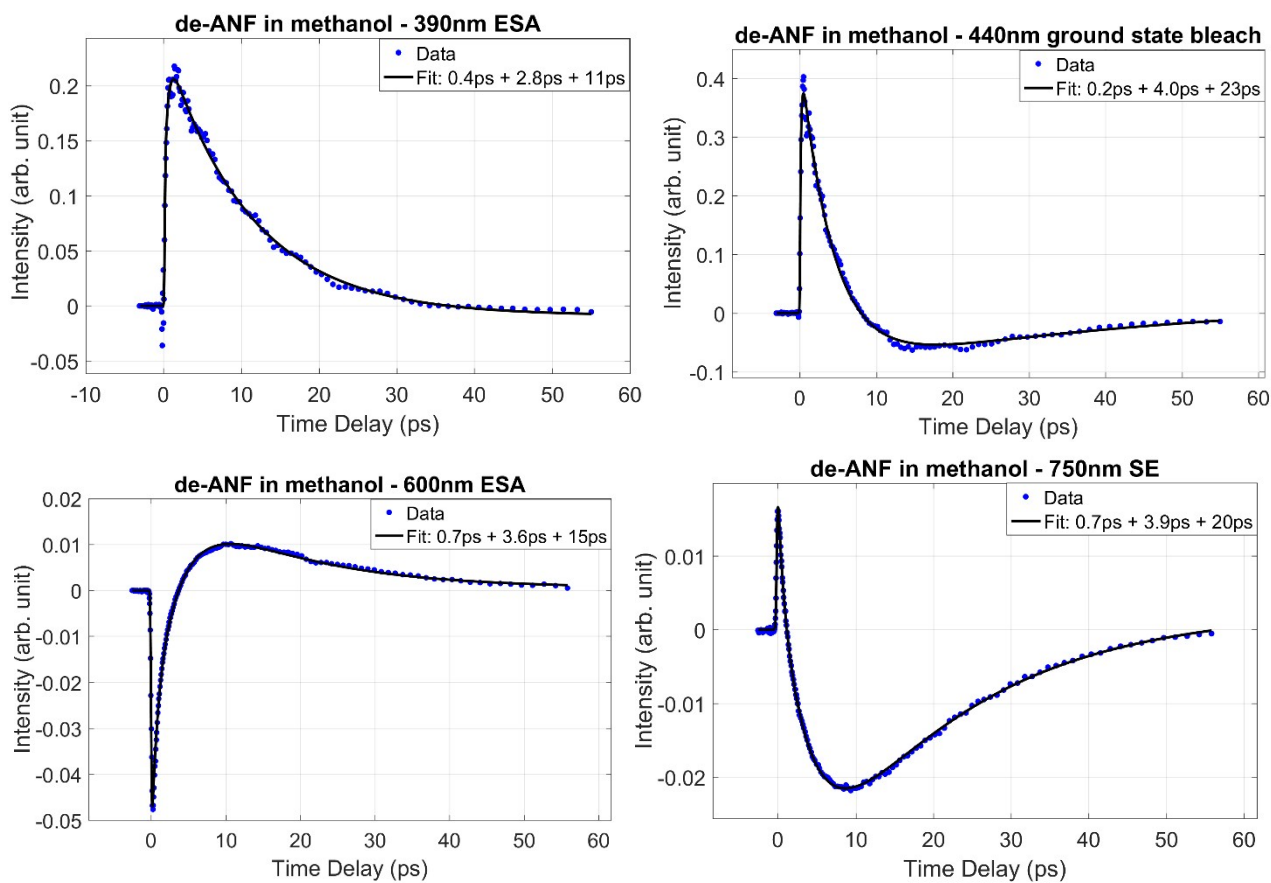
Supporting Figure S1. Long-wavelength fluorescence band of dm-ANF in methanol (dark blue) resulting from excitation at 450nm in top of fluorescence band (orange) resulting from 380 nm excitation (and therefore the second harmonic region removed). The similarity of the two bands is clear from the below comparison and does not affect shape or maximum position of the long-wavelength fluorescence band.



Supporting Figure S2. Absorption (blue), fluorescence (orange) and excitation spectra (red) of dm-ANF in methanol at three different wavelengths covering the two fluorescent bands; 610 nm, 690 nm and 780 nm.

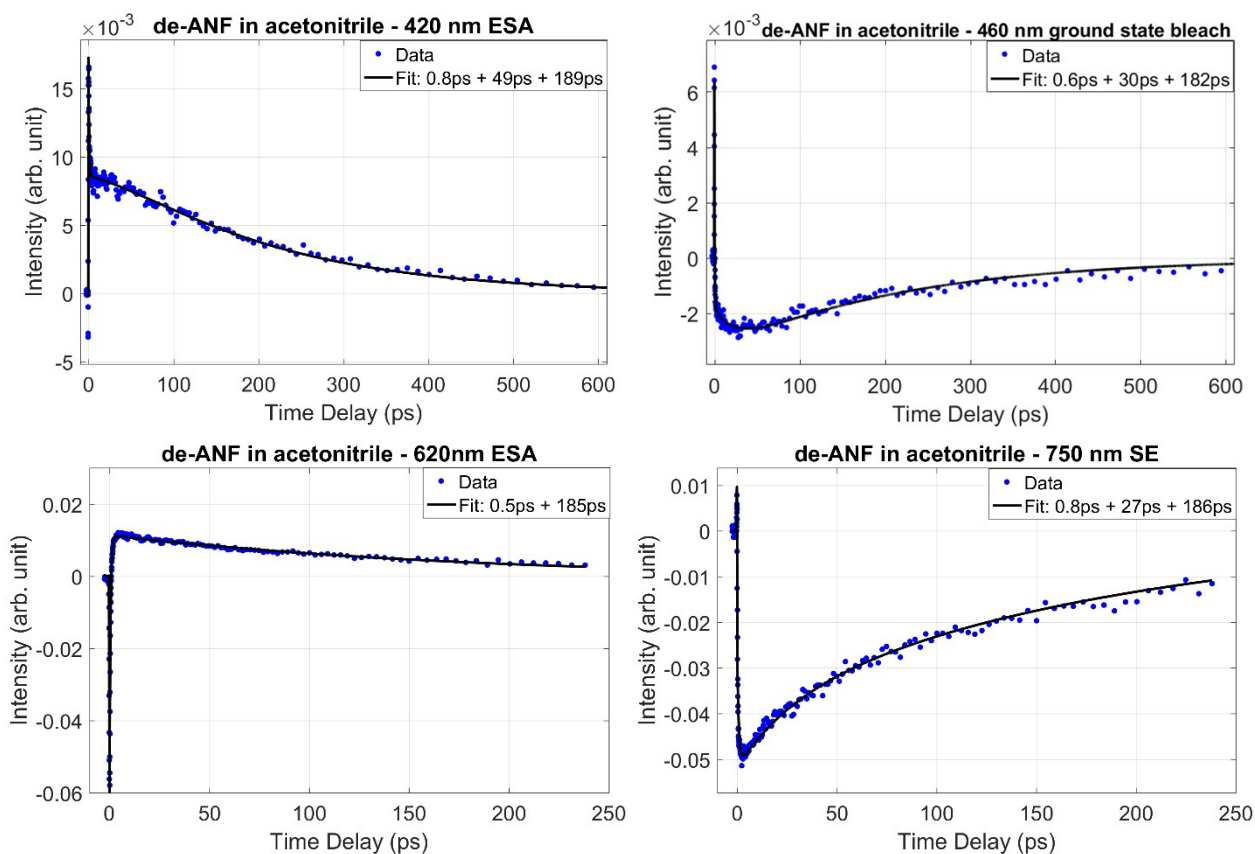


Supporting Figure S3. Transients at specific wavelengths with fits and time constants shown in each graph. The fit consists of the gaussian instrument response function convolved with a number of exponential decays – the timeconstants are given in the figures.

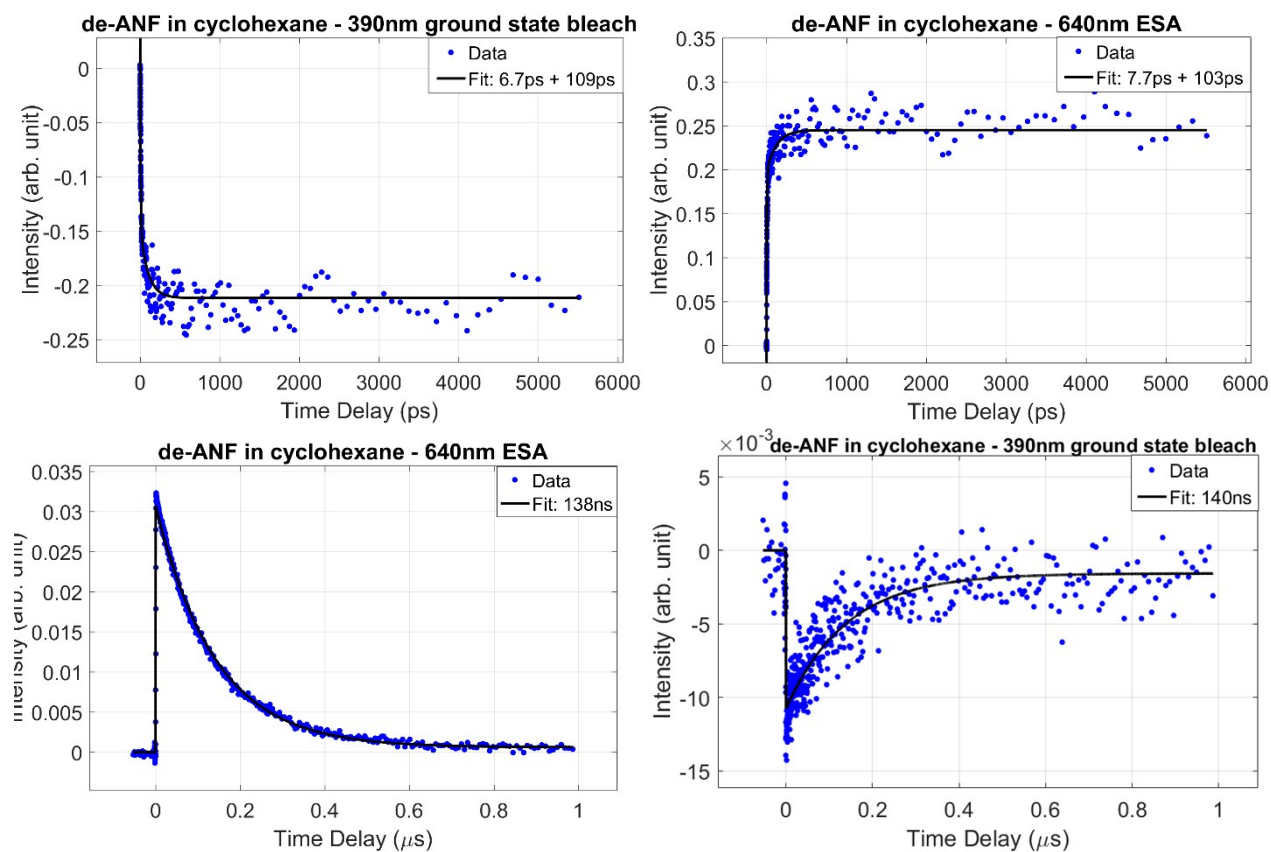


Above: Transients and fits for de-ANF in methanol.

Below: Transients and fits for de-ANF in acetonitrile.



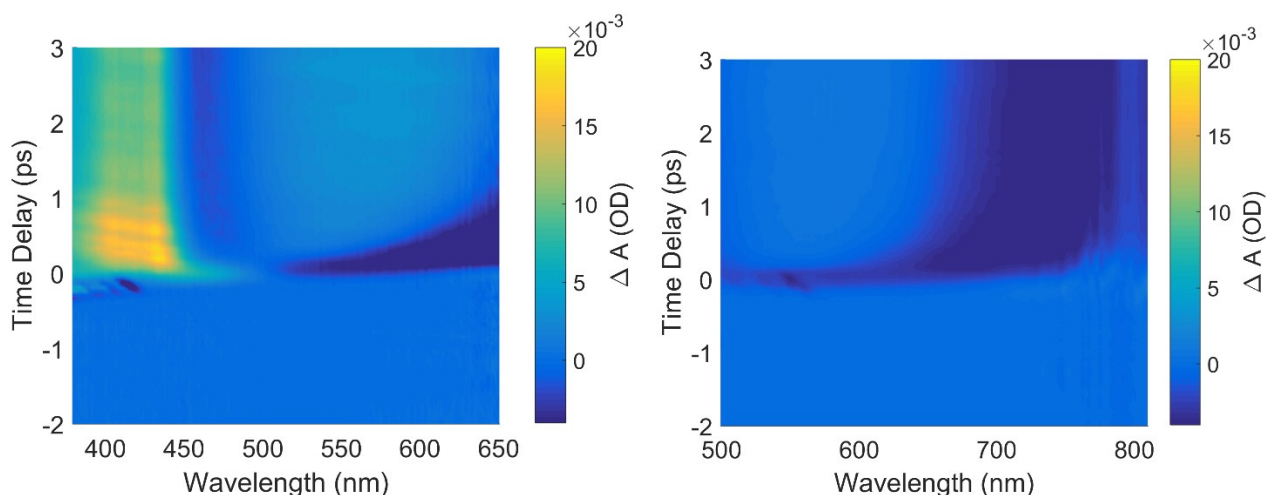
Below: Transients and fits for de-ANF in cyclohexane.



It can be noted that the timescales in methanol correspond closely to the slow (diffusive) solvation timescales (3 ps and 15 ps) associated the solvent.¹ The 3-4 ps component appears to be associated with the appearance of the second excited state minimum and thus represents the time it takes to rotate the amino group in methanol. Likewise, the fast decay of the ESA band at 400 nm in acetonitrile and concomitant rise of the SE at 750 nm (0.5-0.7 ps) is close to the slow, diffusive solvation timescale (0.67 ps) reported for acetonitrile.¹ In acetonitrile the rotation of the amino group and appearance of the second fluorescence peak is thus much faster compared to methanol.

Considering the previously reported timescales for dm-ANF in DMSO, in which the second fluorescence peak appears on a 8.9 ps timescale,² it is clear that the solvent dictates the equilibration between the excited state minima. These observations lead to the notion that there is no or a very small barrier to interconversion between the excited state minima and that twisting is indeed part of the excited state dynamics.

Supporting Figure S4. Transient absorption spectra of de-ANF in acetonitrile near time-zero showing the negative signal in the region from 500 nm to 650 nm at early times. This SE signal arises from the first fluorescent state but is quickly dominated by the positive signal (ESA) from second fluorescent state.

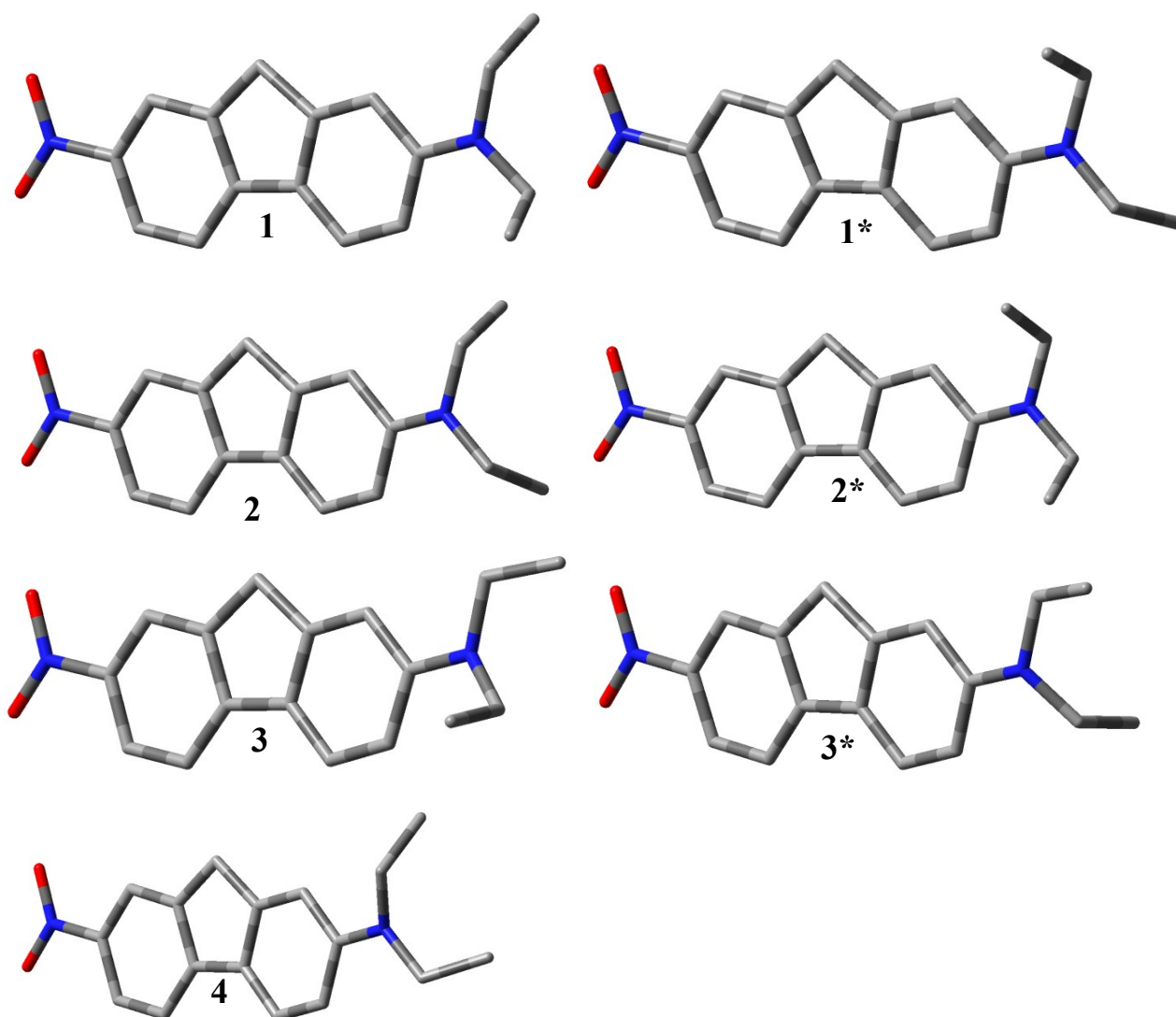


Supporting Table S1. Relative energies of ground state conformers and their gasphase excitation energies ((TD)-PBE0/6-31+G(d,p)).

	Relative Energy (kJ/mol)	Boltzmann population at room temperature (%)	Vertical excitation energy (eV)
1	0	35.5	3.03
1*	0	35.5	3.03
2	2.42	13.4	3.04
2*	2.42	13.4	3.04
3	9.47	0.8	3.07
3*	9.47	0.8	3.07
4	9.55	0.7	3.06

*Indicates enantiomeric pairs.

Supporting Figure S5. Structures of the ground state conformers as referred to by the number in Table S1.



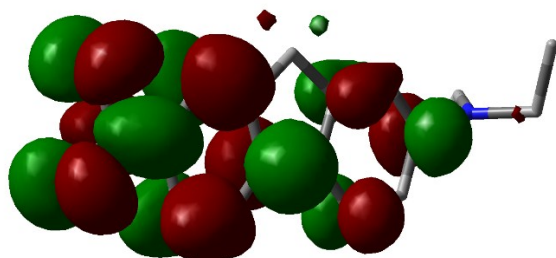
Supporting Table S2. State ordering at the Franck-Condon (FC) geometry and the different excited state minima in de-ANF: S_{1P} , S_{1N} og S_{1A} (PBE0/6-311+G(d,p)).

	FC geometry	S_{1P}	S_{1N}	S_{1A}
S_0	0	0.099	1.4549	0.6753
S_1	3.0277 (π, π^*)	2.9286 (π, π^*)	2.7107 (π, π_N^*)	2.9995 (n_A, π^*)
S_2	3.9161 (n_N, π^*)	3.7295 (n_N, π^*)	4.0399 (π, π_N^*)	4.0925 (n_N, π^*)
T_1	2.260 (π, π^*)	2.2018 (π, π^*)	1.5501 (-)	2.9207 (n_A, π^*)
T_2	2.9272 (π, π^*)	2.6156 (π, π^*)	2.6483 (π, π_N^*)	2.9985 (π, π^*)
T_3	3.3415 (π, π^*)	3.1634 (n_N, π^*)	3.5781 (π, π_N^*)	3.1373 (π, π^*)
T_4	3.3560	3.3978	3.7953	3.5354
T_5	3.5117	3.5226	3.9701	4.1547

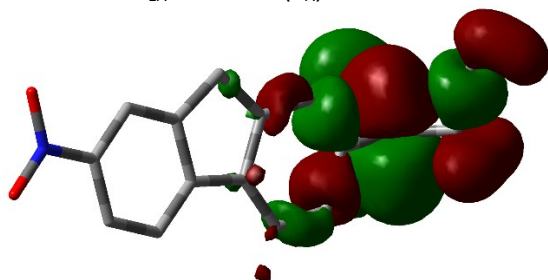
n_N indicates excitation from the lone-pair on the nitro group, whereas n_A indicates excitation from the lone-pair on the amino group. Likewise, π_N^* indicates excitation to a π^* orbital on the nitro group (only seen in the S_{1N} minimum). States with many (>6) contributions are labelled (-) due to the considerable mixed character of the state.

The orbitals involved in the S_1 transition in the S_{1A} minimum is the HOMO and LUMO, given below. The orbitals involved in the T_2 transition in the S_{1A} minimum is the HOMO-5 and HOMO-6 to the LUMO, also given below.

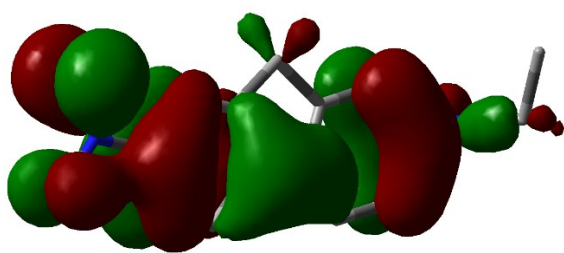
LUMO for the S_{1A} minimum (π^*):



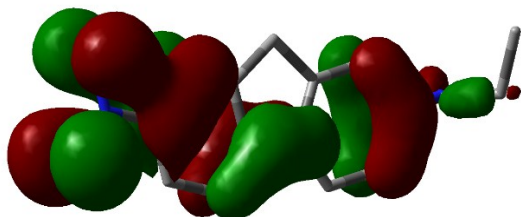
HOMO for the S_{1A} minimum (n_A):



HOMO-5 for the S_{1A} minimum (π):



HOMO-6 for the S_{1A} minimum (π):



Supporting Figures 6-9. NMR spectra of the analytically pure compounds.

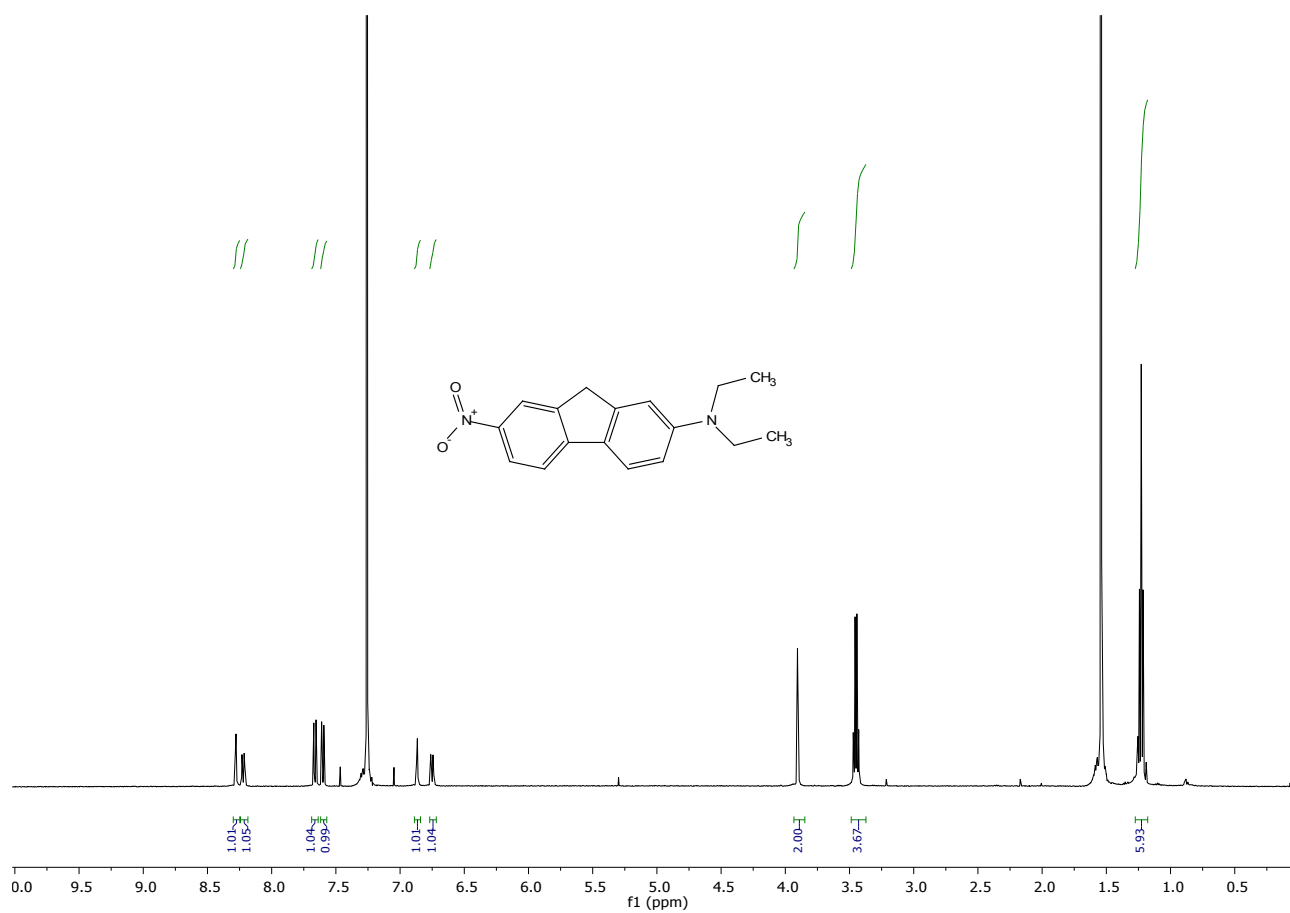


Figure S6: ^1H NMR spectrum of de-ANF in CDCl_3 .

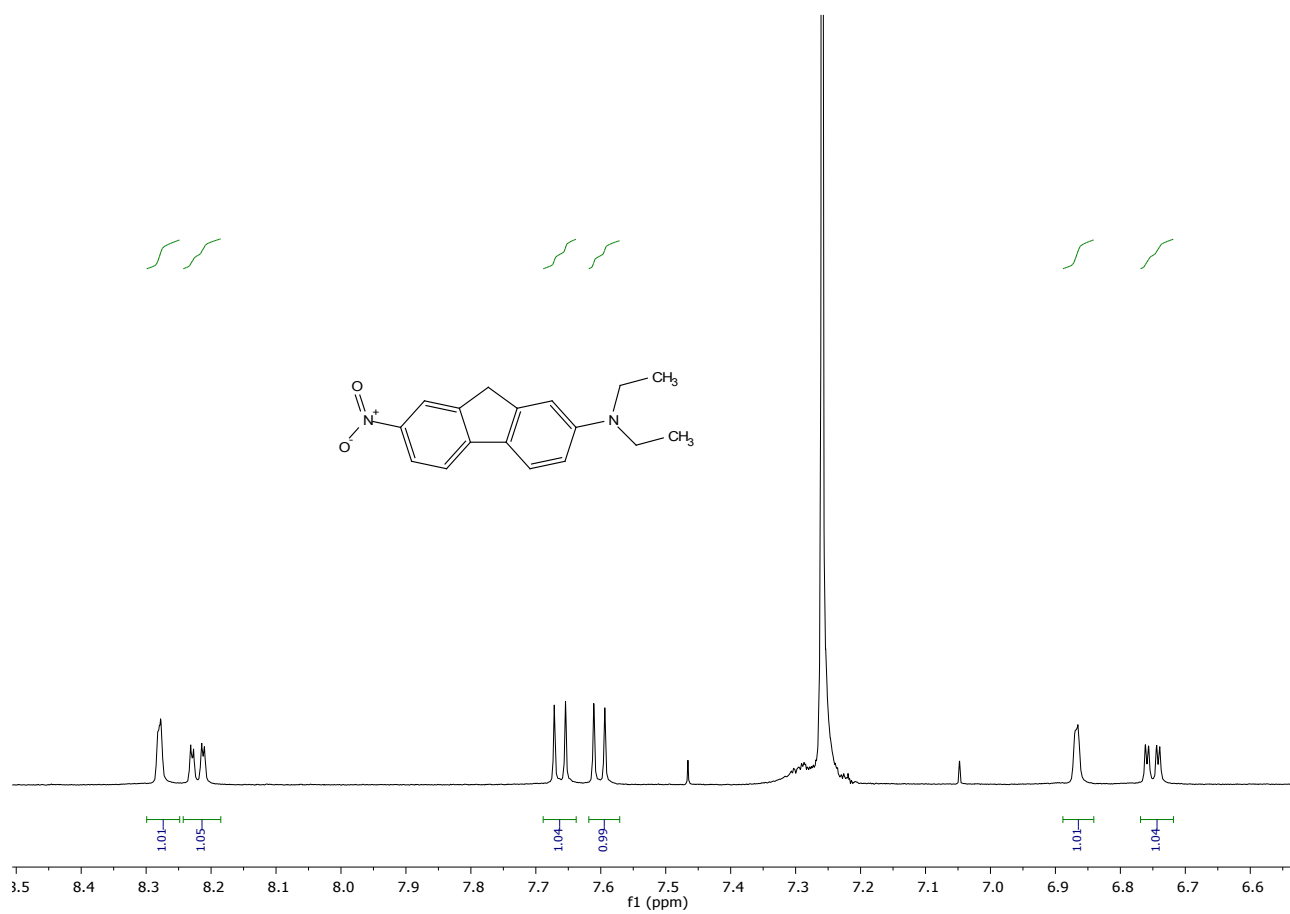


Figure S7. Zoom of the aromatic region of the ^1H NMR spectrum of de-ANF in CDCl_3 . The intense signal at 7.26 is the CHCl_3 residue in the CDCl_3 and its ^{13}C -satellites are seen at 7.05 and 7.47 ppm.

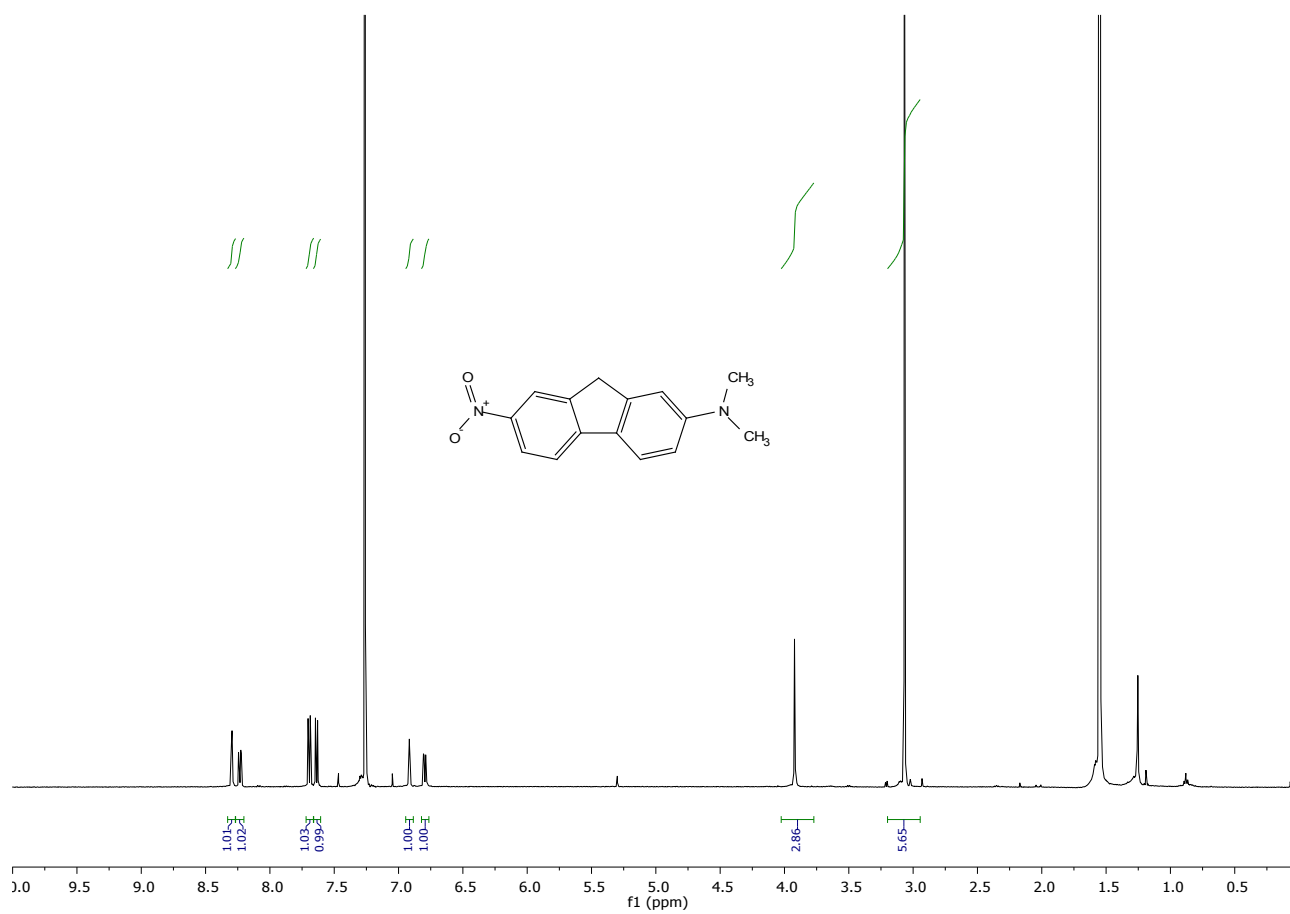


Figure S8. ^1H NMR spectrum of dm-ANF in CDCl_3 .

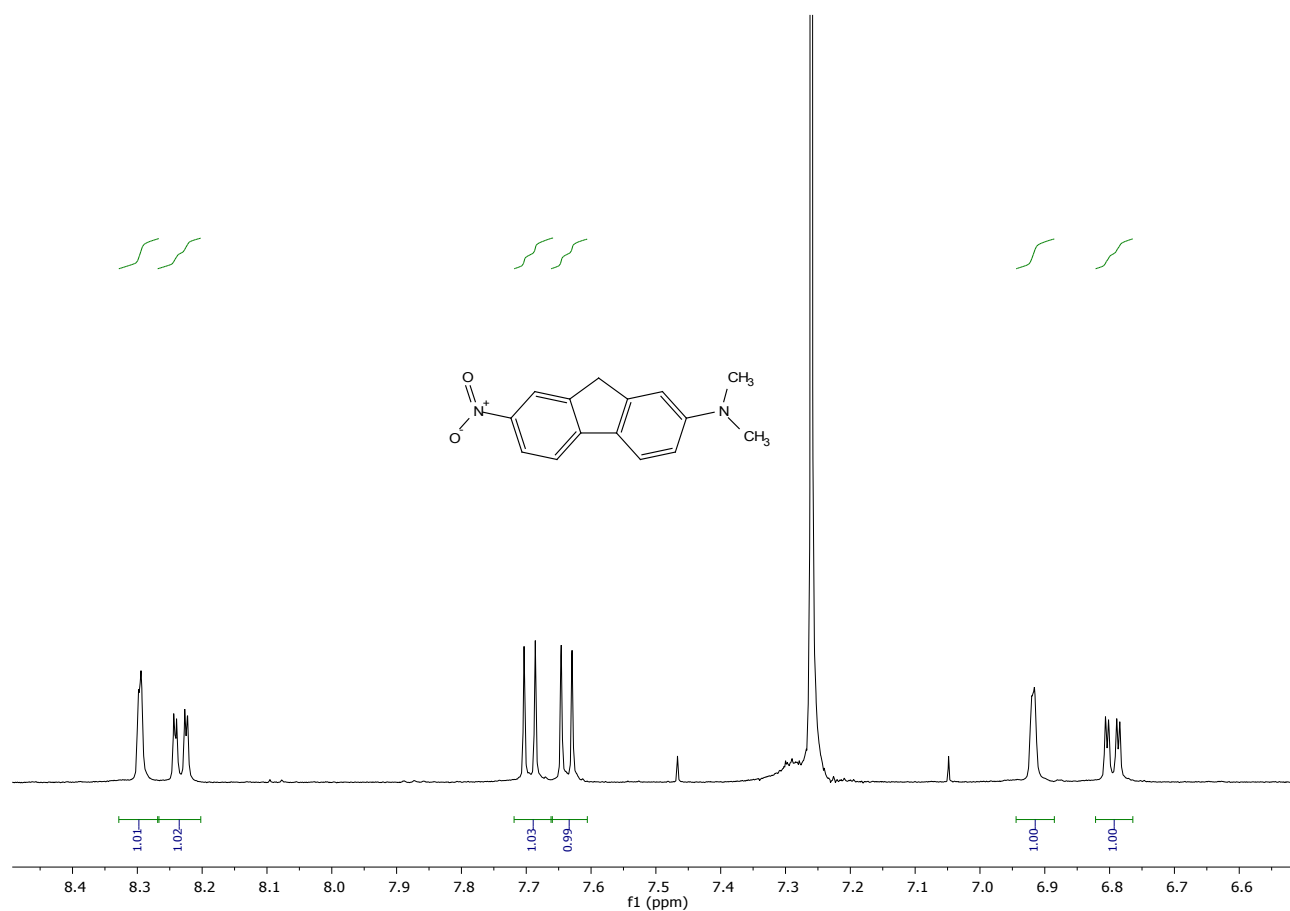


Figure S9. Zoom of the aromatic region of the ^1H NMR spectrum of dm-ANF in CDCl_3 . The intense signal at 7.26 is the CHCl_3 residue in the CDCl_3 and its ^{13}C -satellites are seen at 7.05 and 7.47 ppm.

References

1. Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M., *Journal Of Physical Chemistry* **1995**, 99 (48), 17311-17337.
2. Mondal, J. A.; Sarkar, M.; Samanta, A.; Ghosh, H. N.; Palit, D. K., *Journal Of Physical Chemistry A* **2007**, 111 (28), 6122-6126.