Electronic Supplementary Material for PCCP

Supplementary information for:

Photoexcited triplets of dyes in zeolitic nanostructured channels. A Time Resolved EPR study.

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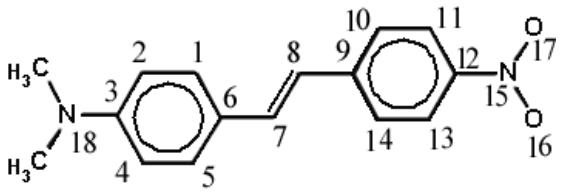
Experiments and methods

Preparation of the PHTP inclusion crystals
NST has been included in PHTP by self-assembly from a 2-butanone solution as described in [26]. For DANS we used the same procedure as Hülliger et al. [28]. The orange inclusion crystals of 1-2 mm length have a typical hexagonal needle shape. The formation of the new phase and the homogeneity of the sample was confirmed by Differential Scanning Calorimetry, that showed a single peak at 141 C, much different from the melting point of PHTP matrix (125 C) and of DANS (above 250 C).

Synthesis of Porosil.
The purely siliceous MFI-type zeolite, Porosil, was prepared according to the procedure reported by J. Patarin et al. [29], using fluoride anions as mineralizing agents (fluoride route). The reactants used in the hydrothermal synthesis were fumed silica (99.8 %, Aldrich), as silica source, tetrapropylammonium bromide (TPABr) (Aldrich) as template, ammonium fluoride (Aldrich) as source of fluorides, and distilled water.
The weighted amount of silica was added to an aqueous solution of NH_4F under stirring in a stainless-steel Teflon-lined autoclave. The required amount of TPABr was successively added to the resulting mixture. After aging at room temperature for 3 h the mixture was heated at 443 K for 15 days. The autoclave was neither shaken nor stirred during the heating period, then cold water was added and the resulting solid was filtered, washed with distilled water and dried at 333 K. The as-synthesised material was then calcined in air at 823 K for 12 h in order to remove the template.
The molar ratio of reagents was: 1 SiO_2, 0.125 TPA-Br, 0.5 NH_4F, 30 H_2O.



Scheme 1: Numbering fo DANS. For Nitrostilbene the numbering is the same, without the dimethylamino group.

Calculated hyperfine tensors of the radical cations 4-nitrostilbene, NST and 4-N,N-dimethylamino-4'-nitrostilbene, DANS

DFT calculations on the radicals DANS and NST molecules by using Gaussian to calculate the hyperfine tensors for protons and nitrogens. The calculation was a single point b3lyp/eprII [1] run on an AM1-optimized geometry.Then the cw-epr spectrum was simulated by taking into account the nuclei with couplings larger than 1 G. The remaining nuclei were considered to give an unresolved inhomogeneous linewidth of 4 G.
The most evident difference with NST is the width of the spectrum. For DANS the hyperfine interactions with the dimethylamino group almost dominate the spectrum because both the number of methyl protons or the high nuclear spin for nitrogen. For NST, this group is missing and the other protons have smaller interactions, moreover the spin density at the nitro group remains low.

Table 1 Calculated isotropic hyperfine interaction a_0, principal values and direction cosines of the hyperfine tensor T_{ii} for $NST^{+\cdot}$ radical cation. The number of the atoms in brackets is referred to scheme 1.

	a_0/G	T_{ii}/G	X	Y	Z
H (C1)	-2.96	-0.93	0.9134	0.4071	0.0004
		-0.845	0.0003	-0.0002	1
		1.775	0.4071	0.9134	0.0001
H (C3)	-6.22	-4.362	0.1186	0.9929	0
		-0.096	0.0001	0	1
		4.458	0.9929	0.1186	-0.0001
H (C5)	-2.64	-1.271	0.9857	-0.1684	0.0001
		-0.602	0.0001	0	1
		1.873	0.1684	0.9857	0
H (C7)	-2.15	-1.127	0.9999	-0.0053	0.0088
		-1.117	0.0088	0	1
		2.245	0.0053	1	0.0001
H (C8)	-6.91	-2.958	0.9861	-0.1663	-0.0001
		-1.12	0	0.0002	1
		4.079	0.1663	0.9861	0.0002
H (C10)	-3.10	-1.187	0.9787	-0.2051	0.0002
		-0.568	0.0002	0	1
		1.755	0.2051	0.9787	0.0001
H (C11)	-1.44	-0.447	0.0002	0.0001	1
		-0.193	0.6471	0.7624	-0.0002
		0.641	0.7624	0.6471	0
H (C13)	-1.47	-0.467	0	0.0001	1
		-0.225	0.3875	0.9219	0
		0.692	0.9219	-0.3875	0.0001
H (C14)	-3.16	-1.01	0.8949	0.4462	0.0001
		-0.704	-0.0001	0	1
		1.713	0.4462	0.8949	0

Table 2 Calculated isotropic hyperfine interaction a_0, principal values and direction cosines of the hyperfine tensor T_{ii} for $DANS^{+\cdot}$ radical cation. The number of the atoms in brackets is referred to scheme 1. Methyl a and b refer to the *cis* or *trans* position of the methyl-C with respect to C4 respectively.

	a_0 (G)	T_{ii} (G)	x	y	z
N 18	-0.60	-4.422	0.9942	0.1073	-0.0001
		-4.416	-0.1073	0.9942	-0.0001
		8.838	0.0001	0.0001	1
H (C2)	-2.59	-0.998	0.9854	0.1705	0
		-0.549	0	0	1
		1.546	-0.1705	0.9854	0
H (C4)	-3.22	-1.245	0.9284	-0.3717	0
		-0.528	0	0	1
		1.773	0.3717	0.9284	0
H (C7)	1.42	-0.808	0.0003	-0.0002	1
		-0.19	0.6897	0.7241	0.0003
		0.997	0.7241	0.6897	-0.0001
H (C8)	-6.61	-2.914	0.9697	0.2445	-0.0001
		-0.683	0	0.0002	1
		3.598	-0.2445	0.9697	-0.0002
H (C10)	-2.26	-0.749	0.9689	0.2473	0.0003
		-0.4	0.0003	0	1
		1.149	-0.2473	0.9689	-0.0001
H (C14)	-2.26	-0.77	0.8913	-0.4534	0
		-0.424	0	0	1
		1.194	0.4534	0.8913	0
H (methyl a)	8.50	-.30	0.9854	0.1705	0
		-.30	0	0	1
		0.60	0.1705	0.9854	0
H (methyl b)	8.50	-.30	0.9284	-0.3717	0
		-.30	0	0	1
		0.60	0.3717	0.9284	0

[1] V. Barone in *Recent Advances in Density Functional Methods, Part I,* Chong, D. P., Ed., World Scientific Publ. Co.: Singapore, 1996.

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TR-EPR spectra of DANS in PHTP and porosil and ZSM-5 zeolites

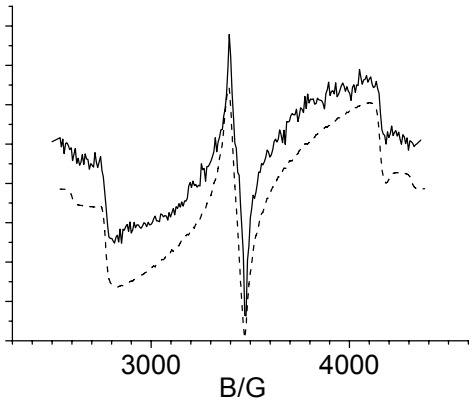

Fig. 1. TR-EPR spectrum of DANS in PHTP: experimental spectrum, continuous line, simulation, dotted line. The parameters are given in Table 1 of the paper.

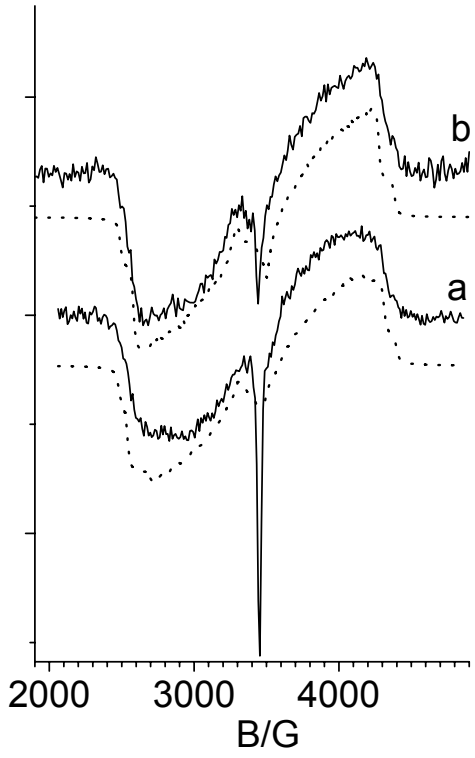

Fig. 2. TR-EPR of DANS at 80K. *a*.: H-ZSM-5, *b*.: Li-ZSM-5. Experimental, continuous lines, simulations, dotted lines. The parameters are given in Table 1 of the paper.

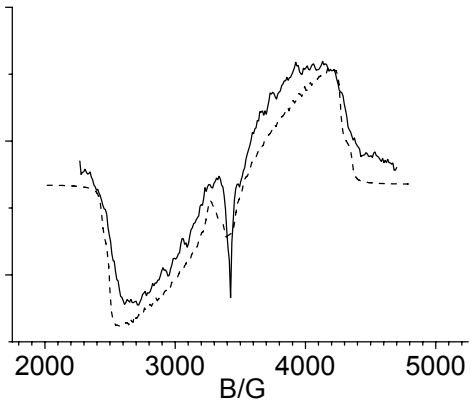

Fig. 3. DANS in porosil. Continuous line, experimental spectrum, dotted line, simulation. The parameters are given in Table 1 of the paper.