Effective Exchange Coupling in Alternating-Chains of a π-Extended 1,2,4-Benzotriazin-4-yl

Electronic Supporting Information

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Fig. S1. Cyclic voltammogram of radical **1**.

Fig. S2 Experimental and simulated solid-state EPR spectrum of radical **1**.

Fig. S3. Experimental and simulated solution EPR spectrum of radical **1**.

Fig. S4. Geometry of radical **1** in the crystal and the crystallographic atom numbering that is used in the discussion of the X-ray structure.

Table T1. Energies of triplet (E_T) and broken symmetry singlet (E_{BS}) states along with spin contaminations before S^2 and after S^2_A annihilation calculated on the X-ray determined geometries at the UB3LYP/6-311G++G(d,p), UB3LYP/6-311++G(2d,p), UMO6-2X/6-311++G(2d,p) and UX3LYP/6-311++G(2d,p) level of theory.

Crystal refinement data for radical 1 (CCDC 953369)

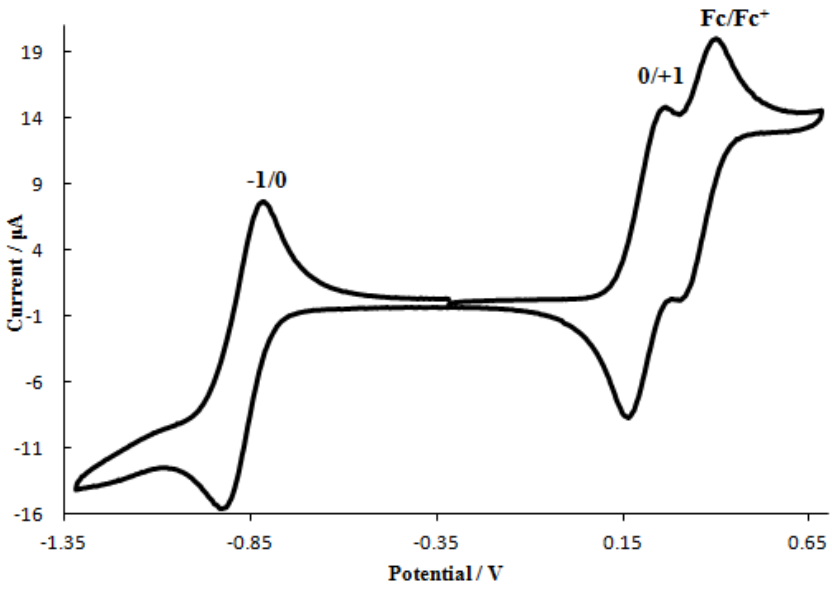

Fig. S1 Cyclic voltammogram of radical **1** (1 mM), *n*-Bu_4NBF_4 (0.1 M), DCM, r.t., 50 mV/S.

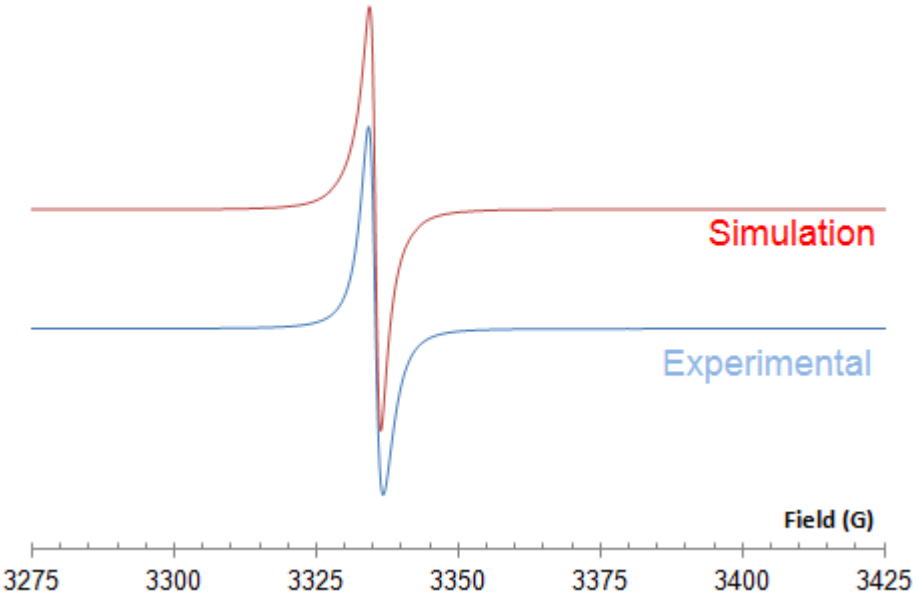

Fig. S2 Experimental and simulated solid-state EPR spectrum of radical **1** at r.t. (g = 2.0028).

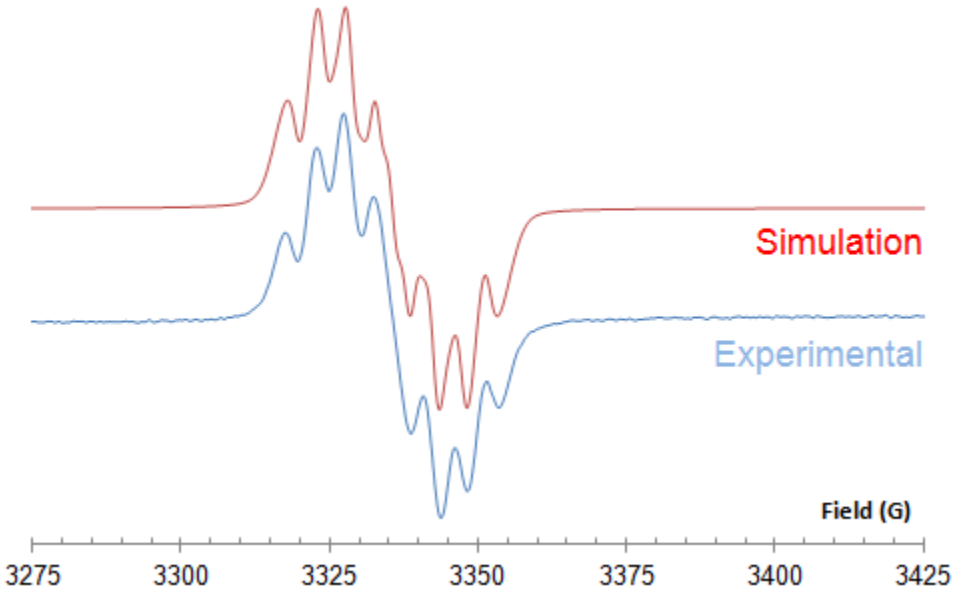

Fig. S3 Experimental and simulated solution EPR spectrum of radical **1** at r.t. in DCM (g = 2.0024).

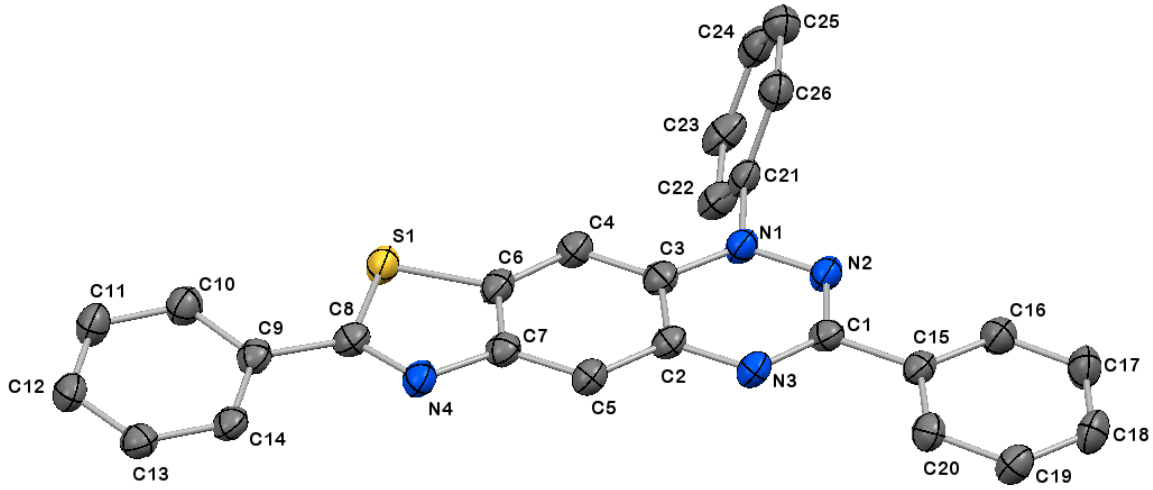

Fig. S4 Geometry of radical **1** in the crystal and the crystallographic atom numbering that is used in the discussion of the X-ray structure, which differs from IUPAC. Thermal ellipsoids are shown at 50% probability. Hydrogens are omitted for clarity.

Table T1 Energies of triplet (E_T) and broken symmetry singlet (E_{BS}) states along with spin contaminations before S^2 and after S^2_A annihilation calculated on the X-ray determined geometries at the UB3LYP/6-311G++G(d,p), UB3LYP/6-311++G(2d,p), UMO6-2X/6-311++G(2d,p) and UX3LYP/6-311++G(2d,p) level of theory

Theory	Radical Pair	Triplet State			BS Singlet State		
		E_T (a.u.)	S^2	S^2_A	E_{BS} (a.u.)	S^2	S^2_A
UB3LYP/	I-II	-3236.3087507	2.03	2.00	-3236.3089632	1.02	0.24
6-311++G(d,p)	II-III	-3236.3050147	2.03	2.00	-3236.3049848	1.03	0.26
UB3LYP/	I-II	-3236.3895325	2.03	2.00	-3236.3900056	1.02	0.24
6-311++G(2d,p)	II-III	-3236.3860577	2.03	2.00	-3236.3860859	1.03	0.22
UMO6-2X/	I-II	-3235.3921863	2.04	2.00	-3235.3924022	1.04	0.34
6-311++G(2d,p)	II-III	-3235.3911078	2.04	2.00	-3235.3910567	1.04	0.36
UX3LYP/	I-II	-3235.1780569	2.03	2.00	-3235.1782707	1.02	0.27
6-311++G(2d,p)	II-III	-3235.1747777	2.04	2.00	-3235.1747296	1.04	0.29

Crystal refinement data for radical 1 (CCDC 953369)

100 K, brown rods: $C_{26}H_{17}N_4S$, M = 417.51, Triclinic, space group *P-1*, a = 9.3437(17) Å, b = 10.538(2) Å, c = 11.5632(15) Å, α = 105.416(15)°, β = 94.821(13)°, γ = 114.063(19)°, V = 978.0(3) Å^3, Z = 2, T = 100(2) K, ρ_{calcd} = 1.418 g cm^{-3}, $2\theta_{max}$ = 67. Refinement of 280 parameters on 3463 independent reflections out of 5933 measured reflections (R_{int} = 0.0323) led to R_1 = 0.0558 [I>2s(I)], wR_2 = 0.1723 (all data), and S = 1.071 with the largest difference peak and hole of 0.588 and -0.748 e^{-3}, respectively.