Electronic Supporting Information

Low Temperature Insights into the Crystal and Magnetic Structure of a Neutral Radical Ferromagnet

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Crystallographic Measurements

Ultra-low temperature crystallographic data were collected on the custom-built XIPHOS system previously described.[1] Temperature control was achieved using a Lakeshore 340 controller with measurements performed by means of a Lakeshore DT-470-CO-13 diode. Crystals of **1a** suitable for X-ray work were grown by electrocrystallization, as previously described (reference 9a, main text). A well-formed single crystal of **1a** (0.250 × 0.075 × 0.070 mm) was selected and mounted onto a graphite fibre with low-temperature epoxy resin (Oxford Instruments, TRZ0004), centred optically at room temperature and then enclosed within a double-walled Be chamber. A dynamic vacuum of ~5.4×10^{-6} mbar was maintained throughout the experiment. The sample was gradually cooled from room temperature to 2 K over an approximately 12 h period and then centred in the X-ray beam via diffraction. All data were collected at a generator setting of 50 kV and 108 mA, using 20 s φ scans (0.5° frame width) at a detector distance of 8 cm from the sample. A total of 12 scans were collected at 2θ angles = ±20° and ±40°. Crystal centring, data collection and processing were performed with APEX2 software.[2] Data were integrated via SAINT[3] and reflections corrected with SADABS.[4] Using Olex2,[5] the structure was solved with the ShelXT[6] structure solution program using Intrinsic Phasing and refined with the XL[7] refinement package using Least Squares minimisation.

Table S1 Crystal Data for **1a**.

CCDC code	701731 [a]	701735 [a]	2096260
Formula	$C_7H_5ClN_3Se_4$	$C_7H_5ClN_3Se_4$	$C_7H_5ClN_3Se_4$
M	482.43	482.43	482.43
a (Å)	16.2708(5)	16.1801(12)	16.1915(4)
c (Å)	4.1720(3)	4.1264(6)	4.07570(10)
V (Å^3)	1104.49(9)	1080.27(8)	1068.50(6)
ρ_{calcd} (g cm^{-1})	2.901	2.966	2.999
space group	$P\overline{4}2_1m$	$P\overline{4}2_1m$	$P\overline{4}2_1m$
Z	4	4	4
temp (K)	296(2)	100(2)	2(1)
μ (mm^{-1})	13.494	13.80	13.949
λ (Å)	0.71073	0.71073	0.71073
solution method	direct methods	direct methods	direct methods
data/restr/params	1209/0/76	1175/0/77	1663/0/83
R, R_w (on F^2)	0.0374, 0.0635	0.0376, 0.0813	0.0252, 0.0408

[a] See reference 9a, main text.

Theoretical Calculations

Unrestricted BS-DFT[8] calculations on the exchange energies in **1a** (J_{π}, $J_{1\text{-}4}$) were performed using the range of functionals listed in the text and the split-valence triple-ξ quality 6-311G(d,p) basis set, as contained in the Gaussian 16W suite of programs.[9] Tight convergence criteria were employed, and atomic coordinates were taken from crystallographic data collected at 296 K, 100 K and 2 K. The magnitude and sign of exchange energies were based on the isotropic Heisenberg Hamiltonian $H_{ex} = -2J_{ij}\ \{S_i \cdot S_j\}$ for interacting pairs (i,j) of radicals and were computed (from eq. 2, main text) using single-point energies of the triplet E_{TS} and broken symmetry singlet E_{BSS} states and their respective $\langle S^2 \rangle$ expectation values. A full listing of all (J_{π}, $J_{1\text{-}4}$) values is provided in Table S2, with details of individual calculations given in Tables S3-S5. The model 1D calculations (Fig. 2a, main text) of J_{π} as a function of the π-stack slippage were performed using coordinates of a model **1** ($R_1 = R_2 = H$) obtained from a UB3LYP/6-31G(d,p) optimization in C_{2v} symmetry.

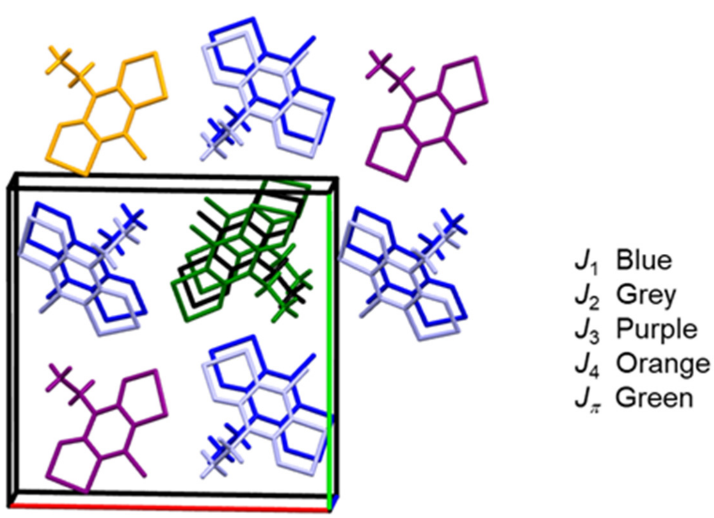

Fig. S1. Color coded pattern of pairwise exchange interactions $J_{1\text{-}4}$ and J_{π}, all referenced to a single radical (black). The total number of pairwise interactions $zJ = 4J_1 + 4J_2 + 2J_3 + J_4 + 2J_{\pi}$.

Table S2. Summary of all BS-DFT Exchange Energies for **1a**.

Functional	T (K)	J_1 (cm^{-1})	J_2 (cm^{-1})	J_3 (cm^{-1})	J_4 (cm^{-1})	J_π (cm^{-1})	Θ (K)[a]
B3LYP	296	4.92	0.13	-0.64	-0.18	-6.97	3.5
	100	5.64	0.15	-0.57	-0.22	-7.75	4.5
	2	5.55	-0.29	-0.81	-0.20	-1.57	11.6
PBE0	296	5.14	0.83	-0.46	-0.11	-4.11	10.5
	100	5.86	0.94	-0.37	-0.15	-4.59	12.3
	2	5.77	0.55	-0.57	-0.13	1.16	18.9
CAM-B3LYP	296	2.90	1.32	-0.33	-0.20	1.23	13.3
	100	3.36	1.45	-0.31	-0.22	1.40	15.2
	2	3.34	1.29	-0.46	-0.22	5.54	20.5
ωB97XD	296	3.16	1.56	-0.31	-0.15	2.27	16.3
	100	3.56	2.04	-0.31	-0.18	3.35	20.4
	2	3.51	2.06	-0.44	-0.18	5.87	23.7
LC-ωHPBE	296	2.15	1.29	-0.24	-0.18	4.49	15.9
	100	2.50	1.47	-0.20	-0.22	5.13	18.4
	2	2.48	1.36	-0.29	-0.20	8.77	23.1

[a] Estimated from mean field approximation as $\Theta = 0.5\ zJ/k_B$, where $zJ = 4J_1 + 4J_2 + 2J_3 + J_4 + 2J_\pi$ (derived from the connectivity pattern shown in Fig. S1).

Table S2. BS-DFT Exchange Energies for **1a** at 296 K.

UB3LYP/6-311G(d,p)

Dimer	Triplet (H)	$<S^2>_{TS}$	BS Singlet (H)	$<S^2>_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-21000.87832080	2.0517	-21000.87829840	1.0516	4.916	7.073
J_2 (d_2)	-21000.87824180	2.0520	-21000.87824120	1.0510	0.132	0.189
J_3 (d_3)	-21000.87817700	2.0526	-21000.87817990	1.0524	-0.636	-0.916
J_4 (d_4)	-21000.87786390	2.0529	-21000.87786470	1.0529	-0.176	-0.253
J_π (δ)	-21000.87247790	2.0522	-21000.87250980	1.0479	-6.971	-10.030

Θ(calc) = 0.5 *zJ (calc) = 3.5 K

UPBE1PBE/6-311G(d,p)

Dimer	Triplet (H)	$<S^2>_{TS}$	BS Singlet (H)	$<S^2>_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-20997.03393340	2.0732	-20997.03391000	1.0731	5.135	7.389
J_2 (d_2)	-20997.03440010	2.0734	-20997.03439630	1.0728	0.834	1.199
J_3 (d_3)	-20997.03171050	2.0744	-20997.03171260	1.0742	-0.461	-0.663
J_4 (d_4)	-20997.03120790	2.0747	-20997.03120840	1.0747	-0.110	-0.158
J_π (δ)	-20997.03434940	2.0740	-20997.03436820	1.0705	-4.112	-5.916

Θ(calc) = 0.5 *zJ (calc) = 10.5 K

UCAM-B3LYP/6-311G(d,p)

Dimer	Triplet (H)	$<S^2>_{TS}$	BS Singlet (H)	$<S^2>_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-21001.14138450	2.1405	-21001.14137130	1.1404	2.897	4.168
J_2 (d_2)	-21001.14210210	2.1401	-21001.14209610	1.1399	1.317	1.894
J_3 (d_3)	-21001.14053320	2.1419	-21001.14053470	1.1418	-0.329	-0.474
J_4 (d_4)	-21001.14016010	2.1425	-21001.14016100	1.1425	-0.198	-0.284
J_π (δ)	-21001.14153680	2.1414	-21001.14153120	1.1398	1.227	1.766

Θ(calc) = 0.5 *zJ (calc) = 13.3 K

UωB97XD/6-311G(d,p)

Dimer	Triplet (H)	$<S^2>_{TS}$	BS Singlet (H)	$<S^2>_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-21000.74575930	2.1732	-21000.74574440	1.1371	3.156	4.541
J_2 (d_2)	-21000.74659090	2.1367	-21000.74658380	1.1364	1.558	2.241
J_3 (d_3)	-21000.74053660	2.1384	-21000.74053800	1.1384	-0.307	-0.442
J_4 (d_4)	-21000.73999030	2.1391	-21000.73999100	1.1391	-0.154	-0.221
J_π (δ)	-21000.76727650	2.1340	-21000.76726620	1.1367	2.267	3.261

Θ(calc) = 0.5 *zJ (calc) = 16.3 K

ULC-ωHPBE/6-311G(d,p)

Dimer	Triplet (H)	$<S^2>_{TS}$	BS Singlet (H)	$<S^2>_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-20997.01700740	2.2409	-20997.01699760	1.2408	2.151	3.094
J_2 (d_2)	-20997.01802740	2.2400	-20997.01802150	1.2398	1.295	1.863
J_3 (d_3)	-20997.01631850	2.2424	-20997.01631960	1.2424	-0.241	-0.347
J_4 (d_4)	-20997.01619280	2.2432	-20997.01619360	1.2443	-0.176	-0.253
J_π (δ)	-20997.02064050	2.2424	-20997.02062000	1.2413	4.494	6.466

Θ(calc) = 0.5 *zJ (calc) = 15.9 K

Table S3. BS-DFT Exchange Energies for **1a** at 100 K.

UB3LYP/6-311G(d,p)

Dimer	Triplet (H)	$\langle S^2 \rangle_{TS}$	BS Singlet (H)	$\langle S^2 \rangle_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-21000.88965690	2.0499	-21000.88963120	1.0498	5.640	8.115
J_2 (d_2)	-21000.88941510	2.0502	-21000.88941440	1.0492	0.153	0.221
J_3 (d_3)	-21000.88989670	2.0508	-21000.88989930	1.0506	-0.571	-0.821
J_4 (d_4)	-21000.88961430	2.0511	-21000.88961530	1.0511	-0.219	-0.316
J_π (δ)	-21000.88311080	2.0504	-21000.88314630	1.0455	-7.753	-11.156
			Θ(calc) = 0.5 *zJ (calc) =		4.5	K

UPBE1PBE/6-311G(d,p)

Dimer	Triplet (H)	$\langle S^2 \rangle_{TS}$	BS Singlet (H)	$\langle S^2 \rangle_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-20997.04509520	2.0706	-20997.04506850	1.0705	5.859	8.430
J_2 (d_2)	-20997.04536720	2.0709	-20997.04536290	1.0702	0.943	1.357
J_3 (d_3)	-20997.04304430	2.0718	-20997.04304600	1.0717	-0.373	-0.537
J_4 (d_4)	-20997.04254760	2.0722	-20997.04254830	1.0722	-0.154	-0.221
J_π (δ)	-20997.04527680	2.0714	-20997.04529780	1.0674	-4.591	-6.605
			Θ(calc) = 0.5 *zJ (calc) =		12.3	K

UCAM-B3LYP/6-311G(d,p)

Dimer	Triplet (H)	$\langle S^2 \rangle_{TS}$	BS Singlet (H)	$\langle S^2 \rangle_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-21001.15237690	2.1349	-21001.15236160	1.1348	3.358	4.831
J_2 (d_2)	-21001.15294230	2.1347	-21001.15293570	1.1344	1.448	2.084
J_3 (d_3)	-21001.15185420	2.1363	-21001.15185560	1.1363	-0.307	-0.442
J_4 (d_4)	-21001.15152740	2.1370	-21001.15152840	1.1370	-0.219	-0.316
J_π (δ)	-21001.15225050	2.1358	-21001.15224410	1.1340	1.402	2.017
			Θ(calc) = 0.5 *zJ (calc) =		15.2	K

UωB97XD/6-311G(d,p)

Dimer	Triplet (H)	$\langle S^2 \rangle_{TS}$	BS Singlet (H)	$\langle S^2 \rangle_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-21000.75720430	2.1319	-21000.75718810	1.1318	3.555	5.115
J_2 (d_2)	-21000.75777690	2.1315	-21000.75776760	1.1312	2.041	2.936
J_3 (d_3)	-21000.75216240	2.1331	-21000.75216380	1.1331	-0.307	-0.442
J_4 (d_4)	-21000.75163540	2.1338	-21000.75163620	1.1339	-0.176	-0.253
J_π (δ)	-21000.77932000	2.1328	-21000.77930470	1.1310	3.352	4.823
			Θ(calc) = 0.5 *zJ (calc) =		20.4	K

ULC-ωHPBE/6-311G(d,p)

Dimer	Triplet (H)	$\langle S^2 \rangle_{TS}$	BS Singlet (H)	$\langle S^2 \rangle_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-20997.02815530	2.2312	-20997.02814390	1.2311	2.502	3.600
J_2 (d_2)	-20997.02903730	2.2304	-20997.02903060	1.2302	1.470	2.115
J_3 (d_3)	-20997.02770920	2.2327	-20997.02771010	1.2327	-0.198	-0.284
J_4 (d_4)	-20997.02761370	2.2336	-20997.02761470	1.2336	-0.219	-0.316
J_π (δ)	-20997.03186820	2.2325	-20997.03184480	1.2313	5.130	7.380
			Θ(calc) = 0.5 *zJ (calc) =		18.4	K

Table S4. BS-DFT Exchange Energies for **1a** at 2 K.

UB3LYP/6-311G(d,p)

Dimer	Triplet (H)	$\langle S^2\rangle_{TS}$	BS Singlet (H)	$\langle S^2\rangle_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-21000.90607280	2.0497	-21000.90604750	1.0496	5.552	7.988
J_2 (d_2)	-21000.90597940	2.0500	-21000.90598070	1.0489	-0.285	-0.410
J_3 (d_3)	-21000.90642880	2.0507	-21000.90643250	1.0504	-0.812	-1.168
J_4 (d_4)	-21000.90613490	2.0509	-21000.90613580	1.0509	-0.198	-0.284
J_p (d)	-21000.89838850	2.0502	-21000.89839570	1.0466	-1.575	-2.265

Θ(calc) = 0.5 *zJ (calc) = 11.6 K

UPBE1PBE/6-311G(d,p)

Dimer	Triplet (H)	$\langle S^2\rangle_{TS}$	BS Singlet (H)	$\langle S^2\rangle_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-20997.06131230	2.0702	-20997.06128600	1.0701	5.772	8.304
J_2 (d_2)	-20997.06172010	2.0705	-20997.06171760	1.0698	0.548	0.789
J_3 (d_3)	-20997.05930900	2.0715	-20997.05931160	1.0713	-0.571	-0.821
J_4 (d_4)	-20997.05880750	2.0718	-20997.05880810	1.0718	-0.132	-0.189
J_p (d)	-20997.06084650	2.0710	-20997.06084120	1.0680	1.160	1.669

Θ(calc) = 0.5 *zJ (calc) = 18.9 K

UCAM-B3LYP/6-311G(d,p)

Dimer	Triplet (H)	$\langle S^2\rangle_{TS}$	BS Singlet (H)	$\langle S^2\rangle_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-21001.16791440	2.1344	-21001.16789920	1.1343	3.336	4.799
J_2 (d_2)	-21001.16863150	2.1342	-21001.16862560	1.1339	1.295	1.863
J_3 (d_3)	-21001.16750050	2.1359	-21001.16750260	1.1359	-0.461	-0.663
J_4 (d_4)	-21001.16717730	2.1366	-21001.16717830	1.1366	-0.219	-0.316
J_p (d)	-21001.16705470	2.1353	-21001.16702940	1.1338	5.544	7.977

Θ(calc) = 0.5 *zJ (calc) = 20.5 K

UωB97XD/6-311G(d,p)

Dimer	Triplet (H)	$\langle S^2\rangle_{TS}$	BS Singlet (H)	$\langle S^2\rangle_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-21000.77274120	2.1313	-21000.77272520	1.1312	3.511	5.052
J_2 (d_2)	-21000.77345840	2.1308	-21000.77344900	1.1305	2.062	2.967
J_3 (d_3)	-21000.76780510	2.1326	-21000.76780710	1.1326	-0.439	-0.632
J_4 (d_4)	-21000.76728410	2.1334	-21000.76728490	1.1334	-0.176	-0.253
J_p (d)	-21000.79491280	2.1323	-21000.79488600	1.1308	5.873	8.450

Θ(calc) = 0.5 *zJ (calc) = 23.7 K

ULC-ωHPBE/6-311G(d,p)

Dimer	Triplet (H)	$\langle S^2\rangle_{TS}$	BS Singlet (H)	$\langle S^2\rangle_{BSS}$	J (cm^{-1})	J (K)
J_1 (d_1)	-20997.04280840	2.2299	-20997.04279710	1.2298	2.480	3.568
J_2 (d_2)	-20997.04384530	2.2290	-20997.04383910	1.2288	1.360	1.957
J_3 (d_3)	-20997.04247370	2.2315	-20997.04247500	1.2315	-0.285	-0.411
J_4 (d_4)	-20997.04235780	2.2324	-20997.04235870	1.2325	-0.198	-0.284
J_p (d)	-20997.04609440	2.2313	-20997.04605440	1.2301	8.768	12.616

Θ(calc) = 0.5 *zJ (calc) = 23.1 K

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