Supplementary Information
for

Slow magnetization dynamics in a six-coordinate Fe(II)-radical complex

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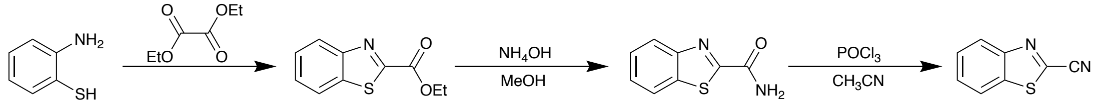
SYNTHESIS OF ORGANIC STARTING MATERIALS



Scheme S1. Synthetic strategy for 2-cyanobenzothiazole (**betaCN**)

Ethyl 2-benzothiazolecarboxylate. A liquid mixture of 2-aminothiophenol (10 mL, 97 mmol) and excess diethyl oxalate (25 mL, 184 mmol) was heated to reflux for 4 hours. Upon cooling, the yellow-green solution was added to 2.4 M HCl (125 mL) and stirred at room temperature for 12 hours. The resulting white precipitate was collected by vacuum filtration and washed with cold deionized water (100 mL). Yield 9.73 g (51%). FTIR (KBr, cm^{-1}): 3063 (w), 2973 (w), 2941 (w), 1750 (s), 1552 (w), 1498 (s), 1485 (w), 1457 (w), 1361 (w), 1316 (m), 1289 (s), 1257 (s), 1227 (s), 1163 (w), 1098 (m), 1050 (w), 1013 (m), 892 (w), 855 (m), 807 (m), 758 (s), 723 (s), 431 (m). ^1H NMR δ_H (300 MHz; DMSO-d_6): 8.24 (m, 2H), 7.65 (m, 2H), 4.44 (2H, q), 1.37 (3H, t) ppm.

Benzothiazole-2-carboxamide. Excess concentrated ammonium hydroxide (9 mL) was added to a solution of ethyl 2-benzothiazolecarboxylate (1.45 g, 6.97 mmol) in methanol (20 mL), immediately producing a white precipitate. The solution was stirred at room temperature for 10 minutes, then the white powder was collected by vacuum filtration and washed with water (50 mL). Yield 1.12 g (90%). FTIR (KBr): 3320 (m), 3223 (m), 1696 (m), 1664 (s), 1619 (m), 1587 (w), 1508 (w), 1457 (w), 1407 (m), 1312 (m), 1117 (m), 1086 (w), 1049 (w), 763 (m), 754 (m), 721 (m), 685 (w), 582 (m). ^1H NMR δ_H (300 MHz; DMSO-d_6): 8.47 (s, 1H), 8.16 (m, 2H), 8.06 (s, 1H), 7.59 (m, 2H) ppm.

2-Cyanobenzothiazole. Phosphorus oxychloride (10 mL, 40 mmol) was added to a slurry of benzothiazole-2-carboxamide (1.12 g, 6.29 mmol) in anhydrous acetonitrile (20 mL). The mixture was refluxed for 3 hours, resulting in a brown solution. Solvent and excess phosphorus oxychloride were removed *in vacuo* to afford a beige residue. The residue was extracted with ethyl acetate (300 mL) and the solution was subsequently washed with water (3x100 mL). The organic layer was dried over magnesium sulfate, then the solvent removed *in vacuo* to produce yellow microcrystalline material. The product was purified by dynamic sublimation (10^{-2} Torr) at 60 °C to yield white crystals; Yield 0.78 g (77%). FTIR (KBr): 3066 (w), 2964 (w), 2230 (s), 1719 (w), 1655 (w), 1629 (w), 1560 (w), 1550 (m), 1499 (w), 1468 (s), 1456 (s), 1421 (m), 1318 (m), 1261 (m), 1242 (m), 1242 (w), 1201 (w), 1149 (m), 1134 (s), 1041 (m), 952 (w), 874 (m), 801 (m), 763 (s), 727 (s), 703 (w), 617 (w), 541 (w), 498 (w), 447 (w). ^1H NMR δ_H (300 MHz; $CDCl_3$): 8.22 (m, 1H), 7.98 (m, 1H), 7.63 (m, 2H) ppm.

CRYSTALLOGRAPHIC DETAILS

BetaDTDA: The crystals of the ligand were grown by sublimation. The crystals were coated with type NVH immersion oil and mounted on Mitegen micromount holders. Six crystals were preliminary tested, all showing the presence of a non-merohedral twin component. Finally, a full data set was collected for a dark-brown prism. All measurements were conducted at 150 K on a SuperNova single-crystal diffractometer equipped with a microfocus MoK_α radiation source (λ = 0.71073 Å), Atlas CCD detector and a CryoJet low temperature device (Guelph, Chemistry Department X-Ray Facility).

Diffraction intensity data were collected to 67.30° (2θ) using ω-scan technique. The unit cell parameters were refined using the entire data set. The data were processed with CrysAlisPro software[1] using two superimposed matrices related by ~180° rotation around the [001] direction. The ratio of twin components was 0.69:0.31 and the fraction of overlapped reflections was 25.6%. The best solution was achieved with the HKLF 4 file generated for the major twin component, and these data are reported here. Absorption corrections were applied using the multiscan method. The structure was solved (direct methods) and refined (full-matrix least-squares on F^2) using SHELXS[2] and SHELXL-2013.[3] All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were included in calculated positions with U_{iso} tied to the carrier atom. Data collection and refinement details are listed in Table S1 and select intermolecular contact distances are listed in Table S2. Full crystallographic data and experimental details have been deposited with the Cambridge Crystallographic Data Centre in CIF format.

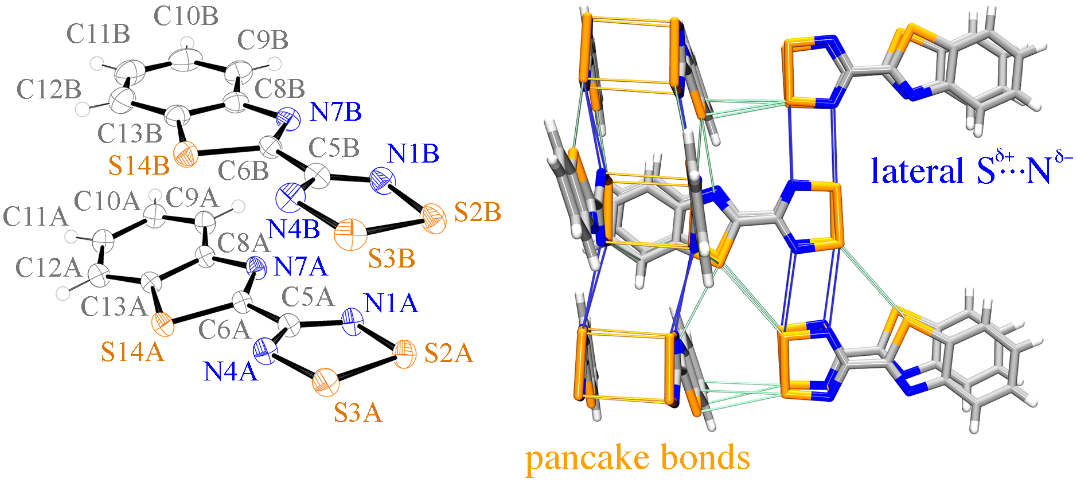


Figure S1. Excerpts from the crystal structure of **betaDTDA** illustrating (left) an ORTEP representation of the pancake bonded dimer (anisotropic thermal ellipsoids at 50% probability) and (right) the dense network of intermolecular contacts, oriented to highlight the pancake bonding and lateral Coulombic interactions; colour code: H, white; C, grey; N, blue; S, yellow.

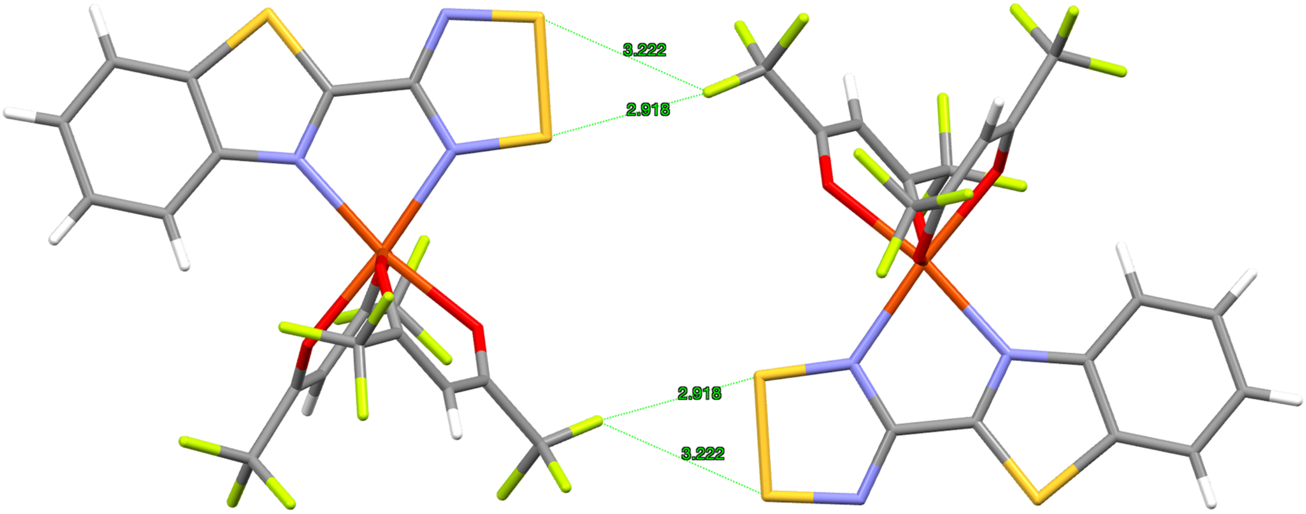


Figure S2. Excerpt from the crystal structure of **Fe(hfac)$_2$(betaDTDA)** illustrating the CF_3…S-S contacts between molecules in neighbouring π-stacks; distances in Ångstroms; colour code: H, white; C, grey; N, blue; S, yellow; O, red; F, green; Fe, rust.

Table S1. Summary of Crystallographic Data for betaDTDA and Fe(hfac)$_2$(betaDTDA)

	betaDTDA	**Fe(hfac)$_2$(betaDTDA)**
Formula	$C_8H_4N_3S_3$	$C_{18}H_6F_{12}FeN_3O_4S_3$
Formula weight, g/mol	238.32	708.29
Crystal dimensions, mm	0.25 × 0.20 × 0.15	0.53 × 0.10 × 0.02
Crystal color and habit	dark-brown prism	red plate
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Temperature, K	150	150
a, Å	9.7286(3)	17.183(2)
b, Å	17.2405(4)	16.421(3)
c, Å	10.7173(3)	8.8532(14)
β,°	92.114(3)	93.124(5)
V, Å^3	1796.35(8)	2494.4(7)
Min & max 2θ for cell determination, °	3.97, 33.69	4.74, 49.94
Index ranges	$-15 \leq h \leq 15$, $-26 \leq k \leq 26$, $-16 \leq l \leq 16$	$0 \leq h \leq 20$, $0 \leq k \leq 19$, $0 \leq l \leq 10$
Z	8	4
$F(000)$	968	1396
Absorption coefficient (mm^{-1})	0.779	0.979
ρ, g/cm	1.762	1.886
λ, Å	0.71073 (MoKα)	0.71073 (MoKα)
Diffractometer type	Rigaku SuperNova	Bruker Kappa Axis Apex2
Scan type(s)	omega scans	phi and omega scans
Completeness to theta = °	33.769, 82.1%	25.045, 87.6%
Number of reflections measured	27775	4485
Unique reflections measured	5909	4485
R_{int}	0.0650	0.0752
Number of reflections included in refinement	5909	4485
Cutoff threshold expression	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Absorption correction	multi-scan	multi-scan
Refinement method	full matrix least-squares using F^2	full matrix least-squares using F^2
Weighting scheme	$w = 1/[\sigma^2(F_O^2) + (0.0749P)^2 + 3.35P]$, where $P = (F_O^2 + 2F_C^2)/3$	$w = 1/[\sigma^2(F_O^2) + (0.0754P)^2]$ where $P = (F_O^2 + 2F_C^2)/3$
Data / restraints / parameters	5909 / 0 / 253	4485 / 429 / 381
R_1	0.0629	0.0549
wR_2	0.1621	0.1240
R_1 (all data)	0.0826	0.0993
wR_2 (all data)	0.1691	0.1381
GOF on F^2	1.067	1.046
Maximum shift/error	0.001	0.000
Min & max peak heights on final ΔF map, e^-/Å	-0.540, 0.659	-0.491, 0.406
CCDC deposition #	1895351	1886640

Where: $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma F_o$; $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{½}$; $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(\text{No. of reflns.} - \text{No. of params.})]^{½}$

Fe(hfac)$_2$(betaDTDA):

Data Collection and Processing. The sample was mounted on a Mitegen polyimide micromount with a small amount of Paratone N oil. All X-ray measurements were made on a Bruker Kappa Axis Apex2 diffractometer at a temperature of 150 K. The crystal was weakly diffracting and exhibited non-merohedral twinning (see below). The unit cell dimensions were determined from a symmetry constrained fit of 9371 reflections with $4.74° < 2\theta < 49.94°$. The data collection strategy used a number of ω and φ scans which collected data up to 50.09° (2θ). The frame integration was performed using SAINT.[4] The resulting raw data were scaled and absorption corrected by applying a multi-scan averaging of symmetry equivalent data using SADABS.[5]

Analysis of Twinning. Two individuals were able to be indexed from the initial set of scans. The orientations of the two sets of unit cell basis vectors is given as follows:

```
===============================================================================
Solution number :   1
---------------------
New Cell: a=17.1841 b=16.4208 c=8.8542 alpha=90.000 beta=93.130 gamma=90.000

Figure of Merit (0=ideal)          :   0.01
Rotation angle  (degrees)          : 179.976
Rotation vector (laboratory)       :   0.9973  0.0327  0.0651
Rotation vector (reciprocal cell)  :  -1.00    0.00    0.00
Rotation vector (direct cell)      : -19.00    0.00   -1.99

Superposition matrix               : H' = +1.000 * H            +0.210 * L
                                     K' =            -1.000 * K -0.001 * L
                                     L' = -0.001 * H            -1.000 * L
===============================================================================
```

During data reduction, the twin law was calculated to be:

```
Twin Law, Sample 1 of 1
   Transforms h1.1(1)->h1.2(2)
     1.00006 -0.00050  0.20934
    -0.00044 -1.00000 -0.00073
    -0.00059  0.00020 -1.00006
```

Structure Solution and Refinement. The structure was solved by using a dual space methodology using the SHELXT program.[3] All non-hydrogen atoms were obtained from the initial solution. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The relative amount of the minor individual was refined during the least-squares procedure and converged to a value of 0.4072(15). One of the CF_3 groups exhibited a disorder over 2 orientations for the F atom positions. The normalized occupancy for the dominant conformer refined to a value of 0.649(8). The structural model was fit to the data using full matrix least-squares based on F^2 The calculated structure factors included corrections for anomalous dispersion from the usual tabulation. The structure was refined using the SHELXL program from the SHELX suite of crystallographic software.[3] Graphic plots were produced using the NRCVAX program suite.[6]

Table S2. Select intra- and inter-molecular distances from the crystal structures of betaDTDA and Fe(hfac)$_2$(betaDTDA)

betaDTDA	**Fe(hfac)$_2$(betaDTDA)**
Characteristic DTDA measures	
S – S bond distance within each thiazyl ring: S2A – S3A 2.098(1) Å S2B – S3B 2.103(1) Å	*S – S bond distance within the thiazyl ring*: S2 – S3 2.090(2) Å
Dihedral angle between planes defined by the atoms of the benzthiazole and the DTDA rings: 16.43(7)° and 10.79(8)°	*Dihedral angle between planes defined by the atoms of the benzthiazole and the DTDA rings*: 5.5(2)°
Intermolecular S – S distance within a pancake bond: S3A – S3B 3.071(1) Å S2A – S2B 2.954(1) Å	N/A
Select intermolecular contact distances	
Lateral contacts illustrated with blue lines in Fig. S1: S3A – N4B 3.365(3) Å S3B – N4A 3.253(3) Å	*S···O contacts*: O21 – S14 3.151(1) Å *S···F contacts*: S2 – F24 2.918(2) Å S3 – F24 3.222(2) Å

Table S3. Bond lengths and angles characterizing the coordination environment of the *hs*-Fe(II) center in Fe(hfac)$_2$(betaDTDA)

Bond lengths (Å)	
Fe1 – N1	2.172(5)
Fe1 – N7	2.199(6)
Fe1 – O21	2.058(5)
Fe1 – O25	2.112(5)
Fe1 – O31	2.062(5)
Fe1 – O35	2.033(5)
Bond angles (°)	
N1 – Fe1 – N7	76.5(2)
N7 – Fe1 – O31	98.6(2)
O31 – Fe1 – O25	90.89(18)
O25 – Fe1 – N1	93.98(19)
O35 – Fe1 – N1	93.18(19)
O35 – Fe1 – N7	95.07(18)
O35 – Fe1 – O31	86.85(19)
O35 – Fe1 – O25	88.90(18)
O21 – Fe1 – N1	93.54(18)
O21 – Fe1 – N7	92.47(18)
O21 – Fe1 – O31	86.98(19)
O21 – Fe1 – O25	84.51(170

ADDITIONAL MAGNET DETAILS

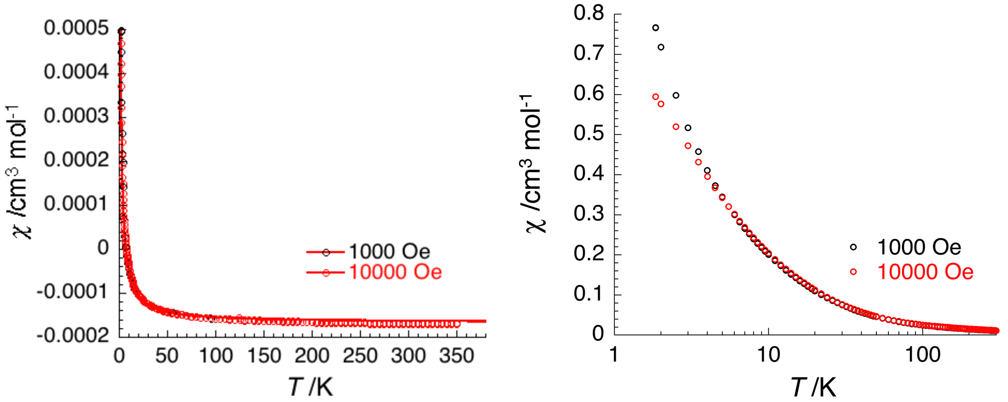


Figure S3. Temperature dependence of the magnetic susceptibility, χ (being calculated from the ratio between the measured magnetization normalized per mole, M, and the applied magnetic field, H) measured for a polycrystalline sample of **betaDTDA** (left) and **Fe(hfac)$_2$(betaDTDA)** (right) at 0.1 (black points) and 1.0 T (red points). Left: The Curie Law fit to each set of experimental data (shown as solid red lines) support the conclusion that **betaDTDA** is diamagnetic with a susceptibility of -1.7 × 10^{-4} cm^3/mol, consistent with the theoretical value of -1.2 × 10^{-4} cm^3/mol calculated from the molecular weight (MW; χ = -MW/2 × 10^{-4} cm^3/mol). A minor (0.32%) S = ½ Curie impurity is observed at low temperature, consistent with crystal packing defects in pancake-bonded radical systems. The magnetic data indicate that radicals form diamagnetic pancake-bonded dimers throughout the measured temperature range.

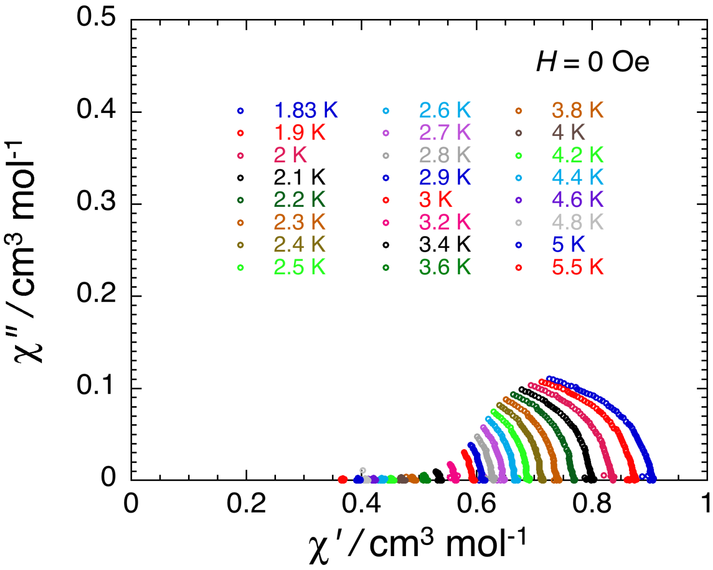


Figure S4. Cole-Cole plot of **Fe(hfac)$_2$(betaDTDA)** in zero-dc field for ac frequencies ranging from 10 to 10000 Hz, an ac-field of 1 to 10 Oe and for temperatures ranging between 1.83 and 5.5 K. This plot demonstrates that the relaxation mode is not of Debye nature (for which a semi-circle is expected).

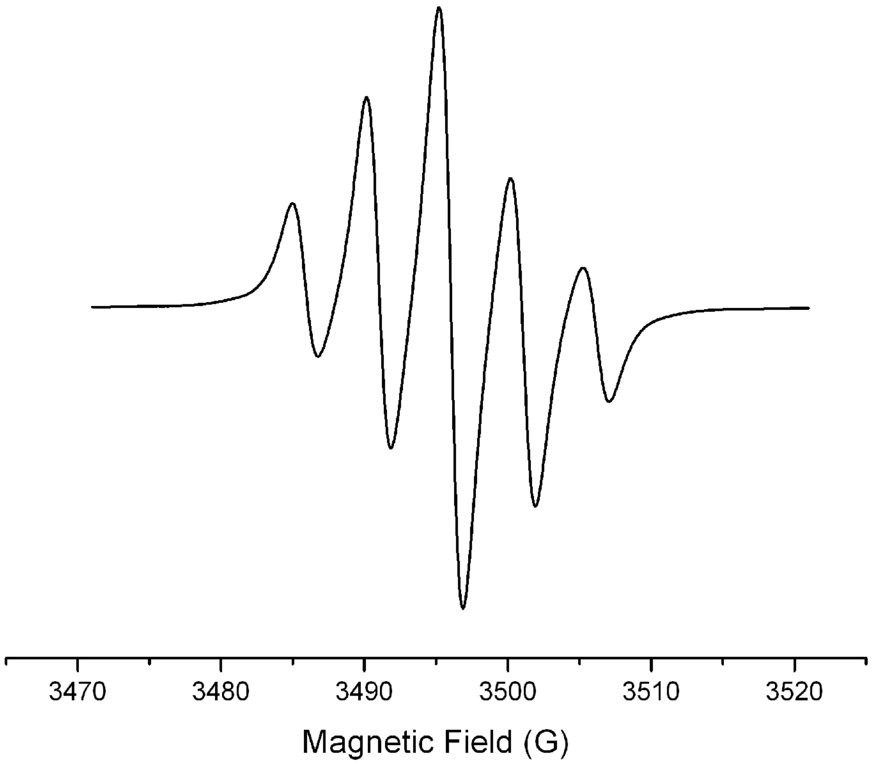


Figure S5. EPR spectrum of **betaDTDA** in toluene at ambient temperature; $a_N = 5.026$ G, $g = 2.010$.

REFERENCES:

[1] *CrysAlisPro Software*, *Version 1.171.35.8*; Agilent Technologies; 2011.
[2] G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *54*, 112-122.
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