

Supporting Information

Effects of Spiro-Cyclohexane Substitution of Nitroxyl Biradicals on Dynamic Nuclear Polarization

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X-ray crystallography

XRD data were obtained at room temperature on a Bruker Kappa Apex II CCD diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) and a graphite monochromator. Absorption corrections were applied empirically using *SADABS* programs [1]. The structures were solved by direct methods using the *SHELX-97* [2] programs set and refined by full-matrix least-squares method against all F^2 in anisotropic (beside the atoms H) approximation using the *SHELXL2014/7* programs set [3]. The H atoms positions were calculated with the riding model. The asymmetric unit contains also molecule of chloroform. The obtained crystal structure geometry and short contacts between non-bonded atoms were analyzed using the *PLATON* program [4].

Crystal solvate of diradical **4** is triclinic, space group P-1, a 12.4262(5), b 13.3902(5), c 13.7759(6) \AA , α 67.121(2), β 67.676(2), γ 77.066(2) $^\circ$, V 1945.7(1) \AA^3 , Z 2, $C_{41}H_{51}C_{13}N_6O_2Fe$, D_c 1.333 g/cm^3 , μ 0.638 mm^{-1} , $F(000)$ 864, crystal size 0.20 \times 0.06 \times 0.05 mm^3 , independent reflections 8868, R 0.0973, R_2 0.2002 for, S 1.028 for all reflections (R 0.0657, wR_2 0.1767 for 6296 $I > 2\sigma$), largest difference peak and hole 1.769 and -1.412 e.\AA^{-3} .

CCDC 2168987 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk

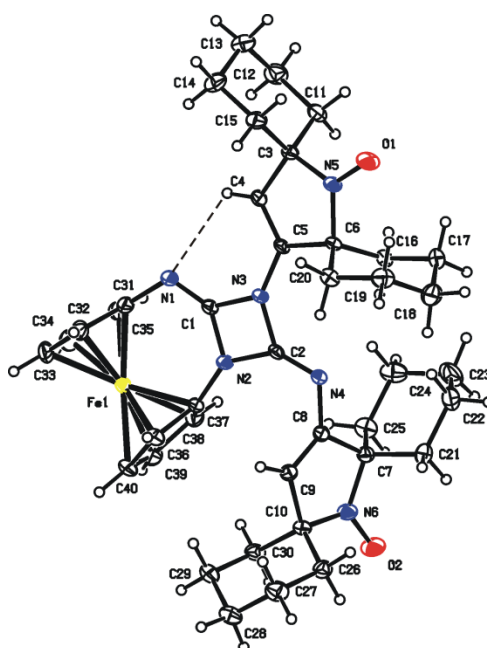


Figure S1. Molecular structure of diradical **4** with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Intermolecular short contact Cl3...O2 equaling to 3.067(3) Å is observed in solvate of **4** (sum of VDW radii [5] is 3.34 Å) (Figure S2). Solvates are bound through H-bond C1S-H...N1 (Table 3) between chloroform and 2,4-diimino-1,3-diazetidino moiety into chains directed along the (*b-c*). The chains, in turn, are formally bound *via* C40-H...O1 h-bond in (*b, c*) plain and then *via* C32-H...O1 and C38-H...O2 h-bonds along axis *a* into 3D-structure.

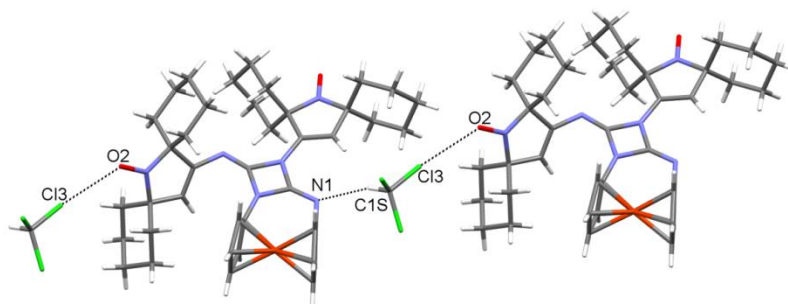


Figure S2. Fragment of molecular chain directed along (*b-c*).

Table S1. Intermolecular hydrogen bonds in crystals of diradical **4** solvate.

| | H...O, Å | C...O, Å | C-H...O, ° |
|------------|----------|----------|------------|
| C1S-H...N1 | 2.59 | 3.536(6) | 161 |
| C32-H...O1 | 2.59 | 3.485(6) | 163 |
| C40-H...O1 | 2.51 | 3.274(5) | 140 |
| C38-H...O2 | 2.61 | 3.403(5) | 144 |

References

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