Electronic Supplementary Material (ESI) for ChemComm.
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Diferrocenyl tosyl hydrazone with an ultrastrong NH···Fe hydrogen bond as double click switch

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Supporting Information

General Procedures

All reactions were performed under argon atmosphere unless otherwise noted. Toluene was distilled from potassium. Diferrocenylketone **1** was prepared according to a literature procedure.[1] Filtrations from precipitated silver after oxidation were performed with syringe filters (Rotilabo-Spritzenfilter, Ø = 25 mm, pore size = 0.20 µm; Carl Roth GmbH + Co. KG, Germany). NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 400.31 MHz (^{1}H) and 100.66 MHz (^{13}C{^{1}H}). All resonances are reported in ppm versus the solvent signal as internal standard [$CDCl_3$ (^{1}H: δ = 7.24; ^{13}C: δ = 77.0 ppm), d_6-DMSO (^{1}H: δ = 2.49 ppm), C_6D_6 (^{1}H: δ = 7.20 ppm)]. IR spectra were recorded with a BioRad Excalibur FTS 3100 spectrometer as KBr disks or in solution in KBr cells. Electrochemical experiments were carried out on a BioLogic SP-50 voltammetric analyzer using platinum wires as counter and working electrodes and a 0.01 M $Ag/AgNO_3$ electrode as reference electrode. The cyclic voltammetry measurements were carried out at scan rate of 50–100 mV s^{-1} using 0.1 M (nBu$_4$N)(B(C_6F_5)$_4$) as supporting electrolytes in CH_2Cl_2. Potentials are referenced to the ferrocene/ferrocenium couple ($E_{½}$ = 250 ± 5 mV under the experimental conditions). UV/Vis/NIR spectra were recorded on a Varian Cary 5000 spectrometer using 1.0 cm cells (Hellma, suprasil). FD mass spectra were recorded on a FD Finnigan MAT90 spectrometer. ^{57}Fe Mößbauer measurements of powder samples were performed in transmission geometry using a constant-acceleration spectrometer and the source ^{57}Co(Rh). The Recoil 1.03 Mössbauer Analysis Software was used to fit the experimental spectra with Lorentzian peaks.[2] Isomer shift values are quoted relative to α-Fe at 293 K.

X-ray structure determinations

Intensity data were collected with a Bruker AXS Smart 1000 CCD diffractometer with an APEX II detector and an Oxford cooling system and corrected for absorption and other effects using Mo K_α radiation (λ = 0.71073 Å) at 173(2) K. The diffraction frames were integrated using the SAINT package, and most were corrected for absorption with MULABS.[3,4] The structure was solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXTL software package.[5,6] All non-hydrogen atoms were refined anisotropically, while the positions of carbon bonded hydrogen atoms were generated with appropriate geometric constraints and allowed to ride on their respective parent atoms with fixed isotropic thermal parameters. The nitrogen bonded hydrogen atom was located in the Fourier map and refined with a fixed N-H distance of 0.88 Å. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-1031559. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (0.44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk].

Table S1. X-ray crystallographic data of **2**.

empirical formula	$C_{28}H_{26}Fe_2N_2O_2S$
Fw	566.27
cryst syst	monoclinic
space group	$P2_1/c$
a / Å	7.1125(6)
b / Å	11.3143(8)
c / Å	29.525(2)
β / deg	95.838(2)
volume / Å^3	2363.6(3)
Z	4
density (calcd), Mg m^3	1.591
absorp coeff, mm^{-1}	1.346
F(000)	1168.0
cryst size, mm^3	0.46×0.06×0.01
θ range for data collection	2.27 to 27.94
index ranges	$-9 \le h \le 9$
	$-14 \le k \le 11$
	$-36 \le l \le 38$
no. of reflns collected	26075
no. of indep reflns	5663
R_{int}	0.0650
completeness to θ_{max}	99.7
max. / min transmn	0.9867 / 0.5764
goodness-of-fit on F^2	0.913
final R indices [$I > 2\sigma(I)$]]	R_1 = 0.0320
	wR_2 = 0.0649
R indices (all data)	R_1 = 0.0551
	wR_2 = 0.0691
Largest diff peak and hole, e / Å^3	0.434 / –0.330

DFT calculations were carried out with the *Gaussian09*/DFT[7] series of programs. The B3LYP formulation of DFT was used employing the LANL2DZ (Fe) and 6-31G* basis sets (C, H, N, O, S). No symmetry constraints were imposed on the molecules. The presence of energy minima was checked by analytical frequency calculations. The integral-equation-formalism polarisable continuum model (IEFPCM, CH_2Cl_2) was employed for solvent modeling.

Synthesis of 2[8]

A mixture of diferrocenylketone[1] (2.00 g, 5.02 mmol), *p*-toluenesulfonyl hydrazide (1.86 g, 10.0 mmol) and *p*-toluenesulfonic acid (0.02 g, 0.12 mmol) in toluene (70 ml) was heated to reflux for 19 h under an inert atmosphere of argon. The mixture was filtered and the solvent was removed under reduced pressure (without inert atmosphere). Purification via column chromatography (silica, 25 cm × 5.5 cm, dichloromethane, R_f = 0.13) yielded **2** as an orange coloured solid after removing the solvent under reduced pressure. Yield 1.67 g (2.95 mmol, 59%). ^{1}H NMR ($CDCl_3$): δ = 2.44 (s, 3 H, H^1), 3.99 (s, 5 H, H^{15}), 4.19 (s, 5 H, H^{11}), 4.27 (pt, 2 H, $^3J_{HH}$ = 1.68 Hz, H^{14}), 4.50 (pt, 2 H, $^3J_{HH}$ = 1.72 Hz, H^{10}), 4.58 (pt, 2 H, $^3J_{HH}$ = 1.68 Hz, H^{13}), 4.71 (pt, 2 H, $^3J_{HH}$ = 1.72 Hz, H^9), 7.41 (d, 2 H, $^3J_{HH}$ = 8.16 Hz, H^3), 8.01 (d, 2 H, $^3J_{HH}$ = 8.16 Hz, H^4), 10.14 (s, 1 H, H^6) ppm (these data conform to ref. 8). ^{13}C NMR ($CDCl_3$): δ = 21.6 (C^1), 68.5 (C^{13}), 69.4 (C^{15}), 69.5 (C^9), 69.5 (C^{11}), 69.7 (C^{14}), 70.5 (C^{10}), 73.0 (C^8), 82.1 (C^{12}), 128.3 (C^4), 129.4 (C^3), 135.4 (C^5), 144.0 (C^2), 150.5 (C^7) ppm. MS (FD): *m/z* (%) = 565.9 (100) $[M]^+$. IR (KBr): 3101 (s, NH), 1596 (w), 1567 (w), 1480 (w), 1400 (m), 1341 (s), 1321 (m), 1295 (m), 1187 (w), 1165 (vs), 1050 (s), 895 (m), 825 (m), 816 (m), 676 (m), 662 (m), 620 (m), 553 (s), 493 (m), 475 (s) cm^{-1}. UV/vis (CH_2Cl_2): λ_{max} (ε) = 455 (844), 354 (1750), 275 (11900 M^{-1} cm^{-1}) nm. CV (CH_2Cl_2, vs Fc/Fc^+): $E_{1/2}$ = 115 (rev.), 595 (rev.) mV. Mößbauer (293 K): δ = 0.4484 mm s^{-1}; ΔE_Q = 2.300 mm s^{-1}. Mößbauer (90 K): δ = 0.5273 mm s^{-1}; ΔE_Q = 2.3080 mm s^{-1}. Anal. Calcd for $C_{28}H_{26}Fe_2N_2O_2S$ (566.2): C, 59.39; H, 4.63; N, 4.95; S, 5.66. Found: C, 58.91; H, 4.64; N, 4.80; S, 5.72.

Synthesis of ^{D}2.

2 (0.10 g, 0.18 mmol) was stirred in a mixture of dry tetrahydrofuran (5 ml), D_2O (1 ml, 99.96% D) and dry CH_2Cl_2 (4 ml) for 1 h. The solvents were removed under reduced pressure. The degree of deuterium incorporation at the NH group was 70%, estimated via ^{1}H NMR spectroscopy.

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3 *SMART Data Collection and SAINT-Plus Data Processing Software for the SMART System*, various versions; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, *2000*.

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8 K.-Y. Kay, L. H. Kim and I. C. Oh, *Tetrahedron Lett.*, *2000*, **41**, 1397-1400.

Fig. S1. IR spectra of **2** (top) and of N deuterated derivative ^{D}**2** (bottom) as KBr disks.

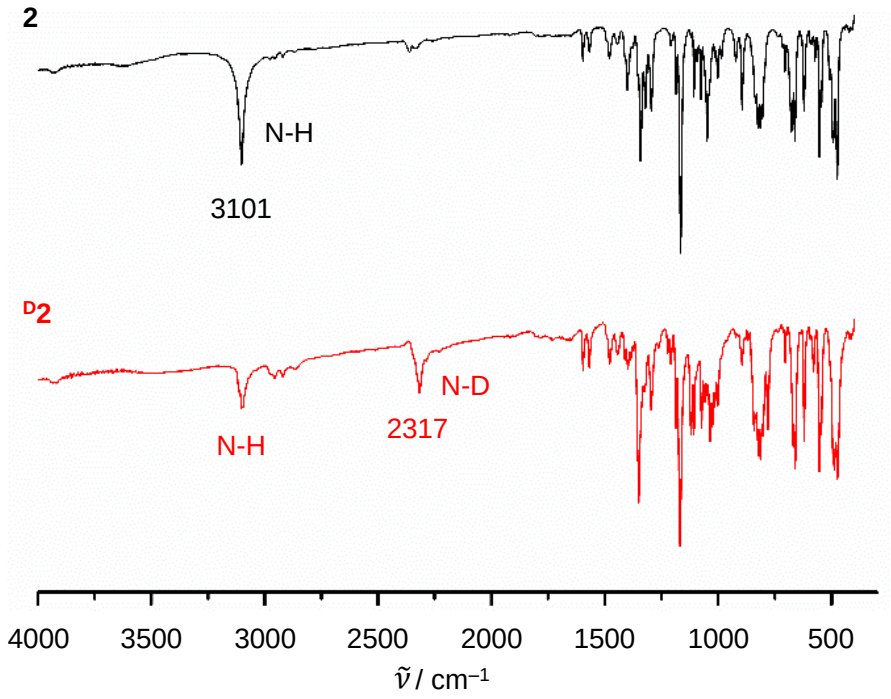


Fig. S2. IR spectrum of **3** as KBr disk.

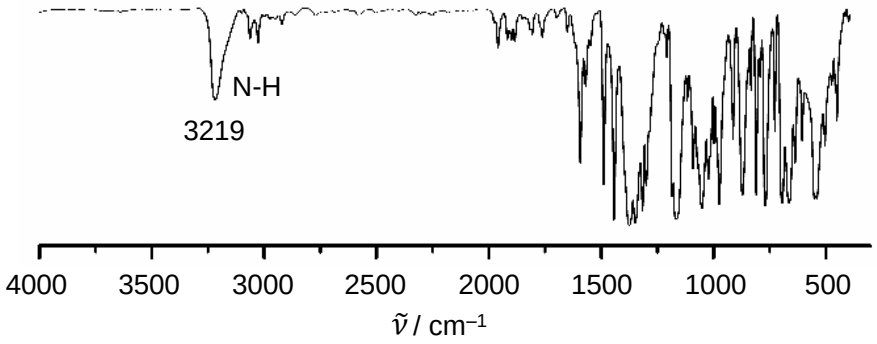


Fig S3. IR spectra of **2** and **3** in CD_2Cl_2 and d_8-THF (NH region).

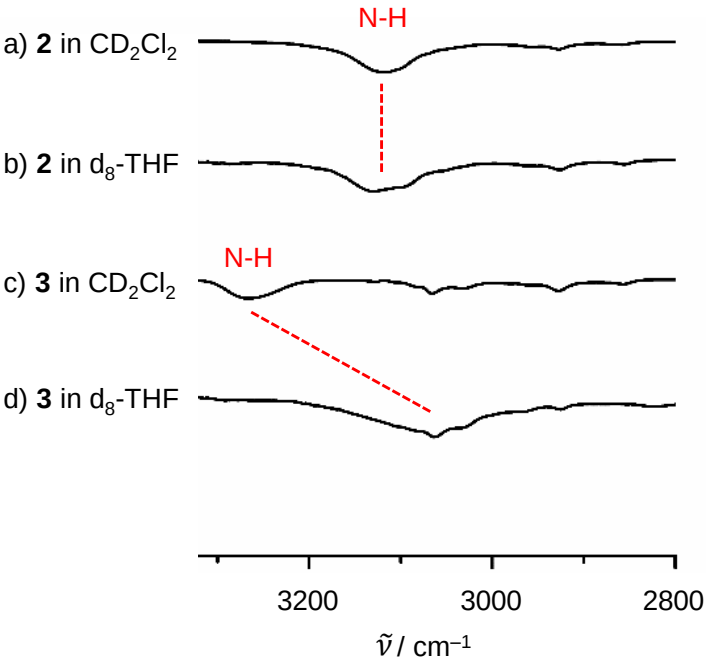


Fig. S4. ^{1}H NMR spectra of **2** a) in $CDCl_3$ and b) in d_6-DMSO.

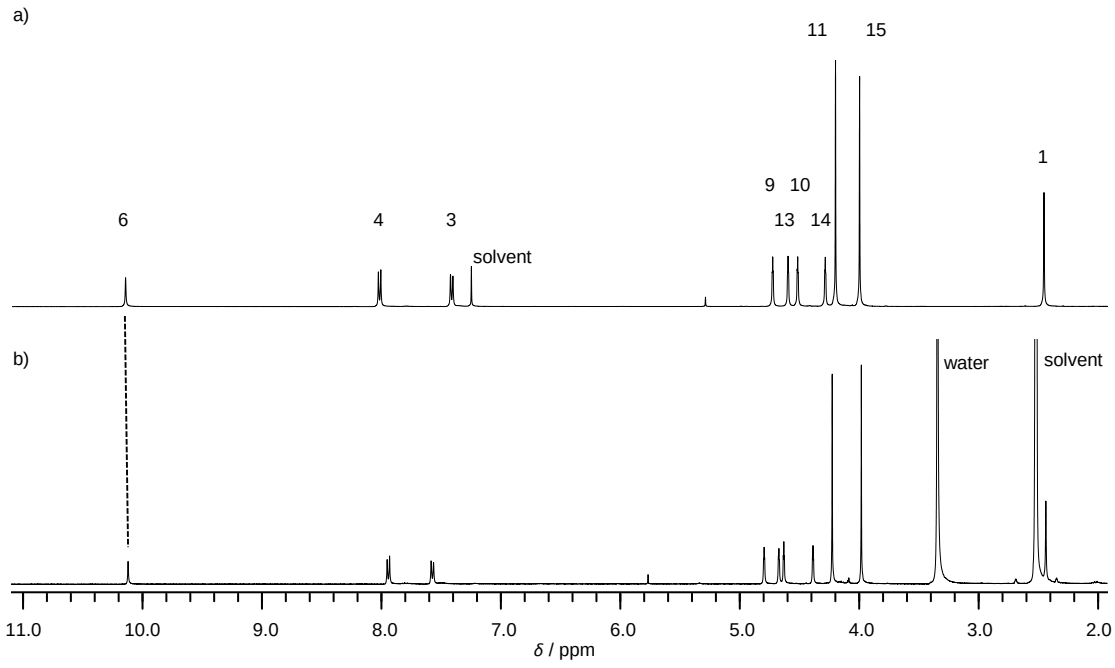


Fig. S5. ^{1}H NMR spectra of **3** a) in $CDCl_3$ and b) in d_6-DMSO.

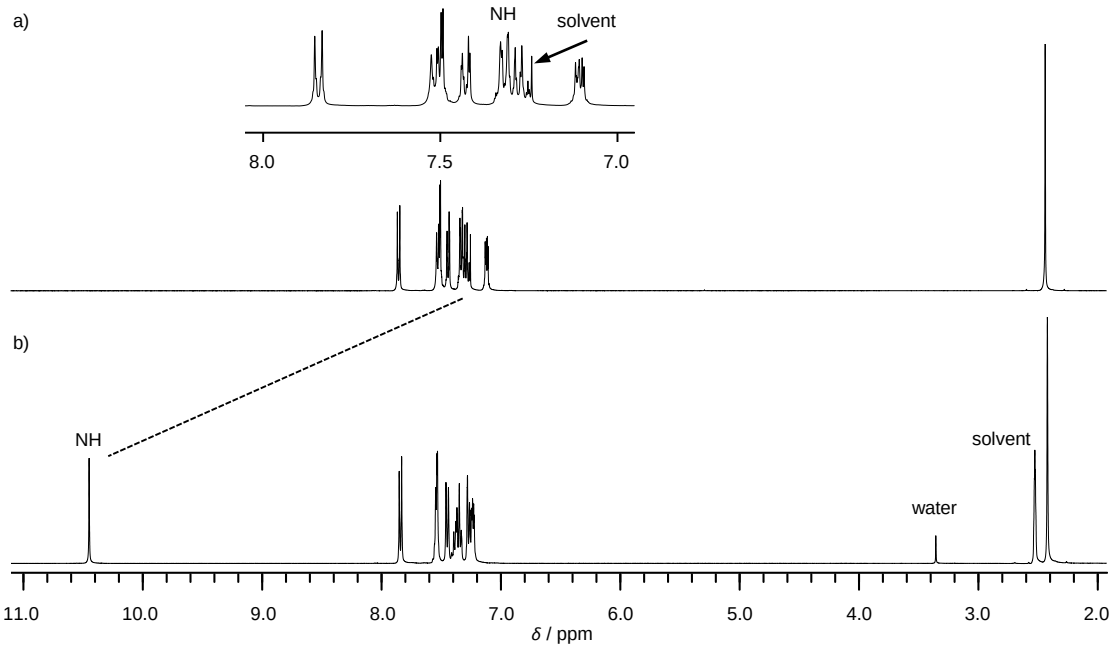


Fig S6. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

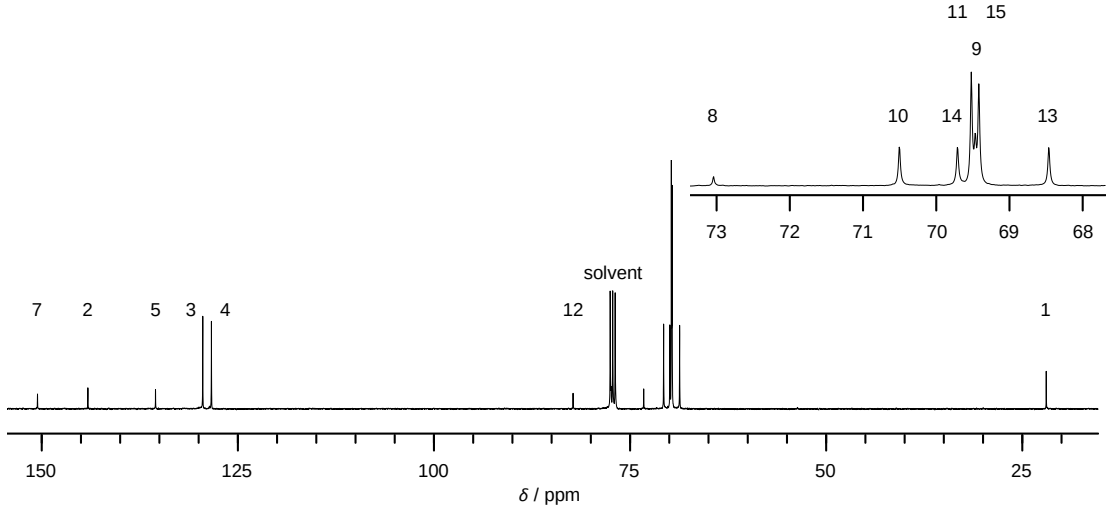
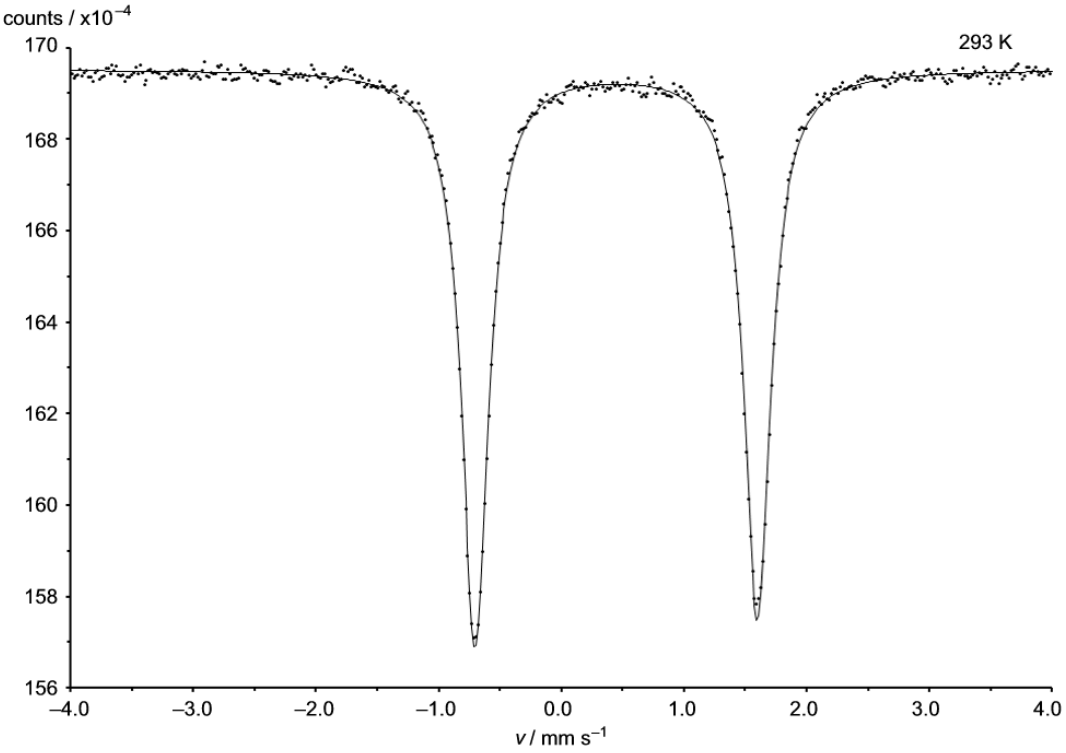


Fig. S7. Mößbauer spectra of **2** a) at 293 K and b) at 80 K.

a)



b)

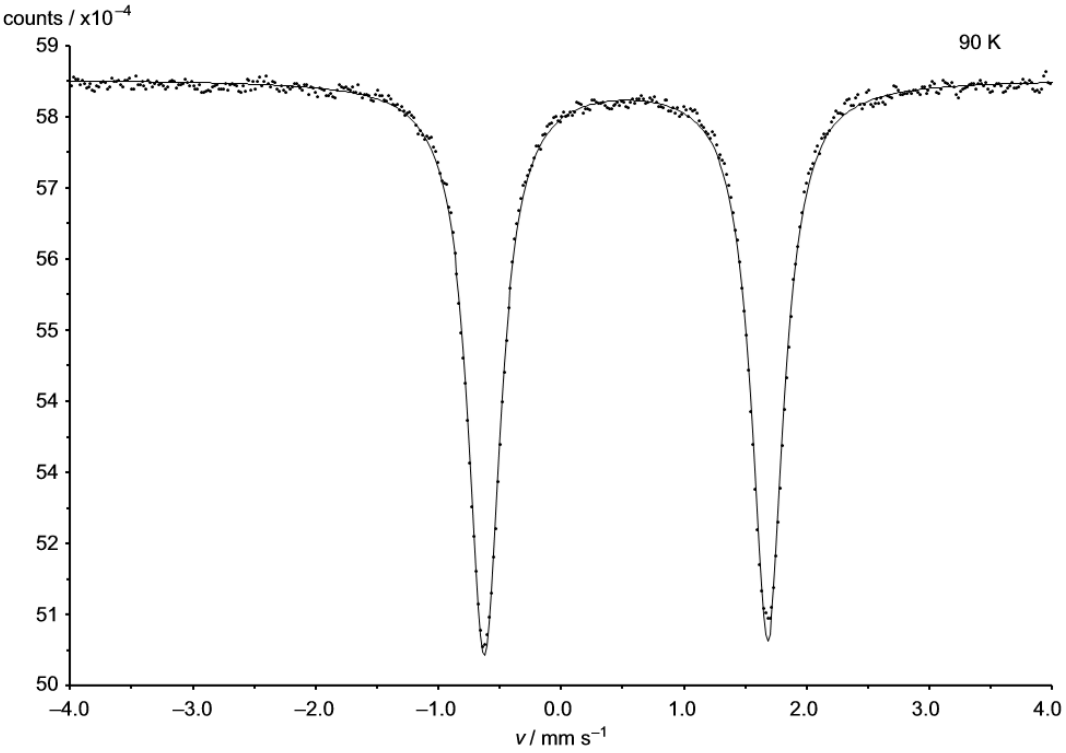


Fig. S8. VT ^{1}H NMR spectra of **2** in C_6D_6 from 298 to 343 K (400 MHz).

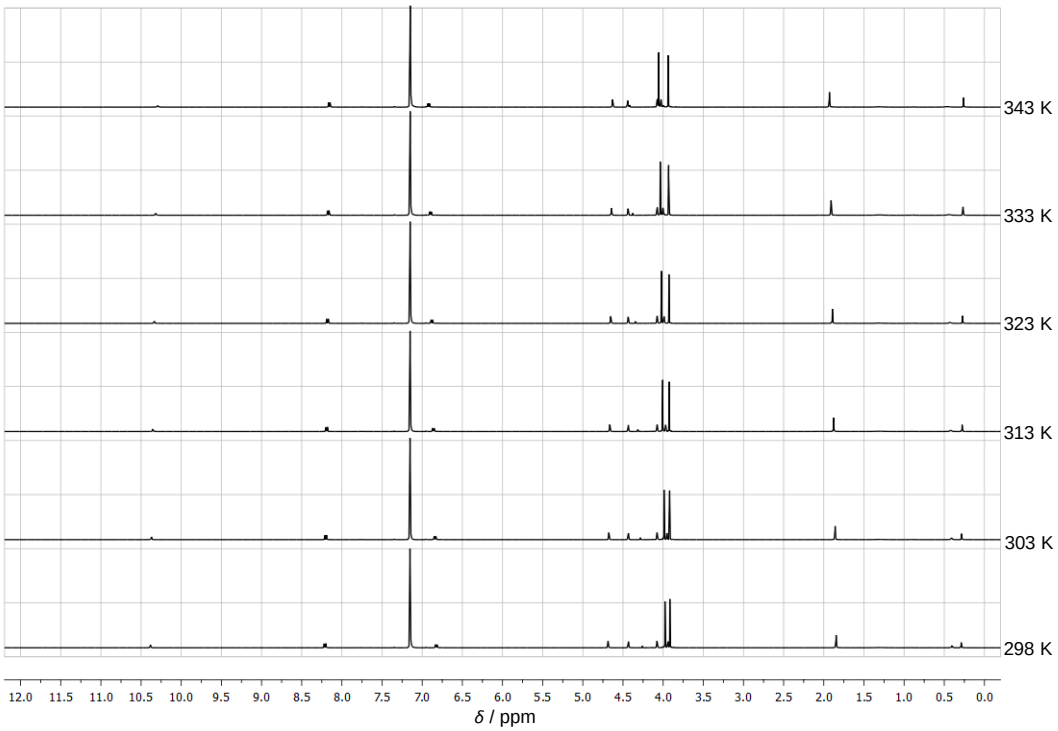


Fig. S9. Cyclic voltammograms of **1** and **2** in CH_2Cl_2.

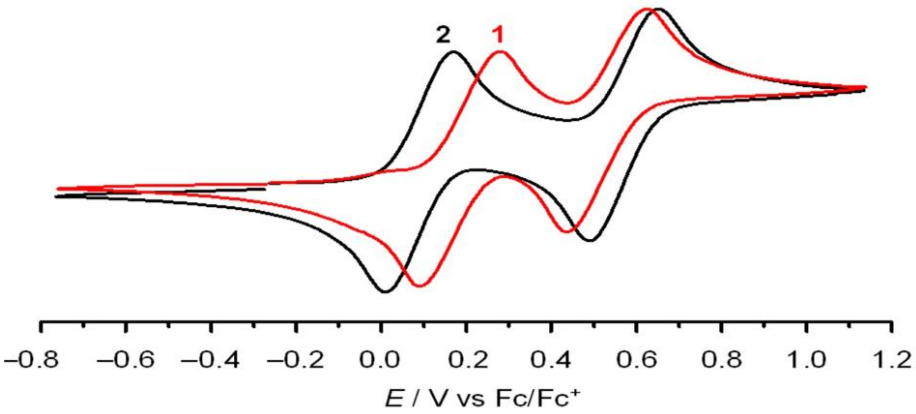


Fig. S10. ^{1}H NMR spectra of **2** upon titration with iodine in $CDCl_3$.

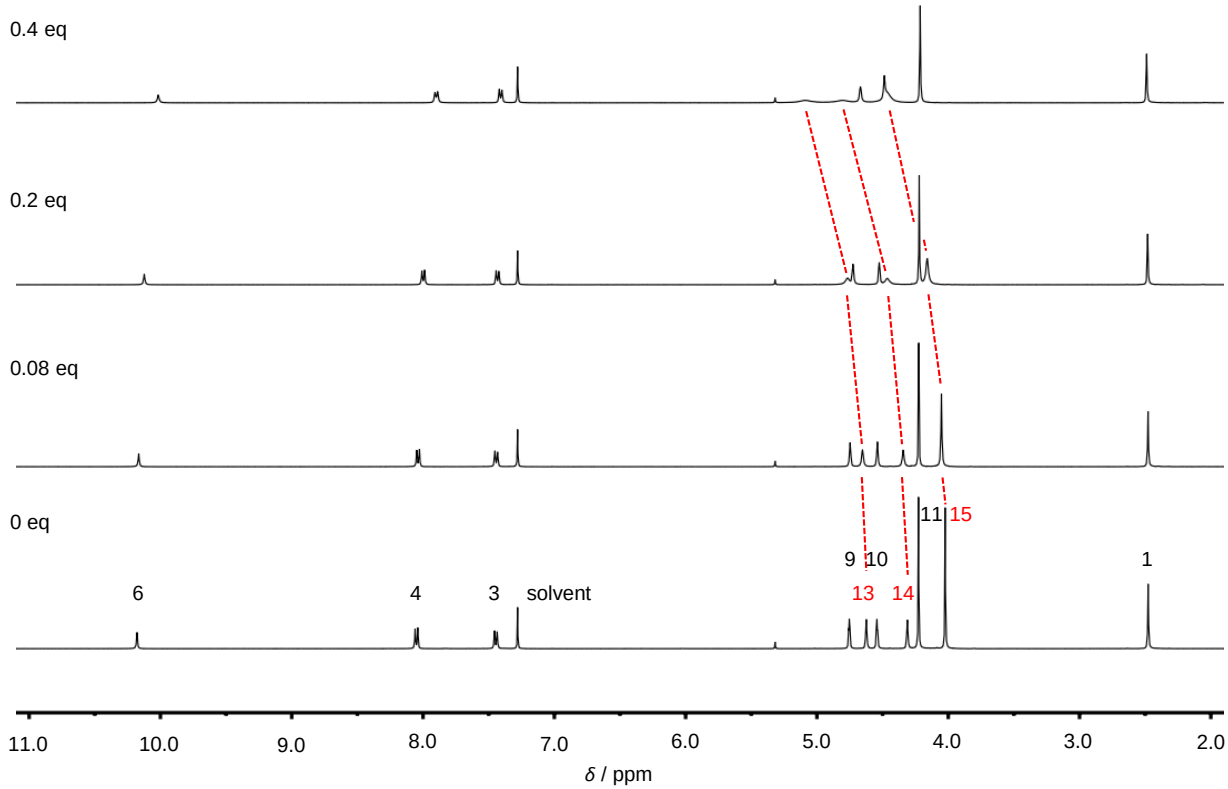


Fig. S11. IR spectra (NH/CH region) of **2** upon oxidation with $AgSbF_6$ in CD_2Cl_2.

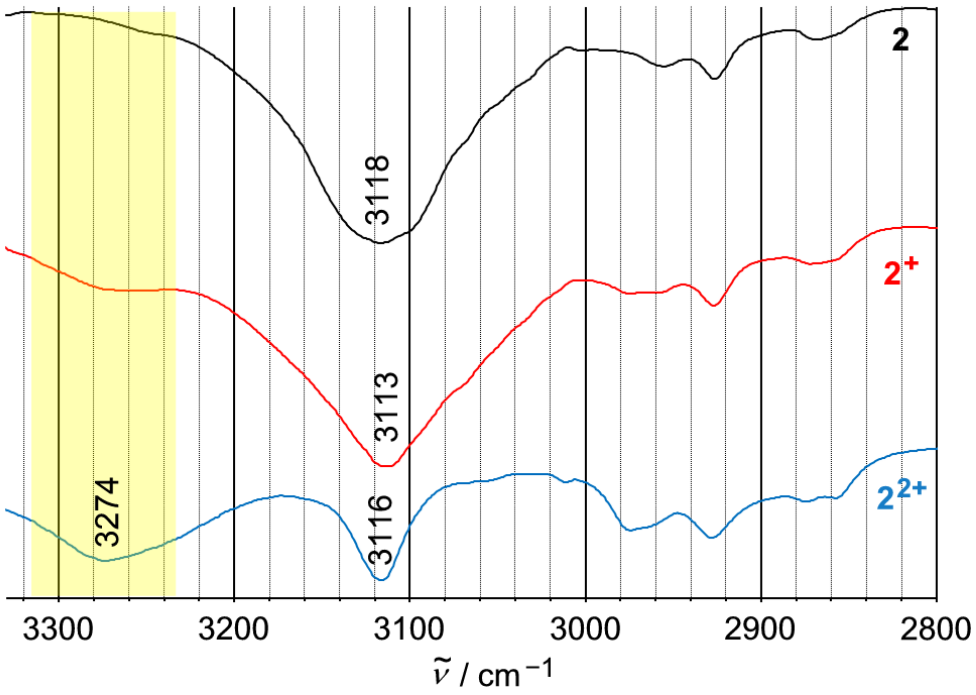
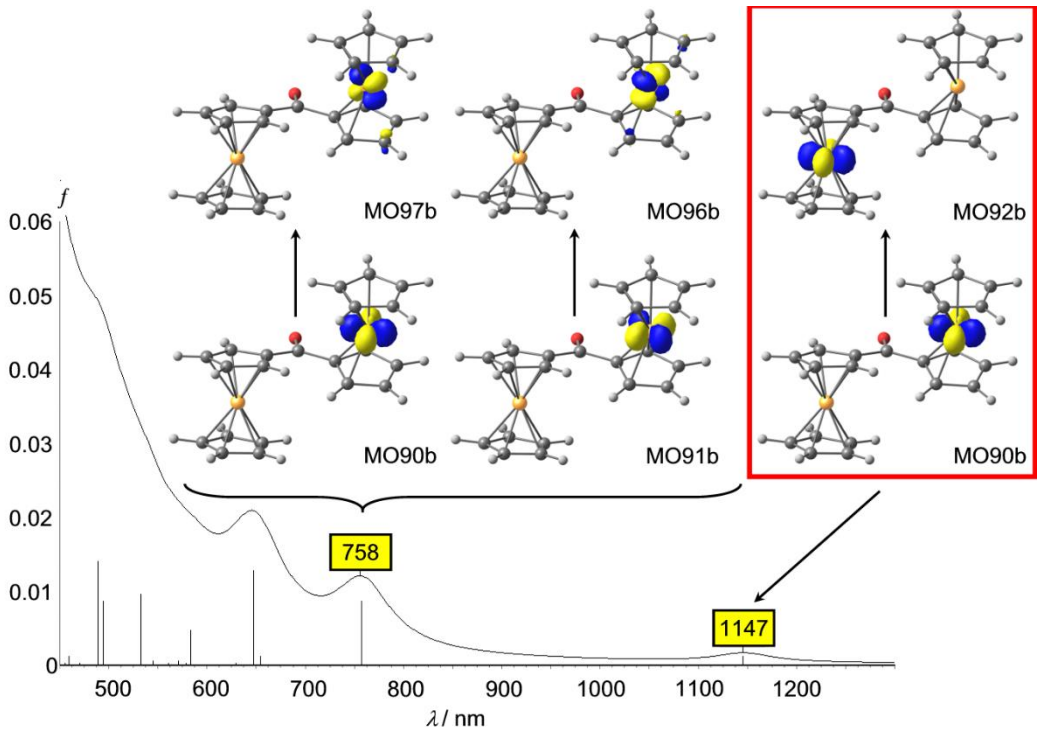


Fig. S12.TD-DFT calculated optical spectra of a) **1**$^{+}$ and b) **2**$^{+}$ (B3LYP, LANL2DZ for Fe, 6-31G* for C, H, N, O, S; IEFPCM CH_2Cl_2; aryl ring of **2**$^{+}$ omitted; contour value 0.1 a.u.).

a)



b)

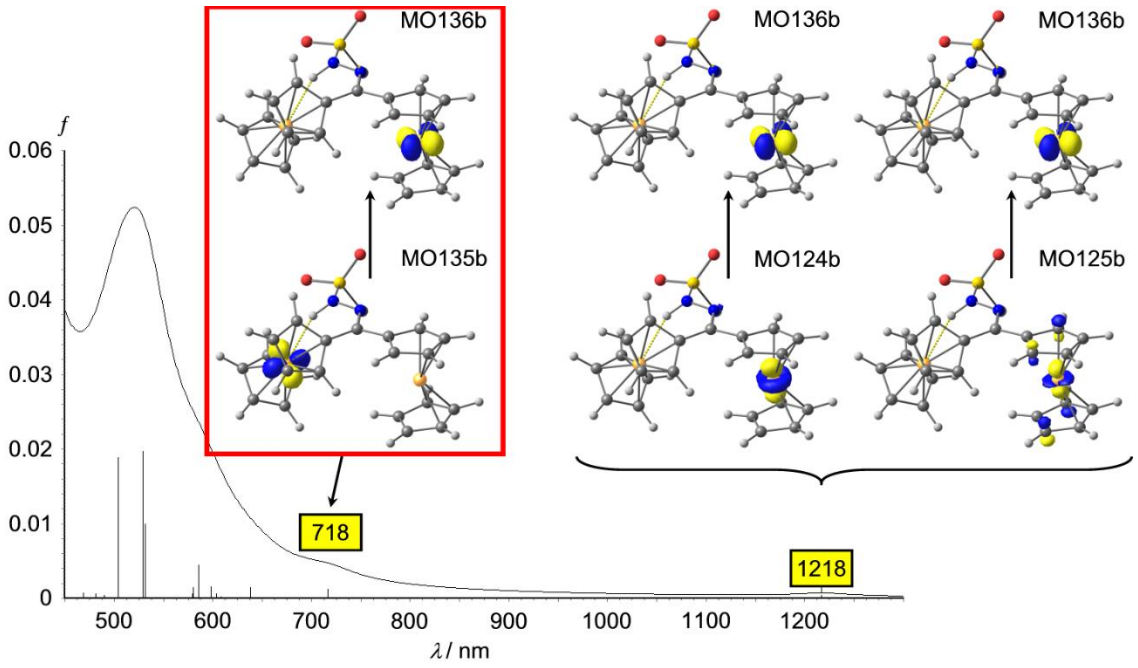
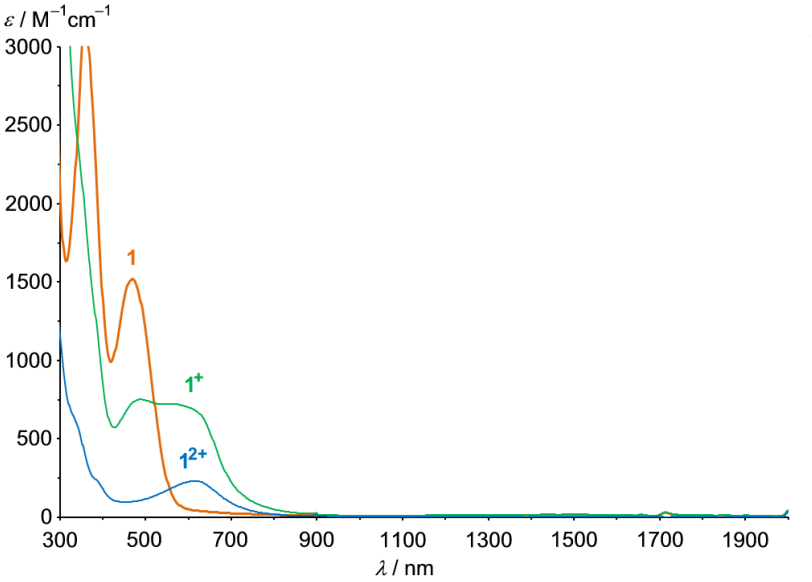


Fig. S13. UV/Vis spectra of a) **1**, $\mathbf{1}^{+}$ and $\mathbf{1}^{2+}$ in CH_2Cl_2 (note that the extinction coefficient of $\mathbf{1}^{2+}$ is higher than shown due to the precipitation of $\mathbf{1}^{2+}$ in CH_2Cl_2) and b) IVCT band of $\mathbf{1}^{+}$ in THF with spectral deconvolution into Lorentz functions (red).

a)



b)

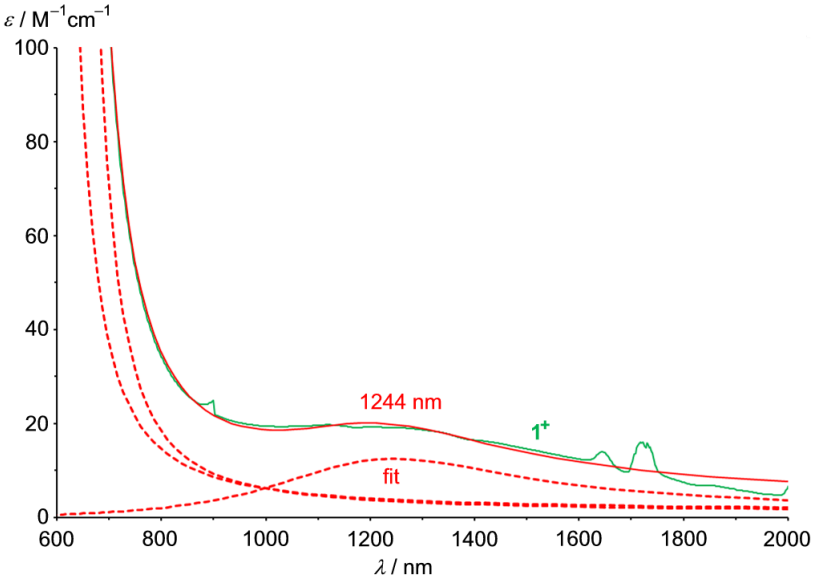
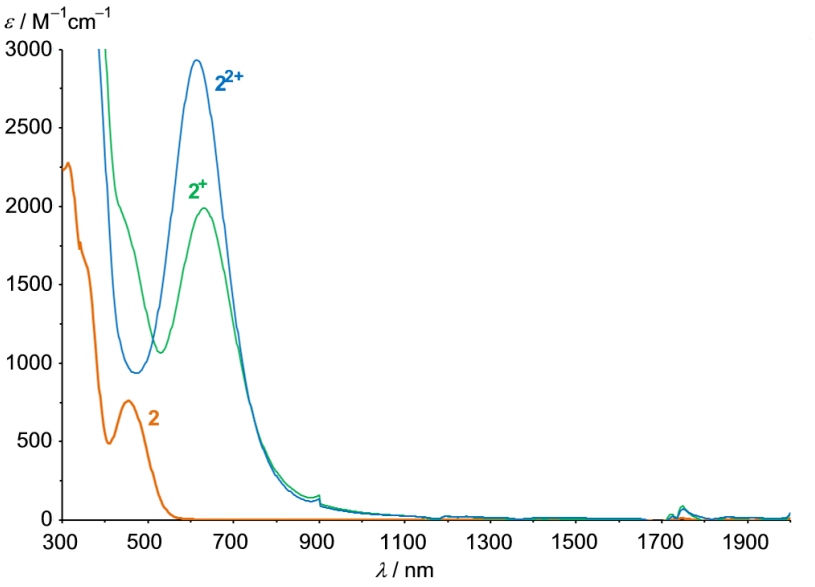
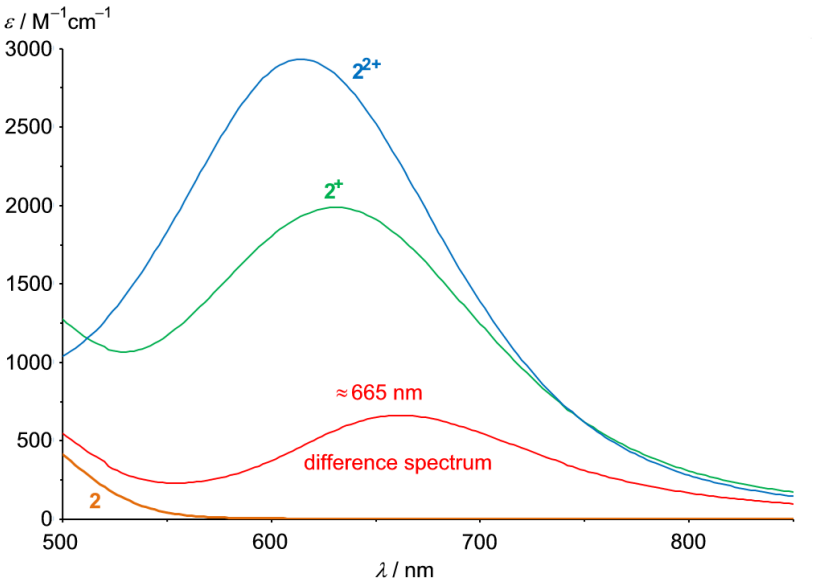


Fig. S14. UV/Vis spectra of a) **2**, $\mathbf{2}^{+}$ and $\mathbf{2}^{2+}$ in THF and b) difference spectrum "$\mathbf{2}^{+}$ – ($\mathbf{2}^{2+}$ + **2**)/2" in red.



b)



Cartesian coordinates of optimised geometries

2 with hydrogen bond

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8	2.646580000	1.910200000	-3.019832000
8	4.138177000	0.688188000	-1.343336000
7	0.445505000	0.293173000	-1.739856000
7	1.776995000	-0.044151000	-1.631421000
1	2.026139000	-0.693106000	-0.873317000
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1	-3.670502000	-1.539155000	1.894354000
6	-4.621104000	0.440364000	1.449947000
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6	-4.054749000	1.745000000	1.320235000
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6	-3.027967000	-0.962297000	-1.590556000
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6	2.975157000	2.401389000	0.804423000
1	3.755034000	1.673850000	1.001695000
6	2.579060000	3.305214000	1.787957000
1	3.054344000	3.269436000	2.764682000
6	1.584384000	4.264157000	1.536711000
6	0.992602000	4.296247000	0.264749000
1	0.225740000	5.035618000	0.049528000
6	1.377037000	3.403014000	-0.734483000
1	0.926579000	3.445718000	-1.719426000
6	1.187756000	5.257680000	2.601649000
1	1.178406000	4.796262000	3.594624000
1	0.197139000	5.679569000	2.407012000
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2 without hydrogen bond

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8	2.199546000	-3.214404000	-2.211403000
8	2.115645000	-4.340839000	0.079454000
7	0.447591000	-1.149204000	-0.911086000
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1	-1.896808000	1.165849000	1.652870000
6	-2.883305000	-0.682294000	2.424474000
1	-3.465609000	-0.308941000	3.256585000
6	-2.835222000	-2.034636000	1.973241000
1	-3.382030000	-2.867951000	2.394019000
6	-1.985261000	-2.089737000	0.832537000
1	-1.789369000	-2.971102000	0.238766000
6	-0.494894000	-0.375034000	-0.466906000
6	-0.493197000	0.974646000	-1.077456000
6	-1.477898000	2.017591000	-0.980542000
1	-2.390479000	1.975116000	-0.407565000
6	-1.044763000	3.121651000	-1.770469000

1	-1.564250000	4.065153000	-1.875656000
6	0.208771000	2.778537000	-2.361630000
1	0.813076000	3.419006000	-2.990765000
6	0.555123000	1.468114000	-1.930343000
1	1.455794000	0.927049000	-2.178893000
6	1.080602000	2.337900000	1.631534000
1	0.966484000	1.391889000	2.144621000
6	0.156398000	3.427338000	1.665343000
1	-0.771231000	3.461748000	2.221826000
6	0.660438000	4.459096000	0.815269000
1	0.175343000	5.403432000	0.604705000
6	1.893760000	4.006148000	0.255429000
1	2.504477000	4.546229000	-0.456428000
6	2.154094000	2.694396000	0.759900000
1	2.995812000	2.065980000	0.499779000
6	3.404458000	-2.034595000	-0.179772000
6	3.849625000	-2.134092000	1.142433000
1	3.435300000	-2.887043000	1.804462000
6	4.842016000	-1.265065000	1.588602000
1	5.194549000	-1.342546000	2.613719000
6	5.399151000	-0.297613000	0.735960000
6	4.930989000	-0.220834000	-0.584580000
1	5.354608000	0.516714000	-1.261067000
6	3.937255000	-1.081635000	-1.050517000
1	3.590807000	-1.026935000	-2.076205000
6	6.498775000	0.614301000	1.223879000
1	6.327426000	0.927457000	2.259085000
1	6.582451000	1.509915000	0.601068000
1	7.468959000	0.101248000	1.196859000

2^{+} with hydrogen bond

26	-3.147677000	-0.967269000	-0.066232000

26	2.289250000	-1.996147000	0.587175000
16	1.917840000	2.367352000	-1.761148000
8	1.412055000	2.765467000	-3.073732000
8	3.346425000	2.423405000	-1.432118000
7	0.277043000	0.336741000	-1.698288000
7	1.573411000	0.691952000	-1.594959000
1	2.163883000	0.206853000	-0.906054000
6	-2.445832000	-0.527341000	1.939148000
1	-1.396805000	-0.468352000	2.199140000
6	-3.249241000	-1.700557000	1.982977000
1	-2.917860000	-2.684758000	2.287787000
6	-4.545942000	-1.371919000	1.493709000
1	-5.374404000	-2.058097000	1.379272000
6	-4.544392000	0.014188000	1.140794000
1	-5.377494000	0.567896000	0.729301000
6	-3.239039000	0.535202000	1.416620000
1	-2.906355000	1.549307000	1.239928000
6	-1.520327000	-1.120334000	-1.557288000
6	-2.224063000	-2.360591000	-1.456058000
1	-1.792900000	-3.313045000	-1.183980000
6	-3.597774000	-2.133577000	-1.758302000
1	-4.375216000	-2.885746000	-1.761713000
6	-3.762561000	-0.741850000	-2.041741000
1	-4.688899000	-0.246194000	-2.299020000
6	-2.492495000	-0.114215000	-1.886782000
1	-2.277286000	0.937319000	-2.005627000
6	-0.082024000	-0.865483000	-1.355567000
6	0.819728000	-1.948751000	-0.912658000
6	2.113924000	-2.253021000	-1.480479000
1	2.621395000	-1.682663000	-2.245986000
6	2.592520000	-3.450431000	-0.884436000
1	3.546721000	-3.917072000	-1.089243000
6	1.625146000	-3.895738000	0.064577000

1	1.719705000	-4.754983000	0.714820000
6	0.537779000	-2.977809000	0.053956000
1	-0.331124000	-3.028890000	0.694475000
6	2.304223000	-0.286374000	1.795717000
1	1.610158000	0.540827000	1.724963000
6	3.551399000	-0.404574000	1.102458000
1	3.982478000	0.324582000	0.427482000
6	4.142153000	-1.649834000	1.474036000
1	5.074361000	-2.047707000	1.095502000
6	3.265204000	-2.298199000	2.394643000
1	3.415199000	-3.275769000	2.833336000
6	2.128896000	-1.455892000	2.592793000
1	1.272629000	-1.679584000	3.215473000
6	0.985260000	3.230589000	-0.510847000
6	1.561555000	3.451791000	0.744172000
1	2.576032000	3.126175000	0.947059000
6	0.820487000	4.118296000	1.717742000
1	1.266299000	4.300266000	2.691718000
6	-0.483818000	4.569098000	1.458132000
6	-1.033649000	4.332956000	0.187823000
1	-2.036684000	4.686411000	-0.035646000
6	-0.309539000	3.669661000	-0.801472000
1	-0.731469000	3.512957000	-1.787697000
6	-1.259962000	5.326098000	2.507771000
1	-0.997451000	4.993621000	3.516943000
1	-2.339399000	5.207875000	2.372011000
1	-1.038579000	6.399783000	2.450481000

2^{+} without hydrogen bond

26	3.078163000	-1.831867000	-0.307984000
26	0.670963000	2.881690000	-0.150518000
16	-2.822493000	-1.383355000	1.947668000

8	-2.825720000	-0.231604000	2.849712000
8	-3.023494000	-2.748599000	2.441893000
7	-0.880635000	-0.355357000	0.567103000
7	-1.240427000	-1.461089000	1.268457000
1	-1.038000000	-2.380706000	0.864922000
6	4.053888000	-0.203486000	0.565805000
1	3.571271000	0.714695000	0.871654000
6	4.614376000	-0.476919000	-0.720159000
1	4.650441000	0.198754000	-1.564854000
6	5.120802000	-1.811913000	-0.702504000
1	5.578151000	-2.328632000	-1.535947000
6	4.874677000	-2.360533000	0.592162000
1	5.107767000	-3.368402000	0.909276000
6	4.212797000	-1.367397000	1.375867000
1	3.866573000	-1.486038000	2.394075000
6	1.006696000	-1.531037000	-0.520582000
6	1.613056000	-1.823946000	-1.797164000
1	1.585893000	-1.188128000	-2.671565000
6	2.219936000	-3.106867000	-1.722494000
1	2.767891000	-3.592503000	-2.518895000
6	2.025377000	-3.618392000	-0.404916000
1	2.411386000	-4.552988000	-0.020918000
6	1.292357000	-2.654604000	0.343170000
1	1.044370000	-2.732726000	1.392399000
6	0.139814000	-0.374462000	-0.234804000
6	0.297468000	0.889201000	-0.994017000
6	-0.770257000	1.810283000	-1.263742000
1	-1.794965000	1.675810000	-0.948038000
6	-0.247222000	2.902518000	-2.017088000
1	-0.809132000	3.754002000	-2.376510000
6	1.154184000	2.678460000	-2.193256000
1	1.849456000	3.336928000	-2.696368000
6	1.484470000	1.445062000	-1.561338000

1	2.472219000	1.016629000	-1.483356000
6	1.047686000	2.844229000	1.973062000
1	1.141330000	1.926316000	2.538267000
6	-0.173256000	3.516231000	1.668405000
1	-1.160645000	3.213618000	1.989560000
6	0.141156000	4.644075000	0.843894000
1	-0.567081000	5.350305000	0.432070000
6	1.556652000	4.658687000	0.643685000
1	2.106861000	5.364401000	0.035767000
6	2.110543000	3.548562000	1.342632000
1	3.153940000	3.261987000	1.346359000
6	-3.951807000	-1.057361000	0.607321000
6	-4.408700000	-2.121139000	-0.177469000
1	-4.101161000	-3.138095000	0.041772000
6	-5.273564000	-1.854706000	-1.235292000
1	-5.634599000	-2.677930000	-1.845823000
6	-5.691170000	-0.544356000	-1.522232000
6	-5.216308000	0.501137000	-0.716316000
1	-5.534805000	1.520121000	-0.918644000
6	-4.349385000	0.256618000	0.348149000
1	-4.000235000	1.066367000	0.978840000
6	-6.652447000	-0.275841000	-2.654034000
1	-6.422110000	-0.893919000	-3.528116000
1	-6.630998000	0.774962000	-2.957428000
1	-7.680981000	-0.512439000	-2.352351000

2^{2+} with hydrogen bond

26	-3.380625000	0.145448000	0.007466000
26	1.528690000	-2.625558000	0.588904000
16	2.462781000	1.672259000	-1.995282000
8	1.901974000	2.275021000	-3.199095000
8	3.851342000	1.216219000	-1.910129000

7	0.272349000	0.233080000	-1.757919000
7	1.600005000	0.178487000	-1.765222000
1	2.112141000	-0.505479000	-1.201806000
6	-2.619521000	0.232934000	2.037170000
1	-1.639880000	-0.117551000	2.335150000
6	-3.812486000	-0.542053000	2.027863000
1	-3.894264000	-1.584669000	2.305657000
6	-4.868238000	0.272467000	1.528535000
1	-5.892592000	-0.039501000	1.374670000
6	-4.324394000	1.559257000	1.221054000
1	-4.868812000	2.399041000	0.810934000
6	-2.927747000	1.531577000	1.536197000
1	-2.227080000	2.344721000	1.401067000
6	-1.915632000	-0.522555000	-1.517865000
6	-2.994229000	-1.454636000	-1.406844000
1	-2.913639000	-2.502681000	-1.154849000
6	-4.214134000	-0.772651000	-1.686942000
1	-5.199953000	-1.217641000	-1.682934000
6	-3.901404000	0.595304000	-1.959962000
1	-4.608515000	1.378620000	-2.197016000
6	-2.492379000	0.755306000	-1.827082000
1	-1.935604000	1.672484000	-1.951815000
6	-0.468348000	-0.767778000	-1.382879000
6	0.025391000	-2.098411000	-0.960330000
6	1.106007000	-2.834687000	-1.550017000
1	1.739697000	-2.498326000	-2.360034000
6	1.204964000	-4.095769000	-0.901288000
1	1.931131000	-4.864432000	-1.128845000
6	0.196462000	-4.155035000	0.109473000
1	0.015384000	-4.978450000	0.786798000
6	-0.515746000	-2.918937000	0.086583000
1	-1.319364000	-2.646908000	0.755339000
6	2.301313000	-0.973685000	1.806627000

1	1.974028000	0.055239000	1.728991000
6	3.359384000	-1.569154000	1.063384000
1	3.992939000	-1.068115000	0.342009000
6	3.431839000	-2.949278000	1.421771000
1	4.125758000	-3.675095000	1.019699000
6	2.409011000	-3.204435000	2.390580000
1	2.193098000	-4.158126000	2.853357000
6	1.707193000	-1.979221000	2.619098000
1	0.855281000	-1.845754000	3.272752000
6	2.073909000	2.690090000	-0.590223000
6	2.910791000	2.651581000	0.530317000
1	3.801086000	2.031841000	0.529529000
6	2.595160000	3.442846000	1.632174000
1	3.246736000	3.425534000	2.501354000
6	1.461085000	4.271860000	1.632436000
6	0.641765000	4.286985000	0.491983000
1	-0.232687000	4.931488000	0.469351000
6	0.938053000	3.504681000	-0.622929000
1	0.313713000	3.543119000	-1.508587000
6	1.156565000	5.153588000	2.817686000
1	1.438684000	4.669942000	3.758229000
1	0.095029000	5.413762000	2.863559000
1	1.722677000	6.091644000	2.752691000

2^{2+} without hydrogen bond

26	3.389534000	-1.598310000	-0.276880000
26	0.313974000	2.857620000	-0.178193000
16	-2.654678000	-1.442964000	1.877840000
8	-2.592838000	-0.222896000	2.680934000
8	-2.746518000	-2.773496000	2.479386000
7	-0.795544000	-0.436464000	0.356925000
7	-1.122658000	-1.528061000	1.055550000

1	-0.908007000	-2.462958000	0.698531000
6	4.349091000	0.097436000	0.739332000
1	3.844640000	1.014510000	1.014463000
6	5.019535000	-0.150469000	-0.489630000
1	5.119551000	0.543645000	-1.314076000
6	5.496115000	-1.493877000	-0.473732000
1	6.030597000	-1.988365000	-1.273732000
6	5.121844000	-2.078195000	0.778528000
1	5.331922000	-3.090143000	1.097825000
6	4.400438000	-1.091875000	1.522474000
1	3.961260000	-1.228108000	2.501574000
6	1.189265000	-1.457659000	-0.698059000
6	1.916054000	-1.660507000	-1.914577000
1	1.905346000	-1.002377000	-2.773337000
6	2.661820000	-2.865778000	-1.808267000
1	3.303343000	-3.280242000	-2.573980000
6	2.421606000	-3.421807000	-0.513350000
1	2.845426000	-4.334705000	-0.117670000
6	1.542911000	-2.539910000	0.183781000
1	1.221295000	-2.662314000	1.208513000
6	0.232677000	-0.364695000	-0.431549000
6	0.318449000	0.923714000	-1.162903000
6	-0.828946000	1.709184000	-1.524835000
1	-1.855504000	1.425823000	-1.340794000
6	-0.376561000	2.904478000	-2.156786000
1	-1.004441000	3.698091000	-2.538511000
6	1.050594000	2.873131000	-2.179430000
1	1.701973000	3.648365000	-2.560065000
6	1.475509000	1.660146000	-1.568768000
1	2.504566000	1.383844000	-1.396596000
6	0.722215000	2.704574000	1.886172000
1	1.118286000	1.804681000	2.337265000
6	-0.661692000	2.992859000	1.669495000

1	-1.490237000	2.347650000	1.931047000
6	-0.743140000	4.263493000	1.018367000
1	-1.649043000	4.752475000	0.685528000
6	0.582690000	4.755669000	0.840054000
1	0.856956000	5.669481000	0.329506000
6	1.486310000	3.794672000	1.372605000
1	2.566044000	3.860658000	1.349445000
6	-3.897767000	-1.252731000	0.622337000
6	-4.386462000	-2.389103000	-0.030337000
1	-4.028667000	-3.376736000	0.240852000
6	-5.350283000	-2.229545000	-1.022406000
1	-5.737890000	-3.107382000	-1.531588000
6	-5.834029000	-0.957607000	-1.370375000
6	-5.323896000	0.162175000	-0.694661000
1	-5.693356000	1.152772000	-0.944906000
6	-4.359004000	0.027442000	0.301089000
1	-3.984462000	0.893780000	0.834040000
6	-6.902596000	-0.800576000	-2.423357000
1	-6.836158000	-1.587098000	-3.181254000
1	-6.833398000	0.171137000	-2.921819000
1	-7.900619000	-0.866128000	-1.970947000