Supporting Information

Nitrosyl iron complexes with enhanced NO donating ability: synthesis, structure and properties of a new type of salts with DNIC cations $[Fe(SC(NH_2)_2)_2(NO)_2]^+$

Nataliya A. Sanina,[a] Sergey M. Aldoshin,[a] Natal'ya Yu. Shmatko,[a] Denis V. Korchagin,[a] Gennadii V. Shilov,[a] Ekaterine V. Knyazkina,[b] Nikolay S. Ovanesyan[a] and Alexander V. Kulikov[a]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences,142432 Chernogolovka, Moscow Region, Russia;*
[b] *M.V. Lomonosov Moscow State University, 1, Leninskie gory, Moscow, 119991, Russia*

[*] *Tel.: 8 (496) 5221168, Fax: 8 (496) 5223507, e- mail:sanina@ icp.ac.ru*

Table S1 Selected bond lengths and angles for **I** and **II**.

Compound **I**				Compound **II**	
1		***2***			
Bond	*d, Å*	*Bond*	*d, Å*	*Bond*	*d, Å*
Fe(1)-N(1)	1.684(2)	Fe(2)-N(8)	1.688(2)	Fe(2)-N(3)	1.688(2)
Fe(1)-N(2)	1.695(2)	Fe(2)-N(7)	1.689(2)	Fe(2)-N(4)	1.689(2)
Fe(1)-S(2)	2.2907(7)	Fe(2)-S(3)	2.2997(7)	Fe(2)-S(4)	2.3130(5)
Fe(1)-S(1)	2.3250(7)	Fe(2)-S(4)	2.3228(7)	Fe(2)-S(3)	2.3353(6)
N(1)-O(1)	1.165(3)	N(8)-O(4)	1.162(3)	N(4)-O(4)	1.163(2)
N(2)-O(2)	1.169(3)	N(7)-O(3)	1.168(3)	N(3)-O(3)	1.175(2)
S(1)-C(1)	1.739(2)	S(3)-C(3)	1.736(2)	S(3)-C(1)	1.755(2)
C(1)-N(3)	1.304(3)	C(3)-N(9)	1.321(3)	N(5)-C(1)	1.321(2)
C(1)-N(4)	1.299(3)	C(3)-N(10)	1.317(3)	N(6)-C(1)	1.311(2)
S(2)-C(2)	1.737(2)	S(4)-C(4)	1.732(2)	S(4)-C(2)	1.729(2)
C(2)-N(6)	1.320(3)	C(4)-N(12)	1.309(3)	N(7)-C(2)	1.323(2)
C(2)-N(5)	1.321(3)	C(4)-N(11)	1.312(3)	N(8)-C(2)	1.324(2)
Bond Angle	*ω, deg*	*Bond Angle*	*ω, deg*	*Bond Angle*	*ω, deg*
O(1)-N(1)-Fe(1)	168.9(2)	O(4)-N(8)-Fe(2)	172.7(3)	O(4)-N(4)-Fe(2)	170.1(2)
O(2)-N(2)-Fe(1)	164.9(2)	O(3)-N(7)-Fe(2)	170.3(2)	O(3)-N(3)-Fe(2)	162.5(2)
N(1)-Fe(1)-N(2)	117.7(1)	N(8)-Fe(2)-N(7)	120.3(1)	N(3)-Fe(2)-N(4)	114.18(9)
S(2)-Fe(1)-S(1)	108.83(3)	S(3)-Fe(2)-S(4)	111.17(3)	S(4)-Fe(2)-S(3)	109.42(2)

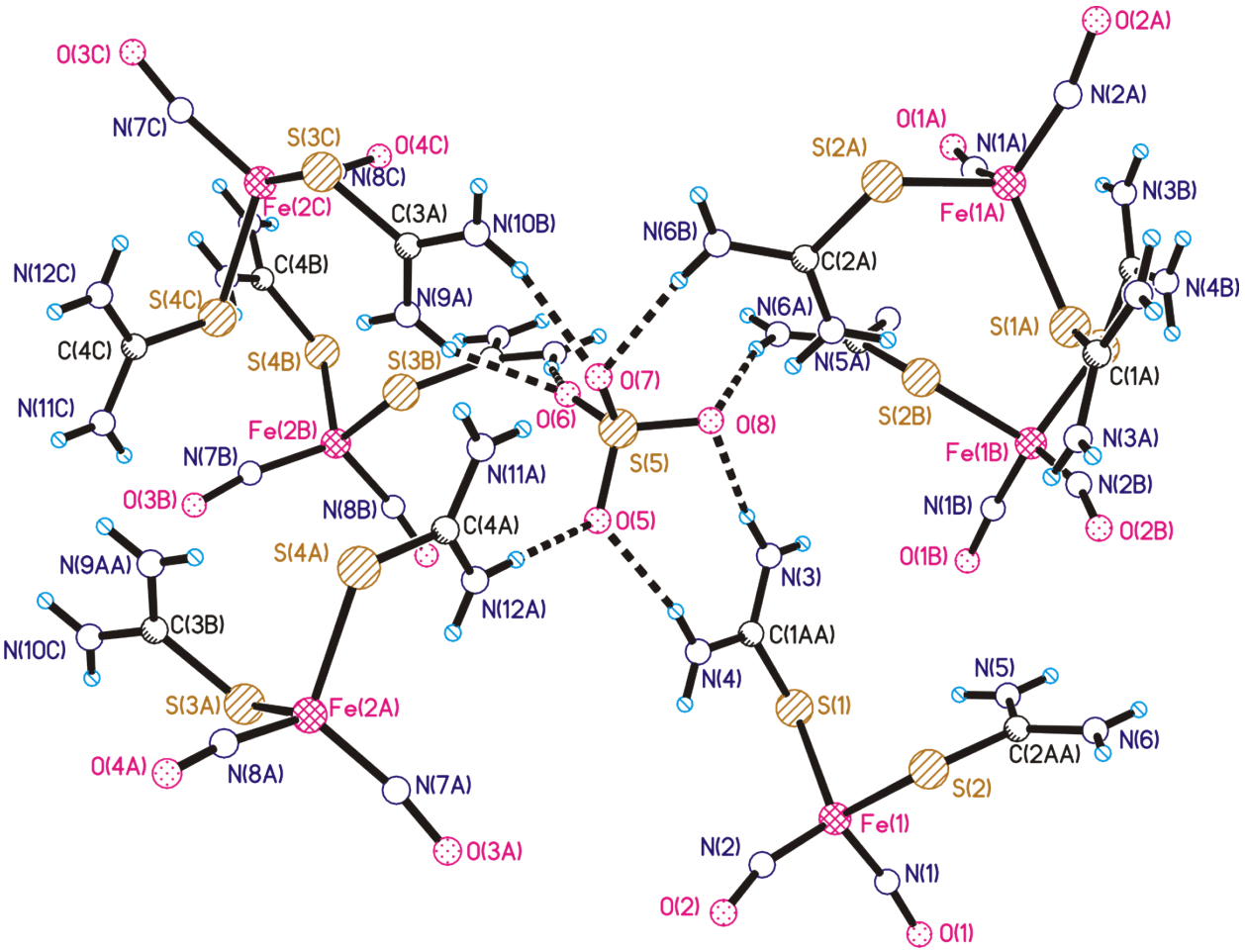


Fig. S1 Fragment of the crystal structure of **I**, the dashed line shows the intermolecular hydrogen bonds.

Table S2 Geometric characteristics of intermolecular and intramolecular hydrogen bonds in the crystal structure of **I**.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N3-H3A	0.860	2.057	170.49	2.909	O8
N4-H4A	0.860	1.969	163.99	2.805	O5
N5-H5A	0.860	2.078	159.88	2.901	O8 [-x+1, y-1/2, -z+1/2]
N6-H6A	0.860	1.994	171.77	2.847	O7 [-x+1, y-1/2, -z+1/2]
N6-H6B	0.860	2.069	163.32	2.903	O8 [x-1/2, y, -z+1/2]
N9-H9A	0.860	2.011	159.58	2.833	O6 [x-1/2, -y+1/2, -z]
N10-H10B	0.860	2.057	160.17	2.881	O7 [x-1/2, -y+1/2, -z]
N10-H10A	0.860	1.978	168.51	2.826	O6 [-x+1, -y, -z]
N11-H11A	0.860	1.991	170.25	2.842	O7 [-x+1/2, y-1/2, z]
N12-H12B	0.860	1.921	174.65	2.779	O5 [-x+1/2, y-1/2, z]

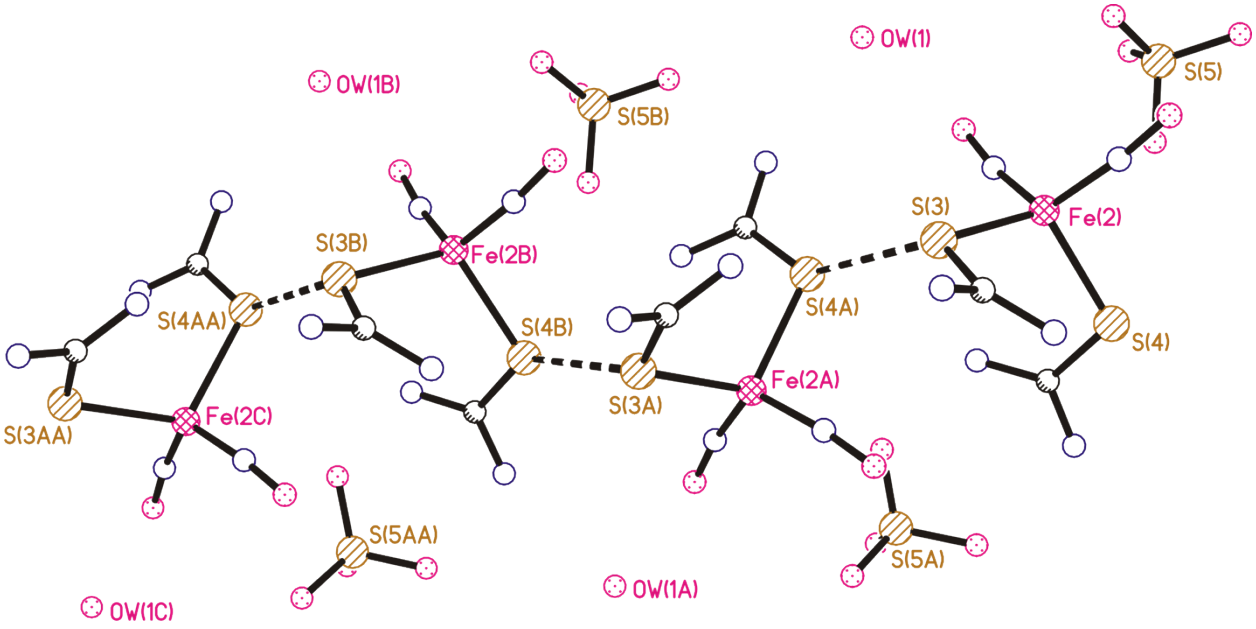


Fig. S2 Intermolecular contacts S (3) ···S (4A) 3.56Å in the crystal structure of **I**.

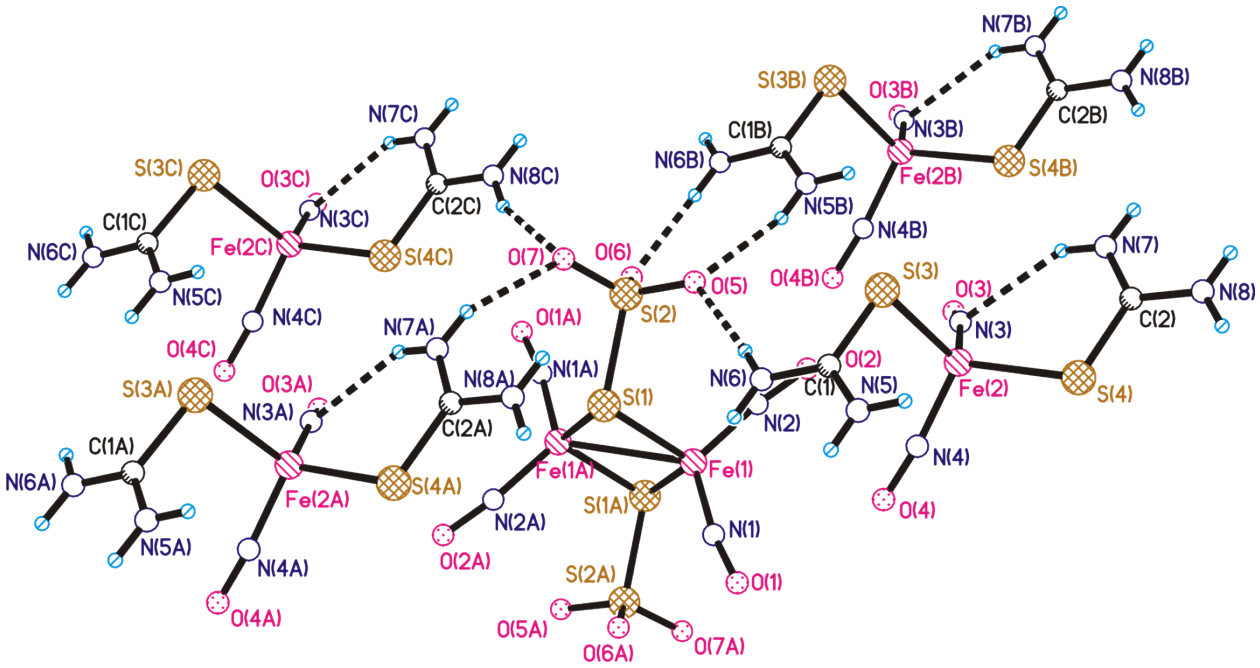


Fig. S3 Fragment of the crystal structure of **II**, the dashed line shows the intermolecular and intramolecular hydrogen bonds.

Table S3 Geometric characteristics of intermolecular and intramolecular hydrogen bonds in the crystal structure of **II**.

D-H	**d(H..A)**	**<DHA**	**d(D..A)**	**A**
N5-H5A	2.214	163.15	3.047	O5 [x+1, y, z]
N6-H6A	2.025	171.52	2.878	O6 [x+1, y, z]
N6-H6B	2.011	169.76	2.862	O5
N7-H7A	2.208	151.22	2.990	O7 [x, y, z-1]
N7-H7B	2.394	150.99	3.173	N3
N8-H8A	2.288	149.28	3.059	O7 [-x, -y+2, -z+1]
N8-H8B	2.146	158.60	2.963	O7 [x+1, y, z-1]

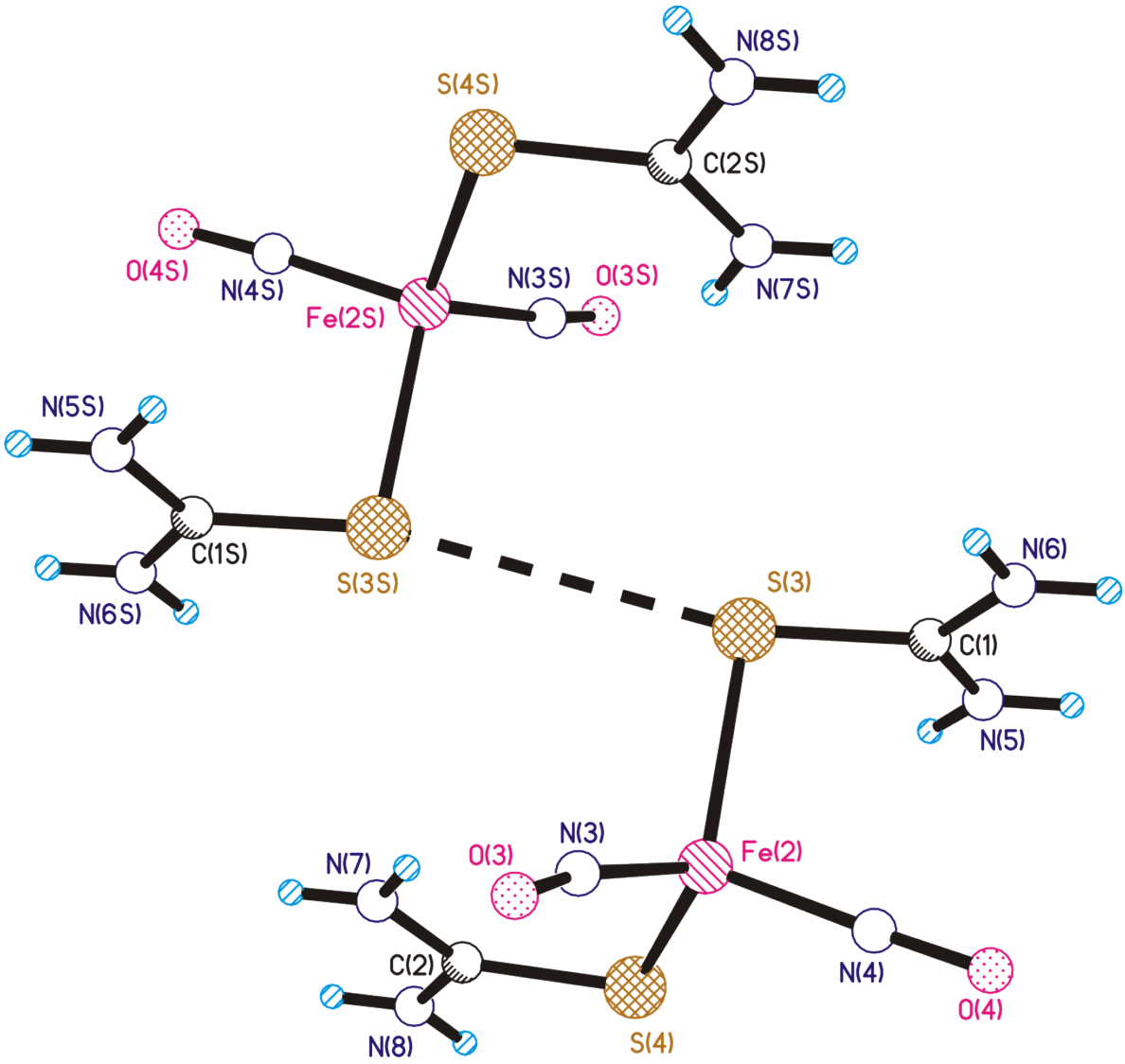


Fig. S4 Intermolecular contacts S (3)···S (4A) 3.56Å in the crystal structure of **II**.

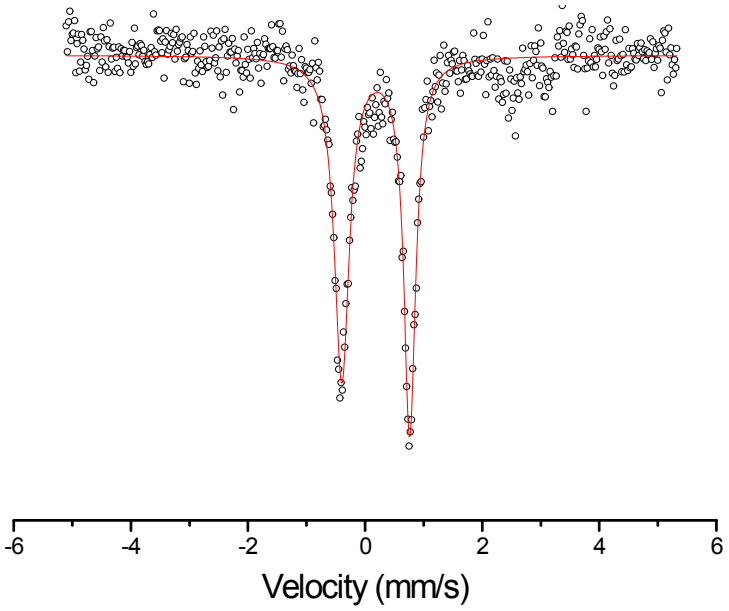


Fig. S5 293 K Mössbauer spectrum of **I** (raw data – black dots, fitted spectrum – red line).

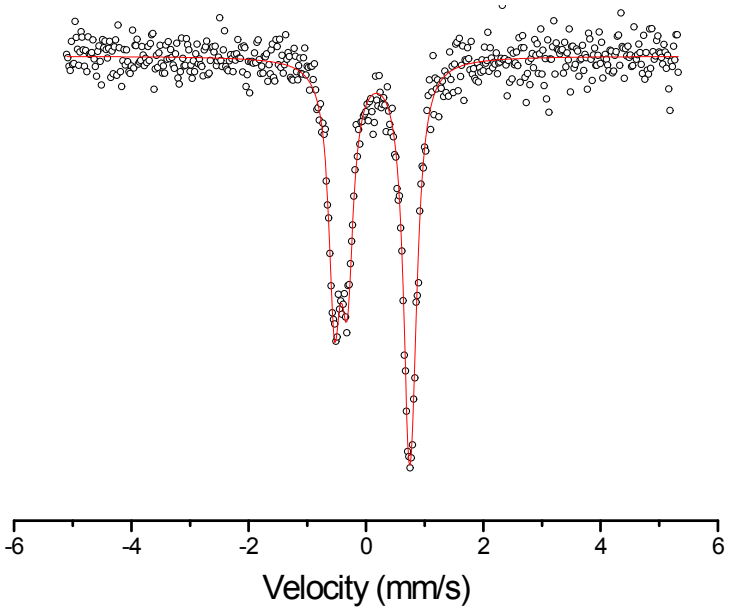
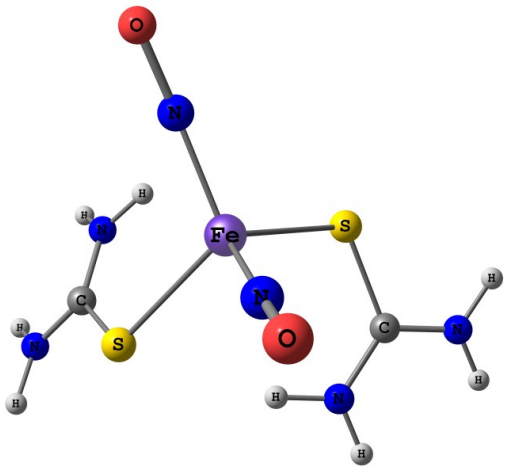


Fig. S6 293 K Mössbauer spectrum of **II** (raw data – black dots, fitted spectrum – red line).

Table S4 Cartesian coordinates and total energy of the cationic DNIC optimized at TPSSh/TZVP level of theory.

X	Charge : +1 Multiplicity : 2 Total energy: -2620.31305047 a.u.



26	0.860962567	1.699788402	-5.106006389
7	-0.704047287	1.216020552	-5.592516168
7	1.862040819	0.479937270	-4.453240173
8	-1.715623390	0.689743773	-5.834234470
8	2.341368905	-0.481209769	-4.001185432
16	0.328046211	3.338595537	-3.555451277
16	2.108847513	2.611700875	-6.866493673
7	2.932918004	3.455823175	-2.849985122
1	3.726919914	3.801853345	-2.326559952
1	3.108378120	2.797117406	-3.594275288
7	1.486806643	4.846604182	-1.726313896
1	2.234311055	5.246183628	-1.174348196
1	0.551035605	5.188125736	-1.564370937
7	0.406525851	4.701189831	-6.818441320
1	-0.085579096	5.493830739	-7.210075486
1	0.284696167	4.506020752	-5.830385834
7	1.512560139	4.302602603	-8.798901147
1	1.117750808	5.124781391	-9.235889422
1	2.120562014	3.718840482	-9.353838875
6	1.709420516	3.919277199	-2.648400875
6	1.253557923	3.979450891	-7.538066069

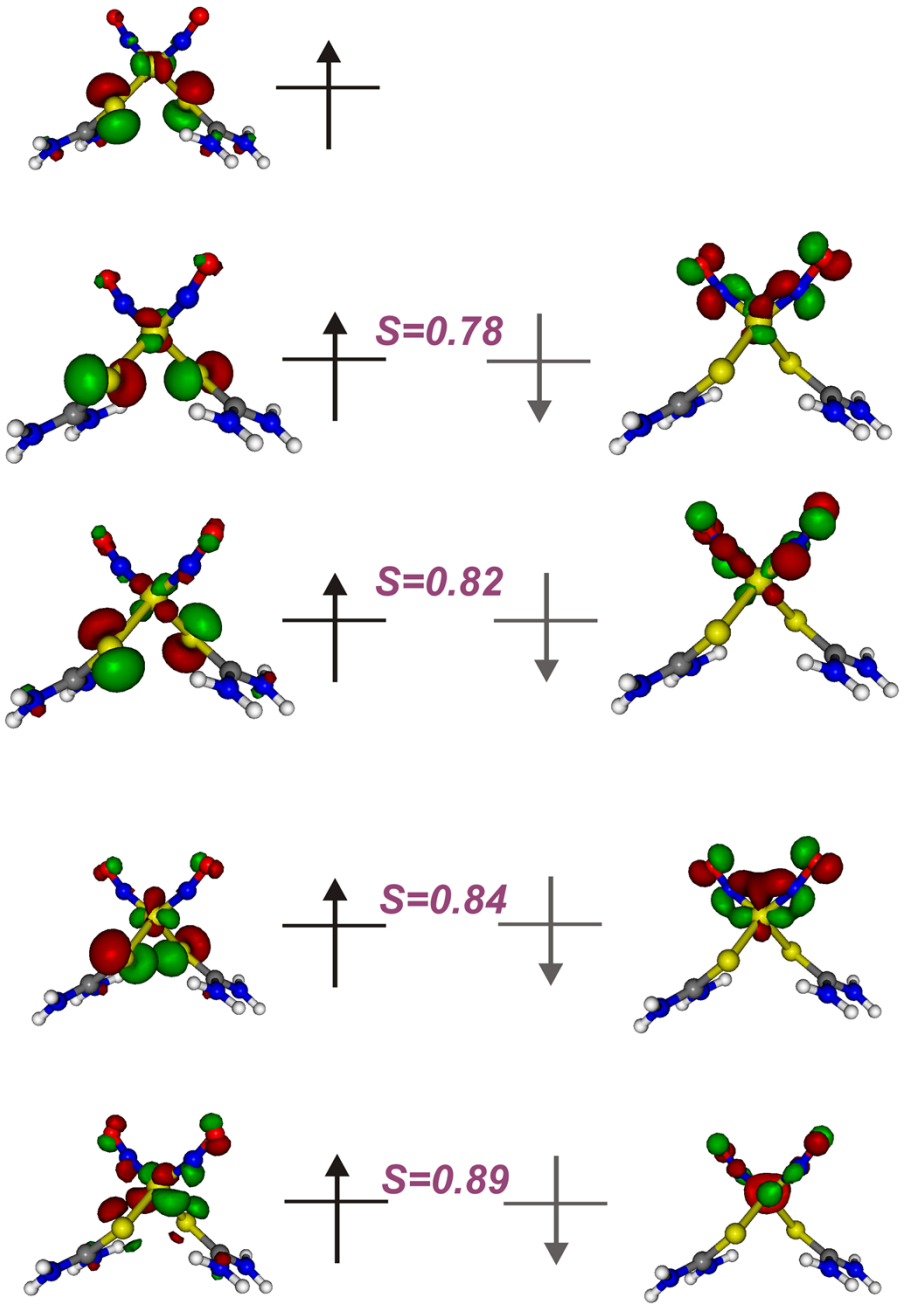


Fig. S7 Schematic MO diagram of cationic DNIC.

Table S5 Comparison of the optimized structural parameters of cationic DNIC using various density functionals with x-ray geometries.

	Fe-N, Å	N-O, Å	Fe-S, Å	<FeNO, °	<NFeN, °	<SFeS, °
BP86	1.668, 1.673	1.174, 1.176	2.301, 2.313	166.0, 169.0	114.5	111.2
TPSS	1.674, 1.676	1.173, 1.173	2.286, 2.314	167.0, 169.8	116.0	110.5
B3LYP	1.756, 1.757	1.166, 1.166	2.387, 2.394	166.2, 169.7	116.6	111.3
TPSSh	1.708,	1.165,	2.318,	168.1,	116.3	110.5

	1.709	1.166	2.343	169.0		
Expt. **I**	1.684(2)-1.695(2)	1.162(3)-1.169(3)	2.2907(7)-2.3250(7)	164.9(2)-172.7(3)	117.7(1)-120.3(1)	108.83(3)-111.17(3)
Expt. **II**	1.688(2), 1.689(2)	1.163(2), 1.175(2)	2.3130(5), 2.3353(6)	162.5(2), 170.1(2)	114.18(9)	109.42(2)

Table S6 The calculated Mössbauer spectroscopic parameters for cationic DNIC using different density functionals in comparison with the experimental values.

	δ, mm/s	$\lvert\Delta E_Q\rvert$, mm/s
BP86	0.325	0.765
TPSS	0.314	0.812
B3LYP	0.261	1.181
TPSSh	0.217	1.029
Expt. **I**	0.184(1)	1.165(1)
Expt. **II**	0.219(1)	1.08(2)