A Dual-Ion-Switched Molecular Brake based on Ferrocene

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91 Stockholm. Sweden.

All solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. Compounds were visualized with UV light at 254 nm and 365 nm. Melting points were determined on a hot-plate melting point apparatus and are uncorrected. ¹H NMR and ¹³C NMR spectra were obtained by using a Bruker AV 400 spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constant (*J*) are recorded in Hertz (Hz). High resolution mass spectra were performed with a HP5989 mass spectrometer, and UV-Vis spectra on a Varian Cary 500 spectrophotometer (1-cm quartz cell used). Fluorescent spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. For tests, the applied H⁺ and OH⁻ are hydrochloric acid and NaOH aqueous solution, and the applied Zn²⁺ is ZnCl₂.

All electrochemical experiments were performed with a Versastat II electrochemical workstation using a normal three-electrode cell with a Pt working electrode, a Pt wire auxiliary electrode, and Ag/AgCl reference electrode in saturated KCl solution. All potentials are quoted with respect to Fc^+/Fc under a nitrogen atmosphere at 25 °C. The experiments were carried out in solutions containing 0.1 M of $[(nBu)_4N]PF_6$ as supporting electrolyte. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min and the working electrode was cleaned after each run. Cyclic voltammetry (CV) curves were recorded at a scan rate of 50 mV s⁻¹ and the differential pulse voltammetry (DPV) curves were recorded at a 20 mV s⁻¹ scan rate.

Computational details

Calculated geometries for complex $FI2-2H^+$ and $FI2-Zn^{2+}$ were fully optimized in the gas-phase with tight convergence criteria at the DFT level with the Gaussian 03 package,¹ using the B3LYP² functional and the 6-31G* basis set for all atoms except Zn and Fe, for which Lanl2DZ-ECP was used.



Scheme S1 Synthesis of the triad FI2 and reference compound FI

Synthesis of 2-Methylene-1,1,3-trimethyl-1H-benzo[e]indoline (4):

A mixture of 1,1,2,3-Tetramethyl-1H-benzo[e]indolinium iodide (20 g, 0.057 mol) and potassium hydroxide (7 g, 0.125 mol) was stirred vigorously at room temperature in water (40 mL) and toluene (100 mL) for 2 h. Upon standing, the organic phase was isolated and dried (MgSO₄) and then concentrated under reduced pressure. The product was then recrystallized from ethanol to give **4** (10.0 g, 79%) as olivine flakes, m.p. 107-108 °C. ¹H NMR (400MHz, CDCl₃, 25 °C, TMS): δ (ppm) 1.69 (s, 6H, CH₃), 3.15 (s, 3H, N-CH₃), 3.95 (d, 2H, CH₂, *J* = 26.4 Hz), 7.01 (d, 1H, *J* = 4.8 Hz), 7.21 (s, 1H), 7.41 (s, 1H), 7.72 (d, 1H, *J* = 5.2 Hz) 7.78(d, 1H, *J* = 4.8 Hz), 7.98 (d, 1H, *J* = 5.6 Hz).

Synthesis of 1,1'-Diacetylferrocene

A mixture of anhydrous aluminum chloride (30 g, 0.225 mol) and dry methylene chloride (85 mL) was stirred under argon at room temperature. Through the addition funnel, acetyl chloride (17.7 g, 0.451mol) was slowly added, dissolving the aluminum chloride. A solution of ferrocene (16.3 g, 0.088 mol) in dry methylene chloride (90 mL) was added dropwise at 0-5 °C over a period of 30 min. The reaction was immediate as evidenced by the evolution of hydrogen chloride and the formation of a dark purple complex. The reaction mixture was stirred 20 h at room temperature, and then hydrogen chloride evolution had ceased. The reaction mixture was hydrolyzed by pouring it onto ice (130 g).

The two-phase system, which was badly emulsified, was filtered under vacuum and the phases were separated. The organic phase was washed until neutral and dried over anhydrous calcium sulfate. The methylene chloride solution was filtered free of drying agent and the solvent evaporated under reduced pressure. The crude product was recrystallized twice from methanol yielding orange-red crystals (17.7 g, 75%). ¹H NMR (400MHz, CDCl₃, 25 °C, TMS): δ (ppm) 2.37 (s, 6H, CH₃), 4.52 (s, 4H), 4.78 (s, 4H).

Synthesis of 1,1'-Ferrocenedicarboxylic Acid

To commercial 5.46% sodium hypochlorite solution (200 mL) protected from light was added powered 1,1'-diacetylferrocene (10.6 g, 39.3 mmol). With rapid stirring the temperature was maintained between 44 and 50 °C. Additional portions of sodium hypochlorite solution (3 \times 100 mL) were added after 1.5, 2, and 3 h. Following the final addition of sodium hypochlorite solution, the reaction mixture was stirred 2 h at 45-50 °C, and then filtered while it was still warm. The clear orange filtrate obtained was treated with aqueous bisulfite and acidified with dilute hydrochloric acid to yield orange precipitate (11.08 g). The crude acid was dissolved in sodium bicarbonate solution, hydrochloric filtered, and reprecipitated with dilute acid to vield of 1,1'-ferrocenedicarboxylic acid (9.56 g, 89%). ¹H NMR (400MHz, DMSO- d_6 , 25 °C, TMS): δ (ppm) 4.47 (d, 4H, J = 6.4 Hz), 4.70 (d, 4H J = 6.4 Hz).

Synthesis of 1,1'-Ferrocenedicarbonyl Chloride³

A mixture of 1,1'-ferrocenedicarboxylic acid (4.11g, 15 mmol), dry methylene chloride (50 mL), freshly distilled oxalyl chloride (8.8 mL, 100 mmol), and DMF (15 drops) was stirred in the dark for 12 h at room temperature. Then the contents evaporated to dryness under reduced pressure. The residue was extracted repeated at 80 °C with petroleum ether (b.p. 100-140 °C) to yield red crystals (4.20 g, 90%), m.p. 98-100 °C. ¹H NMR (400MHz, CDCl₃, 25 °C, TMS): δ (ppm) 4.77 (t, 4H, J = 2.0 Hz), 5.06 (t, 4H J = 2.0 Hz).

Synthesis of FI

A mixture of 1,1'-ferrocenedicarbonyl chloride (3.11 g, 0.01 mol), dry methylene chloride (50 mL) and triethylamine (4 mL) was protected by argon. A solution of 2-methylene-1,1,3-trimethyl-1H-benzo[e]indoline (4) (2.23 g, 0.01 mol) in dry methylene chloride (20 mL) was added dropwise at 0-5 °C over a period of 30 min. The reaction mixture was stirred 10 h at room temperature, and then anhydrous aluminum chloride (3 g) was added. After 10 h of stirring at room temperature, the reaction mixture was slowly poured into aqueous sodium hydroxide (100 mL, 0.2 M). The organic phase was washed until neutral and dried over anhydrous magnesium sulfate. The methylene chloride solution was filtered free of drying agent and the solvent evaporated under reduced pressure. The crude product was further purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/1) to afford FI (3.05 g, 61%), m.p. 68-69 °C. ¹H NMR (400MHz, CDCl₃, 25 °C, TMS): δ (ppm) 2.15 (m, 6H, CH₃), 3.44 (m, 3H, N-CH₃), 4.36 (t, 2H, Cp-H), 4.51 (t, 2H, Cp-H), 4.64 (t, 2H, Cp-H), 4.90 (t, 2H, Cp-H), 5.78 (m, 2H, CHCO), 7.18 (d, 2H J = 8.8 Hz, Ar-H), 7.35 (t, 2H J = 7.6 Hz, Ar-H), 7.54 (t, 2H J = 7.6 Hz, Ar-H), 7.81 (d, 2H J = 8.8 Hz, Ar-H), 7.87 (d, 2H J = 8.8 Hz, Ar-H), 8.09 (d, 2H J = 8.8 Hz, Ar-H).

Synthesis of FI2

A mixture of 2-methylene-1,1,3-trimethyl-1H-benzo[e]indoline (4) (4.46 g, 0.02 mol), dry methylene chloride (30 mL) and triethylamine (4 mL) was protected by argon. A solution of 1,1'-ferrocenedicarbonyl chloride (3.11 g, 0.01 mol) in dry methylene chloride (50 mL) was added dropwise at 0-5 °C over a period of 30 min. The reaction mixture was stirred 10 h at room temperature, and then anhydrous aluminum chloride (5 g) was added. After 30 h of stirring at room temperature, the reaction mixture was slowly poured into aqueous sodium hydroxide (100 mL, 0.2 M). The organic phase was washed until neutral and dried over anhydrous magnesium sulfate. The methylene chloride solution was filtered free of drying agent and the solvent evaporated under reduced pressure. The crude product was further purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/5) to afford FI2 (2.10 g, 31%), m.p. 158-159 °C. ¹H NMR (400MHz, CDCl₃, 25 °C, TMS): δ (ppm) 2.16 (m, 12H, CH₃), 3.33 (m, 6H, N-CH₃), 4.47 (m, 4H, Cp-H), 4.82 (m, 4H, Cp-H), 5.71 (m, 2H, CHCO), 7.12 (d, 2H J = 8.8 Hz, Ar-H), 7.35 (t, 2H J = 7.6 Hz, Ar-H), 7.53 (t, 2H J = 7.6 Hz, Ar-H), 7.81 (d, 2H J = 8.8 Hz, Ar-H), 7.86 (d, 2H J = 8.8 Hz, Ar-H), 8.08 (d, 2H J = 8.8 Hz, Ar-H). ¹³C NMR (400 MHz, CDCl₃, 25 °C, TMS): δ(ppm) 22.46 (4C, CH₃), 29.89 (2C, N-CH₃), 49.95 (2C, C(Me)₂), 70.69 (4C, CpC), 72.81 (4C, CpC), 85.63 (2C, CpC), 91.91 (2C), 109.19 (2C), 122.49 (2C), 123.14 (2C), 126.86 (2C), 128.75 (2C), 129.28 (2C), 129.68 (2C), 130.71 (2C), 130.83 (2C), 140.61 (2C), 172.51 (2C), 188.90 (2C, CO). HRMS (EI) : *m/z* [FI2] calc. 684.6456, found 684.2440.

Crystal of FI2

Single crystals of FI2 with the dimensions $0.327 \times 0.311 \times 0.214$ mm3 was mounted on a Rigaku RAXIS RAPID IP imaging plate system with Mo_{Ka} radiation ($\lambda = 0.71073$ Å) at 293(2) K. Crystal data (CCDC 713480) and structure refinement data are given in Table S2. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif.</u>

Empirical formula	$C_{46}H_{46}Fe\;N_2O_3$			
Formula weight	730.70			
Temperature	293(2) K			
Wavelength	0.71073 Å			
Crystal system, space group	Monoclinic, P2(1)/n	1		
Unit cell dimensions	a = 9.4657(8) Å	$\alpha = 90^{\circ}$		
	b = 19.9920(18) Å	$\beta = 102.495(2)^{\circ}$		
	0			

Table S1	Crystal	data and	structure	refinement	for	FI2
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Volume	3828.0(6) Å ³
Z, Calculated density	4, 1.268 Mg/m ³
Absorption coefficient	0.437 mm ⁻¹
F (000)	1544
Crystal size	$0.327\times0.311\times0.214~\text{mm}^3$
Theta range for data collection	2.01 to 26.00°
Limiting indices	$-11 \le h \le 11, -24 \le k \le 22, -24 \le l \le 25$
Reflections collected / unique	20822 / 7513 [R(int) = 0.0512]
Completeness to theta = 26.00°	99.8 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.75948
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7513 / 2 / 465
Goodness-of-fit on F ²	0.928
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0562, wR2 = 0.1369
R indices (all data)	R1 = 0.0927, wR2 = 0.1516
Largest diff. peak and hole	0.487 and -0.556 e $\text{\AA}^{\text{-3}}$

Notes and references

Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

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Fig. S1 ¹H NMR spectra of FI2 in CDCl₃.



Fig. S2 ¹³C NMR spectra of **FI2** in CDCl₃.

Elemental Composition Report

Multiple Mass Analysis: 31 mass(es) processed Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 5651 formula(e) evaluated with 113 results within limits (up to 50 closest results for each mass)

Minimum:	3.40		-1.5								
Maximum:	100.00)		5.0	5.	.0	50	0.0			
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	For	mula			
684.2440	100.00	684.2439	0.1	0.1	26.0	1	C44	H40	N2	O2	56Fe



Fig. S3 HRMS (EI) spectra of FI2.



Fig. S4 HRMS (ESI) spectra of $[FI2 \cdot Zn^{2+} + Cl]^+$.



Scheme S2 Schematic representation of Zn²⁺ binding in FI2.



Fig. S5 Parts of the ¹H NMR spectra of: free FI2 (up) and FI2-Zn²⁺ (down) in DMSO-d₆.



Fig. S6 Parts of the 13 C NMR spectra of: free **FI2** (up) and **FI2**-Zn²⁺ (down) in DMSO-d₆.



Fig. S7 UV-vis spectra of FI2 (0.02 mM) with Zn^{2+} in CH₃CN at 298 K.



Fig. S8 Fluorescence spectra of FI2 (0.02 mM) with Zn^{2+} in CH₃CN at 298 K.



Fig. S9 UV-Vis spectra (A) and fluorescence spectra (B, $\lambda_{ex} = 380 \text{ nm}$) of **FI** (0.02 mM) and **FI2** (0.02 mM) in CH₃CN in the presence of Zn²⁺ (0.6 mM) at 298 K: **FI** (black), **FI** + Zn²⁺ (red), **FI2** (green), **FI2** + Zn²⁺ (blue).

Fig. S10 CV and DPV (inset) of compound **FI2** (0.2 mM), in CH₃CN using $[(nBu)_4N]PF_6$ (0.1M) as supporting electrolyte, and scanned at 100 mV s-1 from 0.4 to 1.6 V.

Fig. S11 Evolution of the DPV of **FI2** (0.2 mM) in CH₃CN by using $[(n-Bu)_4N]PF_6$ (0.1M) as supporting electrolyte, scanned at 20 mVs⁻¹, from 0.4 V to 1.5 V, when 1 equiv. of ZnCl₂ and 1 equiv. of EDTA is added.

Fig. S12 Change in UV-Vis spectra of complexation/decomplexation of **FI2** (0.02 mM) in CH₃CN: free **FI2** (black), **FI2** + 1 equiv. of Zn^{2+} (red), **FI2** + 1 equiv. of Zn²⁺ + 1 equiv. of EDTA (green), at 298K.

Fig. S13 The colour change response of **FI2** (0.02 mM) with H^+ in CH₃CN at 298 K.

Fig. S14 UV-Vis spectra (A) and fluorescence spectra (B, $\lambda_{ex} = 380$ nm) of **FI2** (0.02 mM) in CH₃CN at 298 K. **FI2** was treated with Zn²⁺ and H⁺ in different order: (1) 30 eq. of Zn²⁺ (blue); (2) first 30 eq. of Zn²⁺ and then 5 eq. of H⁺ (cyan); (3) 5 eq. of H⁺ (green); (4) first 5 eq. of H⁺ and then 30 eq. of Zn²⁺ (red).

Table S2 Fluorescence lifetime of FI2 (λ_{em} =470 nm), excited at 372 nm in CH ₃ CN	1
(0.2 mM, 298K).	

	FI2	$FI2+Zn^{2+}$	$FI2+2H^+$
τ1 (ns)	2.98	3.26	4.39
τ2	15.42	18.87	15.50
χ^2	1.22	1.46	1.43

Fig. S15 IR spectrum of FI.

Fig. S16 IR spectrum of FI2.

Fig. S17 The simulated (bottom) and experimental (top) powder X-Ray diffraction patterns of FI2.

Fig. S18 TGA thermogram of FI2.

Calculated structure:

Coordinates for H complex: Optimized by b3lyp/6-31g*

С	-10.264444	2.273190	1.143069	С	5.972536	1.804127	-0.064138
С	-9.438089	2.684492	0.122482	Н	6.017918	-2.390602	1.778351
С	-8.287761	1.932100	-0.231852	N	4.781160	0.077924	1.252630
С	-7.980628	0.728254	0.500332	C	5.847404	2.156680	-1.566526
С	-8.862128	0.332733	1.541653	С	6.466999	3.038441	0.737348
Н	-7.709137	3.273215	-1.829663	С	4.608293	1.339091	0.455389
Н	-11.143500	2.854776	1.402474	Н	5.151709	2.990027	-1.708803
Н	-9.659312	3.591653	-0.432809	Н	6.809211	2.465861	-1.978505
С	-7.453177	2.359109	-1.302363	Н	5.490612	1.300573	-2.146923
С	-6.809234	0.004569	0.116978	Н	5.771568	3.874858	0.614680
Н	-8.674962	-0.577692	2.097191	Н	6.557434	2.820015	1.805883
С	-6.073303	0.473494	-0.942976	Н	7.448881	3.360026	0.381748
С	-6.346630	1.636192	-1.683188	С	3.405326	1.887732	0.277936
Н	-5.717595	1.958352	-2.507718	Н	3.364891	2.839426	-0.246296
Ν	-4.947755	-0.441330	-1.261485	С	2.084210	1.441133	0.846493
С	-6.199517	-1.269159	0.709077	Ο	1.394272	2.259937	1.433899
С	-7.086504	-2.519843	0.465832	С	-1.830705	-1.037328	-1.077387
Н	-6.569391	-3.423592	0.803507	С	-1.819766	0.259312	-0.435253
Н	-8.024928	-2.439752	1.020028	С	-0.899377	-0.982399	-2.174389
Н	-7.336508	-2.641699	-0.592630	С	-0.908401	1.089222	-1.147462
С	-5.863855	-1.136152	2.214778	Н	-2.360888	0.535180	0.461963
Н	-5.337280	-2.027716	2.570293	Fe	0.050541	-0.587260	-0.412224
Н	-5.236172	-0.260555	2.405782	С	-0.354177	0.328986	-2.222180
Н	-6.771250	-1.038078	2.812711	Н	-0.680194	-1.805216	-2.841117
С	-4.893923	-1.374387	-0.085634	Н	-0.651573	2.107578	-0.885142
С	-3.821771	-2.132574	0.147522	C	0.694514	-0.624688	1.529631
Н	-3.881118	-2.838752	0.972117	Н	0.373424	0.684069	-2.940344
С	-2.573863	-2.259640	-0.686510	C	1.665182	0.027864	0.688827
С	-9.974217	1.085366	1.852023	Н	0.200117	-0.165189	2.374660
Н	-10.636892	0.760942	2.648521	C	1.365853	-2.141452	-0.084210
0	-2.211198	-3.373725	-1.028918	C	2.069632	-0.925236	-0.321535
Н	11.874933	-0.654682	-1.089028	Н	1.427300	-3.040142	-0.683612
С	10.850995	-0.404453	-0.829770	Н	2.744028	-0.730917	-1.147184
С	10.058088	-1.320164	-0.176685	С	0.533818	-1.955904	1.061240
С	10.334918	0.869668	-1.158346	Η	-0.131831	-2.701105	1.476986
С	8.718708	-1.005999	0.173217	С	-5.139549	-1.155739	-2.587853
Н	10.450027	-2.298565	0.086777	Н	-5.209683	-0.401306	-3.372061

Н	10.969707	1.591104	-1.663686	Н	-4.289926	-1.815988	-2.760944
С	9.036778	1.207848	-0.842043	Н	-6.065544	-1.726110	-2.530366
С	8.184638	0.287604	-0.175266	С	4.637688	0.287864	2.749623
С	7.916920	-1.955876	0.866232	Н	3.633358	0.653882	2.961401
Н	8.675933	2.196084	-1.098383	Н	4.813713	-0.667958	3.244075
С	6.829865	0.560747	0.188798	Н	5.386814	1.015092	3.059482
Н	8.347152	-2.923202	1.108008	Н	4.057946	-0.597822	0.967466
С	6.624558	-1.668614	1.239863	Н	-4.058243	0.074625	-1.317545
С	6.135224	-0.402510	0.876996				

Coordinates for Zn complex: Optimized by B3LYP/6-31G*/Lanl2DZ-ecp

С	7.157008	-4.823019	1.287399	С	-3.805397	-2.034157	1.302956
С	6.521982	-4.956162	0.072790	С	-3.776624	-0.657108	-0.607679
С	5.582583	-3.988161	-0.368677	Н	-3.719011	-3.110774	3.208923
С	5.295419	-2.853782	0.475496	Ν	-2.917694	-0.936616	1.537375
С	5.973352	-2.748661	1.721820	С	-4.898443	0.386968	-0.867300
Н	5.188242	-4.985349	-2.246802	С	-2.952638	-0.928255	-1.891365
Н	7.874811	-5.569379	1.612836	С	-2.865970	-0.125525	0.496614
Н	6.734902	-5.807033	-0.568268	Н	-4.488751	1.308375	-1.294826
С	4.938341	-4.126551	-1.630867	Н	-5.625354	-0.019601	-1.574148
С	4.349905	-1.913886	-0.013836	Н	-5.429379	0.634732	0.056515
Н	5.785235	-1.903526	2.374405	Н	-2.521938	-0.000249	-2.284977
С	3.752021	-2.113773	-1.243413	Н	-2.147660	-1.646622	-1.701669
С	4.023832	-3.205585	-2.089671	Н	-3.592098	-1.347659	-2.670828
Н	3.559230	-3.318895	-3.062368	С	-2.102229	1.108612	0.409621
N	2.841566	-1.039161	-1.497269	Н	-2.328419	1.621395	-0.533510
С	3.828749	-0.609507	0.567080	С	-2.239948	2.116488	1.522719
С	4.955382	0.452820	0.696455	0	-2.991781	1.981881	2.469873
Н	4.562293	1.399870	1.081407	С	1.274670	3.265639	-1.514156
Н	5.720282	0.097409	1.390639	С	0.611687	5.473390	-1.438695
Н	5.437057	0.638672	-0.268036	Fe	0.011390	4.073952	-0.009565
С	3.079270	-0.799792	1.910180	С	-0.485587	4.718034	-1.941555
Н	2.663111	0.149985	2.265679	Н	0.615569	6.540153	-1.259041
Н	2.271311	-1.533095	1.813375	С	0.047150	3.283812	1.939472
Н	3.765745	-1.163771	2.677499	Н	-1.453706	5.109447	-2.223752
С	2.849979	-0.156767	-0.514572	С	-1.319952	3.312131	1.458978
С	2.087162	1.078853	-0.456650	Н	0.553063	2.433033	2.386507
Н	2.350089	1.643382	0.445470	С	-0.499769	5.467303	1.464533
С	2.118307	2.013836	-1.632437	С	-1.643770	4.667808	1.175055
С	6.879368	-3.709438	2.114942	Н	-0.426293	6.536850	1.319753

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Н	7.388951	-3.611075	3.068671	Н	-2.587360	5.022540	0.781669
Ο	2.711052	1.788330	-2.671033	С	0.539897	4.620109	1.940879
Н	-7.747389	-5.700878	-1.545052	Н	1.529780	4.932946	2.245097
С	-7.050256	-4.930503	-1.230859	С	2.014660	-1.010169	-2.704920
С	-6.485160	-4.977588	0.023945	Н	1.711543	-2.031320	-2.940624
С	-6.727417	-3.873963	-2.114859	Н	1.128465	-0.402595	-2.522331
С	-5.574687	-3.976303	0.451540	Н	2.574631	-0.575169	-3.534711
Н	-6.733099	-5.783990	0.708433	С	-2.180507	-0.802126	2.794361
Н	-7.182291	-3.842737	-3.100268	Н	-1.278946	-0.213262	2.622937
С	-5.846193	-2.884223	-1.737481	Н	-2.797882	-0.295735	3.539098
С	-5.240670	-2.900361	-0.450237	Н	-1.900105	-1.797329	3.141626
С	-5.006147	-4.024406	1.755982	С	1.695082	4.584759	-1.177632
Н	-5.622878	-2.084440	-2.434502	Н	2.663127	4.859517	-0.779478
С	-4.327523	-1.923444	0.028265	С	-0.087435	3.353320	-1.993196
Н	-5.289763	-4.841122	2.413163	Н	-0.661188	2.548288	-2.439973
С	-4.124251	-3.067390	2.204485	Zn	-0.002424	1.305178	0.007855