Supplementary Information

A novel *o*-vanillin Fe(III) complex catalytically active in C–H oxidation: Exploring the magnetic exchange interactions and spectroscopic properties with different DFT functionals

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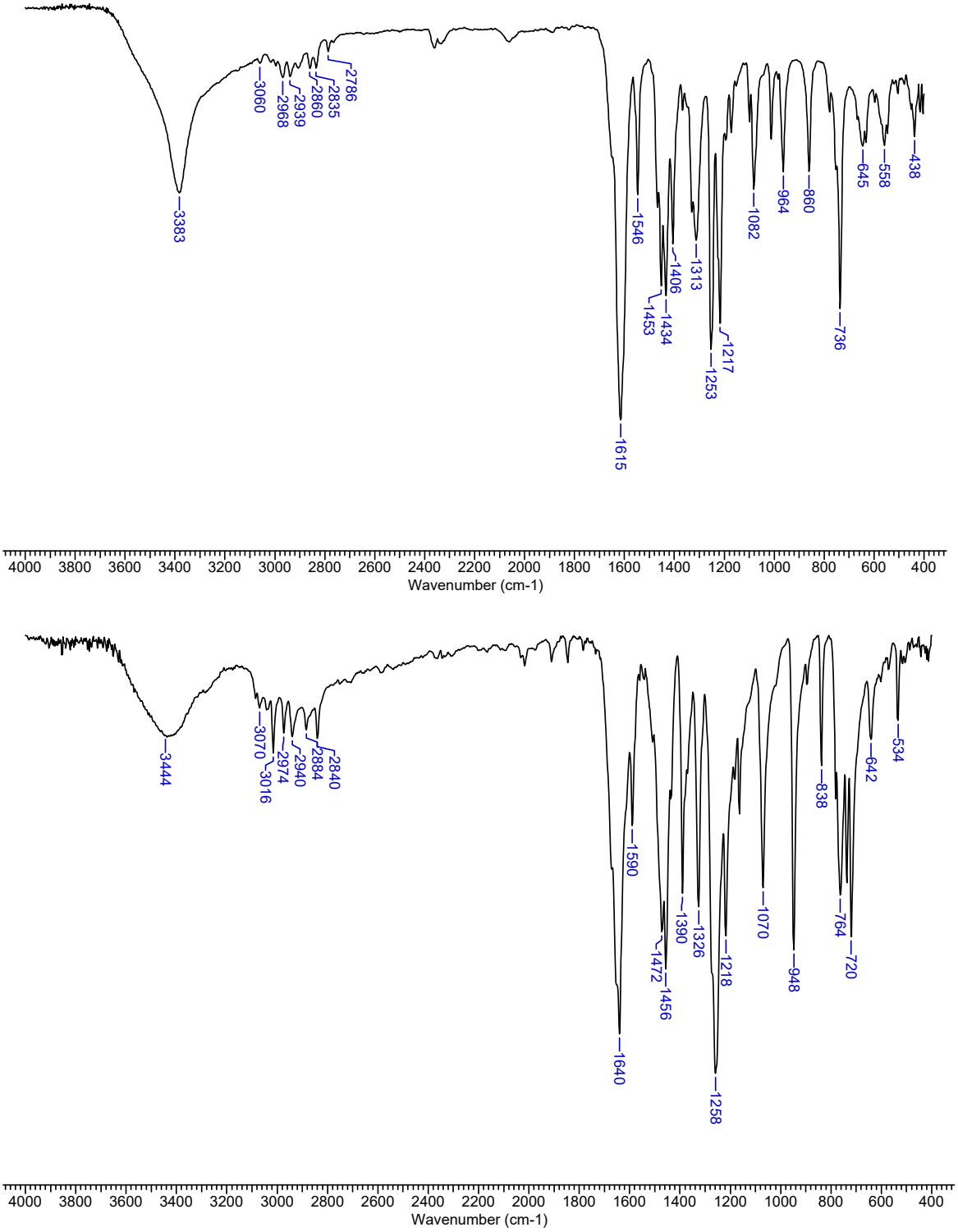

Figure S1. IR spectra of **1** (top) and *o*-vanillin (bottom).

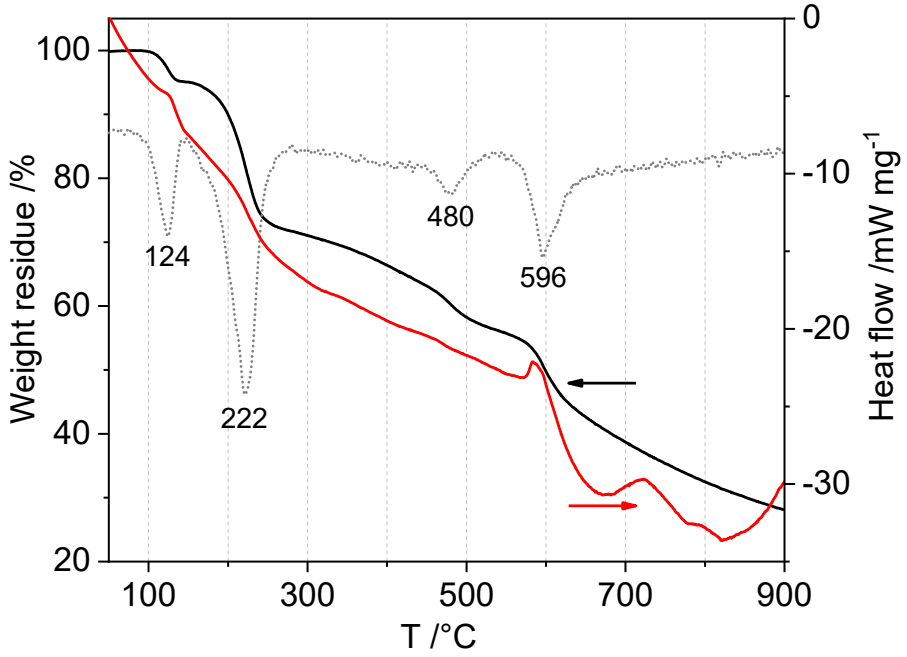

Figure S2. Thermogravimetric plot showing the loss in weight (black line), its first derivative (grey dot line) and heat flow (red line) with the increase of temperature for complex **1** at 10°/min heating speed under N_2 atmosphere. The numbers in the plot show peak temperatures.

Table S1. Crystallographic parameters and refinement data for **1**

Empirical formula	$C_{16}H_{16}ClFeO_7$
Formula weight	411.59
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 9.3705(2) Å
	b = 13.1255(3) Å
	c = 13.9195(3) Å
	β = 104.818(2)°
Volume	1655.06(6) $Å^3$
Z	4
Density (calculated)	1.652 Mg/m^3
μ	9.140 mm^{-1}
Crystal size	0.20 x 0.03 x 0.025 mm^3
θ range for data collection	4.706 to 67.226°
Index ranges	-8<=h<=11, -15<=k<=15, -16<=l<=16
Reflections collected	13206
Independent reflections	2957 [R(int) = 0.0372]
Completeness to θ = 67.226°	99.7 %
Absorption correction	Analytical
Max. and min. transmission	0.820 and 0.424
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2957 / 2 / 236
Goodness-of-fit on F^2	1.057
Final R indices [I>2σ(I)]	R1 = 0.0327, wR2 = 0.0823
R indices (all data)	R1 = 0.0395, wR2 = 0.0869
Largest diff. peak and hole	0.304 and -0.316 $e.Å^{-3}$

Table S2. Selected bond lengths (Å) and angles (°) in **1**

Fe(1)-O(21)	1.9214(16)	Fe(1)-O(261)	2.0592(16)
Fe(1)-O(11)	1.9387(16)	Fe(1)-O(1)	2.1317(18)
Fe(1)-O(161)	2.0488(17)	Fe(1)-Cl(1)	2.3023(7)
O(21)-Fe(1)-O(11)	94.04(7)	O(161)-Fe(1)-O(1)	81.29(7)
O(21)-Fe(1)-O(161)	169.65(7)	O(261)-Fe(1)-O(1)	81.52(7)
O(11)-Fe(1)-O(161)	89.81(7)	O(21)-Fe(1)-Cl(1)	97.19(5)
O(21)-Fe(1)-O(261)	88.70(7)	O(11)-Fe(1)-Cl(1)	96.44(6)
O(11)-Fe(1)-O(261)	170.99(7)	O(161)-Fe(1)-Cl(1)	91.91(6)
O(161)-Fe(1)-O(261)	86.10(7)	O(261)-Fe(1)-Cl(1)	91.72(5)
O(21)-Fe(1)-O(1)	89.09(7)	O(1)-Fe(1)-Cl(1)	170.69(5)
O(11)-Fe(1)-O(1)	89.93(7)		

Table S3. Hydrogen bonding parameters (Å, °) for **1**[a]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(1)-H(1BO)...O(21)[1]	0.765(18)	2.26(3)	2.853(2)	136(3)
O(1)-H(1BO)...O(22)[1]	0.765(18)	2.37(2)	3.075(2)	155(3)
O(1)-H(1AO)...O(11)[1]	0.792(18)	2.08(2)	2.811(2)	153(4)
O(1)-H(1AO)...O(12)[1]	0.792(18)	2.52(3)	3.147(2)	138(3)

[a] Symmetry transformation used to generate equivalent atoms: [1] 1 – x,1 – y, 1 – z.

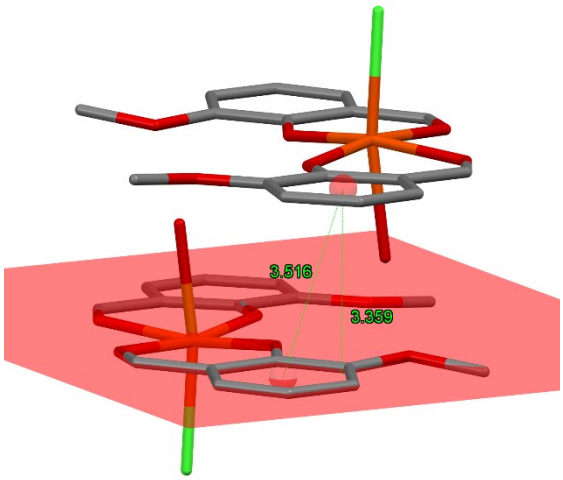

Figure S3. Face-centred stacking between aromatic rings in the hydrogen-bonded dimer of **1**. H atoms are not shown.

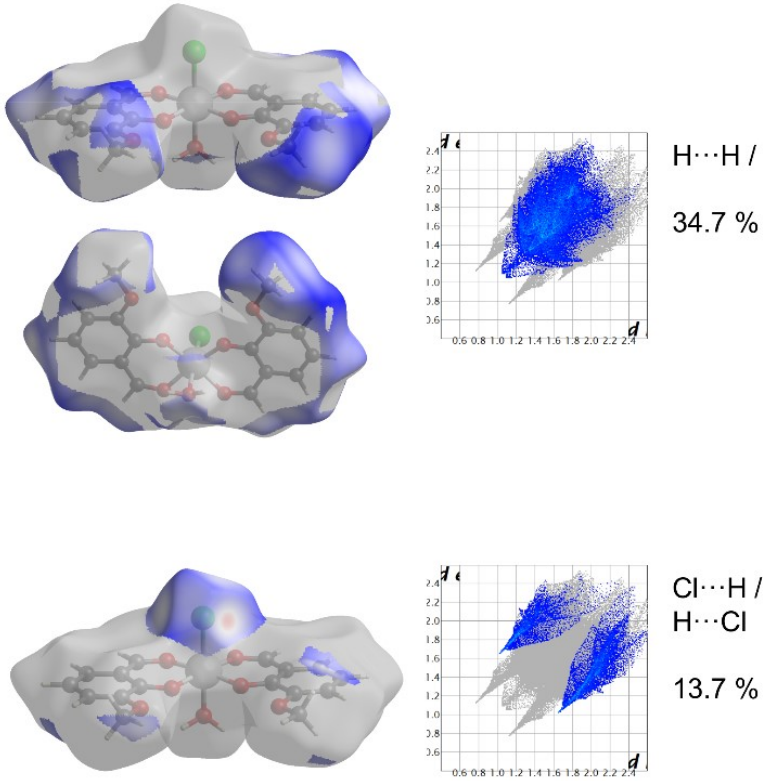

Figure S4. The Hirshfield surfaces and fingerprint plots of the monomer **1** featuring the H···H and Cl···H contacts.

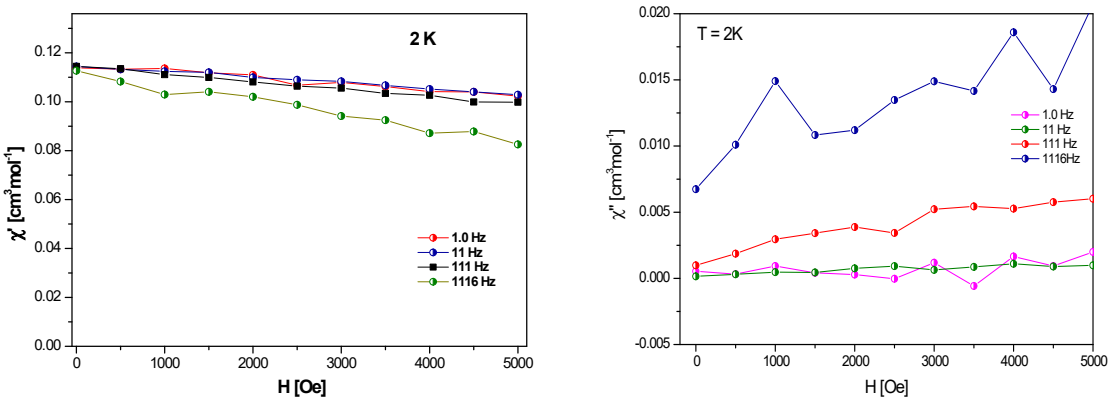

Figure S5. Field dependence of the AC susceptibility components for **1** at T = 2.0 K for a set of frequencies of the AC field.

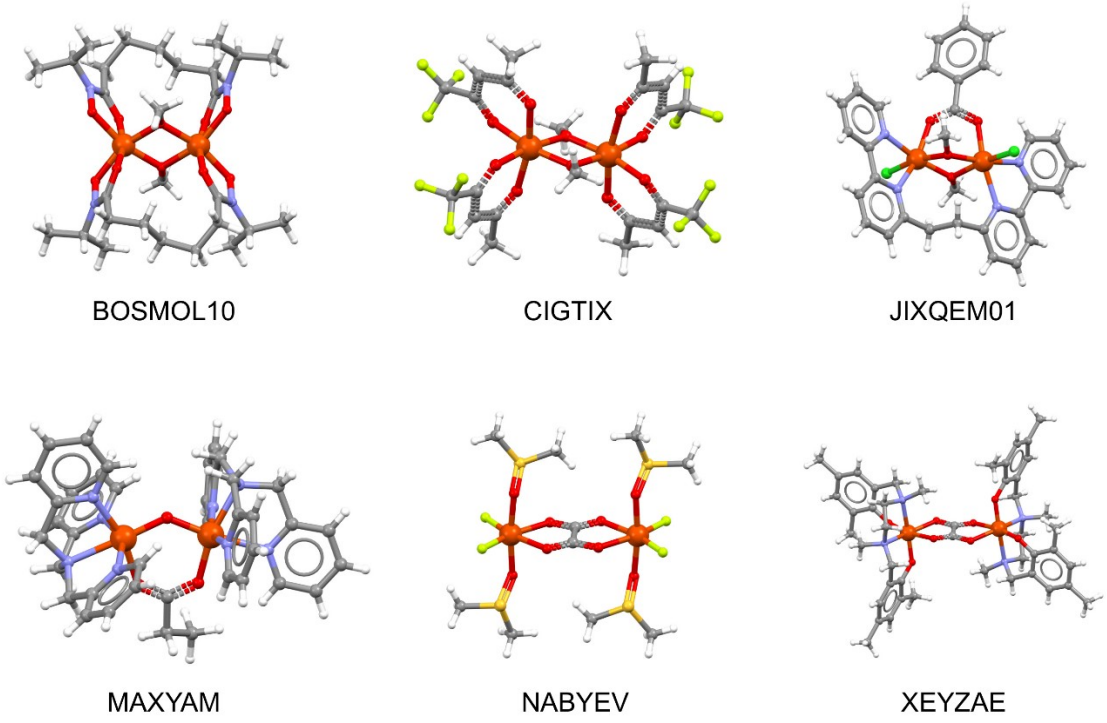

Figure S6. Molecular structures and CSD refcodes of the binuclear Fe(III) complexes used as test models for broken symmetry calculations of the J_{FeFe} exchange coupling constants (see Table S5 for literature references). The original structures CIGTIX and MAXTAM were simplified by replacing the phenyl and naphthyl groups, respectively, with methyl ones.

Table S4. Calculated exchange couplings for compound **1** and its model derivatives.[a]

Conditions	d(Fe···Fe), Å	J_{calcd},[b] cm^{-1}	$E_{HS} - E_{BS}$, cm^{-1}	Overlap[c]
1[d]	4.753	–0.12	3.603	0.01512
Free optimization	4.711	–0.18	5.293	0.01906
Constrained Fe···Fe distance	5.122	–0.09	2.804	0.01419
Constrained Fe···Fe distance	5.500	–0.04	1.256	0.00916
Constrained Fe···Fe distance	6.000	–0.01	0.388	0.00539
MeCN derivative, free optimization[e]	5.122	–0.05	1.573	0.01296
Constrained Fe···Fe distance[e]	4.753	–0.15	4.407	0.01927
Acetone derivative, free optimization[f]	5.122	–0.07	2.092	0.01305

[a] Broken symmetry calculations: B3LYP functional, def2-TZVPP basis set for metal, all coordinated atoms and hydrogen atoms of the water molecules (def2-SVP basis set for all other atoms). Geometry optimization: B97-3c functional and def2-TZVP basis set for all atoms; [b] J_B formalism (see Table S5 footnote for details); [c] magnetic orbitals overlap obtained from the unrestricted coordinating orbitals analysis; [d] X-ray coordinates; [e,f] coordinated water molecules replaced with acetonitrile[e] or acetone[f] ones, methoxy groups replaced with H atoms.

Table S5. Experimental and calculated exchange couplings for selected literature binuclear Fe(III) complexes.

CSD refcode[a]	d(Fe···Fe), Å	J_{exp}[b], cm^{-1}	J_{calcd}[b]				Form.[c]	ref.
			TPSSh	B3LYP	B97-3C	M06-2X		
BOSMOL10	3.168	–21.84	–36.84	–26.2	–48.74	–9.56	J_A	S1
			–30.7	–21.82	–40.62	–7.96	J_B	
			–36.74	–26.14	–48.54	–9.56	J_C	
CIGTIX[d]	3.066	–28	–45.46	–30.96	–69.14	–8.9	J_A	S2
			–37.88	–25.8	–57.62	–7.42	J_B	
			–45.32	–30.9	–68.76	–8.9	J_C	
JIXQEM01	3.088	–20	–38.68	–24.14	–60.46	–6.14	J_A	S3
			–32.24	–20.12	–50.38	–5.12	J_B	
			–38.56	–24.08	–60.12	–6.14	J_C	
NABYEV	5.527	–9.72	–10.8	–8.2	–14.34	–3.6	J_A	S4
			–9.0	–6.82	–11.94	–3	J_B	
			–10.8	–8.2	–14.32	–3.6	J_C	
XEYZAE	5.505	–6	–10.8	–7.94	–16.56	–3.36	J_A	S5
			–9.0	–6.62	–13.8	–2.8	J_B	
			–10.8	–7.94	–16.56	–3.36	J_C	
MAXYAM[e]	3.255	–260	–321.96	–255.12	–438.42	–128.8	J_A	S6
			–268.3	–212.6	–365.34	–107.34	J_B	
			–317.88	–252.94	–428.74	–128.46	J_C	
LOZHOA[f]		–2.62		–7.08			J_A	S7
				–5.67			J_B	
				–7.08			J_C	
			NRMSE$_{small}$[g]					
			0.61	0.15	1.32	0.56	J_A	
			0.37	**0.08**	0.96	0.61	J_B	
			0.61	0.14	1.30	0.56	J_C	
			NRMSE$_{all}$[h]					
			0.11	**0.01**	0.31	0.22	J_A	
			0.03	0.08	0.19	0.25	J_B	
			0.10	0.02	0.29	0.22	J_C	

[a] reference code in the Cambridge Structural Database (CSD). See Figure S6 for the structures of Fe(III) binuclear complexes used for calculations; [b] the literature and calculated J constants were adjusted to the $H = -JS_1S_2$ spin Hamiltonian formalism. The calculations were performed by using Ahlrichs-type basis set def2-TZVPP for metal, all coordinated atoms as well as carbon atoms involved into the Fe···Fe bridges (def2-SVP basis set was used for all other atoms); [c] the J constants were determined from the energies of the high-spin and broken symmetry states (E_{HS} and E_{BS}, respectively), from which the J exchange coupling parameter could be determined through several formalisms: $J_A = -2\ (E_{HS} - E_{BS}) / (S_A + S_B)^2$, $J_B = -2\ (E_{HS} - E_{BS}) / (S_A + S_B)(S_A + S_B + 1)$ and $J_C = -2\ (E_{HS} - E_{BS}) / (\langle S^2\rangle_{HS} - \langle S^2\rangle_{BS})$, implemented in the ORCA system. The equations were multiplied by 2 to adjust them to the $H = -JS_1S_2$ spin Hamiltonian; [d] phenyl groups were replaced with methyl ones; [e] naphthyl group was replaced with methyl one; [f] the Fe(II) binuclear complex;

[g] Normalized Root-Mean-Square Error (NRMSE) for $-J < 30$ cm^{-1} data only: $$NRMSE = \frac{\sqrt{\sum_{i=1}^{n}(J_{calcd} - J_{exp})^2}}{n\left|J_{exp}^{max} - J_{exp}^{min}\right|}$$; [h] NRMSE using all data.

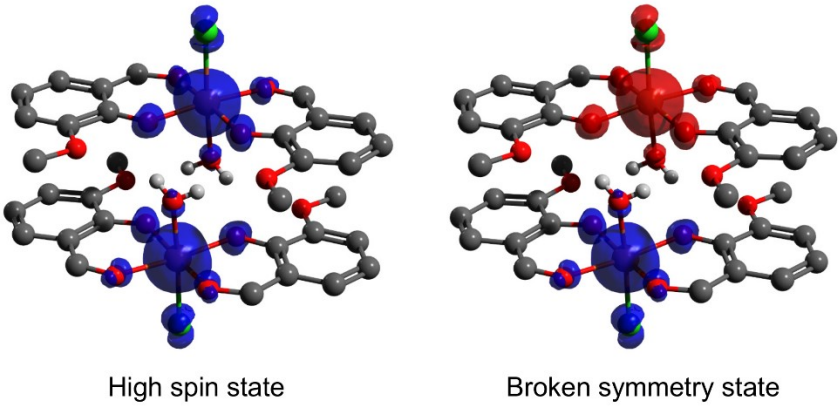

Figure S7. Spin density isosurfaces for **1** shown at 0.01 au level (B3LYP functional, def2-TZVPP basis set for metal, all coordinated atoms and hydrogen atoms of the water molecules; def2-SVP basis set for all other atoms). All H atoms except those from water molecules are omitted for clarity.

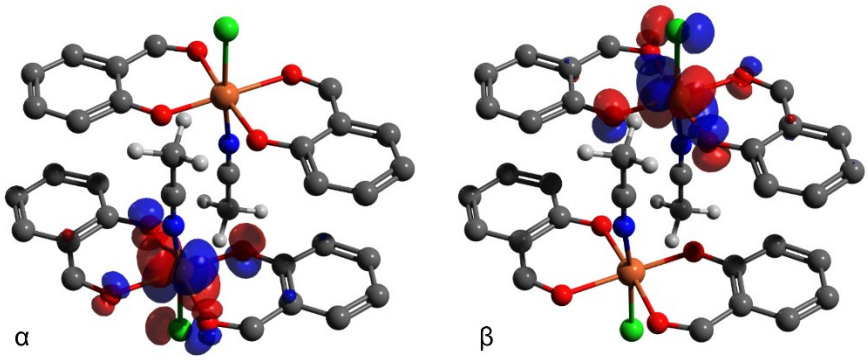

Figure S8. Magnetic orbital pairs in the DFT optimized derivative of **1** (coordinated water molecules and methoxy groups replaced by acetonitrile molecules and H atoms, respectively) with the overlap value of 0.01296 (shown at 0.03 au isosurface; B3LYP functional, def2-TZVPP basis set for metal and all coordinated atoms, def2-SVP basis set for all other atoms). All H atoms except those from acetonitrile molecules are omitted for clarity.

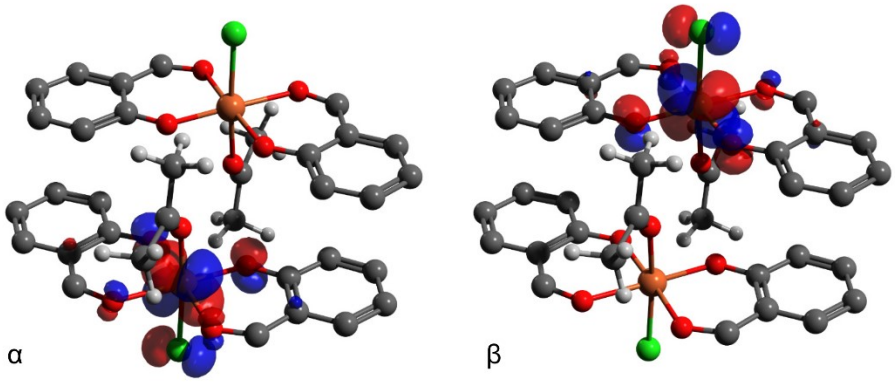

Figure S9. Magnetic orbital pairs in the DFT optimized derivative of **1** (coordinated water molecules and methoxy groups replaced with acetone molecules and H atoms, respectively) with the overlap value of 0.01305 (shown at 0.03 au isosurface; B3LYP functional, def2-TZVPP basis set for metal and all coordinated atoms, def2-SVP basis set for all other atoms). All H atoms except those from acetone molecules are omitted for clarity.

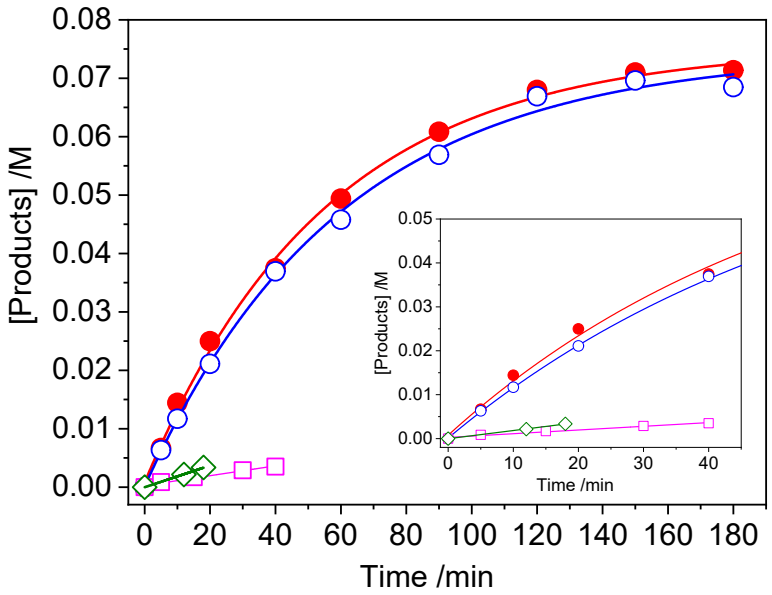

Figure S10. Accumulations of oxygenates (sum of cyclohexanol and cyclohexanone) in the oxidation of cyclohexane (0.2 M) with H_2O_2 (1 M) catalysed by **1** (3.7×10^{-4} M; circles), $FeCl_3$ (3.1×10^{-4} M; squares) or $Fe(NO_3)_3$ (3.9×10^{-4} M; rhombs) in acetonitrile at 40 °C, in the presence of HNO_3 promoter (5×10^{-3} M). Solid and empty circles correspond to immediate addition of H_2O_2 and addition after 1 h, respectively. The inset shows the initial region in detail.

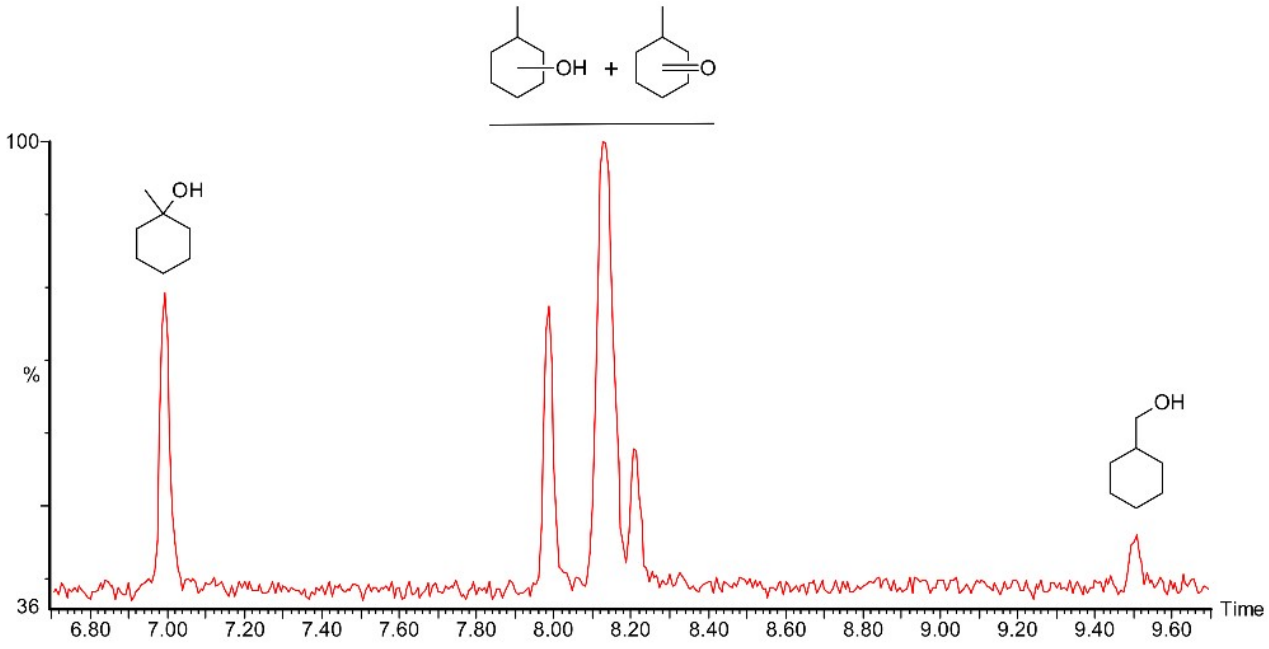

Figure S11. Fragment of the chromatogram showing the main reaction products in the oxidation of methylcyclohexane in the presence of HNO_3 in acetonitrile at 20 min reaction time (other conditions are as those in Figure 7 caption). The following GC conditions have been used: 50 °C (3 min), 50–120 °C (8 degr. per min), 120–300 (30 degr. per min), 300 °C (5.25 min); SGE BPX-5 capillary column.

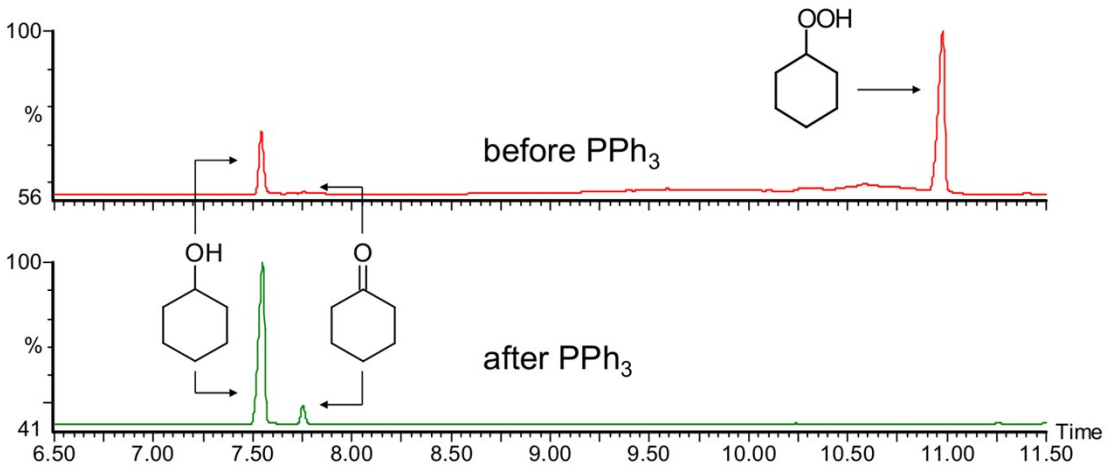

Figure S12. Fragments of the chromatograms recorded before and after addition of PPh_3 to the sample, showing main products in the oxidation of cyclohexane (0.2 M) with H_2O_2 (1 M) catalysed by **1** (3.7×10^{-4} M) in acetonitrile at 40 °C, in the presence of nitric acid (5×10^{-3} M) at 4 h time. The following GC conditions have been used: 50 °C (3 min), 50–120 °C (8 degr. per min), 120–300 (30 degr. per min), 300 °C (5.25 min); SGE BPX-5 capillary column.

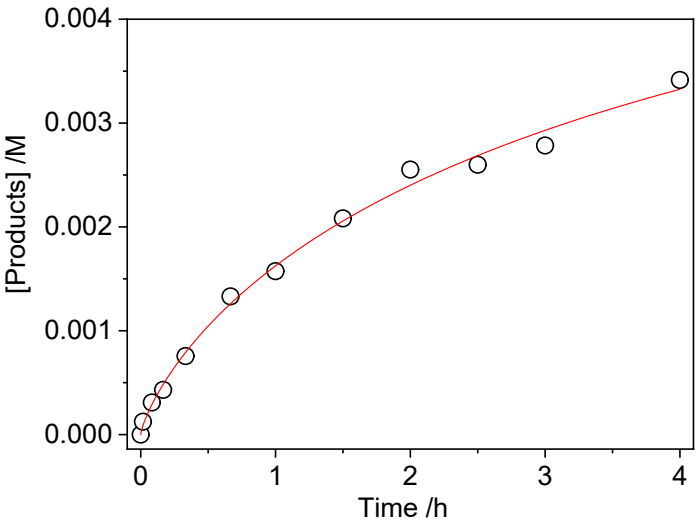

Figure S13. Accumulation of the reaction products (sums of cyclohexanol and cyclohexanone) in the oxidation of cyclohexane (0.2 M) with TBHP (1 M) catalysed by **1** (3.7×10^{-4} M) in acetonitrile at 40 °C, in the presence of nitric acid (5×10^{-3} M).

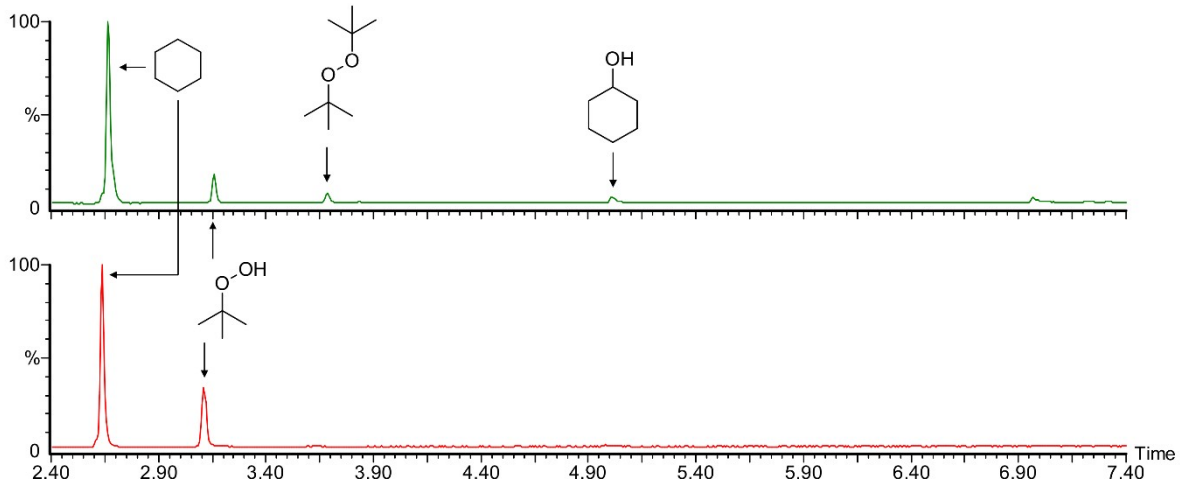

Figure S14. Fragment of the chromatograms showing the main reaction products in the oxidation of cyclohexane in the presence (top) and absence (bottom) of HNO_3 in acetonitrile at 4 h reaction time (other conditions are as those in Figure 7 caption). The following GC conditions have been used: 50 °C (3 min), 50–120 °C (8 degr. per min), 120–300 (30 degr. per min), 300 °C (5.25 min); SGE BPX-5 capillary column.

Table S6. Catalytic parameters exhibited by the catalyst **1** in the oxidation of cyclohexane.[a]

Promoter	Oxidant	Initial reaction rate W_0, M s^{-1}	Yield,[b] %
–	H_2O_2	1.6×10^{-6}	6
HNO_3[c]	H_2O_2	3.9×10^{-6}	3[d]
HNO_3	H_2O_2	2.2×10^{-5}	37
–	TBHP	–	–
HNO_3	TBHP	8.3×10^{-6}	2
HNO_3	*m*-CPBA	8.6×10^{-5}	11
HCl	*m*-CPBA	7.6×10^{-8} [e]	8

[a] General conditions, unless stated otherwise: $[\mathbf{1}]_0 = 3.7 \times 10^{-4}$ M, $[\text{promoter}]_0 = 5 \times 10^{-3}$ M, $[\text{cyclohexane}]_0 = 0.2$ M, $[\text{oxidant}]_0 = 1$ M, acetonitrile, 40 °C; [b] relative to substrate (for H_2O_2 and TBHP) or *m*-CPBA after 4 h; [c] $[HNO_3]_0 = 1.6 \times 10^{-3}$ M; [d] at 20 min; [e] at 4 h. The initial rate was too high for reliable determination.

First, the benchmark calculations using a set of functionals (BP86, OPBE, TPSSh, PBE0, B3LYP, B97-3c, M06L, M06-2X, CAM-B3LYP) were performed to select the most appropriate approach (Table S7 and Figures S15–S17). In general, all the functionals correctly describe the overall spectrum of HL and the nature of transitions, differing in the energies of the excited states. The functionals best matching the experimental UV spectrum of HL were PBE0 and B3LYP, showing the maximum unsigned error (UE) of 40 and 45 nm, respectively (Table S7, Figure S16), while BP86, OPBE and B97-3c functionals revealed a much higher UE value of 137, 125 and 126 nm, respectively. The DFT calculated UV spectrum of HL is depicted in Figure S15. The spectrum consists mainly of three transitions, $S_0 \rightarrow S_1$, $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_7$ (Table S8), while the oscillator strengths of other ones are much weaker. These three transitions involve the frontier molecular orbitals (HOMO and LUMO) as well as the closest lying ones.

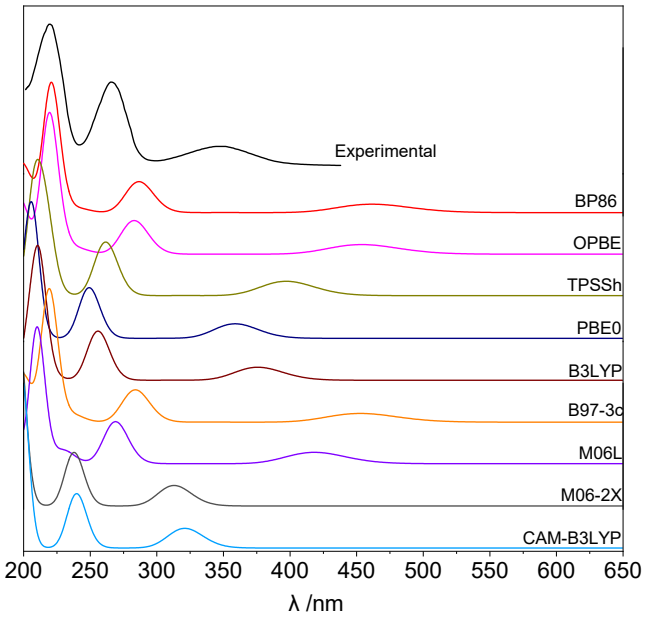

Figure S15. Comparison of the experimental[S8] and TDDFT calculated spectra of HL (see Table S7 footnote for detailed conditions).

Table S7. Experimental and theoretical absorption wavelengths for HL (*o*-vanillin).[a]

Exp.[b]	BP86	OPBE	TPSSh	PBE0	B3LYP	B97-3C	M06L	M06-2X	CAM-B3LYP
220	221	220	210	**206**	211	219	211	196	199
264	286	283	262	**249**	256	284	269	238	240
348	462	454	397	**359**	376	453	418	313	321
Δ_{220}[c]	1	0	-10	**-14**	-9	-1	-9	-24	-21
Δ_{264}[c]	22	19	-2	**-15**	-8	20	5	-26	-24
Δ_{348}[c]	114	106	49	**11**	28	105	70	-35	-27
UE[d]	137	125	61	**40**	45	126	84	85	72
SE[e]	137	125	37	**-18**	11	124	66	-85	-72

[a] General DFT calculations conditions (molecular geometry was optimized at the B97-3C/ma-def2-TZVP level using the CCDC refcode OVANIL01 crystallographic data as starting coordinates): ma-def2-TZVP basis set (auxiliary basis set selected automatically using the AUTOAUX keyword), Grimme's DFT-D3 dispersion correction without (for Minnesota functionals; D3Zero keyword) or with Becke-Johnson damping (all other functionals; D3BJ keyword), numerical precision: Grid7 NoFinalGrid keywords (the chain-of-spheres approximation was applied; GridX7 NoFinalGridX RIJCOSX keywords), CPCM (acetonitrile) solvation model was used; [b] experimental[S8] wavelengths (nm); [c] $\Delta_\lambda = \lambda_{calcd.} - \lambda_{exp.}$; [d] unsigned error (nm), $UE = \Sigma|\lambda_{calcd.} - \lambda_{exp.}|$; [e] signed error (nm), $SE = \Sigma(\lambda_{calcd.} - \lambda_{exp.})$.

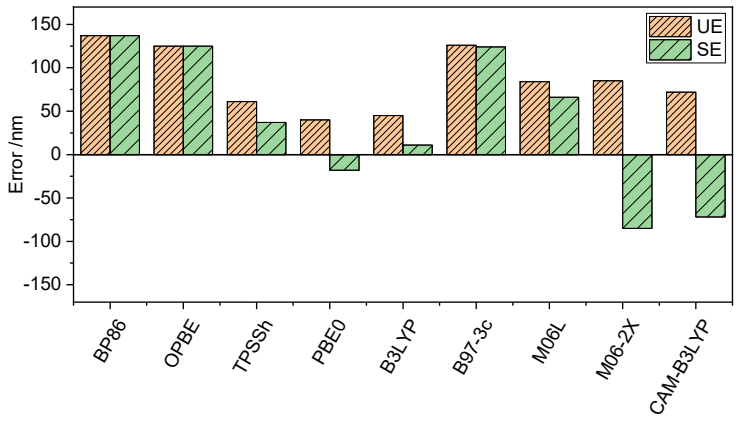

Figure S16. Unsigned (UE) and signed (SE) errors in the DFT calculations of *o*-vanillin absorption wavelengths (see Table S7 footnote for details).

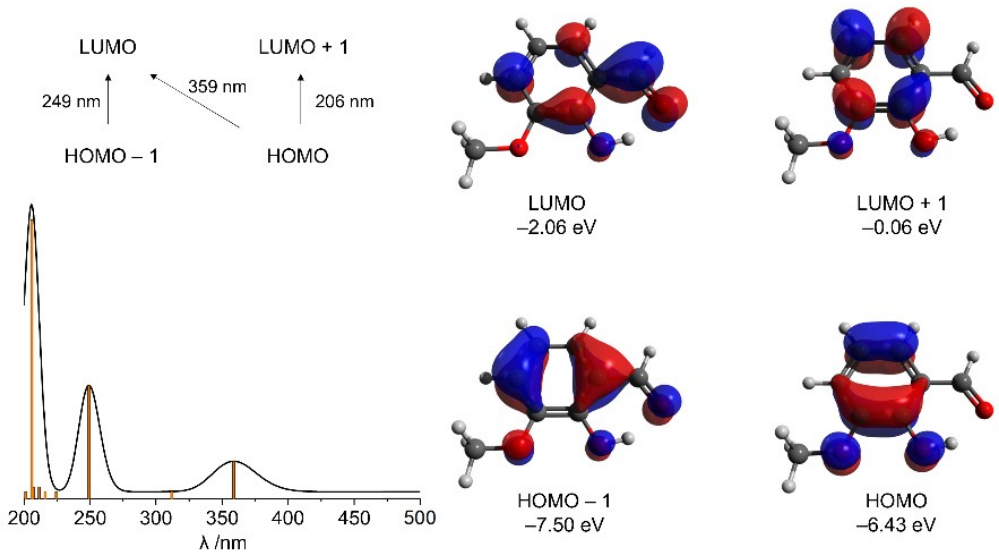

Figure S17. The TDDFT calculated (at the PBE0/ma-def2-TZVP level) UV spectrum of HL in acetonitrile and plots of the frontier molecular orbitals (shown at 0.02 au isosurface) involved into the transitions having the largest oscillator strengths.

Table S8. Selected TDDFT calculated excitation states for HL in the >200 nm region.[a]

State	Excitation energy		λ, nm	Selected transitions (contribution, %)
	eV	cm^{-1}		
S1	3.455	27869.4	358.8	H → L (93.9)
S3	4.976	40131.2	249.2	H–1 → L (86.0)
S7	6.021	48558.7	205.9	H → L+1 (76.4)

[a] H, HOMO; L, LUMO.

Next, the TDDFT calculations of the simple model compound $[Fe(H_2O)_6]^{3+}$ were performed using the same functionals set. This cation, existing at pH < 3, exhibits two absorption bands in the UV region, 190 and 240 nm, assigned to LMCT transitions.[S9] The results of the TDDFT analysis using the B97-3c optimized geometry and the same functionals set as for HL are summarized in the Figures S18–S20 and Tables S9 and S10 (geometry optimization was necessary since the crystal structures found in the CSD involving $[Fe(H_2O)_6]^{3+}$ cation either possess too high symmetry or show distortion caused by the presence of large counteranions). As can be seen, the accuracy of the PBE0 calculations is at the same level as the OPBE and CAM-B3LYP ones, while the best results were obtained for the hybrid meta M06-2X functional which predicts the peak absorptions at 174 and 215 nm (Figures S18 and S19). Both bands are comprised of numerous ligand-to-metal transitions between the spin down molecular orbitals, the most intense of which are listed in Table S10.

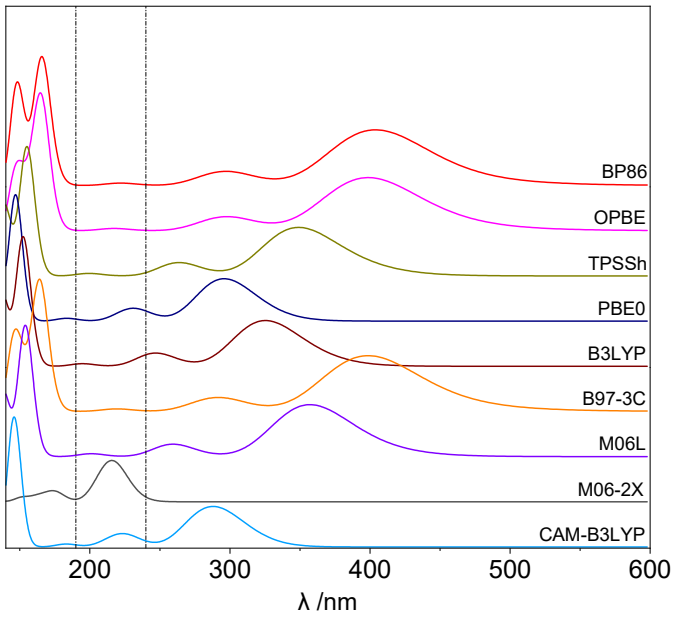

Figure S18. Comparison of the TDDFT calculated spectra of $[Fe(H_2O)_6]^{3+}$ (see the Table S8 footnote for detailed conditions). The experimental bands[S9] at 190 and 240 nm are shown as the dash dot vertical lines. The two absorption bands having the longest wavelengths (in the calculated spectra) are those corresponding to the experimental ones by the nature of transitions.

Table S9. Experimental and theoretical absorption wavelengths for $[Fe(H_2O)_6]^{3+}$.[a]

Exp.[b]	BP86	OBPE	TPSSh	PBE0	B3LYP	B97-3C	M06L	M06-2X	CAM-B3LYP
240	405	399	350	295	325	399	357	**216**	287
190	297	297	264	230	247	290	259	**174**	222
Δ_{240}[c]	0	159	110	55	85	159	117	**–24**	47
Δ_{190}[c]	107	107	74	40	57	100	69	**–16**	32
UE[d]	107	266	184	95	142	259	186	**40**	79
SE[e]	107	266	184	95	142	259	186	**–40**	79

[a] General DFT calculations conditions (molecular geometry was optimized at the B97-3C/ma-def2-TZVP level using the CCDC refcode MEWZAP01 crystallographic data as starting coordinates): ma-def2-TZVP basis set (auxiliary basis set selected automatically using the AUTOAUX keyword), Grimme's DFT-D3 dispersion correction without (for Minnesota functionals; D3Zero keyword) or with Becke-Johnson damping (all other functionals; D3BJ keyword), numerical precision: Grid7 NoFinalGrid keywords (the chain-of-spheres approximation was applied; GridX7 NoFinalGridX RIJCOSX keywords), CPCM (water) solvation model was used; [b] experimental wavelengths (nm); [c] $\Delta_\lambda = \lambda_{calcd.} - \lambda_{exp.}$; [d] unsigned error (nm), $UE = \Sigma|\lambda_{calcd.} - \lambda_{exp.}|$; [e] signed error (nm), $SE = \Sigma(\lambda_{calcd.} - \lambda_{exp.})$.

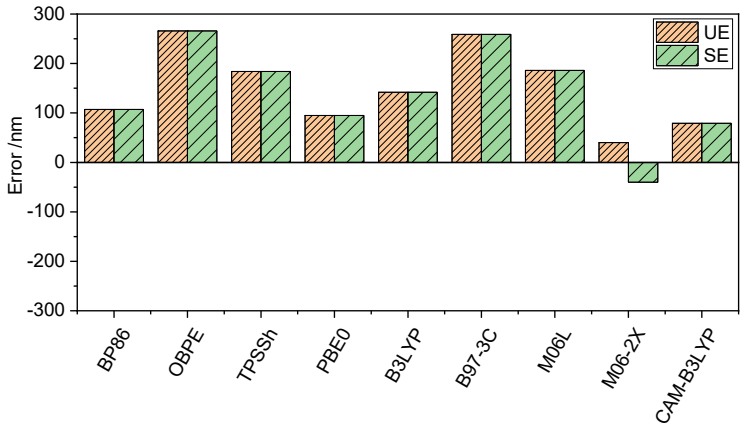

Figure S19. Unsigned (UE) and signed (SE) errors in the DFT calculations of $[Fe(H_2O)_6]^{3+}$ absorption wavelengths (see Table S9 footnote for details).

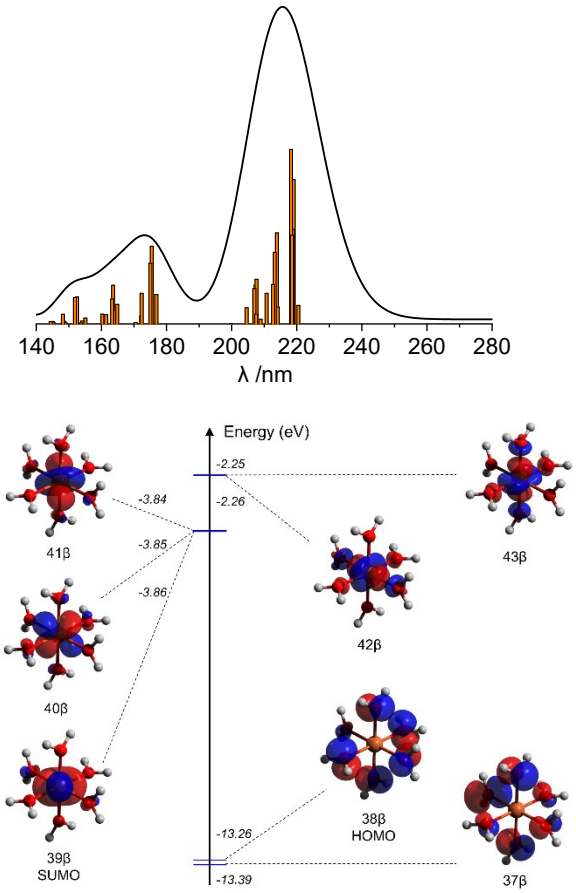

Figure S20. Top: the TDDFT calculated (at the M06-2X/ma-def2-TZVP level) UV absorption spectrum of $[Fe(H_2O)_6]^{3+}$ in water (vertical lines correspond to unbroadened transitions). Bottom: plots of the spin-down HOMO and SUMO frontier molecular orbitals (shown at 0.05 au isosurface) involved into the transitions having the largest oscillator strengths.

Table S10. Selected TDDFT calculated excitation states for $[Fe(H_2O)_6]^{3+}$ in the >120 nm region.[a]

State	Excitation energy		λ, nm	Selected transitions (contribution, %)
	eV	cm^{-1}		
S1	5.660	45653.8	219.0	$38_\beta \rightarrow 41_\beta$ (35.6)
				$38_\beta \rightarrow 39_\beta$ (33.2)
				$38_\beta \rightarrow 40_\beta$ (22.8)
S3	5.681	45819.9	218.2	$38_\beta \rightarrow 40_\beta$ (62.9)
				$38_\beta \rightarrow 41_\beta$ (17.9)
S6	5.797	46752.2	213.9	$37_\beta \rightarrow 40_\beta$ (62.9)
				$37_\beta \rightarrow 41_\beta$ (15.4)
S19	7.067	56997.6	175.4	$38_\beta \rightarrow 43_\beta$ (59.4)
				$37_\beta \rightarrow 42_\beta$ (20.5)

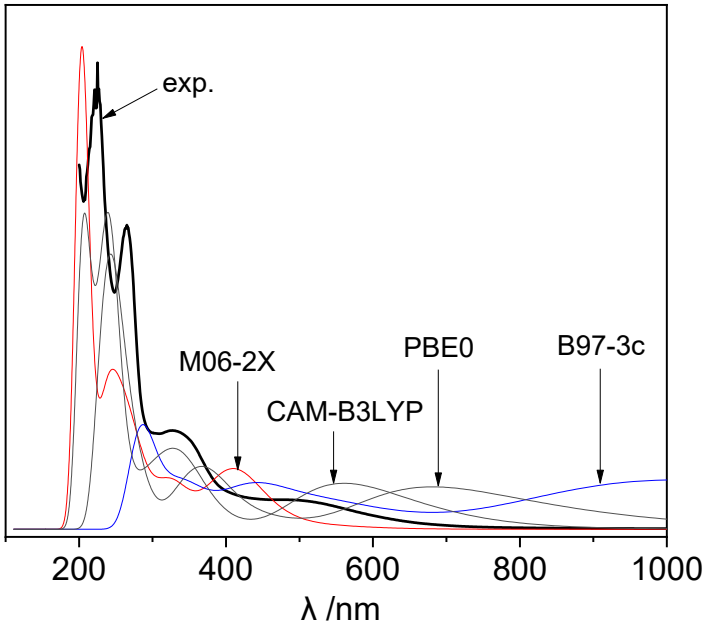

Figure S21. Comparison of the TDDFT calculated spectra of **1** (the ma-def2-TZVP basis set was used for all atoms).

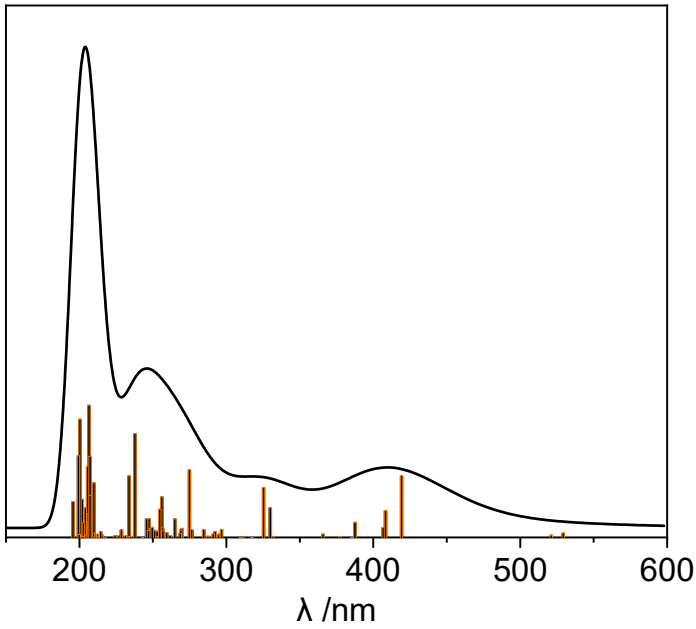

Figure S22. The TDDFT calculated (at the M06-2X/ma-def2-TZVP level) UV absorption spectrum of **1** in acetonitrile (vertical lines correspond to unbroadened transitions).

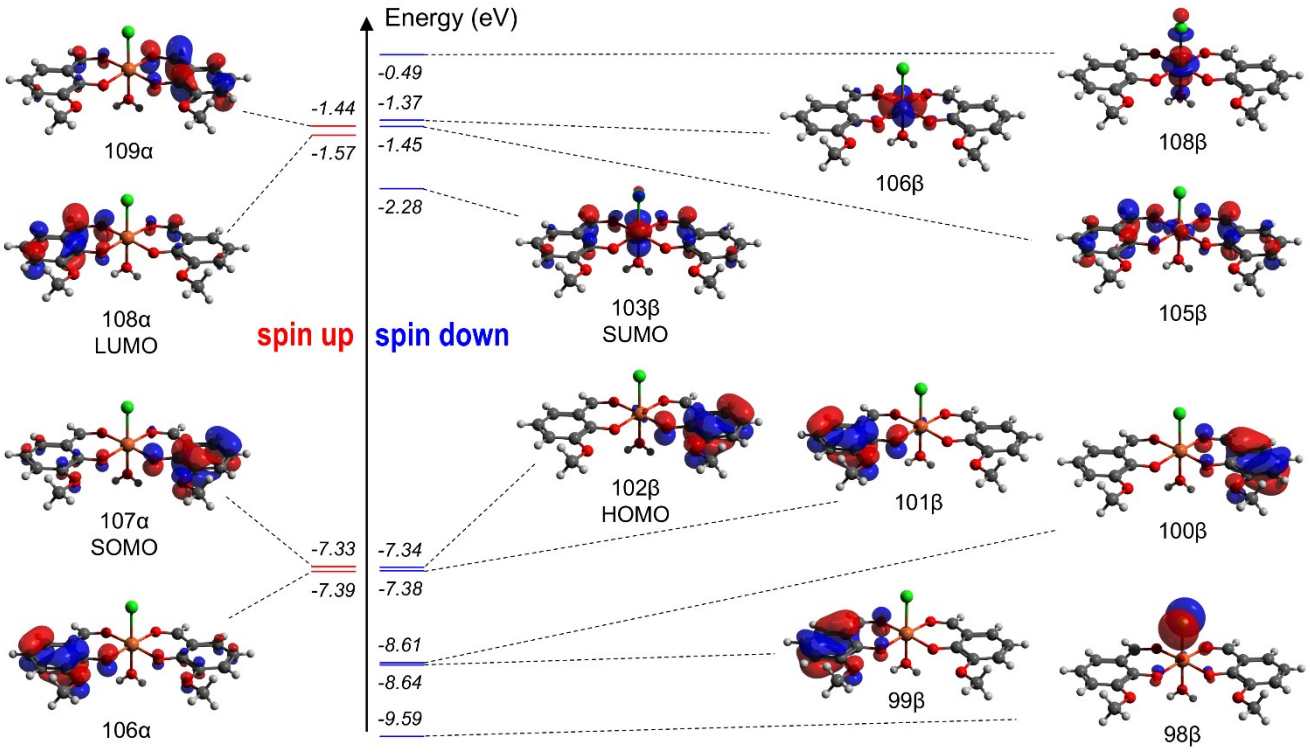

Figure S23. Plots of the frontier molecular orbitals (shown at 0.05 au isosurface) of **1** (at the M06-2X/ma-def2-TZVP level) involved into the UV transitions having the largest oscillator strengths.

Table S11. Selected TDDFT calculated excitation states for **1** in the >200 nm region.

State	Excitation energy		λ, nm	Selected transitions (contribution, %)
	eV	cm^{-1}		
S1	2.342	18892.40	529.3	$101_\beta \rightarrow 103_\beta$ (34.5)
				$106_\alpha \rightarrow 108_\alpha$ (17.3)
S3	2.957	23852.50	419.2	$102_\beta \rightarrow 103_\beta$ (25.7)
				$107_\alpha \rightarrow 108_\alpha$ (11.9)
S12	3.811	30738.20	325.3	$102_\beta \rightarrow 105_\beta$ (28.7)
				$107_\alpha \rightarrow 109_\alpha$ (16.2)
				$102_\beta \rightarrow 107_\beta$ (2.1)
S25	4.511	36380.90	274.9	$98_\beta \rightarrow 105_\beta$ (19.1)
				$99_\beta \rightarrow 103_\beta$ (14.6)
S47	5.215	42058.50	237.8	$100_\beta \rightarrow 106_\beta$ (20.2)
				$99_\beta \rightarrow 108_\beta$ (11.3)
S73	6.005	48431.80	206.5	$107_\alpha \rightarrow 112_\alpha$ (8.5)
				$107_\alpha \rightarrow 113_\alpha$ (6.1)
				$106_\alpha \rightarrow 117_\alpha$ (5.3)
				$104_\alpha \rightarrow 109_\alpha$ (5.3)
				$107_\alpha \rightarrow 114_\alpha$ (4.4)

Table S12. Selected TDDFT calculated excitation states for **1-MeCN** in the >200 nm region.

State	Excitation energy		λ, nm	Selected transitions (contribution, %)
	eV	cm^{-1}		
S1	2.294	18501.1	540.5	$108_\beta \rightarrow 109_\beta$ (46.3)
				$113_\alpha \rightarrow 115_\alpha$ (15.8)
S3	2.586	20857.4	479.4	$107_\beta \rightarrow 110_\beta$ (41.4)
				$107_\beta \rightarrow 109_\beta$ (17.3)
				$108_\beta \rightarrow 110_\beta$ (14.0)
S4	2.750	22179.1	450.9	$108_\beta \rightarrow 109_\beta$ (30.9)
				$113_\alpha \rightarrow 115_\alpha$ (11.5)
				$108_\beta \rightarrow 113_\beta$ (10.6)
S8	2.939	23700.8	421.9	$107_\beta \rightarrow 111_\beta$ (42.3)
				$107_\beta \rightarrow 110_\beta$ (11.7)
				$108_\beta \rightarrow 111_\beta$ (11.0)
S11	3.651	29445.4	339.6	$107_\beta \rightarrow 112_\beta$ (26.6)
				$107_\beta \rightarrow 113_\beta$ (21.6)
				$112_\alpha \rightarrow 114_\alpha$ (18.6)
S12	3.685	29718.2	336.5	$108_\beta \rightarrow 113_\beta$ (27.2)
				$108_\beta \rightarrow 112_\beta$ (18.7)
				$113_\alpha \rightarrow 115_\alpha$ (15.8)
S38	4.498	36279.4	275.6	$106_\beta \rightarrow 110_\beta$ (30.8)
				$104_\beta \rightarrow 111_\beta$ (7.0)
S48	5.208	42003.1	238.1	$105_\beta \rightarrow 112_\beta$ (19.5)
				$106_\beta \rightarrow 113_\beta$ (17.0)
				$105_\beta \rightarrow 113_\beta$ (9.4)
S69	5.805	46823.6	213.6	$108_\beta \rightarrow 123_\beta$ (8.6)
				$113_\alpha \rightarrow 118_\alpha$ (5.3)
				$108_\beta \rightarrow 124_\beta$ (4.8)
				$94_\beta \rightarrow 110_\beta$ (4.4)

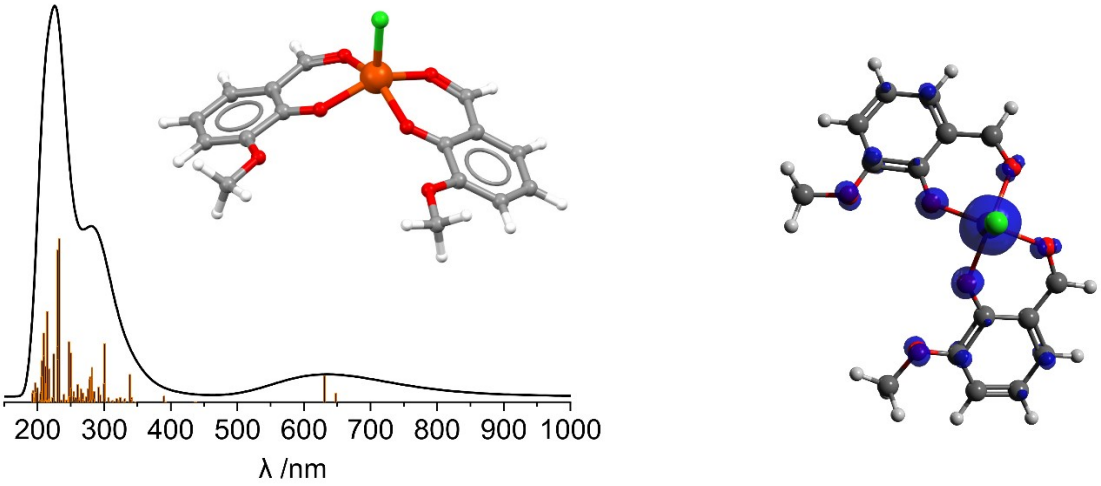

Figure S24. Left: the TDDFT calculated (at the M06-2X/ma-def2-TZVP level) UV absorption spectrum of $[FeCl(L^{\bullet})_2]^{2+}$ (optimized at the B97-3c/def2-TZVP level, shown in the figure) in acetonitrile (vertical lines correspond to unbroadened transitions). Right: spin density isosurface for $[FeCl(L^{\bullet})_2]^{2+}$ shown at 0.02 au level (B97-3c functional, def2-TZVP basis set for all atoms).

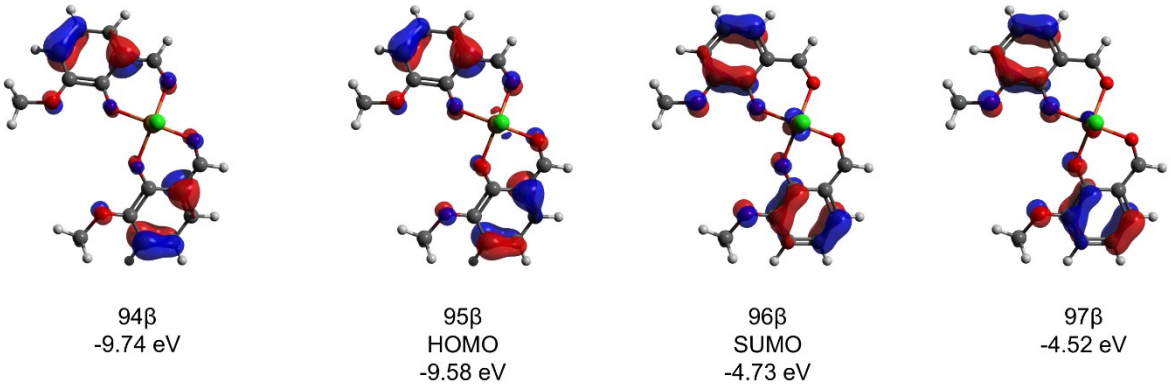

Figure S25. Plots of the spin-down frontier molecular orbitals (shown at 0.05 au isosurface) of $[FeCl(L^{\bullet})_2]^{2+}$ (at the M06-2X/ma-def2-TZVP level) involved into the lowest energy transitions in the visible regions. The respective excitation states are: S1 (1.913 eV, 15432.6 cm^{-1}, 648.0 nm), $95_\beta \rightarrow 96_\beta$ (55.1%), $94_\beta \rightarrow 97_\beta$ (39.1); S2 (1.966 eV, 15860.8 cm^{-1}, 630.5 nm), $94_\beta \rightarrow 96_\beta$ (48.3%), $95_\beta \rightarrow 97_\beta$ (44.7%).

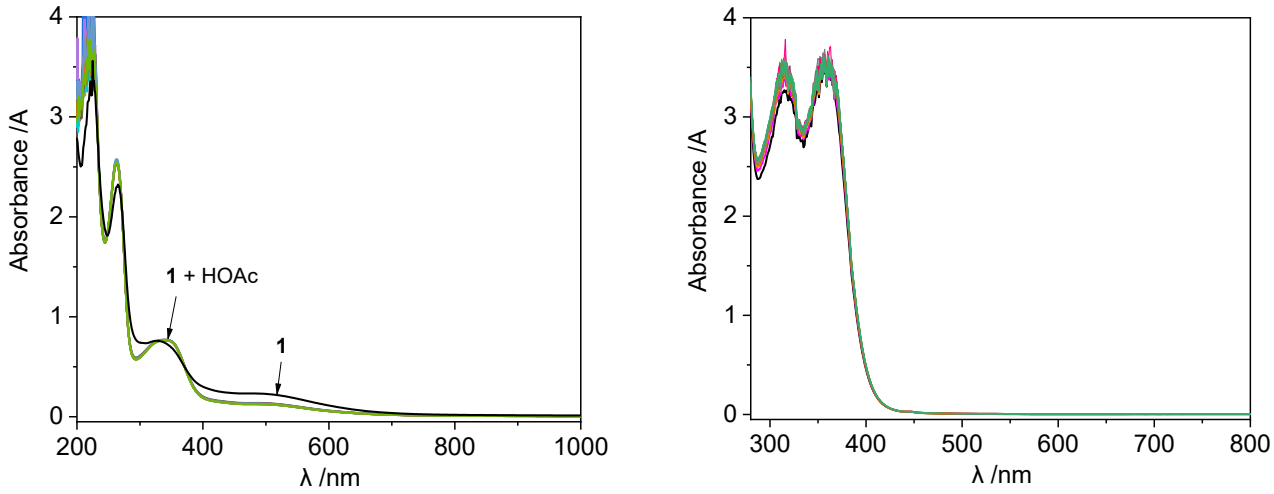

Figure S26. Left: UV/Vis absorption spectra of 3.7×10^{-4} M acetonitrile solution of **1** in the absence (black line) and presence (other lines) of 5×10^{-3} M of acetic acid (HOAc). The spectra with HOAc were recorded each 5 mins for one hour. Right: the UV/Vis spectra of **1** in the presence of HCl (concentrations and timings are the same as for HOAc).

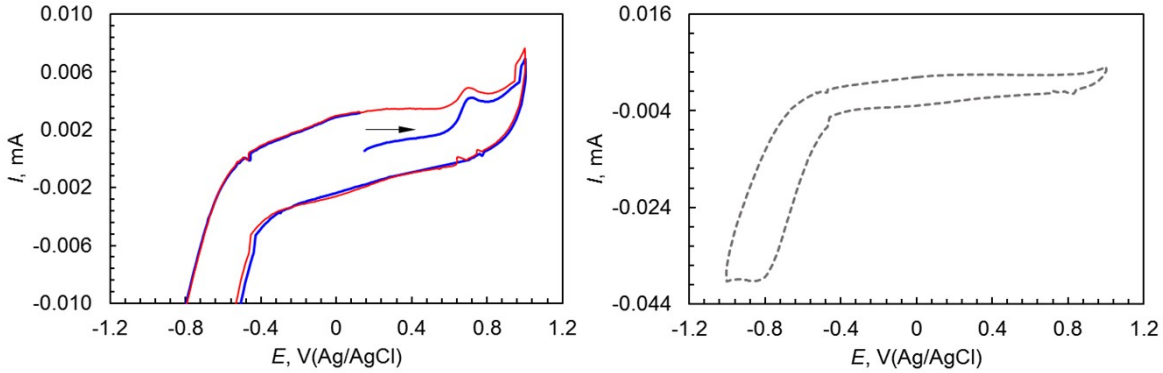

Figure S27: Left: cyclic voltammogram of $[Fe^{III}Cl(L)_2(H_2O)]$ (**1**), 0.1 mM in methanol mixed with 0.1 M acetate buffer (pH 4) and $NaClO_4$ (70:28:2) as supporting electrolyte at a glassy carbon electrode and Ag/AgCl as reference electrode (scan rate: 100 mV s^{-1}; T = 298 K). Right: cyclic voltammogram obtained during the potential scan in the blank solution.

Listing S1. Shortened example of the ORCA input for DFT geometry optimization of the dimer of **1** (only metal atoms are shown).

```
! B97-3C def2-TZVP AutoAux D3BJ VeryTightSCF TightOpt Grid5 FinalGrid6 RIJCOSX
! LARGEPRINT CPCM(ACETONITRILE) PAL5
%scf
MaxIter 500
end
* xyz 0 11
  Fe      4.684853      4.869617      6.732684
  Fe      1.125620      8.255435      6.724196
```

Listing S2. Shortened example of the ORCA input for DFT broken symmetry calculations of the dimer of **1** (only metal atoms are shown).

```
! UKS B3LYP def2-SVP AutoAux D3BJ VeryTightSCF Grid6 FinalGrid7
! RIJCOSX
! KEEPDENS PAL5
%scf brokensym 5,5
end
* xyz 0 11
Fe      4.642859    4.941488    6.707433 newgto "def2-TZVPP" end
Fe      1.167736    8.184012    6.749148 newgto "def2-TZVPP" end
```

Listing S3. Shortened example of the ORCA input for TDDFT calculations of **1** (only metal atom is shown).

```
! M062X ma-def2-TZVP AutoAux D3Zero Grid7 NoFinalGrid GridX7 NoFinalGridX
TightSCF ! RIJCOSX
! LARGEPRINT CPCM(ACETONITRILE) PAL5
%tddft
  maxdim 5
  nroots 100
  end
* xyz 0 6
Fe      1.167736    8.184012    6.749148
```

Listing S4. Cartesian coordinates for DFT optimized dimeric structure of **1**.

```
  Fe  4.68382032321712      5.01626884642515      6.66290553995399
  Fe  1.12732272505948      8.10338043736806      6.79515797279716
  Cl  5.20302802125176      2.86138184889671      7.36787848086472
  Cl  0.60953605898480     10.25973612563269      6.09384807003250
  O   2.85391576906416      8.51093305335383      7.56894701145336
  O   5.36035259042767      9.16401414058145      7.86369536131759
  O   0.27626950446699      8.49957784703821      8.67517406098119
  O   3.34616320663287      6.99390000334938      3.06349401689780
  O   1.81621096329233      7.44522227210269      5.12084448056910
  O   -0.77126553831143      7.42740455193639      6.18138560799250
  O   1.22987153470757      6.06350244586567      7.63830990881698
  O   2.95825934803678      4.60791349864875      5.88936883346509
  O   0.45043217415255      3.96400696598866      5.59342239880006
```

O	5.53445529935801	4.61896355104024	4.78239310551734
O	3.99478739808456	5.67632110771997	8.33700372256053
O	2.46661591721096	6.12812958085776	10.39579414604074
O	6.58238051146773	5.69361826014855	7.27513410928487
O	4.57930308529524	7.05686957447505	5.81999703011153
C	3.17752531417010	9.09369378113752	8.68168614722225
C	4.53798291709278	9.45966529660310	8.89038739329753
C	6.72635168818512	9.55909980280454	7.95586463002609
H	6.80961159158124	10.64248855819621	8.03372435669974
H	7.19296220277692	9.21774920638490	7.03942657665581
H	7.21214648818731	9.09371502271909	8.81205319803888
C	4.92582122251322	10.06895440773142	10.06760535467783
H	5.95809663334631	10.34076165559917	10.21984009870588
C	3.99732225783811	10.33203359667679	11.07945212147245
H	4.33071588458350	10.79738368219306	11.99433849868394
C	2.68000193396583	9.99649913889198	10.90725932857676
H	1.95259827099283	10.19500464240498	11.68182180070716
C	2.24637854777986	9.38553266962233	9.71404827929323
C	0.86654975728747	9.04921231223394	9.62141430120885
H	0.26360646149591	9.30322499150331	10.50139665815478
C	1.23114340913193	7.02030450122295	4.04575416954544
C	2.02866327564297	6.75368345194897	2.89686326024986
C	4.20883603257353	6.84354304249836	1.93839821267262
H	4.18553472400292	5.82287693581282	1.56032718805589
H	5.20348169792681	7.07924468032070	2.29767928765326
H	3.92676083678564	7.53330781579189	1.14403939145594
C	1.44666081106361	6.29225117080669	1.73288738955443
H	2.05676110799685	6.09113547412153	0.86693924724266
C	0.06813666756104	6.06832315951596	1.66108044244136
H	-0.35883813112163	5.69494659947619	0.74293539522312
C	-0.72716240722139	6.31727381866749	2.74928556460947
H	-1.79396814103539	6.14852020376167	2.70515082497961
C	-0.16835474914455	6.80046928414401	3.94851204357308
C	-1.05362158003999	7.01922738339496	5.04169460208028
H	-2.10742617494821	6.78942200051857	4.84343039509883
H	1.96928077540584	6.02124104150525	8.26918995815928
H	1.49495339590551	5.44273503456155	6.93536062296162
C	2.63316625712987	4.02875200407507	4.77545912867543
C	1.27172388156209	3.66701919954025	4.56620421868903
C	-0.91650204638336	3.57148179970422	5.50199807014364
H	-1.00137491471038	2.48828987548794	5.42346433075549
H	-1.38182084645976	3.91366651346784	6.41878097817939
H	-1.40198248745117	4.03768124580519	4.64608488360586
C	0.88205327740646	3.06025459408603	3.38835149848002
H	-0.15100240675346	2.79120025283976	3.23668473848484
C	1.80984650023200	2.79648462167392	2.37594347769843
H	1.47516331087258	2.33330506422235	1.46042174145853
C	3.12804261754647	3.12873636656951	2.54818517372550
H	3.85476787258617	2.93009446184746	1.77299622655096
C	3.56335570435142	3.73688040169335	3.74224151262554
C	4.94361473136742	4.07078529509887	3.83555196852955
H	5.54646259083036	3.81622763011282	2.95567554017614
C	4.58032055595568	6.10444256098498	9.41068872454025
C	3.78363027240116	6.37200177842048	10.56005607353706
C	1.60504789633684	6.27917960919809	11.52166389823378
H	1.62510981185971	7.30117294904789	11.89629519153848
H	0.61086452223496	6.03838845878607	11.16453284636240
H	1.89083467008960	5.59312267728838	12.31793043381744
C	4.36599609514957	6.83768118192921	11.72220897959870
H	3.75627418243962	7.03970743112100	12.58821457097102
C	5.74409091709856	7.06473978941029	11.79195060385916
H	6.17126451170799	7.44177388384768	12.70850685976539
C	6.53869627552308	6.81421866714207	10.70363581925548

H	7.60526384087548	6.98514993114251	10.74611335026699
C	5.97959070210944	6.32670569989602	9.50626446167809
C	6.86470152306511	6.10543631833611	8.41347986534458
H	7.91844527010090	6.33604060693515	8.61114560691914
H	3.84594099350739	7.09656141655684	5.18203644072984
H	4.30283930273660	7.67365223953059	6.52243318936784

Listing S5. Cartesian coordinates for DFT optimized dimeric structure of **1** with *d*(Fe···Fe) fixed to 5.122 Å.

Fe	4.82428286216477	4.86287592455574	6.65981742342081
Fe	0.98465818199055	8.24990983356036	6.80182871790109
Cl	5.31787698786871	2.71781416712800	7.35244773567978
Cl	0.49319434388974	10.39540607163332	6.10987126300766
O	2.74537684859757	8.58025433539759	7.55322112431147
O	5.27189732163426	9.15158078457686	7.83065959510693
O	0.18417127307509	8.60184551253084	8.69351079947698
O	3.31616641329942	7.02280390602307	3.16610565991900
O	1.72871382602444	7.54986279293560	5.16304985226705
O	-0.87478193829284	7.53283304159744	6.17091181024372
O	1.16157111319274	6.14134800919625	7.63587543670118
O	3.06497609388051	4.53133129527001	5.90810483061864
O	0.53575388035354	3.97806746752493	5.62531121980613
O	5.62550285269812	4.51070496813007	4.76680216205884
O	4.08244238400069	5.56516136539170	8.29909482155638
O	2.49982605263413	6.09595480083958	10.29794360772140
O	6.68497901744439	5.57984867499174	7.28589525995205
O	4.64800974389655	6.97171651010579	5.82712955540082
C	3.09508316895391	9.13472922618112	8.66926574311090
C	4.46845873106428	9.46087007233120	8.86906587174206
C	6.64805901661402	9.51235351673818	7.90952406755548
H	6.75858939336158	10.59324333066032	7.98906641902457
H	7.09636226724344	9.16163468728518	6.98743861058521
H	7.13140239929623	9.03334703806071	8.75943819684683
C	4.88381746780952	10.05009357034442	10.04584071033213
H	5.92434594029883	10.29410693450446	10.18893442796921
C	3.97323713980059	10.32679351775596	11.07204740691052
H	4.32931380949561	10.77544443180702	11.98674438213052
C	2.64732291712993	10.02330567586823	10.91434950692171
H	1.93475711140785	10.22874334357675	11.70086873579626
C	2.18405910855797	9.43501432693036	9.71922994404017
C	0.79827986123001	9.12926803102241	9.64029418053778
H	0.21016317875432	9.38272270300278	10.52996492223251
C	1.17370049548715	7.08336095464704	4.09300818685664
C	2.00045344220518	6.77995276745867	2.97280093142489
C	4.20273894728307	6.86546057970742	2.05994745127002
H	4.19454785670551	5.84074468224498	1.69297834947537
H	5.18825500338988	7.11262657491018	2.43626433004035
H	3.93077805789159	7.54452441474020	1.25311352223417
C	1.44836814284448	6.28983623733922	1.80753547237942
H	2.07955575563052	6.06545918007194	0.96269056155454
C	0.07094887027992	6.06250828174480	1.70638632081151
H	-0.33157618075674	5.66495540076524	0.78738062074529
C	-0.75141087748115	6.33523844898714	2.76733206160280
H	-1.81615587165581	6.15996435959393	2.70201498434377
C	-0.22316437919429	6.85166260523138	3.96781709981922
C	-1.13195046279876	7.09489480128467	5.03412833375955
H	-2.18061663764372	6.85638292743570	4.82130671640999
H	1.87159969538406	6.10456909561653	8.29673027815426
H	1.45435548828716	5.52878417374381	6.94138167286881
C	2.71334970435098	3.98569692769754	4.78863727871343

C	1.33836278942457	3.66802900555366	4.58623405432408
C	-0.84133900738109	3.62074175943371	5.54652306789318
H	-0.95396945259712	2.54049075964457	5.46247394286311
H	-1.28791895196092	3.96861325212097	6.47051556769907
H	-1.32462691457077	4.10415977168767	4.69910448474252
C	0.92075174252705	3.08535804352488	3.40710381213239
H	-0.12089018352501	2.84701857920195	3.26247559493783
C	1.83082416189588	2.80848202242108	2.38044057307895
H	1.47316964844263	2.36538606567918	1.46365063492356
C	3.15802416176108	3.10548216089846	2.53985977356546
H	3.86992660471115	2.90103802130813	1.75247237148652
C	3.62345780929827	3.68664565019931	3.73757801683460
C	5.01025102344599	3.98750010947044	3.81840580548888
H	5.59811364581064	3.73417492755217	2.92846931892951
C	4.63938316100093	6.03834388593073	9.36543046480675
C	3.81494810828809	6.34425577322636	10.48675604086815
C	1.61542281518718	6.25774859602980	11.40496958414422
H	1.61969052027490	7.28525300645209	11.76413535410562
H	0.63005651833948	6.00351808471634	11.03294244250517
H	1.89203973827507	5.58592841546123	12.21633040821707
C	4.36886406166642	6.84224125430497	11.64786800438047
H	3.73936840415299	7.06879960098499	12.49342782606414
C	5.74573958552383	7.07485116091815	11.74375311274052
H	6.14970235700683	7.47861403523917	12.65940713922098
C	6.56579179080607	6.79948804922745	10.68168324666564
H	7.63013503800324	6.97863085178711	10.74283438790824
C	6.03576159731320	6.27516304145045	9.48540747802528
C	6.94289017262172	6.02721779181783	8.41869243696154
H	7.99134057311596	6.27013541529706	8.62787621893997
H	3.95076801181261	7.00657496511157	5.15265145254049
H	4.33671164974912	7.57800666266882	6.51922020965497

Listing S6. Cartesian coordinates for DFT optimized dimeric structure of **1** with *d*(Fe···Fe) fixed to 5.5 Å.

Fe	4.98056174283840	4.75511883151144	6.67699771658632
Fe	0.83144148875019	8.36395855664448	6.78224645687710
Cl	5.49528903483847	2.63815189834458	7.41469852315380
Cl	0.31742653575567	10.48060566646327	6.04122254575565
O	2.59828403374772	8.67701884716608	7.50937608702876
O	5.15696514935724	9.09113665322264	7.77805030080395
O	0.06568623952837	8.73461916564399	8.68196087662794
O	3.25412373278817	7.05287420344262	3.22716835315899
O	1.62345726493195	7.62527252589680	5.17710625919721
O	-0.99310611573724	7.59164550874902	6.14756532723605
O	1.05420141144533	6.22365488314883	7.65405815527083
O	3.21300980749438	4.44197427368725	5.95040131945538
O	0.65345803883088	4.03111475569619	5.67871932593246
O	5.74562262367082	4.38871352126065	4.77715189179926
O	4.18721282808784	5.49178018550007	8.28332498723268
O	2.55592770157087	6.07187350790298	10.23076565326643
O	6.80373858644617	5.52855591215401	7.31143508310345
O	4.75575711478981	6.89673477330648	5.80518832076691
C	2.98479951860555	9.17335908393126	8.63596848599113
C	4.37508914189734	9.42565604026182	8.82939578023451
C	6.54274539623482	9.42432319926003	7.83430781908335
H	6.67325130057203	10.50217194110607	7.91990584304145
H	6.96695956613020	9.07301558287121	6.90116946549579
H	7.03234709681062	8.92895184984489	8.67067276305388
C	4.82760926998866	9.97768230410899	10.00906957663284
H	5.87925078533019	10.17201690955733	10.14722331890656

C	3.93952892472158	10.27779636332098	11.04983266820396
H	4.32532951831095	10.69584571907438	11.96691949680943
C	2.60060685302403	10.03101159615648	10.90520538060088
H	1.90734441284897	10.24921425491043	11.70549940505973
C	2.09961931622238	9.48321541543214	9.70592323584289
C	0.70370419635096	9.22736967497168	9.63309161996641
H	0.13007384353275	9.48614563171189	10.53060252385263
C	1.09108533145176	7.13987848745555	4.10659761559514
C	1.94108525969730	6.81660576006336	3.00802897438477
C	4.16254084812382	6.87168807957419	2.14251842770568
H	4.15487320965789	5.84123673200477	1.79208151360041
H	5.14180648346985	7.11742935863817	2.53598963484603
H	3.91339424031822	7.54016442222008	1.31966508207418
C	1.41042683029548	6.31708539473418	1.83752591848966
H	2.05736244191262	6.08055488795475	1.00795671423077
C	0.03371363554188	6.09256496287013	1.71008449508335
H	-0.35046282398477	5.68739430250664	0.78653024816838
C	-0.80923483538735	6.37470384486860	2.75140188591913
H	-1.87225307345311	6.19663719315998	2.66791386853157
C	-0.30402335664791	6.90325939852825	3.95756290457106
C	-1.23043258105927	7.14768206747237	5.00686710688109
H	-2.27425841960272	6.90121372241861	4.78057366290346
H	1.81164020320332	6.17190845315020	8.25691809131687
H	1.25456480910960	5.58320565861160	6.95412470342224
C	2.82638114647781	3.94996305770442	4.82190404712202
C	1.43601027381704	3.69953066391988	4.62687279344757
C	-0.73213568112324	3.69675441020342	5.62066151524623
H	-0.86125585823740	2.61916445664879	5.53072823794238
H	-1.15717180807238	4.04458277683031	6.55472098606192
H	-1.22149483821262	4.19419920163557	4.78539987594443
C	0.98356499470605	3.15200572294002	3.44507036324298
H	-0.06825192930174	2.95976142470167	3.30600845488101
C	1.87178578363823	2.85452650316942	2.40373521318007
H	1.48603227939383	2.43986306567526	1.48508577692113
C	3.21082717389737	3.09980730753978	2.54975244163434
H	3.90423609369381	2.88368466589549	1.74903672199581
C	3.71166992901479	3.64335107130790	3.75101788924674
C	5.10756397968291	3.89885151824757	3.82457341456064
H	5.68107579313225	3.64342172555440	2.92608988188374
C	4.71922693316933	5.98194773491691	9.35187326149431
C	3.86903355283792	6.30911709825326	10.44917385171098
C	1.64768847006342	6.25528494231045	11.31510430850673
H	1.65650192094835	7.28610416618892	11.66444087528735
H	0.66821654014614	6.00976888238593	10.92209148158122
H	1.89595904280297	5.58760648381503	12.13896880094826
C	4.39928155142360	6.81326193892453	11.61785102688238
H	3.75217134175937	7.05363533963719	12.44618635786312
C	5.77590229308757	7.03864401766272	11.74481394494487
H	6.15970022125163	7.44750418033777	12.66689621066298
C	6.61900955335614	6.75322120112130	10.70456170473785
H	7.68193637437636	6.93224902353821	10.78745509510981
C	6.11409715086154	6.22044209780393	9.50011349188012
C	7.04074349548089	5.97449195951609	8.45136549748107
H	8.08429589056640	6.22232692567907	8.67715923706271
H	3.99855965408826	6.94734262351486	5.20195266515079
H	4.55409111890959	7.53729484992494	6.50457016162953

Listing S7. Cartesian coordinates for DFT optimized dimeric structure of **1** with *d*(Fe···Fe) fixed to 6 Å.

Fe	5.13279378816042	4.56121852056167	6.70306989186111

Fe	0.67646015291387	8.57851857256573	6.75196134280037
Cl	5.62456107777041	2.45860100519319	7.45606751908756
Cl	0.18129101681148	10.68069773769545	6.00253339215278
O	2.45386847763112	8.83629361086304	7.47434815188649
O	5.03911041548928	9.09115165250511	7.77015648317347
O	-0.06329110956585	8.90970922780620	8.65556697557659
O	3.16409861404747	7.08154370599982	3.30253099118118
O	1.49173181831740	7.79406292512258	5.18067047826351
O	-1.12204652662571	7.76516080188000	6.13247926764199
O	0.95615850502551	6.33716393222840	7.65024407555994
O	3.35801491180646	4.30173156139273	5.97559556715354
O	0.77524222030854	4.03538251277960	5.67679589554279
O	5.87894295557170	4.22389785139310	4.80193257412463
O	4.31388382359768	5.34513693051167	8.27299787517262
O	2.63762536166946	6.05156873745497	10.15089332551013
O	6.93099249471713	5.37113897995107	7.32982632737945
O	4.85821190274800	6.79392461669186	5.80273135563330
C	2.86338038065511	9.26289093548893	8.61911852806432
C	4.26436769721613	9.43929700220648	8.82445620486217
C	6.43553277523897	9.37830408248809	7.84074273135940
H	6.60036795951703	10.44843229911042	7.95713189349606
H	6.85260011304221	9.04109940473418	6.89910196860908
H	6.90511398810957	8.84325321516733	8.66388962025901
C	4.73452631465009	9.94064837392001	10.01932850654834
H	5.79315862987304	10.08150018537432	10.16788024418573
C	3.85700136244445	10.25457851338126	11.06602004250147
H	4.25892438307020	10.63295870767458	11.99333123630803
C	2.51000399078119	10.06500371232920	10.91559401897593
H	1.82495280132932	10.28632492439746	11.72207671824575
C	1.99019738829510	9.56966611561210	9.70109436400592
C	0.58825941787489	9.35921038227115	9.62086617297876
H	0.02041521664342	9.60855134564683	10.52434686851853
C	0.98090855813867	7.24476606093879	4.13299266494821
C	1.84974429587316	6.85621543016494	3.06992527000865
C	4.08223674511296	6.86076546066191	2.23197036798786
H	4.07638439155966	5.81875357584058	1.91792643314967
H	5.05842868919565	7.11947976012795	2.62496683370526
H	3.84203404341030	7.50102297190209	1.38444585875718
C	1.33377406526394	6.31022927818559	1.91420208910192
H	1.99247641908083	6.02628793749526	1.10917703219544
C	-0.04339418210307	6.09338380872607	1.77013042357023
H	-0.41352570603779	5.65202484708343	0.85751651582548
C	-0.90205859740463	6.42246759774183	2.78379529240273
H	-1.96420278945009	6.24340460435084	2.69178165230624
C	-0.41263843099134	6.99926699088166	3.97479282283495
C	-1.34906106106118	7.28133517272280	5.00425077347660
H	-2.39046064399171	7.02523415173268	4.77897479789471
H	1.70970926779687	6.29235786875602	8.25680777352544
H	1.17495452608469	5.70686485341576	6.94871268307609
C	2.95257293313364	3.86619935434762	4.83268677388146
C	1.55251030034559	3.68402368730758	4.62584740357761
C	-0.62044498416685	3.74494660070523	5.60538048619452
H	-0.78264913443466	2.67359816946846	5.49629049989063
H	-1.03992632787559	4.08834849190112	6.54368723172724
H	-1.08972289544190	4.27316147331340	4.77758943355861
C	1.08628464287285	3.17517058367929	3.43255966704595
H	0.02839251639616	3.03015391195959	3.28262401358145
C	1.96690315281018	2.85880491190931	2.38917275048831
H	1.56795997460391	2.47467014612377	1.46292717391543
C	3.31311903731415	3.05276414074953	2.54146116711273
H	4.00047209036761	2.82902798103327	1.73761008381195
C	3.82904088723817	3.55553817492516	3.75456481297558
C	5.23047617105242	3.76933556237474	3.83700223832381

```
H   5.80075125635785      3.51734946890659      2.93580167265922
C   4.82284010474320      5.88730829249577      9.32522936750781
C   3.95203154793780      6.27194749718853     10.38813256108778
C   1.71755777835029      6.26658611744820     11.22092185010288
H   1.72532290601644      7.30621875245625     11.54270509124066
H   0.74157704813676      6.01330314173288     10.82391323768687
H   1.95441632821400      5.61960885085961     12.06426666187246
C   4.46609535548277      6.80978650751213     11.54853076047396
H   3.80587283727067      7.09004941839290     12.35361330202603
C   5.84325477516772      7.02323641115196     11.69743266981397
H   6.21181362202177      7.45866162737472     12.61353177557744
C   6.70390574086431      6.69840485377852     10.68413263632300
H   7.76615149644602      6.87485894470322     10.78007638318771
C   6.21658246682787      6.12887440569278      9.48876240479440
C   7.15546604100142      5.84996252056655      8.46064656360313
H   8.19653633856431      6.10396773209631      8.68980107952643
H   4.10040599213317      6.83915323228019      5.20172054819109
H   4.64706509063449      7.42799958243454      6.50342880484992
```

Listing S8. Cartesian coordinates for DFT optimized dimeric structure of **1** with water molecules substituted with acetonitrile ones.

```
Fe  4.51499121547289      4.68470493457616      6.96365259596749
Fe  1.20539221691478      8.58088290430316      6.63760532234732
Cl  4.58285350882366      2.51358994548078      7.85173573095669
Cl  1.14025081372082     10.74084610086086      5.72519374502759
O   2.86031521821269      8.77311387093952      7.55314286624805
H   5.28884780495418      9.00814177271388      8.31647503728510
O   0.23728201597811      9.32169580843830      8.40175661316691
H   3.17557422805829      6.77019887016987      3.09762906755481
O   1.85930103526334      7.70270225246261      5.08246097869820
O   -0.77652965078336      8.23461024261898      5.90288641186836
N   0.83416921922754      6.64486790778296      7.63010179142619
O   2.85841920557817      4.49904911254330      6.04942299911456
H   0.42823144047792      4.25553789522055      5.29398788225358
O   5.48043633416672      3.96128943006948      5.19163751681288
O   3.86079298834206      5.54966990592399      8.52565577865692
H   2.54414719341737      6.49387454694868     10.50531428831863
O   6.49661712310723      5.02271920013384      7.70407904691719
N   4.88876819379032      6.62814554197059      5.98681832510766
C   3.19991648524919      9.27881390961409      8.69382503160059
C   4.56494317762755      9.37520604767122      9.02761894372980
C   4.96177951986961      9.90717070676665     10.23167130969342
H   6.01622879040724      9.96201905736942     10.46257226151476
C   4.02554071180996     10.36189842370428     11.16805850417432
H   4.35361866656561     10.76585901788590     12.11365734894815
C   2.68799468748434     10.27879028231501     10.87007679974741
H   1.94681364356931     10.62403219006128     11.57882284370524
C   2.24336075542415      9.75152125074880      9.64391356404081
C   0.83801277890388      9.72402685907452      9.41268375748128
H   0.22324643161358     10.11252421281343     10.23513190585157
C   1.29956977132519      7.25984995280370      4.00425695038944
C   2.10562156291225      6.76984470978908      2.95795320343505
C   1.54393584803789      6.29055374056829      1.79831125916136
H   2.18810696934819      5.91555360740450      1.01561560221515
C   0.15536087399039      6.26448831390509      1.62108346279737
H   -0.26979742848111      5.87361062627908      0.70924460778350
C   -0.65499616217251      6.73415604856910      2.62459152631495
H   -1.73086200589180      6.72363313126968      2.50961703975143
C   -0.11738180000207      7.24368321326017      3.82079118102335
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C	-1.03401392243721	7.72862093614041	4.79706186001456
H	-2.09380274644947	7.64262713818873	4.52389675204033
C	2.51699805875421	3.99548414202412	4.90828706342160
C	1.15123616849387	3.89465863507117	4.57874813525742
C	0.75254823853101	3.36557699361415	3.37402569373200
H	-0.30245053132166	3.30698768117108	3.14652917778513
C	1.68757918396184	2.91847068022153	2.43277403813990
H	1.35801715523814	2.51710106642112	1.48659039903414
C	3.02576418373808	3.00574613516714	2.72665761736373
H	3.76596491232700	2.66637106028725	2.01407102303722
C	3.47231136595338	3.52984054051657	3.95346859796256
C	4.87826754888785	3.56198489511446	4.18033669685821
H	5.49207014586473	3.18050868649209	3.35392369469808
C	4.42038323784008	6.00069612014867	9.60064789948622
C	3.61419458746635	6.49541962549725	10.64459714672321
C	4.17598310129313	6.98111154247441	11.80160243759663
H	3.53172657376252	7.35977093134306	12.58246606182427
C	5.56454473423231	7.00932733690444	11.97818362578998
H	5.98969174248841	7.40502924107941	12.88794555134041
C	6.37504148127375	6.53588722213579	10.97652596097116
H	7.45095119525854	6.54841336755132	11.09085104494658
C	5.83743469060931	6.02028498661808	9.78297014249739
C	6.75413577133528	5.53185336890300	8.80847000655133
H	7.81388961314603	5.61804007380509	9.08168349800491
C	4.84280901845481	9.00267480080229	4.96807953089425
H	5.69229408937202	9.57277815561533	5.33700118693011
H	3.91937260673451	9.50161238254681	5.24905581024083
H	4.90301692736057	8.93644760300192	3.88439873381446
C	0.86078367321607	5.58419377405145	8.07115355224549
C	0.87346037622503	4.26186280099206	8.62918190736625
H	1.79225038184791	3.76026592142455	8.33808569105292
H	0.01848394068909	3.69921846334294	8.26154171467196
H	0.82104079049489	4.31994150226010	9.71371021027379
C	4.85904832304305	7.68490664403936	5.53665443634376

Listing S9. Cartesian coordinates for DFT optimized dimeric structure of **1** with water molecules substituted with acetonitrile ones and with *d*(Fe···Fe) fixed to 4.753 Å.

Fe	4.43321214555222	4.86198137588660	6.92101915842093
Fe	1.28479274708936	8.41429911331309	6.67708765238356
Cl	4.45855074096287	2.67427632870105	7.82491976954023
Cl	1.26129289759948	10.59615907596760	5.75817476542334
O	2.92033871410595	8.63538509135382	7.60413710233321
H	5.34722067844759	8.94696724242466	8.33846985606875
O	0.29610859432097	9.21674565158016	8.42085942663330
H	3.21642476884814	6.69370055490412	3.08885999282229
O	1.90657018518603	7.56730040260215	5.10188394649664
O	-0.71748276958595	8.14909348300181	5.91813228913158
N	0.82019334097153	6.53199896932775	7.67178422819127
O	2.79747242901634	4.64395840202865	5.99322837443146
H	0.36969396774652	4.32446979616423	5.26333320097232
O	5.42161671483167	4.06798182051971	5.17315582017873
O	3.81160043854609	5.70348541877441	8.49926596128543
H	2.50191461357598	6.57718482236867	10.51224805239075
O	6.43535974311529	5.12099444709347	7.68300335458205
N	4.90090449761114	6.74780115986299	5.93496019768688
C	3.25742075813784	9.21108023094535	8.71196975876408
C	4.62216842048520	9.33794616930376	9.03545430581894
C	5.01665213860727	9.92105611578993	10.21660030533773
H	6.07103849913886	9.99351742548950	10.44334398109971
C	4.07772812276288	10.40561498106596	11.13490463590535

H	4.40323567829033	10.85003252275395	12.06312090877381
C	2.74024351595073	10.30381195147865	10.84041773714462
H	1.99735377655997	10.67479793759569	11.53422775058809
C	2.29865200896321	9.72220178664302	9.63869884137498
C	0.89256682410644	9.66985388228353	9.41131290161447
H	0.27544590574783	10.08758243353204	10.21789771652854
C	1.34514773310929	7.19092949266497	3.99938693943751
C	2.14790834241273	6.72238762511257	2.94131099532827
C	1.58363649749036	6.29107767669734	1.76390385376127
H	2.22464650152942	5.92610399627493	0.97380257729126
C	0.19614964925084	6.30159266843956	1.57847373529327
H	-0.23206726994221	5.94832863929813	0.65280914413715
C	-0.61008192393630	6.76258534990447	2.59001425228103
H	-1.68493668870688	6.78282301969571	2.46706680600794
C	-0.06928834424343	7.22047860915216	3.80470853704629
C	-0.98064779556842	7.69279280830309	4.79344601772901
H	-2.04039364219024	7.64370222093756	4.50998211465311
C	2.45981195775862	4.06372741932413	4.88793414032876
C	1.09486436717439	3.93260136535991	4.56695956321202
C	0.69987382929192	3.34477161750835	3.38833055461775
H	-0.35470254183542	3.26865005101651	3.16372240127509
C	1.63846143630236	2.85976818672815	2.46992434686154
H	1.31249300397787	2.41167802605920	1.54364345942276
C	2.97615758093836	2.96600391558595	2.76178723050176
H	3.71885250941994	2.59519075146873	2.06765826105852
C	3.41828799273268	3.55216377069800	3.96108960952631
C	4.82465854009672	3.61036162768521	4.18510203935204
H	5.44152408086732	3.19355906159063	3.37785854952600
C	4.37301183611462	6.07782469192171	9.60243557937117
C	3.57027033283908	6.54631074293804	10.66060473789415
C	4.13456104015805	6.97515236953812	11.83890530820303
H	3.49358673235715	7.34018292440245	12.62902476122541
C	5.52190501418219	6.96209709202477	12.02536695606481
H	5.95021790408168	7.31314759549374	12.95183668837089
C	6.32806923411906	6.50151065205725	11.01356005575196
H	7.40281809210496	6.47953103744246	11.13714765150270
C	5.78735528885415	6.04632412225425	9.79782571274703
C	6.69857976967949	5.57462816189701	8.80880608231375
H	7.75821300954899	5.62156464785151	9.09300203657698
C	4.80175946460466	9.12636970127898	4.93254730444227
H	5.60440155993586	9.73344533630397	5.34473965927976
H	3.84213672989855	9.57769715249815	5.17723522010437
H	4.91221157704897	9.07633383668719	3.85186706765306
C	0.86483053337369	5.47165065313111	8.11198204127975
C	0.91718180657571	4.14866406056301	8.66310815627203
H	1.87646609158812	3.69725549658165	8.41738013793813
H	0.11408407949811	3.54370690042911	8.24870154659503
H	0.80622283858817	4.19501876158415	9.74392472923325
C	4.85537115222545	7.80561757085655	5.48884144660529

Listing S10. Cartesian coordinates for DFT optimized dimeric structure of **1** with water molecules substituted with acetone ones.

Fe	4.59989382588858	4.81943684317680	6.88333998237108
Fe	1.06210365474809	8.51970730109898	6.73272888534997
Cl	4.90894891512468	2.65931655206043	7.75331350553914
Cl	0.78426581654209	10.70188483814993	5.91685938260107
O	2.72502011673388	8.79736173128359	7.60540342608571
H	5.17612658520976	9.15556970466356	8.28242620627699
O	0.11465353338822	9.12294228468804	8.55568281160684

H	3.06246174015501	6.89850487897023	3.11413809825963
O	1.71611689153556	7.73659654782121	5.13332912504527
O	-0.90967788163382	8.05590743919605	6.04186005413483
O	0.93045867732587	6.54587476344142	7.63750165683053
O	2.93142363145700	4.51677667559877	6.03194334041994
H	0.47442046832443	4.20682382503297	5.35314430301626
O	5.53473278827173	4.17531566541908	5.06871990423898
O	3.95735355428849	5.62228636780102	8.47850372890294
H	2.62614301716909	6.42656615030416	10.52150153418077
O	6.57620515025575	5.31390866493115	7.54661361738545
O	4.72001040215966	6.77603115289853	5.95015956721906
C	3.07892429331914	9.26728610465952	8.75712165303248
C	4.45594922935305	9.44034985689198	9.04661728200368
C	4.86570842062012	9.94853222451471	10.26433714342084
H	5.93124703238525	10.06860842472693	10.46020066621679
C	3.93364256742008	10.29903568753009	11.26083990675409
H	4.27568868697264	10.68655893492658	12.21908099116517
C	2.58623780666343	10.13711682790152	11.00931903777484
H	1.84703586262249	10.40175590282621	11.76722719129205
C	2.12638807720432	9.63355767507660	9.76919278327218
C	0.71472735759983	9.52070399369673	9.57366491017363
H	0.09192205952641	9.82911189952454	10.43518971179419
C	1.16543428093129	7.25070306833775	4.06934385584257
C	1.98400549026244	6.82008707664905	2.99458448421975
C	1.42541571293116	6.31039156641935	1.83834336112644
H	2.07949595151170	5.98583681442288	1.02899343241617
C	0.02934494379039	6.18882697290568	1.69274826198511
H	-0.39229738393694	5.77387091645890	0.77871822921264
C	-0.79266642131589	6.59156388923490	2.72555539357575
H	-1.87658821184788	6.50322921591468	2.63557206491372
C	-0.25945916484567	7.13154665076121	3.92028206764562
C	-1.17607934539458	7.54405785676709	4.93611602212452
H	-2.24595113784817	7.38766069627669	4.70007224690091
C	2.56912830330661	4.06012889109712	4.87763377840779
C	1.18916230192225	3.90970640154273	4.58865973188343
C	0.77047982524779	3.40780848221668	3.37141545325286
H	-0.29698440011514	3.30451691507192	3.17647087322272
C	1.69587693265746	3.04246172555312	2.37399887709317
H	1.34680351759349	2.65962211896454	1.41641696158153
C	3.04569368560135	3.18601345250887	2.62306378673617
H	3.77983466707289	2.91215649786157	1.86354880649698
C	3.51458193152743	3.68376129218973	3.86223399467421
C	4.92760745547114	3.78170972677237	4.05280231090584
H	5.54465223789883	3.46487612356116	3.19044189354933
C	4.51559281373071	6.10225067445594	9.54179088379063
C	3.70504257208485	6.51702779145672	10.62840475031864
C	4.27164930865408	7.02595347337162	11.78116075135897
H	3.62386497498481	7.33911004811896	12.59999428355164
C	5.66794539734985	7.16072204801029	11.91117764550559
H	6.09599184460558	7.57489429981448	12.82258199384668
C	6.48227876680606	6.76996990116766	10.86756591423011
H	7.56635922419555	6.86644488352955	10.94668637845730
C	5.94081005808661	6.23074945899356	9.67632832152605
C	6.84990360490175	5.82644387378840	8.64986765491911
H	7.92095698559510	5.99108511774457	8.87529465481741
C	4.96462613266949	8.91372353330668	4.98845717605350
H	5.72702180071372	9.67353172803836	5.20379645675427
H	4.02345212704044	9.13275960907804	5.49655620712062
H	4.80832205726606	8.93250226766125	3.89943295853226
C	0.21787933315732	5.80430200382242	8.30936017286394
C	0.72235525697439	4.45276871261409	8.70065128405510
H	1.79441170661326	4.36980847428558	8.51129677903824
H	0.18449868264259	3.70299210910609	8.10124204604075

H	0.47918270553778	4.24162865277585	9.74998659890828
C	5.46406956257560	7.55487052653315	5.35924662093574
C	6.87305305088700	7.21002033700106	4.99791506292315
H	7.15928327150228	7.67650762041791	4.04816761570671
H	7.02998048853363	6.12988049764564	4.97349116561186
H	7.52593774227493	7.64128523957276	5.77167820306391
C	-1.14744292075000	6.19753710439416	8.77443636732959
H	-1.55876564811110	7.01150795221932	8.17440117272788
H	-1.05442766259174	6.54120553273225	9.81577836922188
H	-1.82028669098530	5.33217125803938	8.78794621665398

Listing S11. Cartesian coordinates for DFT optimized dimeric structure of **1** with non-planar disposition of the L ligands and water molecule substituted with acetonitrile one.

Fe	1.17374587310885	9.13682283241360	6.27646668876091
Cl	0.27891522670343	11.04736208128598	7.32780109589612
O	2.94080642384387	9.37203435664859	7.00802657969845
O	5.20300461813436	10.58510855975427	7.56374309269798
O	0.74778886281916	7.97463015330732	7.94778079364008
O	1.69765331849412	7.60650426940984	5.18364463381782
O	3.23600133506278	6.08109230985452	3.69727934267586
O	-0.80293704345185	8.70495544263635	5.58983132981320
C	3.31364602501944	9.38437411631598	8.24447869309264
C	4.54443431738532	10.01790382471823	8.59542528162520
C	6.43531310716467	11.24435577379227	7.84228079120284
H	6.28787448511497	12.07154347002863	8.53670410386922
H	6.78703704431143	11.62484591605944	6.89008815835736
H	7.16708713065170	10.54898727776521	8.25351040928111
C	4.97149591793814	10.02386725128189	9.90857228196774
H	5.89848264252656	10.50905054619267	10.17104945407703
C	4.22233650203967	9.40382854266763	10.91937383133389
H	4.58881545030938	9.42488604753125	11.93460523436386
C	3.04454460891639	8.77749328099492	10.61492909145881
H	2.46043101497717	8.28733503528193	11.38129265258211
C	2.56680880244391	8.76581160793941	9.28756627523905
C	1.35741864580348	8.06721724207629	9.03161920605906
H	0.92169468642548	7.54354098750587	9.89037424784525
C	1.16004944112752	7.06615555382652	4.14336451179255
C	1.95467202305516	6.22215069621866	3.30601203505257
C	4.08922505115659	5.25475410665424	2.90894691644954
H	3.72053389419689	4.22958821855077	2.87791704548847
H	5.05659030553025	5.28121853314545	3.39729362406994
H	4.17876756500856	5.64173233339504	1.89400136659898
C	1.39766476512335	5.62726159240908	2.18943683107396
H	2.00215464574703	4.99557154550031	1.55764602749762
C	0.05146158395344	5.82629814437937	1.85771726193296
H	-0.35227039320892	5.34459836503690	0.97998264624657
C	-0.74014939159772	6.62157160993793	2.64474377492457
H	-1.78296115870206	6.77757623301427	2.40555504298041
C	-0.20418931232966	7.25298812963027	3.78355242920238
C	-1.08415004015949	8.04102124122025	4.57624675834990
H	-2.13146624569316	8.04942801993586	4.24827773947279
N	1.53610358047486	10.32817514983368	4.48543097022345
C	1.66281465974963	10.87469347977700	3.48190414886653
C	1.82187061869961	11.56203480773551	2.23199491681460
H	2.87498703638852	11.58787887171613	1.96216893144454
H	1.44774352828551	12.57901816847146	2.32277229203015
H	1.26590884745119	11.04134427414783	1.45578146013101

Listing S12. Cartesian coordinates for DFT optimized dimeric structure of $\mathbf{1}^{2+}$ with eliminated solvent molecule and $S = 3.5$.

Fe	0.80573531114821	9.24328401840918	6.35338729921109
Cl	0.39135500633622	11.21693777219276	5.54970323010928
O	2.61898256360844	9.31264579336481	7.17244369854810
O	5.19088405761756	9.43879549582919	7.56667859789881
O	0.10429975821876	9.24876945253199	8.24572593155152
O	1.67788958696051	8.21736041940441	4.88555413291063
O	3.33699416185164	7.34300315292015	3.07496700633488
O	-0.82166082727545	8.10848575708389	5.99334938138003
C	3.00646677523358	9.36808731437989	8.37509378594108
C	4.45115879810043	9.44237136293082	8.64015195273573
C	6.62288910108675	9.50393117554108	7.64703000064260
H	6.92516259415072	10.43457641694981	8.14103738416492
H	6.97451139156805	9.48647916523080	6.61442373014698
H	7.00363804215899	8.63617441840046	8.19808271175801
C	4.92791084124429	9.50716155755759	9.96272265923390
H	5.99655633354227	9.55875143801534	10.15556110393934
C	4.03711810517519	9.50449605886430	11.02189598549985
H	4.41378461968711	9.55569784842065	12.04140882898769
C	2.64696692078702	9.43763071795319	10.80054268681747
H	1.96495633593048	9.44081797118690	11.65037645338375
C	2.12345675623286	9.36835137700179	9.50760656955018
C	0.70241005081909	9.31567527832866	9.33595803535640
H	0.08558921344838	9.34146100955313	10.24951361780788
C	1.25118363040283	7.30995796647703	4.11514476144158
C	2.15735569131923	6.78781769252099	3.08110185910360
C	4.34040896249757	6.95208893600391	2.12497736689600
H	4.58152234679544	5.89061850905028	2.25475426903625
H	5.20996595286558	7.57235789916811	2.34714742603308
H	3.98164590714709	7.14247182195188	1.10683360788293
C	1.72592489519672	5.77409854743534	2.20563424676808
H	2.39918964956955	5.38792801099006	1.44469702619542
C	0.44279497132959	5.26623683690578	2.31046394352270
H	0.11764755447462	4.48226506273217	1.62960666393455
C	-0.45198399346771	5.75153056624403	3.28487135640478
H	-1.45941539857606	5.34085017907062	3.34401716321563
C	-0.07217344800158	6.75489926709763	4.17910223784649
C	-1.02503128229238	7.22472047315059	5.13941807932107
H	-2.02777093689184	6.76668325915001	5.11615520848715

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