Supporting Information

Ultrafast Reaction Mechanisms in Multimolecular Ir-Co Multimolecular Catalytic Assemblies for Hydrogen Evolution

Lucia Velasco[a], Asterios Charisiadis[a], Xiaoyi Zhang[b], Dooshaye Moonshiram[a*]

[a] Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Sor Juana Inés de la Cruz, 3, 28049, Madrid, Spain

[b] X-ray Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Lemont, IL 60439, U.S.A

Table of Contents

Experimental Methods:

Steady-state and time-resolved X-ray absorption Structure (XAS) measurements. Steady-state and time-resolved X-ray absorption spectra were collected at 11 ID-D[1] beamlines at the Advanced Photon Source using undulator radiation at electron energy 7.71 KeV (Co K-edge) in solvent grade acetonitrile and millipore water. The samples were circulated through a stainless-steel nozzle into a free-flowing cylindrical jet inside an airtight aluminum chamber, and continuously degassed with nitrogen. This sample handling technique ensures proper sample recovery such that the subsequent laser pulse can hit a "fresh" sample position.

Cooled running water from a chiller was additionally circulated around the jacketed sample flask to prevent heating damage of the complexes by radiation. The X-ray fluorescence signals were collected with two avalanche photodiodes (APDs) positioned at 90˚ on both sides of the liquid jet, and a combination of Z-1 filters and soller slits with conical geometry were used to reduce the background from elastically scattered X-rays.

The experiments were carried out using the 24 bunch timing mode of APS (in top up mode with a constant 102 mA ring current) which consists of a train of X-rays separated by 153 ns. This mode easily allows for gateable detectors that selects X-ray pulses. This timing mode was suitable for this type of experiments in which the separation between adjacent X-ray pulses was long enough for the Avalanche Photodiode (APD) detector to resolve individual X-ray pulses.

The time-resolved experiments were carried out by pumping the samples at 400 nm wavelength using a regenerative amplified laser with 10 kHz repetition rate 5 ps-FWHM pulse length and laser power of 630 mW at the sample. The X-ray and laser beam was spatially overlapped with an X-ray spot size of 100 μm(V) x 450 μm(H) and laser spot size of 170 μm(V) x 550 μm. With a liquid flow speed of around 3.5 m/s, the pumped laser volume was calculated to move out of the FWHM laser pulse region in around 24 μs. This temporal range ensured that the excited state volume was probed more at the centre and less at the edges where the excitation fraction would be less, due to movement of the sample. Beamline 11 ID-D has an automated data digitization system which allows for all X-ray pulses after laser excitation to be collected. Such a system, together with the larger X-ray beam spot size, was very useful for our experiments, as multiple X-ray pulses after laser excitation were averaged to monitor the dynamics for the formation and decay of the Co(I) transient signal in the nano-microsecond time regime.

The UV-vis measurements of the dyads before and after X-ray and laser exposure were checked after each run to ensure lack of X-ray and laser damage of the complexes. The delay between the pump and X-ray pulses was adjusted by a programmable delay line (PDL-100A-20NS, Colby

Instruments). A Co metal foil was placed between two ionization chambers downstream to the X-ray beam, and its transmission recorded with each scan for energy calibration.

Extended X-ray Absorption Fine Structure (EXAFS) Analysis. Athena software[2] was used for data processing. The energy scale for each scan was normalized using copper metal standard. Data in energy space were pre-edge corrected, normalized, deglitched (if necessary), and background corrected. The processed data were next converted to the photoelectron wave vector (k) space and weighted by *k*. The electron wave number is defined as $k = [2m(E - E_0)/\hbar^2]^{1/2}$, E_0 is the energy origin or the threshold energy. K-space data were truncated near the zero crossings k = 2 to 13.173 Å^{-1} for the cobalt-based solution complexes, in Co EXAFS before Fourier transformation. The k-space data were transferred into the Artemis Software for curve fitting. In order to fit the data, the Fourier peaks were isolated separately, grouped together, or the entire (unfiltered) spectrum was used. The individual Fourier peaks were isolated by applying a Hanning window to the first and last 15% of the chosen range, leaving the middle 70% untouched. Curve fitting was performed using *ab initio*-calculated phases and amplitudes from the FEFF8[3] program from the University of Washington. *Ab initio*-calculated phases and amplitudes were used in the EXAFS equation

$$\chi(k) = S_0^2 \sum_j \frac{N_j}{kR_j^2} f_{eff_j}(\pi, k, R_j) e^{-2\sigma_j^2 k^2} e^{\frac{-2R_j}{\lambda_j(k)}} \sin(2kR_j + \phi_{ij}(k)) \qquad \text{(Equation S1)}$$

where N_j is the number of atoms in the j^{th} shell; R_j the mean distance between the absorbing atom and the atoms in the j^{th} shell; $f_{eff_j}(\pi,k,R_j)$ is the *ab initio* amplitude function for shell *j*, and the Debye-Waller term $e^{-2\sigma_j^2 k^2}$ accounts for damping due to static and thermal disorder in absorber-backscatterer distances. The mean free path term $e^{\frac{-2R_j}{\lambda_j(k)}}$ reflects losses due to inelastic scattering, where $\lambda_j(k)$, is the electron mean free path. The oscillations in the EXAFS spectrum are reflected in the sinusoidal term $\sin(2kR_j + \phi_{ij}(k))$, where $\phi_{ij}(k)$ is the *ab initio* phase function for shell *j*. This sinusoidal term shows the direct relation between the frequency of the EXAFS oscillations in k-space and the absorber-backscatterer distance. S_0^2 is an amplitude reduction factor.

The EXAFS equation[4] (Eq. S2) was used to fit the experimental Fourier isolated data (q-space) as well as unfiltered data (k-space) and Fourier transformed data (R-space) using *N*, S_0^2, E_0, *R*, and σ^2 as variable parameters (Table S1). *N* refers to the number of coordination atoms surrounding Co for each shell. The quality of fit was evaluated by R-factor and the reduced Chi^2 value. The deviation in E_0 ought to be less than or equal to 10 eV. R-factor less than 2% denotes that the fit is good enough. R-factor between 2 and 5% denotes that the fit is correct within a consistently broad model. The reduced Chi^2 value is used to compare fits as more absorber-backscatter shells are included to fit the data. A smaller reduced Chi^2 value implies a better fit. Similar results were obtained from fits done in k, q, and R-spaces.

Optical Transient Absorption Measurements. Ultrafast transient absorption spectroscopy was carried out at the Center for Nanoscale materials at Argonne National Laboratory, using an EOS broadband pump-probe nanosecond transient absorption spectrometer (Ultrafast Systems, EOS). The set up featured a sub-nanosecond pulsed probe generated by a photonic crystal fiber-based supercontinuum laser. Pump-probe delays were electronically controlled, and the pump laser operated at a repetition rate of 1 KHz with automated data. The Co multimolecular assemblies were pumped with 355 nm excitation and typical pulse energy of 300 nJ per pulse, and probed with a super-continuum source. The transient absorption data consisted of two-dimensional spectra and kinetic traces across 390- 900 nm. The temporal chirp in the optical transient absorption data of the probe beam were corrected using the non-resonant response of blank water and acetonitrile, the latter providing an instrument response function (IRF) of 5 ns. The samples were degassed with N_2 gas and continuously stirred magnetically in a 2 mm cuvette. Global fit analysis for the OTA spectra, used to model the kinetics spectra with a single unified model, were further conducted through the surface Xplorer software by Ultrafast Systems.

DFT Calculations. DFT optimization calculations were performed using the ORCA (Version 6.1.) program package developed by Neese[5] and co-workers. The calculations employed the B3LYP[6, 7], a hybrid exchange-correlation functional, in combination with the Zeroth Order Regular Approximation (ZORA)[8] method to account for relativistic effects. A relativistic decontracted version of the triple zeta valance polarization basis set (ZORA-def2-TZVP)[8] with SARC/J[9] as auxiliary basis set were chosen. The dispersion correction was described with the D4 model[10] and the Conductor-like Polarizable Continuum Model (CPCM)[15] using acetonitrile as the solvent was used for the complexes in solution. The RIJCOSX[11] approximation was utilized to accelerate the calculations. The default GRID settings were further used for the self-consistent field iterations and for the final energy evaluation.

XANES and Optical Simulations analysis. XANES and optical simulations were performed using time-dependent Density Functional Theory (TD-DFT) within the ORCA[5] program package (Version 6.1.0). Similar to the optimization calculations, B3LYP[6, 7] was used as functional, ZORA[8] to take into account the relativistic effects and ZORA-def2-TZVP[8] and SARC/J [9] as basis set and auxiliary basis set, respectively. The RIJCOSX[11] approximation was further applied with the atom-charge dependent dispersion correction D4[10] and CPCM solvent model for the solvent effects[12]. In order to account for the higher-order interactions, the Semiclassical Full Mater Interaction Operator[13] was added to the calculations.

The TD-DFT XANES spectra were shifted by 13 eV relative to the experimental data and a broadening of 2.0 eV was applied to all calculated spectra. The donor orbitals for XAS calculations were chosen as Co 1s and all virtual orbitals were selected as acceptor orbitals. For the optical

spectra, a gaussian broadening of 20 nm was applied. Up to 150 roots were computed for XANES, and 30 roots for optical spectra.

Table S1. EXAFS Fits parameters

Sample	Fit	Peak	Shell,N	R, Å	E_0	ss.^{2} (10^{-3})	R-factor	Reduced Chi-square
1^{H}-Co^{II}	1	I	Co-N,3 Co-N,3	2.04 2.21	3.9	3.0 0.9	0.0033	432
	2	**All**	**Co-N,3** **Co-N,3** **Co-C,11**	**2.02** **2.18** **2.91**	**1.6**	**6.7** **4.2** **18.6**	**0.0041**	**18**
1^{COOEt}-Co^{II}	3	I	Co-N,3 Co-N,3	2.02 2.19	2.9	4.3 1.8	0.0048	747
	4	**All**	**Co-N,3** **Co-N,3** **Co-C,12**	**1.99** **2.16** **2.90**	**1.7**	**7.8** **4.3** **24.2**	**0.0076**	**29**

***** The fit I was carried out between 1.2 – 2.5 Å and fit all to 1.2 –3 Å in apparent distance. The amplitude reduction factor S_0^2 was set to 1. The bond distance resolution given by $\pi/2\Delta k$ is equal to 0.141 Å.

Table S2. DFT calculated parameters of all calculated cobalt complexes

	Co-N_1	Co-N_2	Co-N_3	Co-N_4	Co-N_5	Co-N_6	Co-H
1^{H}-Co^{II} (CH_3CN)$_2$	2.117	2.177	2.198	2.240	2.065	2.112	
1^{H}-Co^{I}	1.935	2.130	2.064	2.165			
1^{H}-Co^{I} (CH_3CN)	2.077	2.209	2.243	2.193	1.918		
1^{H}-Co^{II}H	2.109	2.267	2.203	2.130			1.642
1^{H}-Co^{II}H (CH_3CN)	2.182	2.215	2.195	2.350	2.077		1.729
1^{H}-Co^{III}H	1.925	2.022	1.949	1.920			1.461
1^{H}-Co^{III}H (CH_3CN)	1.946	1.946	1.995	2.107	1.891		1.452
1^{COOEt}-Co^{II} (CH_3CN)$_2$	2.129	2.173	2.187	2.189	2.075	2.146	
1^{COOEt}-Co^{I}	1.903	2.120	2.065	2.148			
1^{COOEt}-Co^{I} (CH_3CN)	1.934	1.976	2.026	2.183	1.901		
1^{COOEt}-Co^{II}H	2.111	2.265	2.198	2.132			1.642
1^{COOEt}-Co^{II}H (CH_3CN)	2.152	2.186	2.224	2.300	2.099		1.749
1^{COOEt}-Co^{III}H	1.928	2.022	1.944	1.920			1.461
1^{COOEt}-Co^{III}H (CH_3CN)	1.943	1.947	1.994	2.103	1.891		1.452

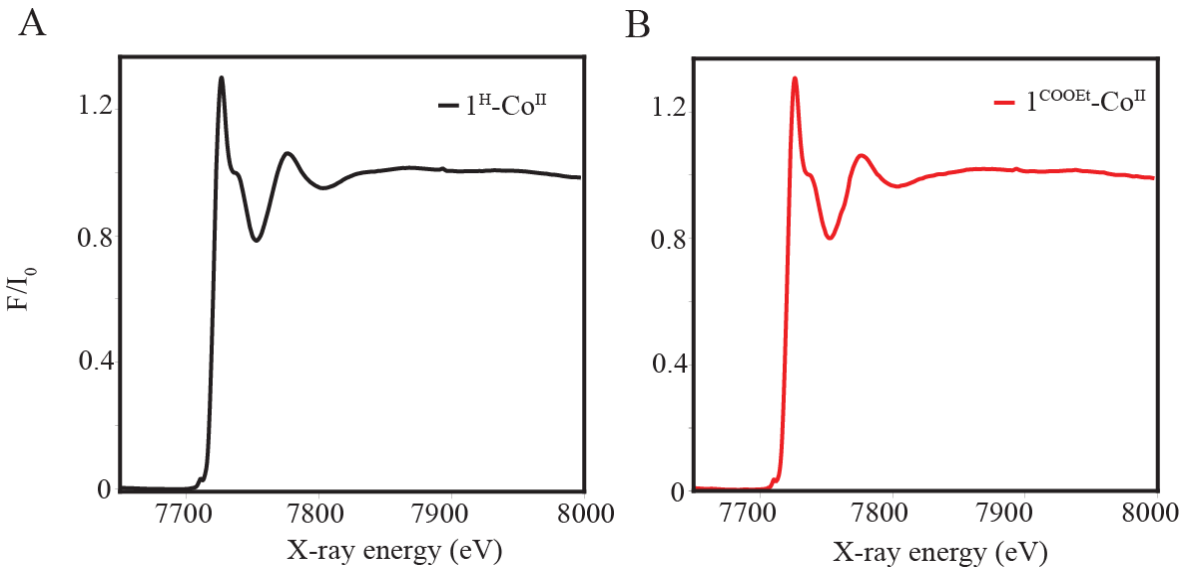


Figure S1. **A**. Normalized Co K-edge XANES of 1 mM 1H-Co^{II} and **B**. 1COOEt-Co^{II} complexes in a solution mixture of 4:1 CH_3CN:H_2O showing the full spectra extending to the EXAFS region.

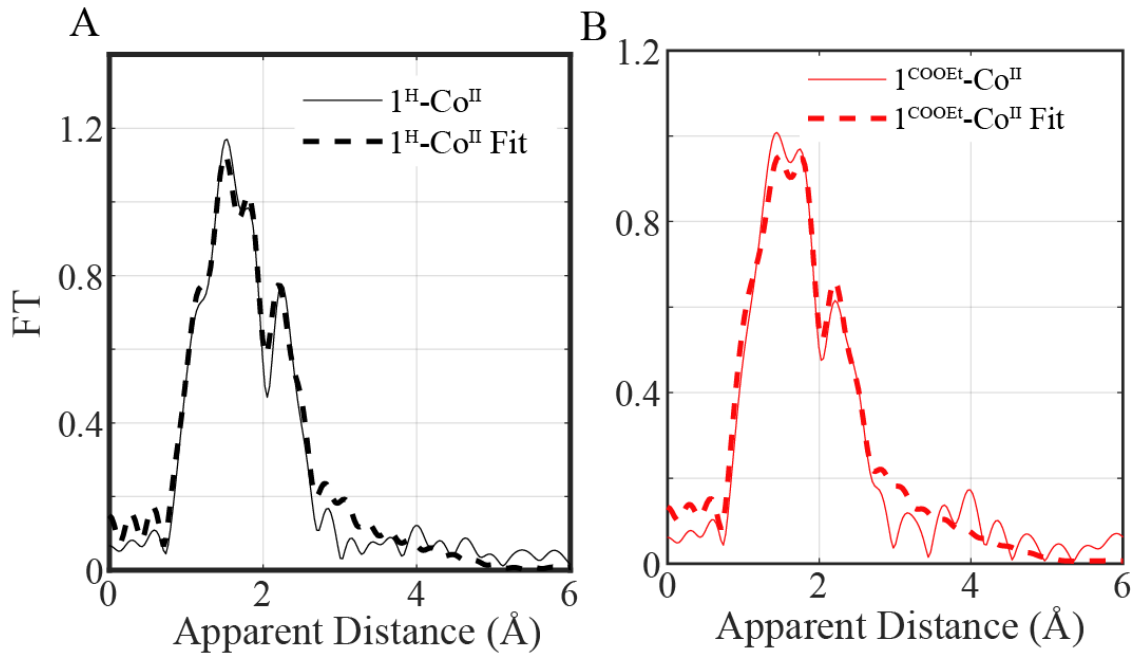


Figure S2. Comparison of the Fourier transform of **A**. 1^{H}-Co^{II} (Fit 2 in **Table S1**) and **B**. 1^{COOEt}-Co^{II} complex (Fit 4 in **Table S1**). EXAFS fits were carried from 1-2.9/3 Å.

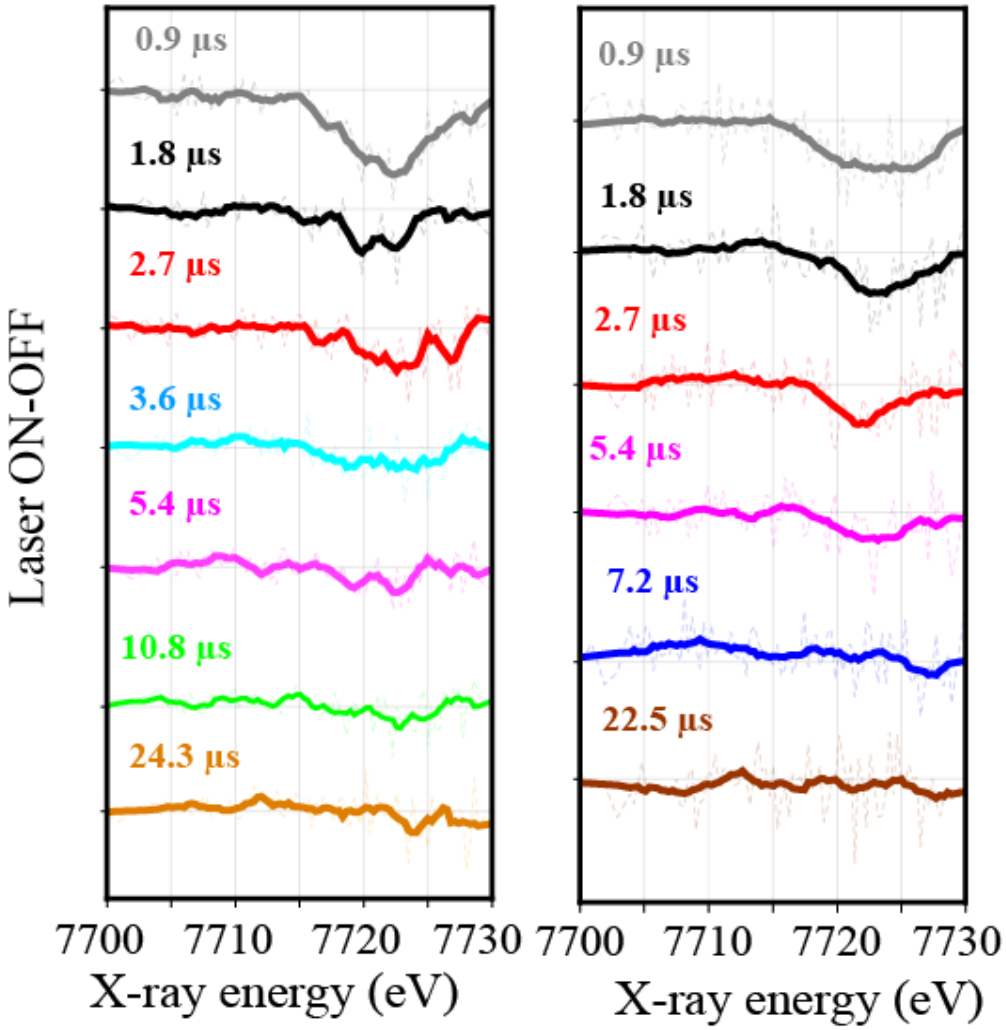


Figure S3. Stacked Spectra corresponding to a series of time-delays between laser and X-ray pulses. These measurements were carried out for a range of averaged time delays 1.8 µs to 23.9 µs for the 2 sets of photocatalytic systems with the **A**. $[1^{H}\text{-}Co^{II}]^{2+}$ and **B**. $1^{COOEt}\text{-}Co^{II}$ complexes.

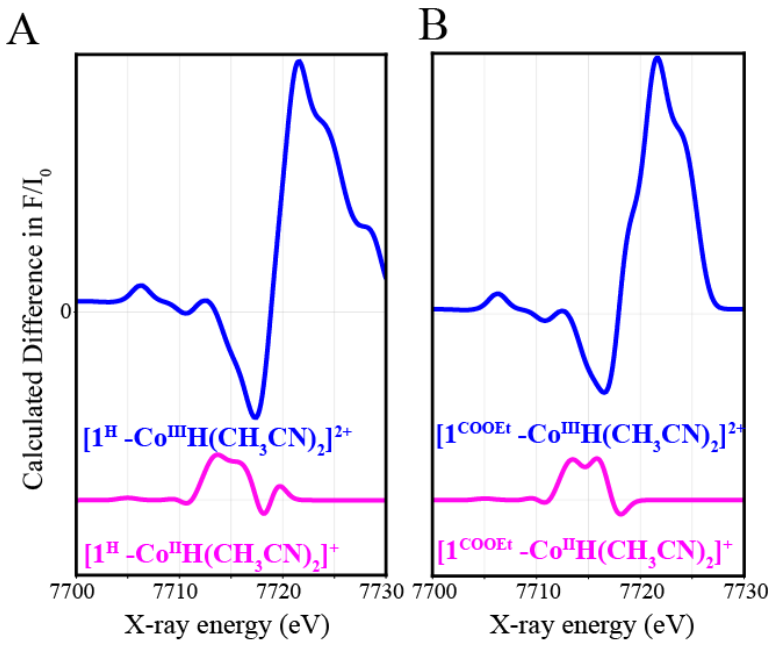


Figure S4. Theoretical XANES simulations corresponding to the formation of an octahedral $[LCo^{III}H](CH_3CN)_2)^{2+}$ (blue) and $[LCo^{II}H](CH_3CN)_2)^{+}$ (magenta) hydride species for **A**. $[1^{H}\text{-}Co^{II}]^{2+}$ and **B**. $[1^{COOEt}\text{-}Co^{II}]^{2+}$.

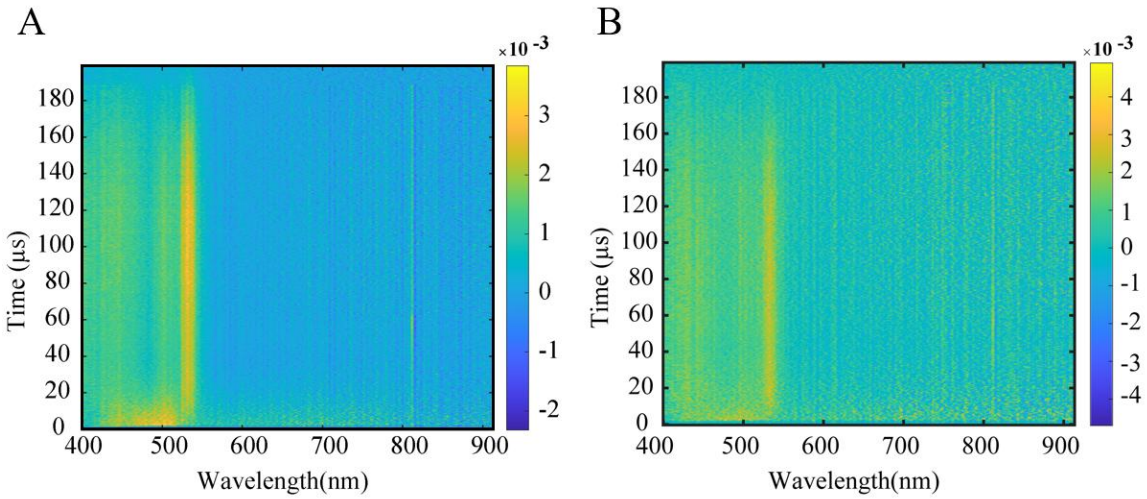


Figure S5. Color-coded 2D Intensity plots showing the magnitude of the optical transient absorption (OTA) spectra of a solution of 0.3 mM **A**. $1^{H}Co^{II}$ **B**. $1^{COOET}Co^{II}$ catalyst with 0.6 mM $[Ir^{III}(ppy)_2(bpy)]^{+}$, 0.3 M triethylamine and 10 mM ascorbic acid in 4:1 solution mixture of CH_3CN: H_2O . The color gradient here shows the magnitude of the OTA signal at each wavelength and time coordinate.

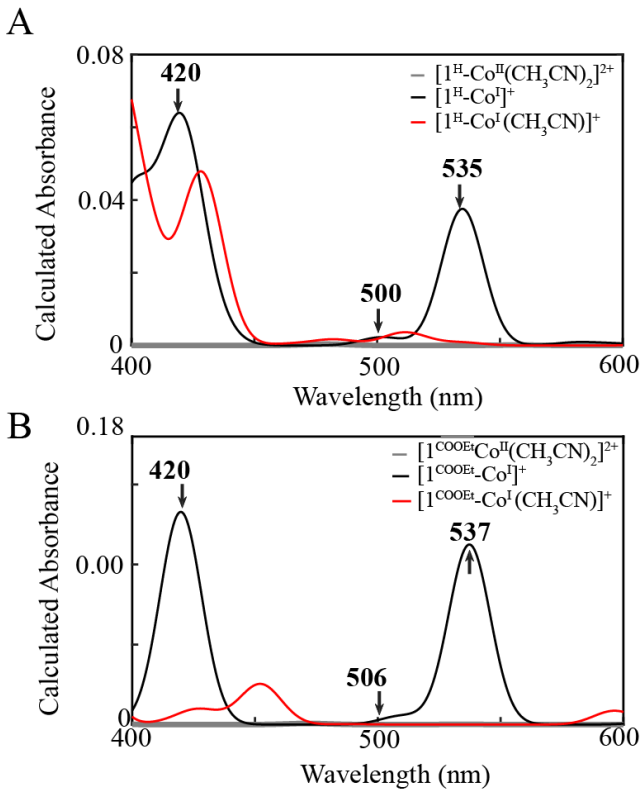


Figure S6. Calculated optical spectra extracted with a broadening of 20 nm of **A.** $[1^{H}\text{-}Co^{II}(CH_3CN)_2]^{2+}$, $[1^{H}\text{-}Co^{I}]^{2+}$ and $[1^{H}\text{-}Co^{I}(CH_3CN)_2]^{+}$ **B.** $[1^{COOEt}\text{-}Co^{II}(CH_3CN)_2]^{2+}$, $[1^{COOEt}\text{-}Co^{I}]^{2+}$ and $[1^{COOEt}\text{-}Co^{I}(CH_3CN)_2]^{+}$

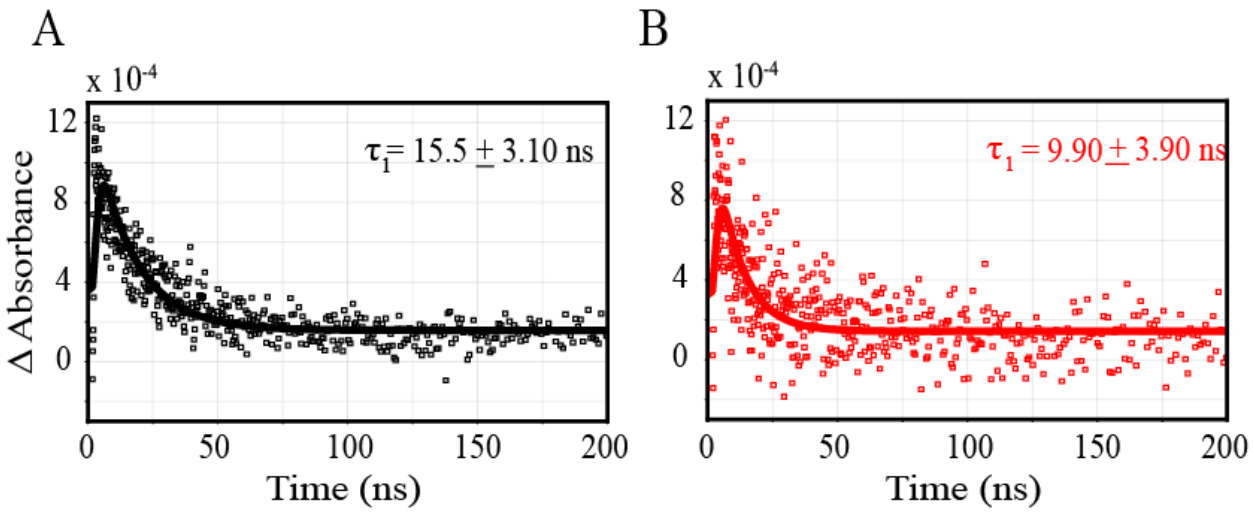
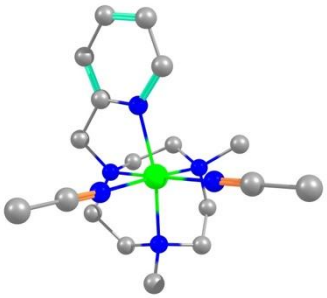


Figure S7. Kinetic decay profiles at λ= 728 nm after excitation at λ^{exc} = 355 nm for multimolecular assemblies composed of **A**. the $1^{H}Co^{II}$ **B**. $1^{COOET}Co^{II}$ with 0.6 mM $[Ir^{III}(ppy)_2(bpy)]^{+}$, 0.3 M triethylamine and 10 mM ascorbic acid in 4:1 solution mixture of CH_3CN: H_2O . τ_1 are the resulting decay lifetimes of the $[Ir^{III}(ppy)_2(bpy^{\cdot -})]$ which in the presence of the 0.3 M excess triethylamine electron donor corresponds to the formation of the photoreduced Co^{I} species.

Appendix- DFT optimized coordinates using B3LYP[6, 7], hybrid exchange-correlation functional, in combination with ZORA-def2-TZVP basis[14] set.

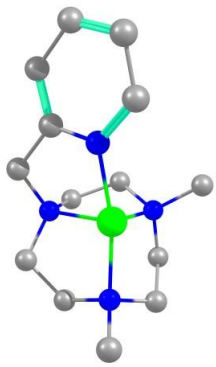
1^{H}-$Co^{II}(CH_3CN)_2$



Co	0.317156000	0.187358000	0.014627000
N	-0.438083000	-1.513621000	1.143486000
N	-1.738153000	0.242926000	-0.490307000
N	0.775587000	-1.426488000	-1.469215000
N	2.225413000	-0.513482000	0.849708000
C	-1.808245000	-1.130959000	1.510405000
H	-1.756788000	-0.420741000	2.337765000
H	-2.390884000	-1.990570000	1.853384000
C	-2.509611000	-0.457284000	0.355595000
C	-3.885448000	-0.521394000	0.193262000
H	-4.480656000	-1.107983000	0.880309000
C	-4.473489000	0.170925000	-0.855744000
H	-5.545534000	0.134170000	-1.000785000
C	-3.669467000	0.903923000	-1.719484000
H	-4.087417000	1.455215000	-2.550250000
C	-2.302738000	0.909534000	-1.502441000
H	-1.632405000	1.456911000	-2.152305000
C	0.483038000	-1.601506000	2.295333000
H	0.295797000	-2.500075000	2.893259000
H	0.295585000	-0.735059000	2.927056000
C	1.937450000	-1.602583000	1.829117000
H	2.584480000	-1.497986000	2.701783000
H	2.188296000	-2.559861000	1.378749000
C	2.964587000	-0.997735000	-0.337021000
H	3.898997000	-1.489056000	-0.041243000
H	3.227020000	-0.119857000	-0.927837000
C	2.135305000	-1.958587000	-1.174020000
H	2.667028000	-2.159065000	-2.106236000
H	2.041960000	-2.917896000	-0.670218000

C	-0.273409000	-2.432355000	-1.198149000
H	-0.059124000	-3.368861000	-1.726631000
H	-1.207886000	-2.044161000	-1.597533000
C	-0.412150000	-2.734607000	0.291706000
H	-1.324162000	-3.314539000	0.447730000
H	0.408672000	-3.365368000	0.623273000
C	2.974910000	0.579094000	1.498824000
H	3.969273000	0.236754000	1.804549000
H	2.432868000	0.918578000	2.378081000
H	3.082777000	1.412385000	0.806569000
C	0.694968000	-0.973218000	-2.868227000
H	0.815756000	-1.815959000	-3.558007000
H	1.480911000	-0.246243000	-3.060325000
H	-0.270171000	-0.504193000	-3.050280000
N	1.083191000	1.690303000	-1.176148000
N	-0.049783000	1.549857000	1.586276000
C	1.482699000	2.554112000	-1.814795000
C	-0.285748000	2.373860000	2.347447000
C	1.991652000	3.636360000	-2.625853000
H	2.090963000	3.301355000	-3.659101000
H	1.301129000	4.479600000	-2.581554000
H	2.966815000	3.946097000	-2.247654000
C	-0.569912000	3.409663000	3.314968000
H	0.353466000	3.930718000	3.571044000
H	-1.281501000	4.119174000	2.890731000
H	-0.996578000	2.961463000	4.213234000

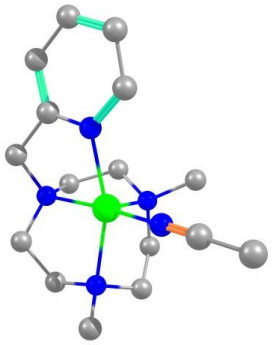
1^{H}-Co^{I}



Co	0.268069000	-0.033500000	0.003789000
N	-0.459131000	-1.665991000	1.162542000
N	-1.594664000	0.327227000	-0.373938000
N	0.735668000	-1.559173000	-1.460026000

N	2.124734000	-0.467076000	0.793848000
C	-1.828740000	-1.245102000	1.473458000
H	-1.786195000	-0.592207000	2.349061000
H	-2.475157000	-2.090388000	1.732943000
C	-2.442630000	-0.454645000	0.340479000
C	-3.800672000	-0.491780000	0.075823000
H	-1.409038000	1.717046000	-1.889889000
C	-4.327847000	0.307132000	-0.932576000
H	-4.437013000	-1.145843000	0.657802000
C	-3.463255000	1.123030000	-1.651105000
H	-5.387202000	0.288118000	-1.152593000
C	-2.114140000	1.103900000	-1.344807000
H	-0.386593000	-0.682934000	-3.004558000
C	0.477905000	-1.642123000	2.297881000
H	0.378963000	-2.524087000	2.944631000
H	0.235098000	-0.763694000	2.896399000
C	1.924321000	-1.547358000	1.813291000
H	2.575377000	-1.374085000	2.672882000
H	2.233917000	-2.496572000	1.382995000
C	2.895882000	-0.956887000	-0.376122000
H	3.860927000	-1.376611000	-0.063655000
H	3.098837000	-0.090305000	-1.006913000
C	2.120540000	-2.004675000	-1.167081000
H	2.659833000	-2.216567000	-2.094159000
H	2.086262000	-2.943337000	-0.617817000
C	-0.275500000	-2.591770000	-1.160996000
H	-0.059611000	-3.529319000	-1.691475000
H	-1.229181000	-2.220695000	-1.536176000
C	-0.385954000	-2.890171000	0.336048000
H	-1.268307000	-3.515636000	0.501229000
H	0.469465000	-3.478399000	0.663235000
C	2.801931000	0.693279000	1.403929000
H	3.801992000	0.424826000	1.766119000
H	2.208991000	1.054482000	2.243156000
H	2.891174000	1.490517000	0.667323000
C	0.611465000	-1.089104000	-2.845036000
H	0.785527000	-1.899786000	-3.564701000
H	1.341363000	-0.300111000	-3.025604000
H	-3.820933000	1.764243000	-2.445447000

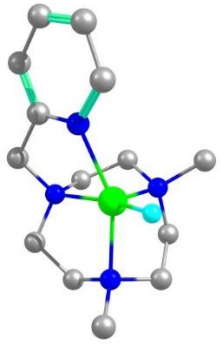
1^{H}-Co^{I} (CH_3CN)



Co	0.176257000	0.057224000	-0.126576000
N	-0.489785000	-1.621534000	1.144689000
N	-1.877326000	0.155568000	-0.424021000
N	0.675204000	-1.581588000	-1.495745000
N	2.139227000	-0.527281000	0.788323000
C	-1.856342000	-1.261863000	1.532328000
H	-1.792697000	-0.515800000	2.328791000
H	-2.414855000	-2.117579000	1.928686000
C	-2.603999000	-0.646223000	0.375768000
C	-3.956261000	-0.867326000	0.164384000
H	1.665516000	4.630285000	-1.491525000
C	-4.590451000	-0.231341000	-0.895849000
H	-4.499601000	-1.533567000	0.822080000
C	-3.842873000	0.607464000	-1.713547000
H	-5.644619000	-0.391481000	-1.082289000
C	-2.494411000	0.771257000	-1.441721000
H	-4.291195000	1.123755000	-2.551938000
C	0.454987000	-1.619528000	2.272642000
H	0.312996000	-2.486446000	2.932384000
H	0.252710000	-0.721897000	2.858541000
C	1.902677000	-1.594234000	1.788092000
H	2.557405000	-1.460134000	2.653703000
H	2.168922000	-2.557723000	1.358422000
C	2.857029000	-1.005527000	-0.405748000
H	3.831356000	-1.443483000	-0.141880000
H	3.048835000	-0.133105000	-1.031701000
C	2.056726000	-2.035285000	-1.195648000
H	2.592948000	-2.253253000	-2.123521000
H	2.014004000	-2.976446000	-0.650374000
C	-0.334950000	-2.602318000	-1.166818000
H	-0.119709000	-3.555986000	-1.669666000
H	-1.289516000	-2.244471000	-1.550610000

C	-0.439056000	-2.862140000	0.336870000
H	-1.328866000	-3.471466000	0.521321000
H	0.407934000	-3.459242000	0.668825000
C	2.831087000	0.614359000	1.393956000
H	3.833996000	0.340572000	1.749875000
H	2.250882000	0.981651000	2.240679000
H	2.922636000	1.416850000	0.663772000
C	0.553019000	-1.164101000	-2.896333000
H	0.718902000	-2.003312000	-3.585736000
H	1.287396000	-0.387937000	-3.107355000
H	-0.441503000	-0.755356000	-3.071012000
N	0.756509000	1.647325000	-1.029626000
C	1.103535000	2.616085000	-1.556122000
C	1.551395000	3.825275000	-2.219757000
H	2.512995000	3.651914000	-2.706207000
H	0.824701000	4.133866000	-2.973484000
H	-1.873212000	1.410342000	-2.056800000

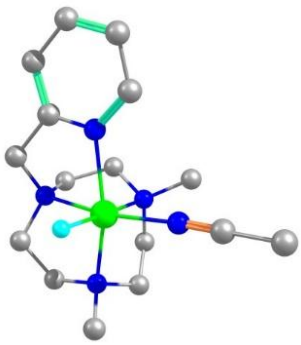
1^{H}-$Co^{II}H$



Co	0.350378000	0.115078000	-0.206422000
N	-0.450258000	-1.559964000	1.094491000
N	-1.739287000	0.340911000	-0.385409000
N	0.786242000	-1.527681000	-1.489742000
N	2.181552000	-0.505403000	0.848883000
C	-1.823897000	-1.195799000	1.468083000
H	-1.774423000	-0.524656000	2.328915000
H	-2.409391000	-2.068199000	1.772076000
C	-2.519255000	-0.454260000	0.359354000
C	-3.887993000	-0.531806000	0.149811000
H	-1.609028000	1.717789000	-1.909491000
C	-4.460183000	0.242738000	-0.849522000
H	-4.489420000	-1.191520000	0.761020000
C	-3.647800000	1.074097000	-1.610646000

H	-5.525790000	0.196266000	-1.034092000
C	-2.289553000	1.092539000	-1.345489000
H	-0.264624000	-0.672372000	-3.103581000
C	0.451571000	-1.583980000	2.264401000
H	0.255563000	-2.449535000	2.908025000
H	0.246535000	-0.683941000	2.845066000
C	1.909672000	-1.584340000	1.833686000
H	2.540985000	-1.457707000	2.715477000
H	2.180814000	-2.544975000	1.402717000
C	2.942624000	-0.988126000	-0.327215000
H	3.895295000	-1.435246000	-0.018542000
H	3.170732000	-0.113948000	-0.938370000
C	2.158582000	-2.004889000	-1.150338000
H	2.714615000	-2.212793000	-2.066332000
H	2.084832000	-2.951493000	-0.620453000
C	-0.253989000	-2.540425000	-1.202601000
H	-0.033774000	-3.482803000	-1.717745000
H	-1.190661000	-2.158510000	-1.607780000
C	-0.395972000	-2.808333000	0.291709000
H	-1.297804000	-3.402762000	0.455516000
H	0.434703000	-3.414867000	0.645253000
C	2.874798000	0.625034000	1.487123000
H	3.862871000	0.325037000	1.854528000
H	2.279720000	0.983502000	2.326457000
H	2.985678000	1.433600000	0.767209000
C	0.714541000	-1.104475000	-2.900512000
H	0.876255000	-1.954445000	-3.572296000
H	1.476498000	-0.350517000	-3.089369000
H	-4.053797000	1.694360000	-2.397634000
H	0.876218000	1.542821000	-0.823898000

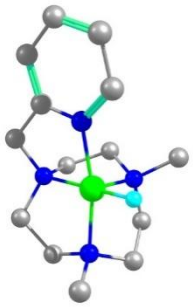
1^{H}-$Co^{II}H$ (CH_3CN)



Co	0.198014000	0.184285000	0.146928000
N	-0.499573000	-1.667171000	1.143543000
N	-1.902209000	0.084054000	-0.437094000
N	0.726505000	-1.443819000	-1.463746000
N	2.129675000	-0.542797000	0.892957000
C	-1.878729000	-1.349345000	1.521986000
H	-1.843146000	-0.636547000	2.348969000
H	-2.424914000	-2.233902000	1.865838000
C	-2.622893000	-0.694799000	0.382514000
C	-3.992105000	-0.852529000	0.217430000
H	1.745595000	4.536933000	-2.017222000
C	-4.630927000	-0.172420000	-0.809677000
H	-4.542700000	-1.501286000	0.885954000
C	-3.880331000	0.641401000	-1.648958000
H	-5.697939000	-0.280731000	-0.956816000
C	-2.516130000	0.735170000	-1.428473000
H	-4.336620000	1.186622000	-2.463793000
C	0.423970000	-1.748907000	2.289370000
H	0.279237000	-2.673030000	2.862527000
H	0.198933000	-0.907242000	2.942146000
C	1.879330000	-1.672855000	1.830715000
H	2.517203000	-1.574844000	2.711782000
H	2.169532000	-2.604684000	1.350988000
C	2.883023000	-0.954995000	-0.309091000
H	3.844716000	-1.407991000	-0.035560000
H	3.096241000	-0.047610000	-0.875679000
C	2.097698000	-1.928638000	-1.173344000
H	2.647413000	-2.088551000	-2.104361000
H	2.042046000	-2.902092000	-0.690397000
C	-0.288022000	-2.486223000	-1.226363000
H	-0.051286000	-3.399582000	-1.788499000
H	-1.234693000	-2.111884000	-1.610398000
C	-0.420482000	-2.848882000	0.250611000
H	-1.307219000	-3.475268000	0.378186000
H	0.425491000	-3.458809000	0.559302000
C	2.831436000	0.555348000	1.577483000
H	3.833419000	0.244092000	1.895381000
H	2.257418000	0.861944000	2.449173000
H	2.921943000	1.407348000	0.904176000
C	0.630730000	-0.954484000	-2.844504000
H	0.771251000	-1.770165000	-3.565079000
H	1.394030000	-0.199197000	-3.018576000

H	-0.347127000	-0.504925000	-3.009686000
N	0.760676000	1.682116000	-1.178111000
C	1.098123000	2.565025000	-1.828034000
C	1.522387000	3.677152000	-2.650261000
H	2.415277000	3.398922000	-3.211389000
H	0.725204000	3.939725000	-3.346967000
H	-1.887183000	1.347488000	-2.062280000
H	-0.193887000	1.210377000	1.481843000

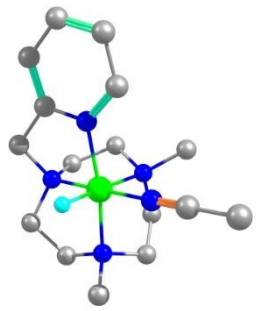
1^{H}-$Co^{III}H$



Co	0.294933000	-0.200688000	-0.050893000
N	-0.426603000	-1.678208000	1.125836000
N	-1.552584000	0.153635000	-0.461556000
N	0.722919000	-1.510675000	-1.388024000
N	2.046941000	-0.487216000	0.752635000
C	-1.824693000	-1.312054000	1.451696000
H	-1.817734000	-0.700685000	2.356560000
H	-2.431330000	-2.193936000	1.662475000
C	-2.424825000	-0.493662000	0.342221000
C	-3.792166000	-0.349029000	0.181631000
H	-1.272877000	1.473599000	-2.024542000
C	-4.269915000	0.490264000	-0.813026000
H	-4.465756000	-0.889981000	0.832079000
C	-3.366510000	1.169491000	-1.621950000
H	-5.335452000	0.612777000	-0.956963000
C	-2.015486000	0.975640000	-1.419642000
H	-0.433116000	-0.634591000	-2.929784000
C	0.485009000	-1.657018000	2.300998000
H	0.355742000	-2.543265000	2.927374000
H	0.221852000	-0.782877000	2.896512000
C	1.919626000	-1.554962000	1.814737000
H	2.583255000	-1.320098000	2.646227000

H	2.256821000	-2.499174000	1.398072000
C	2.909659000	-0.932357000	-0.374535000
H	3.851251000	-1.344220000	-0.004077000
H	3.125722000	-0.057359000	-0.983333000
C	2.147226000	-1.970252000	-1.168230000
H	2.617025000	-2.142886000	-2.134444000
H	2.121745000	-2.923255000	-0.648817000
C	-0.248448000	-2.627235000	-1.151738000
H	0.070102000	-3.506091000	-1.715841000
H	-1.209596000	-2.304886000	-1.544951000
C	-0.336235000	-2.941217000	0.331400000
H	-1.204813000	-3.570547000	0.523243000
H	0.535720000	-3.498467000	0.662288000
C	2.550392000	0.770913000	1.355535000
H	3.530603000	0.598243000	1.805715000
H	1.860023000	1.100724000	2.132130000
H	2.625873000	1.535018000	0.587176000
C	0.574583000	-1.007842000	-2.778940000
H	0.758819000	-1.835494000	-3.466698000
H	1.296005000	-0.215746000	-2.953865000
H	-3.699220000	1.836893000	-2.404100000
H	0.799894000	0.892780000	-0.878271000

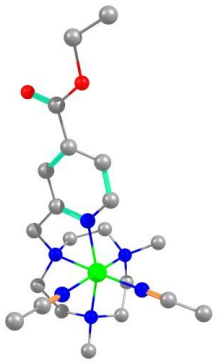
1^{H}-$Co^{III}H$ (CH_3CN)



Co	0.167515000	-0.113576000	0.051136000
N	-0.439931000	-1.625398000	1.114563000
N	-1.710262000	0.061244000	-0.428478000
N	0.637725000	-1.506683000	-1.458533000
N	1.998697000	-0.459951000	0.763032000
C	-1.834625000	-1.313275000	1.521359000
H	-1.791303000	-0.614817000	2.358577000
H	-2.359713000	-2.210237000	1.850542000

C	-2.526223000	-0.643975000	0.378640000
C	-3.893093000	-0.691311000	0.171517000
H	1.370671000	4.382857000	-1.645187000
C	-4.437841000	0.024889000	-0.884369000
H	-4.513099000	-1.281466000	0.832325000
C	-3.593992000	0.762552000	-1.703147000
H	-5.504179000	0.004686000	-1.067059000
C	-2.235178000	0.754655000	-1.446528000
H	-3.974124000	1.335747000	-2.536902000
C	0.481869000	-1.689878000	2.285141000
H	0.337711000	-2.620701000	2.838209000
H	0.237057000	-0.854223000	2.935822000
C	1.901236000	-1.572563000	1.776372000
H	2.584153000	-1.377808000	2.602167000
H	2.226218000	-2.498997000	1.312672000
C	2.800671000	-0.883091000	-0.421839000
H	3.772779000	-1.266801000	-0.100224000
H	2.971723000	0.005354000	-1.026471000
C	2.052877000	-1.931774000	-1.219328000
H	2.559140000	-2.095988000	-2.170955000
H	2.053707000	-2.887915000	-0.702606000
C	-0.318538000	-2.606591000	-1.187817000
H	-0.029939000	-3.516043000	-1.723926000
H	-1.290274000	-2.298537000	-1.567662000
C	-0.383110000	-2.895099000	0.300500000
H	-1.253692000	-3.508891000	0.527295000
H	0.489344000	-3.457631000	0.619188000
C	2.639418000	0.717805000	1.401541000
H	3.657010000	0.457955000	1.702572000
H	2.064084000	1.007602000	2.276539000
H	2.671079000	1.545965000	0.700724000
C	0.484795000	-1.037022000	-2.849945000
H	0.666421000	-1.859956000	-3.546900000
H	1.200395000	-0.242511000	-3.046947000
H	-0.522555000	-0.659193000	-3.006128000
N	0.705345000	1.407917000	-0.934350000
C	1.009054000	2.336366000	-1.530751000
C	1.394896000	3.503009000	-2.289467000
H	2.404274000	3.364250000	-2.679215000
H	0.700447000	3.639896000	-3.119640000
H	-1.548190000	1.309645000	-2.065845000
H	-0.112052000	0.761304000	1.175231000

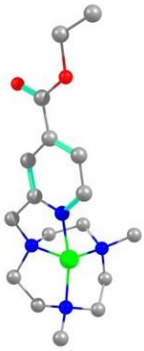
1^{COOEt}-Co^{II} $(CH_3CN)_2$



Co	1.461060000	0.190944000	-0.016374000
N	1.149101000	-1.885098000	0.546323000
N	-0.665438000	0.104360000	0.051567000
N	1.705156000	-0.711748000	-1.995508000
N	3.565539000	-0.364656000	0.195006000
C	-0.122811000	-1.910157000	1.284911000
H	0.062990000	-1.548386000	2.298026000
H	-0.523212000	-2.923568000	1.369204000
C	-1.140366000	-0.997468000	0.650004000
C	-2.500079000	-1.250667000	0.722116000
H	-2.863836000	-2.150817000	1.196915000
C	-3.389697000	-0.334334000	0.175382000
C	-2.888567000	0.811742000	-0.433369000
H	-3.542583000	1.549587000	-0.872173000
C	-1.517030000	0.988487000	-0.474143000
H	-1.082071000	1.860808000	-0.943780000
C	2.318987000	-2.178299000	1.405128000
H	2.371228000	-3.242431000	1.658905000
H	2.188116000	-1.622197000	2.332195000
C	3.622395000	-1.756478000	0.732768000
H	4.429050000	-1.837766000	1.462962000
H	3.874165000	-2.442374000	-0.072267000
C	4.040150000	-0.282264000	-1.207299000
H	5.066362000	-0.658153000	-1.291713000
H	4.052499000	0.773785000	-1.478247000
C	3.145748000	-1.053488000	-2.165849000
H	3.460781000	-0.839051000	-3.188783000
H	3.274205000	-2.124277000	-2.028661000
C	0.854365000	-1.920827000	-1.941779000
H	1.028489000	-2.557300000	-2.816641000

H	-0.181686000	-1.588936000	-1.982589000
C	1.104601000	-2.732374000	-0.676258000
H	0.323450000	-3.488852000	-0.579730000
H	2.044449000	-3.272877000	-0.755976000
C	4.347212000	0.553741000	1.042673000
H	5.412450000	0.302181000	1.007482000
H	4.000322000	0.482352000	2.070866000
H	4.210474000	1.576463000	0.695209000
C	1.250858000	0.175852000	-3.082399000
H	1.282118000	-0.343909000	-4.045748000
H	1.895582000	1.050366000	-3.132153000
H	0.229487000	0.501131000	-2.890156000
N	1.737763000	2.153990000	-0.629132000
N	1.332269000	0.934609000	1.992410000
C	1.878888000	3.243165000	-0.956607000
C	1.177784000	1.385315000	3.034995000
C	2.060363000	4.614050000	-1.374963000
H	1.867495000	4.695017000	-2.445569000
H	1.368479000	5.257541000	-0.830235000
H	3.085586000	4.923405000	-1.166889000
C	0.985561000	1.951055000	4.351942000
H	1.720477000	2.738844000	4.521828000
H	-0.018935000	2.369519000	4.425801000
H	1.109230000	1.171365000	5.104600000
C	-4.856961000	-0.623840000	0.259802000
O	-5.305653000	-1.631033000	0.760835000
O	-5.591659000	0.345608000	-0.273588000
C	-7.037723000	0.174368000	-0.248510000
H	-7.279042000	-0.742026000	-0.787621000
H	-7.346696000	0.059192000	0.790633000
C	-7.649802000	1.393022000	-0.893530000
H	-7.318588000	1.496971000	-1.927980000
H	-7.387728000	2.299564000	-0.345726000
H	-8.736513000	1.291427000	-0.889527000

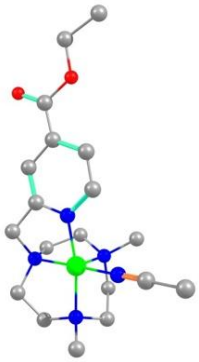
1^{COOEt}-Co^{I}



Co	1.338214000	-0.036440000	-0.055683000
N	1.167407000	-2.059865000	0.553886000
N	-0.555745000	0.040573000	0.113464000
N	1.602235000	-0.854086000	-2.024670000
N	3.378690000	-0.278576000	0.153611000
C	-0.118977000	-2.065970000	1.263000000
H	0.067531000	-1.743589000	2.290380000
H	-0.560474000	-3.066031000	1.311414000
C	-1.097468000	-1.095466000	0.644387000
C	-2.454173000	-1.317843000	0.660968000
H	-2.841487000	-2.240365000	1.070965000
C	-3.331784000	-0.351911000	0.155107000
C	-2.776813000	0.823354000	-0.361615000
H	-3.401957000	1.606449000	-0.764134000
C	-1.409229000	0.978634000	-0.365247000
H	-0.953149000	1.872037000	-0.769637000
C	2.356557000	-2.209288000	1.411753000
H	2.545421000	-3.254335000	1.687368000
H	2.161603000	-1.654555000	2.330026000
C	3.602286000	-1.645615000	0.728585000
H	4.418160000	-1.613654000	1.453137000
H	3.927352000	-2.311143000	-0.067270000
C	3.872741000	-0.182284000	-1.244616000
H	4.932552000	-0.458235000	-1.303605000
H	3.784103000	0.864020000	-1.540104000
C	3.064726000	-1.060626000	-2.193333000
H	3.364607000	-0.838431000	-3.220211000
H	3.298693000	-2.110519000	-2.030862000
C	0.851403000	-2.124653000	-1.933023000
H	1.047881000	-2.764129000	-2.802972000
H	-0.208008000	-1.869714000	-1.948802000

C	1.181781000	-2.907001000	-0.660266000
H	0.465004000	-3.726771000	-0.560325000
H	2.163700000	-3.367751000	-0.747758000
C	4.022632000	0.748492000	0.997362000
H	5.108891000	0.607603000	1.029043000
H	3.628285000	0.682234000	2.010576000
H	3.802717000	1.737244000	0.597123000
C	1.060117000	0.001231000	-3.090098000
H	1.148518000	-0.478113000	-4.072717000
H	1.606223000	0.943955000	-3.109684000
H	0.009854000	0.209763000	-2.891248000
C	-4.784129000	-0.611412000	0.187405000
O	-5.283785000	-1.633292000	0.622101000
O	-5.500815000	0.403018000	-0.314799000
C	-6.942787000	0.249073000	-0.326995000
H	-7.190941000	-0.633845000	-0.917488000
H	-7.281211000	0.084629000	0.696786000
C	-7.529706000	1.507419000	-0.919811000
H	-7.176032000	1.661245000	-1.940718000
H	-7.267172000	2.381418000	-0.321318000
H	-8.617617000	1.421381000	-0.942756000

1^{COOEt}-Co^{I} (CH_3CN)

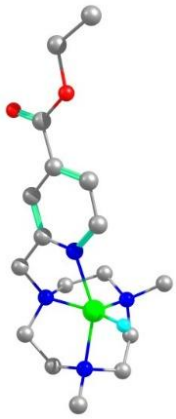


Co	-1.548821000	0.098164000	-0.387443000
N	-1.332259000	-1.866263000	-0.400774000
N	0.372882000	0.129648000	-0.605438000
N	-1.649580000	-0.071304000	1.786903000
N	-3.545094000	-0.242774000	-0.321494000
C	-0.100742000	-2.132430000	-1.196895000
H	-0.367522000	-2.003591000	-2.248656000
H	0.248035000	-3.156902000	-1.056571000

C	0.924003000	-1.117173000	-0.808417000
C	2.254533000	-1.375994000	-0.687924000
H	3.208818000	1.811872000	0.066250000
C	3.167622000	-0.329232000	-0.362669000
C	2.588064000	0.960982000	-0.173801000
H	0.800256000	2.113525000	-0.137714000
C	1.240612000	1.139346000	-0.292498000
H	8.420192000	1.555778000	0.643014000
C	-2.555621000	-2.384115000	-1.066012000
H	-2.620663000	-3.473415000	-0.990720000
H	-2.483768000	-2.120564000	-2.121141000
C	-3.768796000	-1.725119000	-0.443758000
H	-4.654070000	-1.919451000	-1.049504000
H	-3.971486000	-2.134454000	0.541702000
C	-3.980992000	0.260912000	1.010592000
H	-5.021523000	-0.021167000	1.200255000
H	-3.929344000	1.348133000	0.971847000
C	-3.082898000	-0.266394000	2.120493000
H	-3.332054000	0.247179000	3.051740000
H	-3.271128000	-1.323085000	2.298612000
C	-0.835394000	-1.281308000	2.000034000
H	-0.955862000	-1.674168000	3.017061000
H	0.207236000	-0.992897000	1.880662000
C	-1.196724000	-2.377879000	1.004738000
H	-0.436045000	-3.158248000	1.034796000
H	-2.135555000	-2.847599000	1.285014000
C	-4.292385000	0.450422000	-1.396351000
H	-5.361301000	0.236590000	-1.311000000
H	-3.935429000	0.102923000	-2.364945000
H	-4.136071000	1.522335000	-1.322070000
C	-1.087975000	1.078228000	2.508058000
H	-1.080048000	0.900511000	3.589899000
H	-1.687247000	1.963636000	2.302452000
H	-0.069327000	1.259321000	2.170608000
N	-1.734366000	1.981091000	-0.570783000
C	-1.833453000	3.115236000	-0.703932000
C	-1.965342000	4.544954000	-0.868565000
H	-1.732146000	5.043967000	0.073037000
H	-1.276897000	4.889738000	-1.641173000
H	-2.988474000	4.784651000	-1.161540000
C	4.566806000	-0.606041000	-0.238460000
O	5.099103000	-1.712951000	-0.388950000
O	5.309351000	0.501934000	0.073591000

C	6.727925000	0.315161000	0.213132000
H	6.919694000	-0.406709000	1.010169000
H	7.130706000	-0.095923000	-0.715069000
C	7.339318000	1.661488000	0.530415000
H	6.935975000	2.065299000	1.461173000
H	7.146673000	2.376826000	-0.271543000
H	2.619288000	-2.380888000	-0.850411000

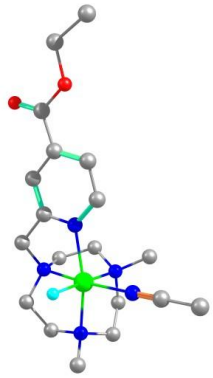
1^{COOEt}-$Co^{II}H$



Co	1.401579000	0.216665000	-0.215603000
N	1.131006000	-1.908848000	0.519395000
N	-0.681850000	0.089855000	0.100544000
N	1.680721000	-0.805432000	-2.065311000
N	3.490599000	-0.350311000	0.166193000
C	-0.140039000	-1.956207000	1.254414000
H	0.043163000	-1.613270000	2.275408000
H	-0.536291000	-2.973017000	1.321993000
C	-1.162111000	-1.033824000	0.648541000
C	-2.522152000	-1.290106000	0.699376000
H	-2.890852000	-2.207344000	1.136286000
C	-3.406453000	-0.352980000	0.179303000
C	-2.899736000	0.817488000	-0.377750000
H	-3.550715000	1.571836000	-0.792350000
C	-1.528285000	0.996827000	-0.395989000
H	-1.080976000	1.886472000	-0.820164000
C	2.290682000	-2.134653000	1.407403000
H	2.357315000	-3.181103000	1.727200000
H	2.135156000	-1.524331000	2.297771000
C	3.589770000	-1.719183000	0.735550000
H	4.396115000	-1.763366000	1.470329000

H	3.859434000	-2.421357000	-0.049401000
C	3.984754000	-0.275543000	-1.229177000
H	5.027443000	-0.609186000	-1.291647000
H	3.955529000	0.775188000	-1.520403000
C	3.138002000	-1.101776000	-2.191049000
H	3.470350000	-0.898633000	-3.210651000
H	3.298350000	-2.164440000	-2.025719000
C	0.860983000	-2.033953000	-1.967016000
H	1.048255000	-2.696962000	-2.819626000
H	-0.182906000	-1.725370000	-2.016529000
C	1.126785000	-2.794845000	-0.672902000
H	0.368800000	-3.573931000	-0.563390000
H	2.083626000	-3.308502000	-0.729487000
C	4.194141000	0.623704000	1.016336000
H	5.268740000	0.411433000	1.050714000
H	3.791786000	0.576374000	2.027767000
H	4.035837000	1.626355000	0.624122000
C	1.217983000	0.033247000	-3.186322000
H	1.306257000	-0.501964000	-4.137990000
H	1.818658000	0.939847000	-3.229209000
H	0.175831000	0.309305000	-3.029762000
C	-4.873882000	-0.644643000	0.236617000
O	-5.329491000	-1.666450000	0.701266000
O	-5.602991000	0.340251000	-0.276238000
C	-7.048927000	0.168075000	-0.273369000
H	-7.283244000	-0.733882000	-0.839235000
H	-7.370457000	0.025866000	0.758616000
C	-7.653099000	1.403248000	-0.893870000
H	-7.309213000	1.533739000	-1.921154000
H	-7.397410000	2.295137000	-0.319652000
H	-8.739828000	1.302379000	-0.905801000
H	1.586282000	1.841597000	-0.358640000

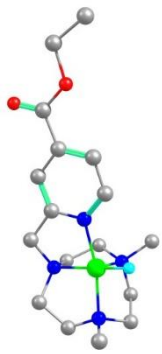
1^{COOEt}-$Co^{II}H$ (CH_3CN)



Co	-1.555253000	0.237579000	-0.545578000
N	-1.249765000	-1.912610000	-0.292925000
N	0.588362000	0.122891000	-0.391950000
N	-1.856347000	0.025490000	1.724417000
N	-3.694530000	-0.367861000	-0.478891000
C	0.028254000	-2.163360000	-0.968123000
H	-0.144249000	-2.095011000	-2.044907000
H	0.416816000	-3.163716000	-0.754426000
C	1.051876000	-1.117246000	-0.608253000
C	2.406270000	-1.403381000	-0.560681000
H	3.482781000	1.733466000	0.123060000
C	3.308232000	-0.378172000	-0.301137000
C	2.820486000	0.907267000	-0.086214000
H	1.027408000	2.089711000	0.030873000
C	1.451896000	1.108211000	-0.137078000
H	8.676776000	1.418676000	0.258004000
C	-2.409941000	-2.462424000	-1.023791000
H	-2.463808000	-3.553585000	-0.931800000
H	-2.267197000	-2.219127000	-2.075846000
C	-3.725238000	-1.856202000	-0.534891000
H	-4.523000000	-2.187329000	-1.203205000
H	-3.976085000	-2.247560000	0.448238000
C	-4.180441000	0.160955000	0.811542000
H	-5.207826000	-0.170399000	1.011126000
H	-4.197064000	1.247859000	0.724039000
C	-3.293162000	-0.251240000	1.977159000
H	-3.626693000	0.277522000	2.873419000
H	-3.420514000	-1.310320000	2.190530000
C	-1.001695000	-1.124416000	2.073389000
H	-1.183012000	-1.451269000	3.105346000
H	0.032123000	-0.787365000	2.020354000

C	-1.220402000	-2.308366000	1.136845000
H	-0.429921000	-3.043182000	1.307908000
H	-2.155214000	-2.809502000	1.377549000
C	-4.460627000	0.214946000	-1.589077000
H	-5.525524000	-0.035304000	-1.509812000
H	-4.073733000	-0.164181000	-2.532768000
H	-4.347665000	1.298219000	-1.579109000
C	-1.421837000	1.218707000	2.466167000
H	-1.455944000	1.043410000	3.548223000
H	-2.073965000	2.055607000	2.226849000
H	-0.402479000	1.479755000	2.185207000
N	-1.845459000	2.313979000	-0.454110000
C	-1.967183000	3.454574000	-0.452811000
C	-2.121012000	4.892985000	-0.452493000
H	-2.004719000	5.272135000	0.563616000
H	-1.365057000	5.343516000	-1.096741000
H	-3.113507000	5.153057000	-0.822871000
C	4.767491000	-0.701927000	-0.259563000
O	5.204656000	-1.823904000	-0.396870000
O	5.518752000	0.376951000	-0.060146000
C	6.959796000	0.181732000	-0.006417000
H	7.178214000	-0.512492000	0.805443000
H	7.276110000	-0.271280000	-0.946383000
C	7.592227000	1.533576000	0.214784000
H	7.255760000	1.974264000	1.154571000
H	7.351662000	2.216320000	-0.601703000
H	2.758022000	-2.412253000	-0.724269000
H	-1.421223000	0.245771000	-2.289153000

1^{COOEt}-$Co^{III}H$

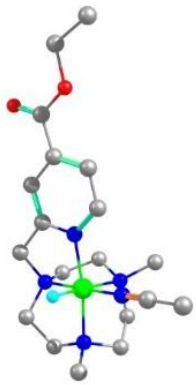


Co	1.349758000	-0.169117000	-0.202408000

N	1.189041000	-2.065506000	0.481322000
N	-0.576800000	-0.158339000	-0.142496000
N	1.657561000	-0.858625000	-1.967546000
N	3.261463000	-0.259114000	0.140270000
C	-0.130776000	-2.165924000	1.145293000
H	-0.010650000	-1.882333000	2.193020000
H	-0.515660000	-3.186377000	1.128104000
C	-1.106370000	-1.209693000	0.518783000
C	-2.474532000	-1.350706000	0.661242000
H	-2.881461000	-2.206884000	1.180024000
C	-3.314868000	-0.381667000	0.132162000
C	-2.759608000	0.711105000	-0.527143000
H	-3.376929000	1.489766000	-0.947599000
C	-1.387464000	0.785870000	-0.647170000
H	-0.909878000	1.608704000	-1.156734000
C	2.339196000	-2.187913000	1.416917000
H	2.516249000	-3.227509000	1.704046000
H	2.083719000	-1.628731000	2.317053000
C	3.575510000	-1.600850000	0.760456000
H	4.372807000	-1.484032000	1.493665000
H	3.953331000	-2.258981000	-0.015901000
C	3.892117000	-0.109918000	-1.199173000
H	4.951459000	-0.373270000	-1.160388000
H	3.800907000	0.935289000	-1.486053000
C	3.150685000	-1.004210000	-2.168628000
H	3.396106000	-0.748721000	-3.197604000
H	3.415061000	-2.047636000	-2.025999000
C	0.974828000	-2.193382000	-1.979645000
H	1.292787000	-2.752170000	-2.861986000
H	-0.092893000	-2.007522000	-2.067089000
C	1.301049000	-2.960526000	-0.710619000
H	0.626777000	-3.810688000	-0.610244000
H	2.310504000	-3.359534000	-0.748592000
C	3.666949000	0.833084000	1.058160000
H	4.739759000	0.771058000	1.253634000
H	3.130536000	0.728535000	2.001545000
H	3.427085000	1.791401000	0.606757000
C	1.095788000	0.000955000	-3.043011000
H	1.238981000	-0.504529000	-4.000073000
H	1.614769000	0.954230000	-3.048701000
H	0.035110000	0.156107000	-2.875775000
C	-4.796230000	-0.556940000	0.293436000
O	-5.287708000	-1.512220000	0.851034000

O	-5.478443000	0.446175000	-0.241024000
C	-6.932093000	0.386495000	-0.146794000
H	-7.263430000	-0.527390000	-0.640489000
H	-7.199130000	0.330482000	0.908750000
C	-7.480413000	1.625410000	-0.809697000
H	-7.190362000	1.668728000	-1.860780000
H	-7.127311000	2.527525000	-0.307434000
H	-8.570308000	1.606059000	-0.754520000
H	1.446447000	1.213459000	-0.664617000

1^{COOEt}-$Co^{III}H$ (CH_3CN)



Co	-1.515483000	0.040490000	-0.323206000
N	-1.340530000	-1.898016000	-0.301125000
N	0.427461000	0.034317000	-0.283792000
N	-1.782043000	-0.070009000	1.760083000
N	-3.486356000	-0.225243000	-0.462882000
C	-0.050734000	-2.206499000	-0.970110000
H	-0.207830000	-2.147197000	-2.048321000
H	0.288812000	-3.214285000	-0.729994000
C	0.952036000	-1.169554000	-0.583108000
C	2.315576000	-1.389059000	-0.580066000
H	3.244127000	1.760427000	0.238958000
C	3.168421000	-0.332722000	-0.288020000
C	2.621089000	0.911098000	0.004752000
H	0.788453000	2.001710000	0.234466000
C	1.246315000	1.053264000	0.002261000
H	8.451758000	1.723747000	0.174693000
C	-2.507123000	-2.414806000	-1.073446000
H	-2.600117000	-3.496688000	-0.955433000
H	-2.326554000	-2.191055000	-2.122030000
C	-3.750538000	-1.704556000	-0.586523000
H	-4.575985000	-1.873076000	-1.276733000

H	-4.067817000	-2.086441000	0.379054000
C	-4.041414000	0.311511000	0.814506000
H	-5.097195000	0.042962000	0.907240000
H	-3.973478000	1.396373000	0.763751000
C	-3.253288000	-0.217154000	1.995329000
H	-3.541783000	0.321816000	2.898147000
H	-3.480691000	-1.264567000	2.176375000
C	-1.043735000	-1.306281000	2.114743000
H	-1.302114000	-1.640714000	3.124150000
H	0.017648000	-1.067708000	2.111729000
C	-1.353358000	-2.408989000	1.119497000
H	-0.631625000	-3.218551000	1.219384000
H	-2.332767000	-2.835833000	1.312165000
C	-4.117558000	0.474324000	-1.611132000
H	-5.200119000	0.334356000	-1.569246000
H	-3.732654000	0.059935000	-2.538923000
H	-3.889453000	1.534390000	-1.567809000
C	-1.260309000	1.070798000	2.539362000
H	-1.360095000	0.872869000	3.610243000
H	-1.821056000	1.968468000	2.291259000
H	-0.210110000	1.229805000	2.307153000
N	-1.649223000	1.923596000	-0.425875000
C	-1.723316000	3.062921000	-0.504676000
C	-1.823530000	4.500173000	-0.599706000
H	-1.703262000	4.939778000	0.391311000
H	-1.043801000	4.876452000	-1.263178000
H	-2.802315000	4.767727000	-1.000581000
C	4.645771000	-0.581416000	-0.300796000
O	5.128433000	-1.673943000	-0.499504000
O	5.342454000	0.525401000	-0.076166000
C	6.794485000	0.406764000	-0.072958000
H	7.073599000	-0.296884000	0.711672000
H	7.101819000	-0.003574000	-1.035022000
C	7.361979000	1.783587000	0.166890000
H	7.033162000	2.181562000	1.128164000
H	7.061898000	2.473826000	-0.623114000
H	2.709671000	-2.368782000	-0.808664000
H	-1.402935000	0.013301000	-1.770531000

References:

1. L. X. Chen and X. Zhang, *J. Phys. Chem. Lett.*, 2013, **4**, 4000-4013.
2. B. Ravel and M. Newville, *J. Synchrotron. Radiat.*, 2005, **12**, 537-541.
3. J. J. Rehr, R. C. Albers and S. I. Zabinsky, *Phys. Rev. Lett.*, 1992, **69**, 3397-3400.
4. D. C. Koningsberger and R. Prins, *X Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, John Wiley & Sons, New York, 1988.
5. F. Neese, *WIREs Comput. Mol. Sci.*, 2025, **15**, e70019.
6. A. D. Becke, *J.Chem.Phys.*, 1993, **98**, 5648-5652.
7. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J.Phys.Chem.* 1994, **98**, 11623-11627.
8. E. van Lenthe, E. J. Baerends and J. G. Snijders, *J.Phys.Chem*, 1994, **101**, 9783-9792.
9. J. D. Rolfes, F. Neese and D. A. Pantazis, *J.Comput.Chem.*, 2020, **41**, 1842-1849.
10. E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth and S. Grimme, *J.Chem.Phys.* 2019, **150**.
11. S. Kossmann and F. Neese, *J.Chem.Theory.Comput*, 2010, **6**, 2325-2338.
12. V. Barone and M. Cossi, *J.Phys.Chem.A.*, 1998, **102**, 1995-2001.
13. S. Bernadotte, A. J. Atkins and C. R. Jacob, *J.Chem.Phys*, 2012, **137**.
14. F. Weigend and R. Ahlrichs, *Phys.Chem.Chem.Phys*, 2005, **7**, 3297-3305.