

Supporting Information

Combining gas phase electron capture and IRMPD action spectroscopy to probe the electronic structure of a metastable reduced organometallic complex containing a non-innocent ligand

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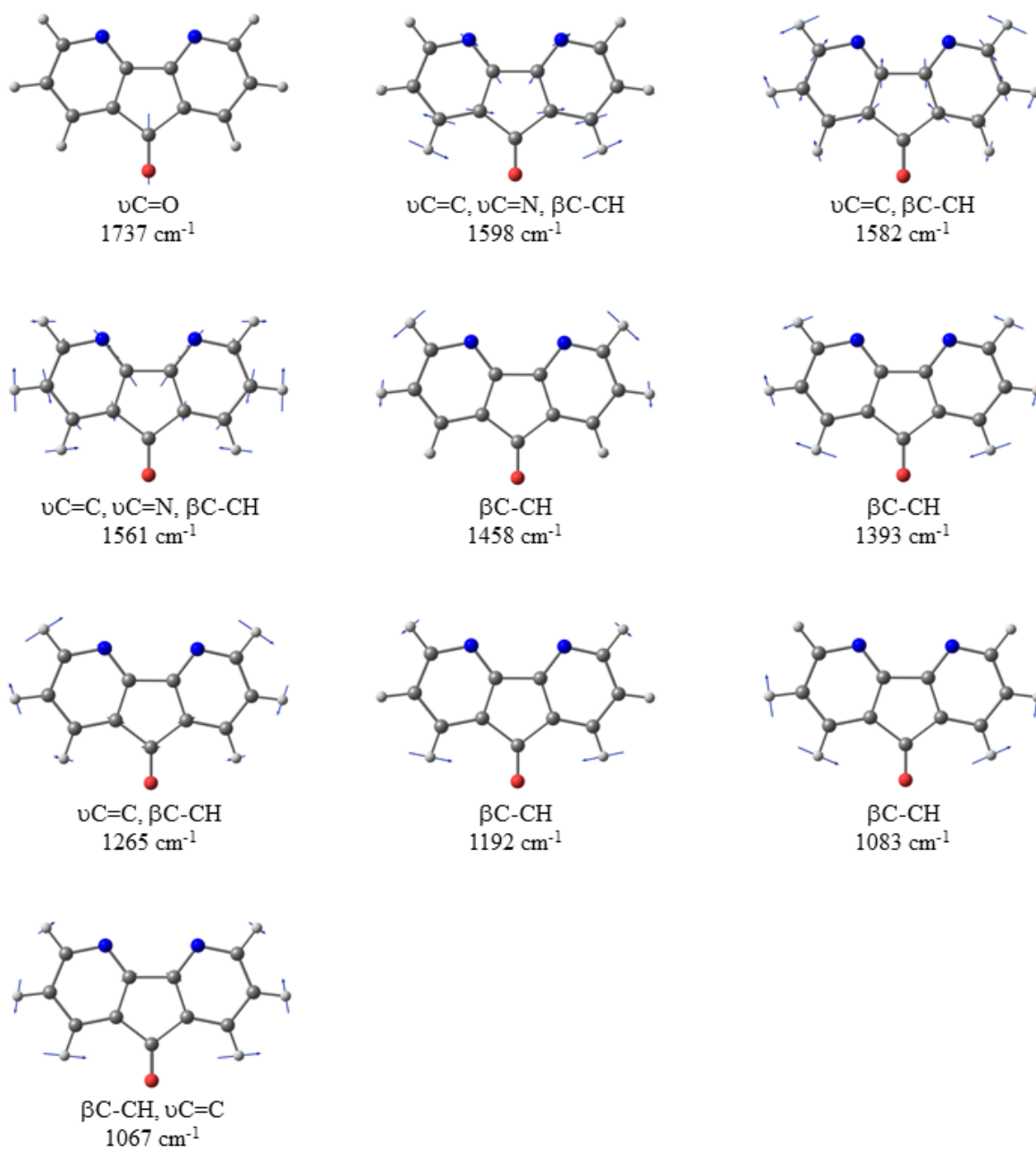


Figure S1. B3LYP/6-31+G(d,p) (scaling factor 0.97) calculated most intense vibrational frequencies of dafoo and associated vibrational modes (β = bending)

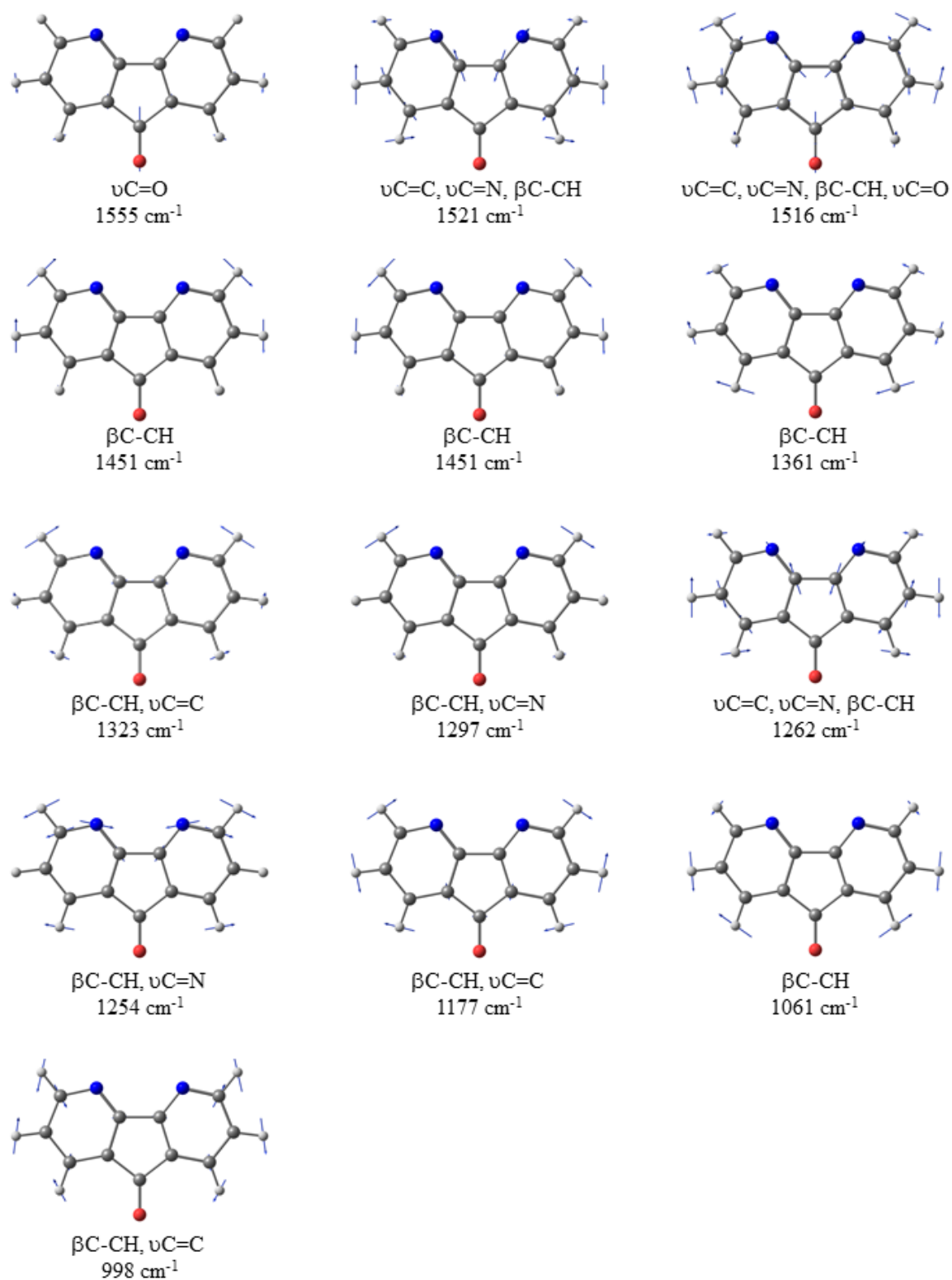


Figure S2. B3LYP/6-31+G(d,p) (scaling factor 0.97) calculated most intense vibrational frequencies of (dafo)⁻ and associated vibrational modes (β = bending)

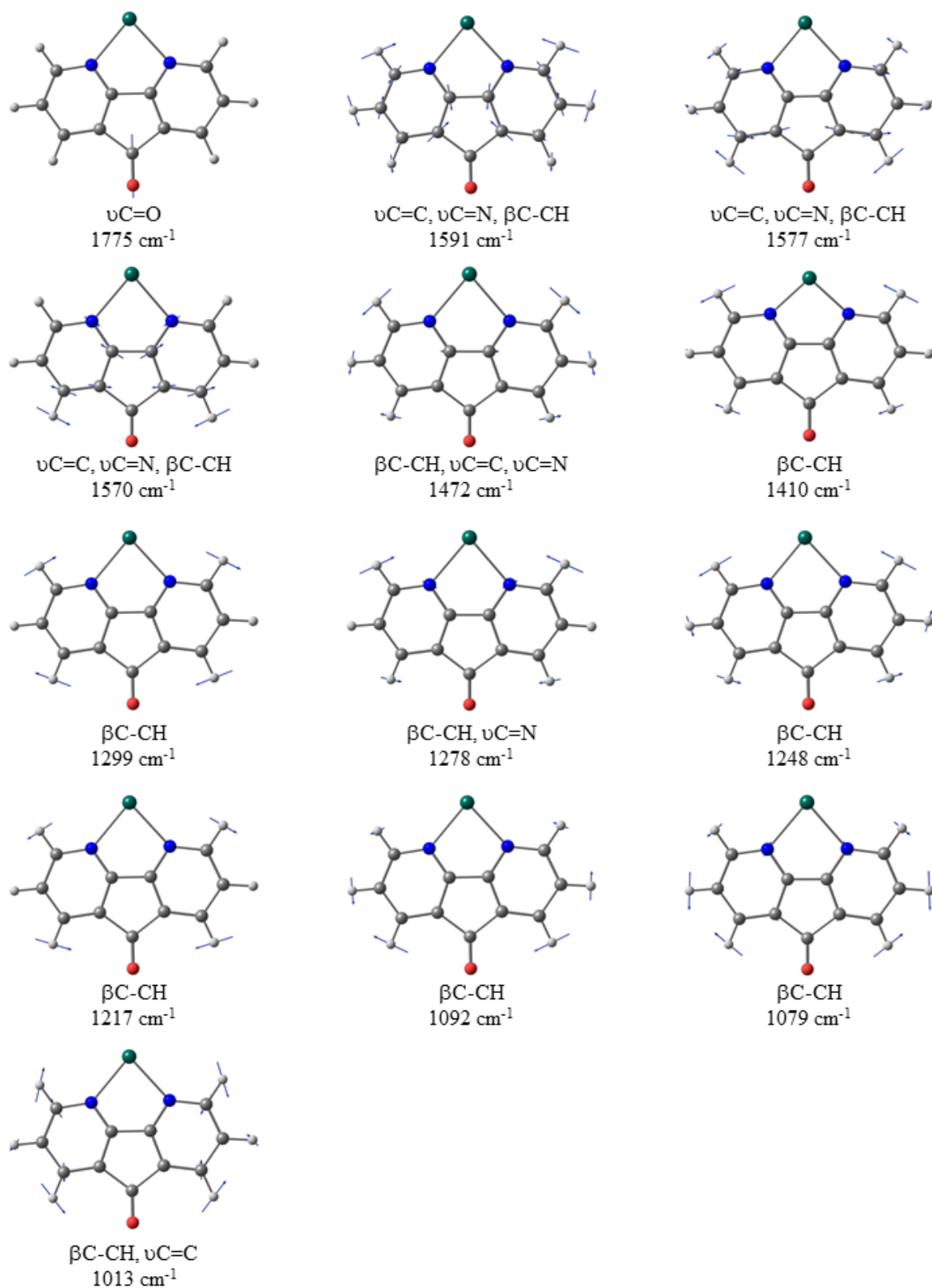


Figure S3. B3LYP/6-31+G(d,p) (scaling factor 0.97) calculated most intense vibrational frequencies of $[\text{Zn}(\text{dafa})]^{2+}$ and associated vibrational modes (β = bending)

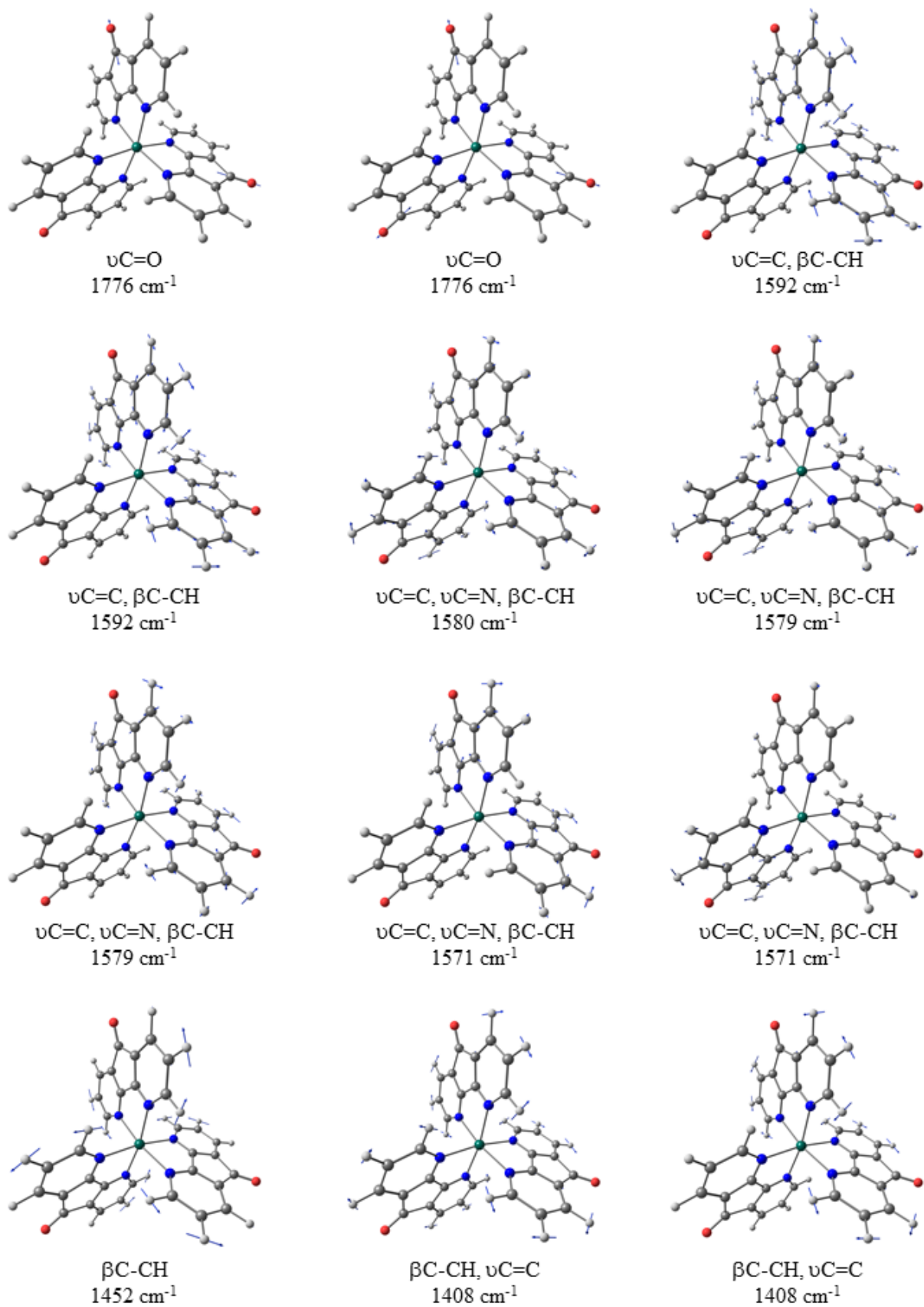


Figure S4. B3LYP/6-31+G(d,p) (scaling factor 0.97) calculated most intense vibrational frequencies of $[\text{Zn}(\text{dafa})_3]^{2+}$ and associated vibrational modes (β = bending) (*continued*)

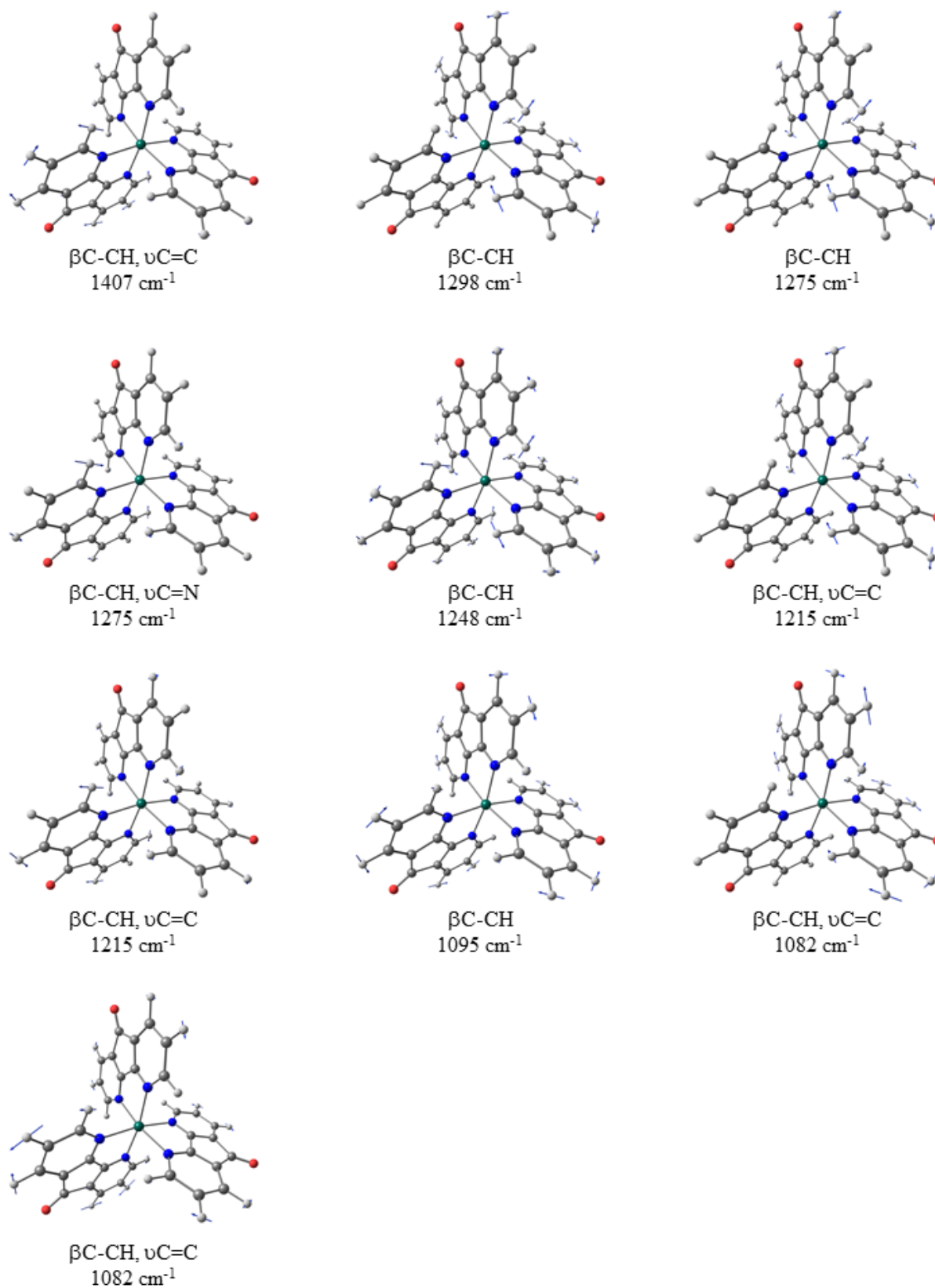


Figure S4. (continued) B3LYP/6-31+G(d,p) (scaling factor 0.97) calculated most intense vibrational frequencies of $[\text{Zn}(\text{dafo})_3]^{2+}$ and associated vibrational modes (β = bending)

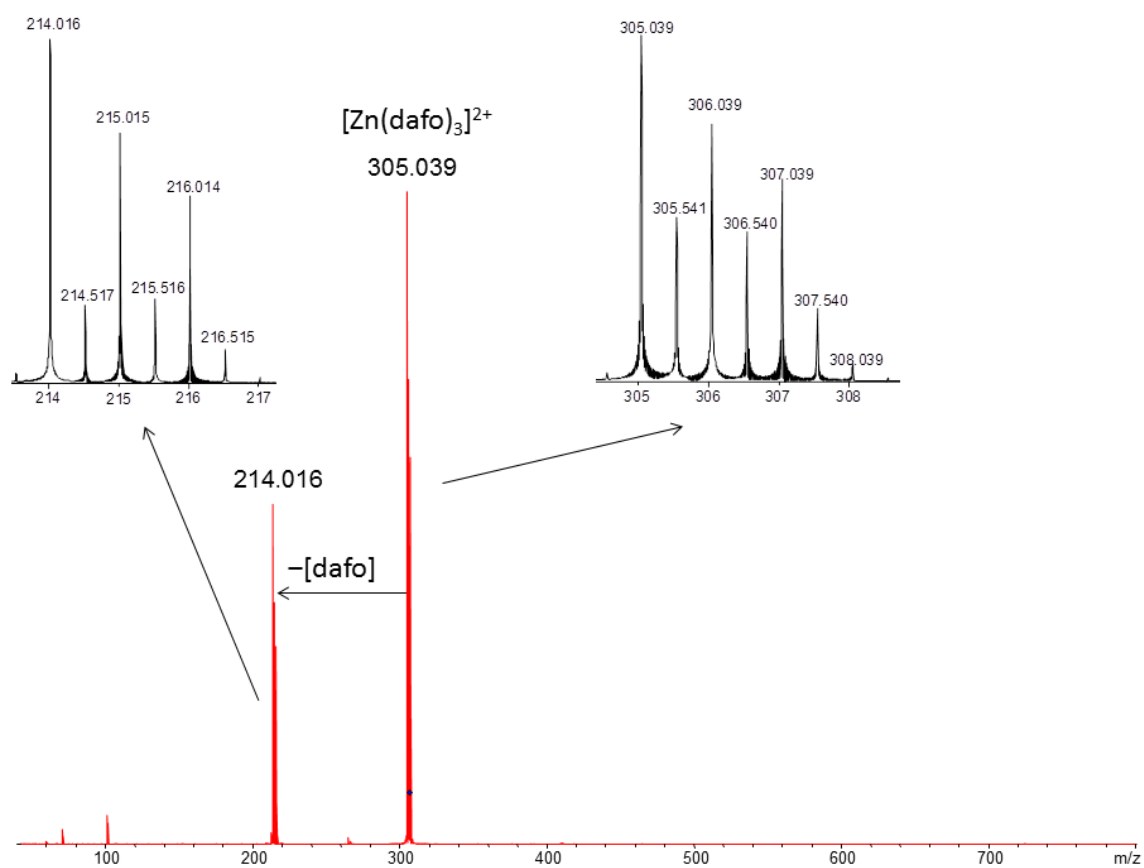


Figure S5. IRMPD mass spectrum (Ion intensity in arbitrary units) obtained after mass selection of $[\text{Zn}(\text{dafo})_3]^{2+}$ (m/z 305) in a 7T Fourier transform ion cyclotron resonance (FT-ICR) tandem mass spectrometer (Bruker Apex Qe) followed by irradiation with tunable free electron laser IR radiation on resonance at 1408 cm^{-1} .

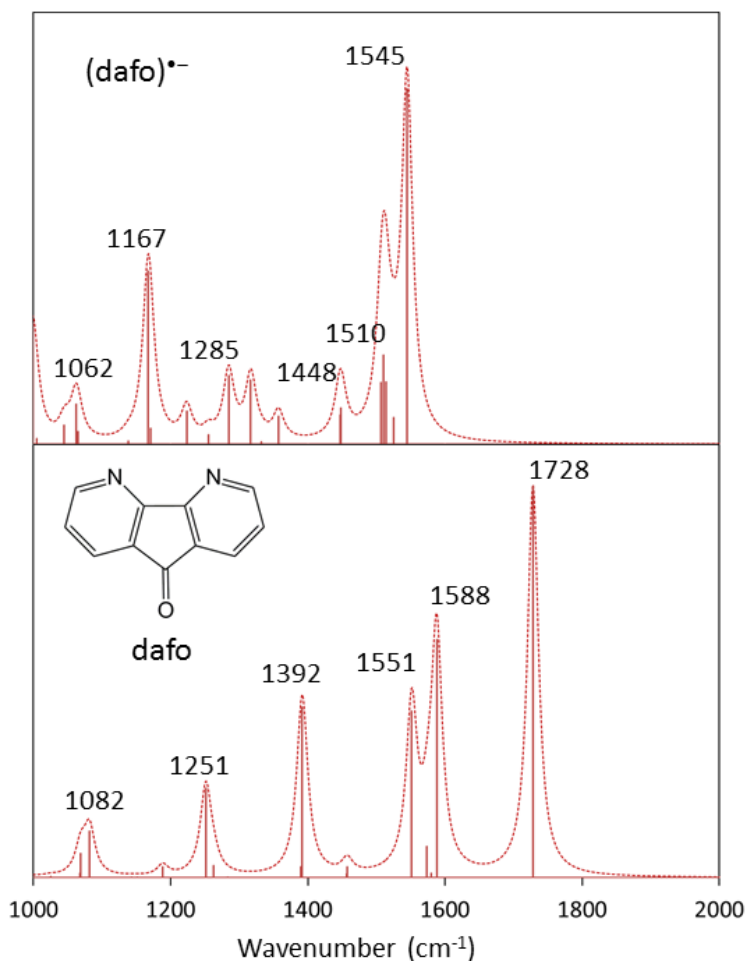


Figure S6. B3LYP/aug-cc-pVTZ calculated IR spectra (scaling factor 0.97) of 4,5-diazafluoren-9-one (bottom) and its reduced form (top).

Methods

Experimental methods

The solution was prepared in a 1:2 water/acetonitrile solution by mixing 4,5-diazafluorenone-9 and zinc(II) tetrafluoroborate. Dicationic complex $[\text{Zn}(\text{dafo})_3]^{2+}$ was formed in an electrospray source in positive mode and observed by high resolution mass spectrometry with a 7T Fourier Transform Ion Cyclotron Resonance (FT-ICR) tandem mass spectrometer (Bruker Apex Qe). The $[\text{Zn}(\text{dafo})_3]^{2+}$ ion was isolated in the quadrupole with an isolation window of m/z 5 and accumulated in the collision cell for 2 seconds. The radical cation $[\text{Zn}(\text{dafo})]^{•+}$ was obtained by Electron Capture Dissociation (ECD) experiments performed on the mass-selected $[\text{Zn}(\text{dafo})_3]^{2+}$ ion with an indirectly heated cathode at 1.6 A. The ECD pulse length was set at 0.1 second, the ECD Bias at 6 V and the ECD Lens at 10 V. The radical cation $[\text{Zn}(\text{dafo})]^{•+}$ was mass-selected in the ICR Cell. The ion of interest is then irradiated for either 0.45 ($[\text{Zn}(\text{dafo})_3]^{2+}$) or 2 seconds ($[\text{Zn}(\text{dafo})]^{•+}$) with an IR laser. Vibrational spectra were obtained in the 1000-2000 cm⁻¹ region by IRMPD using the FT-ICR spectrometer coupled to a tunable free electron laser at the Centre Laser Infrarouge d'Orsay (CLIO).^[1] In IRMPD action spectroscopy, when the laser wavelength becomes resonant with a vibrational transition of the mass-selected species, a sequential absorption of multiple photons that is coupled to fast intramolecular vibrational redistribution can deposit internal energy within the species up to threshold energy for

fragmentation. The intensity of parent and fragment ions after laser irradiation are monitored as a function of the excitation wavelength, with the photofragmentation yield being calculated for each wavelength according to $-\ln[I_{parent}/(I_{parent} + \sum I_{fragments})]$. At each wavelength step, 4 mass spectra were averaged.

Computational Method

Calculations were carried out with the Gaussian09 package^[2] and all structures were fully optimized without any symmetry constraints at the DFT level by means of the B3LYP functional.^[3] The 6-31+G(d,p) basis set was applied for all atoms. For each stationary point, we carried out a vibrational frequency calculation at the same level to characterise their nature as minima. To get accurate geometries and energies, the SCF convergence criterion was systematically tightened to 10^{-8} au, and the force minimizations were carried out until the rms force became smaller than (at least) 1×10^{-5} au ("tight" optimization keyword in Gaussian 09). The "UltraFine" grid (99 radial shells and 590 angular points per shell) was used throughout the calculations, as recommended when using Gaussian 09. It should be noted that almost identical results (in terms of geometries, relative energies and IR frequencies and intensities) have been obtained using the default "FineGrid" (75 radial shells and 302 angular points per shell). Lorentzian line shapes, with a full width at half maximum (FWHM) of 10 cm^{-1} , was used to generate the calculated IR spectra. A scaling factor of $0.97^{[4]}$ was applied to the calculated IR frequencies.

The B3LYP/6-31+G(d,p) level of calculation was shown previously to provide reliable structure and IR spectra.^[4] However, it is known that DFT calculations are not always suitable for calculations of negative ions due to the fact that they overestimate the negative ion stability. Furthermore, augmented basis set with diffuse functions are usually required to better describe a negative ion.^[5] In order to evaluate the accuracy of our level of calculation for neutral and reduced 4,5-diazafluoren-9-one (dafo) containing molecules, we have computed the optimized geometries and IR spectra of (dafo)⁰ and (dafo)^{*-} at the B3LYP/aug-cc-pVTZ (Figure S6). Comparison between Figures 1 and S6 confirms the reliability of the B3LYP/6-31+G(d,p) level of calculation to evaluate the vibrational modes of negative ions. The value of the adiabatic electron affinity of dafo is 146 kJ.mol^{-1} at the B3LYP/aug-cc-pVTZ level (149 kJ.mol^{-1} at the B3LYP/6-31+G(d,p) level). A lower value of 99 kJ.mol^{-1} has been obtained at the MP2/6-311++G(2d,2p)//B3LYP/6-31+G(d,p) level, in which the spin-contamination observed for the open-shell (dafo)^{*-} specie was treated by Schlegel's spin annihilation protocol^[6] to give the spin-projected MP2 (PMP2) energy. This justifies the high ability of dafo to accept an electron to form a radical anion.

The vertical electron affinity of $[\text{Zn}(\text{dafo})_3]^{2+}$ has been computed as the difference between the energy of $[\text{Zn}(\text{dafo})_3]^{2+}$ in its optimized geometry and the energy of $[\text{Zn}(\text{dafo})_3]^{*+}$ in the optimized geometry of the dication.

Cartesian coordinates and energies of the optimized geometries

dafo

$E(\text{B3LYP}/6-31+\text{G}(\text{d},\text{p})) = -607.524174 \text{ u.a.}$

N -0.000011 -1.716236 1.548405
C -0.000001 -1.441559 2.867724
C -0.000015 -0.656931 0.746370
C 0.000007 -0.150397 3.410053
H 0.000002 -2.306331 3.527567

C -0.000009 0.682213 1.188610
C 0.000004 0.954874 2.548632
H 0.000015 -0.020047 4.487500
N -0.000011 -1.716236 -1.548405
C -0.000001 -1.441559 -2.867724
C -0.000015 -0.656931 -0.746370
C 0.000007 -0.150397 -3.410053
H 0.000002 -2.306331 -3.527567
C -0.000009 0.682213 -1.188610
C 0.000004 0.954874 -2.548632
H 0.000015 -0.020047 -4.487500
H 0.000008 1.975959 -2.918968
H 0.000008 1.975959 2.918968
C -0.000023 1.594207 0.000000
O 0.000007 2.813623 0.000000

(dafo)⁻

E(B3LYP/6-31+G(d,p)) = -607.580756 u.a.

N -0.000016 -1.732649 1.563036
C -0.000005 -1.448094 2.872795
C -0.000018 -0.682796 0.729432
C 0.000006 -0.136655 3.401205
H -0.000006 -2.303752 3.548521
C -0.000007 0.692363 1.156927
C 0.000007 0.953688 2.533485
H 0.000013 0.004560 4.480027
N -0.000016 -1.732649 -1.563036
C -0.000005 -1.448094 -2.872795
C -0.000018 -0.682796 -0.729432
C 0.000006 -0.136655 -3.401205
H -0.000006 -2.303752 -3.548521
C -0.000007 0.692363 -1.156927
C 0.000007 0.953688 -2.533485
H 0.000013 0.004560 -4.480027
H 0.000013 1.978516 -2.897815
H 0.000013 1.978516 2.897815
C -0.000020 1.586891 0.000000
O -0.000001 2.854914 0.000000

[Zn(dafo)₃]²⁺

E(B3LYP/6-31+G(d,p)) = -3601.360258 u.a.

Zn 0.000443 -0.000118 0.000229
C 1.844804 -2.196754 0.609903
C 0.403552 -2.429727 2.343671
C 2.645474 -3.270112 1.005845
C 2.380136 -1.601464 -0.611174
C 1.133880 -3.520868 2.826047
H -0.485211 -2.085839 2.863221
C 2.287577 -3.966709 2.153485
C 3.532249 -2.284046 -1.006958
H 0.797560 -4.020206 3.728466
C 2.460326 -0.142563 -2.343907
C 4.187609 -1.853887 -2.154082
C 3.622716 -0.753282 -2.826171
H 2.025033 0.705461 -2.863041

H 4.084214 -0.365468 -3.728075
 C 0.196315 2.861599 -0.610775
 C -1.105493 2.200679 -2.344482
 C 0.210881 4.200632 -1.006641
 C 0.979154 2.696064 0.610587
 C -1.158231 3.512638 -2.826848
 H -1.621123 1.399224 -2.864007
 C -0.488704 4.552610 -2.154294
 C 1.507621 3.926415 1.006681
 H -1.724191 3.717987 -3.729253
 C 1.902688 1.564572 2.343859
 C 2.289952 3.965026 2.154241
 C 2.481700 2.742934 2.826440
 H 2.050316 0.622893 2.863050
 H 3.082566 2.701545 3.728692
 N 1.139611 1.526592 1.224842
 N -0.423401 1.857091 -1.225287
 N 1.820921 -0.561812 -1.225288
 N 0.752252 -1.750254 1.224462
 H 2.732959 4.887684 2.517656
 H -0.520508 5.575663 -2.517578
 H 5.089392 -2.338158 -2.517251
 H 2.864685 -4.812040 2.516773
 N -1.891606 0.223721 1.225581
 C -2.305980 0.865722 2.344507
 C -2.824334 -0.499564 0.611114
 C -3.616095 0.778513 2.826868
 H -1.564074 1.464063 2.863819
 C -4.154204 -0.656603 1.007010
 C -4.578749 0.001750 2.154518
 H -3.880629 1.319690 3.729066
 N -1.396586 -1.295298 -1.224647
 C -1.353195 -2.057964 -2.343736
 C -2.576391 -1.260390 -0.610217
 C -2.463190 -2.759293 -2.826152
 H -0.401209 -2.104202 -2.863060
 C -3.743491 -1.916915 -1.006189
 C -3.698663 -2.698890 -2.153759
 H -2.358142 -3.352296 -3.728440
 H -4.568904 -3.237684 -2.517088
 H -5.599382 -0.075580 2.517763
 C -4.830179 -1.573926 0.000393
 O -5.977984 -1.947913 0.000352
 C 1.050865 4.970444 0.000128
 C 3.778045 -3.396960 -0.000599
 O 1.300415 6.151561 0.000266
 O 4.675645 -4.204196 -0.000602

[Zn(dafo)₃]²⁺

E(B3LYP/6-31+G(d,p)) = -3601.633189 u.a. (at the B3LYP/6-31+G(d,p) optimized geometry of [Zn(dafo)₃]²⁺)

[Zn(dafo)]²⁺

E(B3LYP/6-31+G(d,p)) = -2386.067955 u.a.
 Zn 0.000000 -2.291245 -0.000019

N 1.464562 -0.946740 -0.000008
C 2.819516 -0.798534 -0.000007
C 0.729808 0.176900 0.000001
C 3.392143 0.476059 0.000004
H 3.424385 -1.698454 -0.000014
C 1.215982 1.475163 0.000012
C 2.600494 1.644382 0.000013
H 4.475250 0.549565 0.000004
N -1.464562 -0.946740 -0.000007
C -2.819516 -0.798534 -0.000006
C -0.729808 0.176900 0.000002
C -3.392143 0.476059 0.000005
H -3.424385 -1.698454 -0.000013
C -1.215982 1.475163 0.000012
C -2.600494 1.644382 0.000014
H -4.475250 0.549565 0.000005
H -3.058690 2.630174 0.000022
H 3.058690 2.630174 0.000021
C 0.000000 2.410117 0.000020
O 0.000000 3.609841 0.000031

[Zn(dafo)]⁺⁺

E(B3LYP/6-31+G(d,p)) = -2386.473514 u.a.

Zn 0.001387 -2.550645 -0.000018
N 1.466261 -0.873493 -0.000006
C 2.808619 -0.691312 -0.000005
C 0.729978 0.234817 0.000003
C 3.385603 0.582882 0.000005
H 3.422501 -1.585984 -0.000013
C 1.205308 1.545621 0.000014
C 2.582158 1.738714 0.000015
H 4.467018 0.666198 0.000006
N -1.465312 -0.875088 -0.000006
C -2.807867 -0.694368 -0.000004
C -0.730235 0.234023 0.000003
C -3.386237 0.579197 0.000006
H -3.420775 -1.589708 -0.000012
C -1.206992 1.544309 0.000014
C -2.584050 1.735902 0.000016
H -4.467742 0.661336 0.000007
H -3.024410 2.728550 0.000024
H 3.021437 2.731841 0.000023
C -0.001346 2.471528 0.000023
O -0.002003 3.679233 0.000031

Zn⁰

E(B3LYP/6-31+G(d,p)) = -1779.177373 u.a.

Zn⁺⁺

E(B3LYP/6-31+G(d,p)) = -1778.828580 u.a.

(dafo)⁺⁺

E(B3LYP/6-31+G(d,p)) = -607.205927 u.a.

N 0.000026 -1.735858 1.519767

C 0.000024 -1.473677 2.821744
C 0.000005 -0.655789 0.725036
C 0.000003 -0.153386 3.382912
H 0.000040 -2.333327 3.487956
C -0.000018 0.703332 1.186617
C -0.000019 0.967883 2.547846
H 0.000004 -0.044920 4.463291
N 0.000026 -1.735858 -1.519767
C 0.000024 -1.473677 -2.821744
C 0.000005 -0.655789 -0.725036
C 0.000003 -0.153386 -3.382912
H 0.000040 -2.333327 -3.487956
C -0.000018 0.703332 -1.186617
C -0.000019 0.967883 -2.547846
H 0.000004 -0.044920 -4.463291
H -0.000036 1.982069 -2.935275
H -0.000036 1.982069 2.935275
C -0.000038 1.626019 0.000000
O -0.000051 2.835138 0.000000

[Zn(dafo)₂]²⁺

E(B3LYP/6-31+G(d,p)) = -2993.776388 u.a.

Zn 0.000000 -0.000023 -0.000017
N 1.523882 -1.021921 -1.017334
C 1.690426 -1.977802 -1.968930
C 2.650828 -0.514780 -0.512468
C 2.959097 -2.394058 -2.383325
H 0.792543 -2.408960 -2.398157
C 3.954138 -0.858444 -0.854594
C 4.129085 -1.836620 -1.828390
H 3.029126 -3.161261 -3.147094
N 1.523843 1.021915 1.017336
C 1.690351 1.977799 1.968935
C 2.650808 0.514797 0.512491
C 2.959006 2.394082 2.383353
H 0.792451 2.408938 2.398147
C 3.954105 0.858488 0.854640
C 4.129015 1.836669 1.828437
H 3.029005 3.161285 3.147124
H 5.114555 2.160417 2.150737
H 5.114637 -2.160349 -2.150671
C 4.885991 0.000030 0.000032
O 6.089790 0.000039 0.000046
N -1.523860 1.017332 -1.021921
C -1.690383 1.968941 -1.977793
C -2.650817 0.512480 -0.514792
C -2.959045 2.383360 -2.394053
H -0.792490 2.398158 -2.408940
C -3.954119 0.854629 -0.858461
C -4.129044 1.828435 -1.836630
H -3.029056 3.147139 -3.161247
N -1.523866 -1.017361 1.021892
C -1.690395 -1.968971 1.977763
C -2.650820 -0.512492 0.514773
C -2.959059 -2.383375 2.394030
H -0.792505 -2.398201 2.408902

C -3.954125 -0.854625 0.858450
C -4.129056 -1.828435 1.836615
H -3.029075 -3.147154 3.161223
H -5.114603 -2.150723 2.160353
H -5.114589 2.150737 -2.160361
C -4.885991 0.000011 0.000001
O -6.089790 0.000025 0.000011

References

- [1] R. Prazeres, F. Glotin, C. Insa, D. A. Jaroszynski, J. M. Ortega, *Eur. Phys. J. D* **1998**, *3*, 87-93.
- [2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010. Gaussian 09 (Revision B.01).
- [3] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652; b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789.
- [4] A. M. Rijs, G. Ohanessian, J. Oomens, G. Meijer, G. von Helden, I. Compagnon, *Angew. Chem. Int. Ed.* **2010**, *49*, 2332-2335.
- [5] a) J. Kalcher, A. F. Sax, *Chem. Rev.* **1994**, *94*, 2291-2318; b) J. Kalcher, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **2001**, *97*, 149-189.
- [6] H. B. Schlegel, *J. Chem. Phys.* **1986**, *94*, 4530-4534.