Electronic Transitions in Different Redox States of Trinuclear 5,6,11,12,17,18-Hexaazatrinaphthylene-Bridged Titanium Complexes: Spectroelectrochemistry and Quantum Chemistry

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SI-1 Instrumentation

NIR spectra were measured with a fiber-coupled Matrix-F FT-NIR spectrometer (Bruker Optik GmbH, Ettlingen, Germany) equipped with a halogen lamp as NIR source and an InGaAs detector. Spectra were taken in the range from 12000 to 4000 cm\(^{-1}\) with a resolution of 8 cm\(^{-1}\). For each measurement 16 scans were accumulated. UV-Vis spectra were taken with a GetSpec 2048 CCD array spectrometer (GetSpec, Sofia, Bulgaria). The device configuration allowed a resolution of 2.4 nm in the range of 200 to 1000 nm. For the measurements, an integration time of 100 ms was used. Both spectrometers were coupled to a spectroelectrochemical cell (ALS Co., LTD, Tokyo, Japan) located inside an Ar-filled glove box (Figure S1) using 600 µm-diameter N227 quartz fibers (Bruker Optik GmbH).

![Experimental setup for spectroelectrochemical measurements.](image)

**Figure S1.** Experimental setup for spectroelectrochemical measurements.
SI-2 Attempted interpretation of the electronic spectra within single electron model

Attempted orbital model and assignment of transitions
Despite very coarse assumptions required and their known severe limitations,[1] we attempted an assignment of all transitions in an experimentally derived single electron (orbital) picture for all redox states using the formal potential $E^\circ$ of the electron transfer reactions from Table 1 and the energies of the electronic transitions in Figure 4. This attempt is documented here. Despite its the perceived inner consistency, this assignment could not be reproduced by quantum chemical calculations due to the inherent limitations of the MO model discussed in 2.2 and the consequences of the coarse assumptions required.

The correlation between the spectroscopic and electrochemical data in a semi-quantitative approach involved

i) Definition of a ground state configuration using experimental solid-state magnetic data

ii) The definition of a Fermi energy for dispersed molecular systems

iii) Interpretation of observed electronic transitions within a single electron picture, i.e. equating the spectroscopically observed energy of the electronic transition as the difference between two orbital energies

iv) Definition of a “Fermi energy” of molecular systems as the mean between HOMO and LUMO or to the value of a SOMO. This energy is equated with the Fermi energy from ii)

v) Recalculation of the electrochemical data to the vacuum level

Definition of the ground state configuration (i). The general MO scheme is derived from common textbook MO schemes, where metal orbitals and ligand orbitals form MOs, in which the metal-centered $d$-type orbitals are the frontier orbitals (2 $e_g$ and 3 $t_g$ orbitals for tetrahedral complexes).[2] The highest occupied ligand $\pi$ orbital (referred to as HOMO in the following schemes) is the first orbital below the $d-e_g$ set and the lowest unoccupied $\pi^*$ orbital of the ligand (referred to as LUMO) represents the first orbital above the $d$ $t_2$ set. Note that the MO-scheme of the HATN-ligand as represented schematically in Figure 5 has already been simplified in this approach.

For the neutral complex it is known from magnetic susceptibility measurements that this compound is not a closed shell system in respect to the ligand.[3] At least one electron has to be transferred from one Ti(II) center to a ligand orbital, forming a Ti(III) center and one ligand-centered SOMO. Based on the irreversibility of the reduction of HATN, the transfer of only one electron has been assumed, although a transfer of more than one electron would be an option. Ground states of other redox states were derived from this ground state by subsequent addition or removal of electrons. Note that theoretical calculations in section 2.3-2.5 of the main manuscript showed that actually all metal centers of the neutral complex are Ti(III).

Definition of Fermi levels for dispersed molecules (ii). In case two redox forms of one molecular system are dissolved in an electrolyte, the “Fermi level of electrons” can be set to the Nernst-Potential of an inert electrode in this solution[4] and recalculated to the vacuum level (vi). In our case, one redox form of a complex with total charge $z^+$ is dissolved in an electrolyte solution. This metal complex can undergo a one-electron oxidation with a formal potential $E^\circ(X^{z+}/X^{(z+1)})$. The complex can also undergo a one-electron reduction with a formal potential $E^\circ(X^{(z-1)}/X^{z})$. The Fermi energy of the redox state $X^{\pm n}$ on the electrochemical
potential scale is than taken as midterm potential \( E_m = \frac{1}{2} \left[ E^o(X^{(z-1)} / X^{(z+1)}) + E^o(X^{(z)} / X^{(z+1)}) \right] \) between two adjacent one-electron oxidation and one-electron reduction in the cyclic voltammogram. At the potential \( E_m \), there is an equal probability that the complex accepts an electron from an inert electrode or transfers an electron to the electrode. The concentrations of the adjacent redox states are exactly equal, provided the oxidation and reduction is kinetically fast, which is the case in our system.

**Equating the energy of the spectroscopy transition to the difference of orbital energies (iii).** This is a consequence of assuming a single electron picture for the interpretation of the spectroscopic transitions. In that picture transitions can be interpreted as electron transitions between discrete orbitals.

The starting point for assignment of transitions between ligand orbitals is the energy spacing between HOMO, LUMO and if applicable SOMO. The energetic position of the SOMO within the MO scheme is fixed by the \( \pi-\pi^* \), \( \pi-\pi' \) and \( \pi'-\pi^* \) transitions. Typically, those electronic transition can be identified in the experimental spectra due to their characteristic shape. The index \( r \) marks transitions involving single occupied (radical) orbitals because these show special spin selection rules. Please, note that the SOMO may be filled or emptied in other redox states. The transitions which could not be assigned to this set of \( \pi \) orbitals were assumed to be charge transfer transitions between ligand and metal centers. The energies of the \( d \)-type orbitals are then derived from these assumed charge transfer bands. However, this empirical approach does not guarantee for correctness of the assumption as the quantum chemical calculations illustrate for [(Cp₂Ti)₃HATN(Ph)₆].

**Definition of a “Fermi energy” of molecular systems as the mean between HOMO and LUMO (iv).** The “Fermi energy” is taken as the mid-value between HOMO and LUMO, or as the energy of the SOMO. This value is equated to the value derived in ii) from electrochemical data and is used to place energy levels of different redox states on an absolute scale.

**Recalculation of the electrochemical data to the absolute energy scale (v).** The assessment of the spectroscopic data provides the relative orbital energies for one oxidation state, whereas the electrochemical data show the relative shift of the orbital sets if one compound is reduced or oxidized. To provide a complete picture for comparison of all redox states, the relative energies are referred to the vacuum level. The electrode potentials are measured against the ferrocene/ferrocenium (Fc/Fc⁺) redox couple, which is referenced to the standard hydrogen electrode by

\[
E^\circ(\text{Fc/Fc}^+) = (0.400 \pm 0.005) \text{ V vs. SHE.}[5]
\]  

(S1)

The electrode potentials against the SHE are than recalculated against the SHE scale according to the IUPAC recommendation[6]

\[
E_{\text{vac}} = -e \cdot E_{\text{SHE}} - (4.44\pm0.02) \text{ eV.}
\]  

(S2)

Combining Eq (S1) and (S2) yields

\[
E_{\text{vac}} = -e \cdot E_{\text{Fc/Fc}^+} - (4.84\pm0.025) \text{ eV.}
\]  

(S3)

**Assignment of transitions for each charge state**

Below the qualitative assignment is detailed, which is summarized in Figure S2. The codes for the transitions are from Figure 4.
**Charge state 0.** The assumed electronic structure of the neutral complex allows several characteristic electronic transitions. The UV-vis part of the spectra is dominated by the $\pi-\pi^*$ transition from the HOMO to the LUMO orbital of the ligand at around 3.0 eV (0/X). The energy of this transition does not change significantly between the different redox states. In the UV-vis region, there are also the $\pi-\pi'$ transition from the HOMO to the SOMO orbital at around 1.9 eV (0/VI), ligand to metal charge transfer (LMCT) from the HOMO orbital of the ligand to Ti(t) at around 2.3 eV (0/I), and the degenerate metal to ligand charge transfer (MLCT) from the Ti(II)(e) to the LUMO orbital of the ligand at around 2 eV (0/I). The NIR part of the spectra is characterized by two MLCT from the Ti(II)(t) and Ti(III)(t) to the LUMO' at 0.9 eV (+1/I) and 1.1 eV (+1/II), and two MLCT from the Ti(II)(e) to the LUMO' at 0.75 eV (+1/II) and 1.05 eV (+1/III), and 1.25 eV (+1/IV). The signals at 0.68 eV (*) and 0.9 eV (*) are experimental artifacts caused by overtones of molecular vibration of the solvent, which are not fully compensated during measurement. They appear in each of the NIR spectra in Figure 4. Transition 0/V is a vibronic progression of 0/IV corresponding to C=C valence vibration (~1600 cm$^{-1}$).

**Charge state +1.** After a one-electron oxidation, an electron is removed from the SOMO orbital which becomes the new LUMO orbital (denoted as LUMO' in Figure S2). This charge state has two $\pi-\pi^*$ transitions from the HOMO to the LUMO' and the LUMO orbital at around 2.5 eV (+1/V) and 2.9 eV (+1/VI). The NIR part of the spectra is characterized by two MLCT from the Ti(II)(t) and Ti(III)(t) to the LUMO' at 0.9 eV (+1/I) and 1.1 eV (+1/II), and two MLCT from the Ti(II)(e) and Ti(III)(e) to the LUMO at 1.05 eV (+1/III) and 1.25 eV (+1/IV).

**Charge state +2.** In this charge state, an electron is removed from the one Ti(II)(t). All other transitions are observed as in the charge states discussed before. These transitions and the participating states are slightly shifted to lower energies. The MLCT cannot be seen clearly in the NIR part of the spectra, there is only a general rise in absorption in the spectra which indicate those transitions.

**Charge state -1.** After the first one electron reduction (overall charge 0 to -1), an electron is added to the Ti(III)(t) orbital, after which no mixed valence systems exists. In the NIR part of the spectra, one can see the MLCT at 0.75 eV (-1/I), the $\pi-\pi^*$ at 1.1 eV (-1/II). The LMCT from the SOMO orbital of ligand to the Ti(t)(II) orbital is not observed in the recorded wavelength range, but one can see the rise in absorption at low photon energies which indicates that there is the transition in the energy range below 0.5 eV. In the UV-vis range, there are 3 transitions: the $\pi-\pi^*$ at 2.8 eV (-1/V), the $\pi-\pi'$ at 1.7 eV (-1/IV) and the LMCT from the HOMO orbital of the ligand to the Ti(t)(II) orbital at 2.3 eV (-1/V).

**Charge state -2.** After the second one electron reduction (overall charge state -1 to -2), an electron is transferred into the SOMO orbital of the ligand and this orbital becomes the new HOMO orbital (denoted as HOMO' in Figure S2). In this charge state, some transitions are lost. One can still see two $\pi-\pi^*$ transitions from the HOMO and the HOMO' to the LUMO orbital at 2.6 eV (-2/V) and 0.8 eV (-2/I) as well as the MLCT from the Ti(e)(II) to the LUMO orbital at 1.7 eV (-2/III). The LMCT from the HOMO to the Ti(t)(II) is at 2.2 eV (-2/IV). However, the LMCT from the HOMO' to the Ti(t)(II) cannot be observed, yet there is a rise in absorption which indicate that there is the transition at energies below 0.5 eV. In the third reduction, an electron is accepted by one of the Ti centers. The complex is then composed of one Ti(I) and two Ti(II) centers. The transitions are similar to that of the charge state -2. The only difference is the MLCT from the Ti(e)(II) to the LUMO orbital.
Figure S2. Orbital energy diagram and transitions (in eV) observed in electronic spectra in the visible and NIR range for \([\text{Cp}_2\text{Ti}\text{HATN(Ph)}_6]\) and its oxidation products \((\text{Cp}_2\text{Ti}\text{HATN(Ph)}_6)^{1+}\), \((\text{Cp}_2\text{Ti}\text{HATN(Ph)}_6)^{2+}\) and reduction products \((\text{Cp}_2\text{Ti}\text{HATN(Ph)}_6)^{3-}\), \((\text{Cp}_2\text{Ti}\text{HATN(Ph)}_6)^{2-}\), \((\text{Cp}_2\text{Ti}\text{HATN(Ph)}_6)^{1-}\)). Transitions involving single occupied ligand orbital are marked with \(\pi^*\) (radical). As spins are parallel within one Ti center but may be antiparallel between different Ti centers, d electron spins are indicated as II.

Construction of an Energy Diagram

From the assignments in Figure S2 and the spectra (Figure 4 of the main manuscript) one can construct the “orbital diagram” in an energy scale\(^7\) (Figure S3). For this purpose, the data from the electrochemical experiments are transformed to the absolute energy scale by Eq. (S3). From the assignments Figure S3, it is evident that the positions of Ti-centered orbitals are not affected if an electron is removed from the SOMO (HOMO’, LUMO’) orbital, which seems to be purely ligand-centered. However, if electrons are instead removed from the Ti centers the energetic position of all orbitals in the complex is affected indicating an interaction of the d-orbitals with the ligand.

When the complex is oxidized from -3 to -2 charge state, an electron is removed from antibonding t orbital (because of simplicity all \(t_2\) orbitals are denoted in the text as t orbitals), and this influences all orbitals by shift of -0.5 eV. In the next oxidation (from -2 to -1), the electron is removed from the \(\pi\)-system (HOMO’ becomes SOMO). The Ti-centered orbitals do not change energy because these orbitals are not interacting with the HOMO’ (now SOMO). In next oxidation, an electron is removed from the Ti-centered orbital and, because of \(\pi\)-back bonding, all orbitals are shifted by about -0.5 eV. In the ground state the complex is in the triplet state because of electron paring of two single occupied orbitals (Ti(III)(e) and SOMO). When the titanium complex is oxidized from 0 to +1, removing an electron from the SOMO orbital (now LUMO’) and again the titanium centered orbitals do not change energy. The energy difference between LUMO and LUMO’ becomes smaller because one unpaired electron is removed from the SOMO orbital, and the complex is again in the doublet state. In oxidation from +1 to +2 charge state, an electron is removed from a Ti-centered orbital and because of \(\pi\)-back bonding, all orbitals are shifted by -0.5 eV to lower energies.
**Calculation of orbital diagrams.** The midterm potential \( (E_m) \) is taken as the arithmetic mean of two neighboring redox potentials determined from DPV measurement (vs. Fc/Fc\(^+\)), (Figure 2 of main manuscript). It indicates a potential at which a certain charge state of the complex is stable, i.e. an oxidation to the next higher or a reduction to a lower charge state are equally likely. In the absence of a SOMO orbital in a certain charge state of the complex, this value is taken to be equal to the mean value of the LUMO and the HOMO in that charge state. In the presence of a SOMO orbital, this value corresponds to the energy of SOMO orbital. After this assignment which places the different charge states relatively to each other, the remaining orbital positions were constructed using transition energies from absorption spectra. Orbitals which do not contribute to an electronic transition were omitted from orbital diagrams.

The orbitals of Ti(III) centers have lower energies than those of Ti(II) because removing further electrons from the same metal center becomes increasingly difficult when electrons have already been removed before. The energetic difference between the Ti(III) and the Ti(II) orbitals is always the same and calculated to be 0.16 eV from the optical transition of the neutral complex.

The energetic difference between the Ti(t) and the Ti(e) was taken to be 1.65 eV. This value was calculated from data of the neutral complex.

**Charge state 0.**
The \( E_m \) was determined to be -1.34 V vs. Fc/Fc\(^+\) or 3.50 eV vs. Vac according to Eq. (S3). This is the energy of the SOMO.

Calculation from absorption spectra
- LUMO (-2.40 eV) = SOMO (-3.50 eV) + \( \pi^-\pi^* \) (1.10 eV, 0/IV)
- HOMO (-5.40 eV) = SOMO (-3.50 eV) - \( \pi^-\pi^* \) (1.90 eV, 0/VI)
- Ti(II)(e) (-4.40 eV) = SOMO (-3.50 eV) - MLCT (0.90 eV, 0/III)
- Ti(II)(t) (-2.75 eV) = SOMO (-3.50 eV) + LMCT (0.75 eV, 0/I)
- Ti(III)(t) (-2.90 eV) = SOMO (-3.50 eV) + LMCT (0.60 eV, 0/I)
- Ti(III)(e) (-4.56 eV) = Ti(II)(e) (-4.40 eV) - 0.16 eV

**Charge state +1.**
The \( E_m \) was determined to be -0.785 V vs. Fc/Fc\(^+\) or -4.05 vs Vac according to Eq. (S3). This value of -4.05 eV corresponds to the mean value between the lowest unoccupied (in this case LUMO’) and the highest occupied level (Ti(II)(e)).

Calculation from absorption spectra
- The transition between LUMO’ and the Ti(II)(e) is the MLCT (0.90 eV, +1/I). From this information the energy of the LUMO’ (-3.60 eV) and the Ti(II)(e) (-4.50 eV) was calculated
- Ti(II)(e) (-4.50 eV) = Ti(III)(e) (-4.66 eV) + 0.16 eV
- Ti(III)(t) (-3.00 eV) = Ti(III)(e) (-4.66 eV) + 1.65 eV
- Ti(II)(t) (-2.85 eV) = Ti(II)(e) (-4.50 eV) + 1.65 eV
- HOMO (-6.10 eV) = LUMO’ (-3.60 eV) - \( \pi^-\pi^* \) (2.50 eV, +1/V)
- LUMO (-3.20 eV) = HOMO (-6.10 eV) + \( \pi^-\pi^* \) (2.90 eV, +1/VI)

**Charge state +2.**
The $E_m$ was determined to be -0.315 V vs. Fc/Fc$^+$ or -4.52 vs. Vac according to Eq. (S3). The value of -4.52 eV corresponds to the mean value between the lowest unoccupied (LUMO') and the highest occupied level (Ti(II)(e)).

Calculation from absorption spectra
The transition between LUMO and the Ti(II)(e) is the MLCT. Since the exact values of the MLCTs are not known for this state, approximation was made that the MLCT has the same value as in +1 charge state, this laces the Ti(II)(e) (-4.97 eV) and the LUMO' (-4.07 eV).

$$\text{Ti(III)(e)} (-5.12 \text{ eV}) = \text{Ti(II)(e)} (-4.97 \text{ eV}) - 0.16 \text{ eV}$$
$$\text{Ti(III)(t)} (-3.32 \text{ eV}) = \text{Ti(II)(e)} (-4.97 \text{ eV}) + 1.65 \text{ eV}$$
$$\text{HOMO} (-6.57 \text{ eV}) = \text{LUMO'} (-4.07 \text{ eV}) - \pi^* - \pi^* (2.50 \text{ eV}, +2/II)$$
$$\text{LUMO} (-3.77 \text{ eV}) = \text{HOMO} (-6.57 \text{ eV}) + \pi^* - \pi^* (2.80 \text{ eV}, +2/II)$$

**Charge state -1.**
The $E_m$ was determined to be -1.840 V vs. Fc/Fc$^+$ or -3.00 eV vs. Vac according to Eq. (S3). This is the energy of the SOMO.

Calculation from absorption spectra
LUMO (-1.90 eV) = SOMO (-3.00 eV) + $\pi^* - \pi^* (1.1 \text{ eV}, -1/II)$
HOMO (-4.70 eV) = SOMO (-3.00 eV) - $\pi - \pi' (1.7 \text{ eV}, -1/IV)$
$$\text{Ti(II)(e)} (-3.75 \text{ eV}) = \text{SOMO} (-3.00 \text{ eV}) - \text{MLCT} (0.75 \text{ eV}, -1/I)$$
$$\text{Ti(II)(t)} (-2.10 \text{ eV}) = \text{Ti(II)(e)} (-3.75 \text{ eV}) + 1.65 \text{ eV}$$

**Charge state -2.**
The $E_m$ was determined to be -2.44 V vs. Fc/Fc$^+$ or -2.40 eV vs. Vac according to Eq. (S3). The value of -2.40 eV corresponds to the mean value between the lowest unoccupied (Ti(II)(t)) and the highest occupied level (HOMO').

Calculation from absorption spectra
The transition between Ti(III)(t) and HOMO' is the LMCT. Energy of this transition is lower than 0.5 eV (in this case it was taken the approximation that this transition is at 0.4 eV). From this information the energy of the HOMO' (-2.60 eV) and the Ti(II)(t) (-2.20 eV) was calculated.

$$\text{Ti(II)(e)} (-3.85 \text{ eV}) = \text{Ti(II)(t)} (-2.20 \text{ eV}) - 1.65 \text{ eV}$$
$$\text{HOMO} (-4.40 \text{ eV}) = \text{Ti(II)(t)} (-2.20 \text{ eV}) - \text{LMCT} (2.20 \text{ eV}, -2/IV)$$
$$\text{LUMO} (-1.80 \text{ eV}) = \text{HOMO} (-4.40 \text{ eV}) + \pi - \pi^* (2.60 \text{ eV}, -2/V)$$
At the end the approximation was checked by:
$$\text{LUMO} (-1.80 \text{ eV}) - \pi - \pi^* (0.80 \text{ eV}, -2/I) = \text{HOMO'} (2.60 \text{ eV})$$

**Charge state -3.**
For this charge state it was approximated that the $E_m$ was -2.97 V vs. Fc/Fc$^+$ or -1.87 eV vs. Vac according to Eq. (S3). This approximation is based on the observation that the potential difference between the $E^*$ values of the 0/-1, -1/-2, -2/-3 redox pair is very similar. This differences were averaged and half of that difference was subtracted from $E^*''(-2/-3)$ to arrive at an estimation of $E_m$ for the -3 charge state. The value of -1.87 eV corresponds to the middle value between the lowest unoccupied (Ti(II)(t)) and the highest occupied level (HOMO').
Calculation from absorption spectra.
The transition between these two levels is the LMCT which energy is lower than 0.5 eV (in this case it was taken the approximation that this transition is at 0.3 eV). From this information the energy of the HOMO' (-2.02 eV) and the Ti(II)(t) (-1.72 eV) was calculated.

\[
\text{Ti (II)(t)} (-3.37 \text{ eV}) = \text{Ti(II)(t)} (-1.72 \text{ eV}) - 1.65 \text{ eV}
\]

HOMO (-3.82 eV) = Ti(II)(t) (-1.72 eV) - LMCT (2.1 eV, -3/III)
LUMO (-1.22 eV) = HOMO (-3.82 eV) + π-π* (2.6 eV, -3/IV)

At the end the approximation was checked by:
LUMO (-1.22 eV) - π-π* (0.8 eV, -3/I) = HOMO' (-2.02 eV)
This value matched the value of the HOMO' calculated before.

Table S1. Energy levels [eV vs. vacuum potential scale] of the complex (purple values indicate approximated values, red numbers in the SOMO column are actually the mean value between the LUMO and the HOMO of a certain charge state.

|       | SOMO   | LUMO   | HOMO   | Ti(I)(t) | Ti(II)(t) | Ti(III)(t) | Ti(I)(e) | Ti(II)(e) | Ti(III)(e) | HOMO'   | LUMO'   |
|-------|--------|--------|--------|----------|-----------|------------|----------|-----------|------------|---------|--------|
| 0     | -3.50  | -2.40  | -5.40  | /        | -2.75     | -2.90      | /        | -4.40     | -4.56      | /       | /      |
| +1    | -4.05  | -3.20  | -6.10  | /        | -2.85     | -3.00      | /        | -4.50     | -4.66      | /       | -3.60  |
| +2    | -4.52  | -3.77  | -6.57  | /        | -3.32     | -3.47      | /        | -4.97     | -5.12      | /       | -4.07  |
| -1    | -3.00  | -1.90  | -4.70  | /        | -2.10     | /          | /        | -3.75     | /          | /       | /      |
| -2    | -2.40  | -1.80  | -4.40  | /        | -2.20     | /          | /        | -3.85     | / -2.60    | /       | /      |
| -3    | -1.87  | -1.22  | -3.82  | -1.57    | -1.72     | /          | -3.22    | -3.37     | / -2.02    | /       | /      |

Figure S3. The energy accurate orbital diagram of the [(Cp₂Ti)₃HATN(Ph)₆] and its oxidation products [(Cp₂Ti)₃HATN(Ph)₆]⁺, [(Cp₂Ti)₂HATN(Ph)₆]²⁺ and reduction products [(Cp₂Ti)₃HATN(Ph)₆]⁻, [(Cp₂Ti)₃HATN(Ph)₆]⁻², [(Cp₂Ti)HATN(Ph)₆]¹. The charge state of the complex is stated in the first row of the table. The energy is referenced to the vacuum level on the left ordinate and to the formal potential of the Fc/Fc⁺ redox couple on the right ordinate. As spins are parallel within one Ti center but may be antiparallel between different Ti centers, d electron spins are indicated as II.
The orbital picture discussed above is not a good approximation of the ground state of $[(\text{Cp}_2\text{Ti})_3\text{HATN(Ph)}_6]$. Although the susceptibility measurements showed the electron transfer to the ligand, the number of transferred electrons cannot be ascertained from the solid-state measurements. In connection with the electrochemical stability of the Ti-free ligand, the transfer of only one electron was assumed in a first assessment. This was also in line with the necessity of a SOMO for explaining the NIR $\pi-\pi$ transitions.

Concerning the NIR CT transitions, the MO model discussed above could not explain the disappearance of CT bands for the charge state $+2$. For assessing the contradictions between experimental results and the MO based assignment, DFT calculations were conducted. At this point the limitations of a such simple model became obvious: The arising multiconfigurational problem as evident from DFT calculation needs to be solved by high level quantum calculations. Afterwards, this can be translated back to “partially occupied (single particle) orbitals”. However, in such a situation it becomes impossible to describe an electronic transition as a transition between two orbitals. Rather it should be considered as a transition between two $N$-electron wave functions. Furthermore, our quantum chemical calculations demonstrate, that the MO-diagram of the ligand in the experimental approach was oversimplified and the electronic configuration with the assumption of a transfer of only one electron to the ligand was not justified. In conclusion, the attempt to derive “orbital diagrams” from experimental data alone should be regarded with great caution, since experimental data simply do not allow for an unambiguous assignment of spectral transitions and a subsequent “construction” of “orbital diagrams” due to a lack of atomistic information.
SI-3 Calculated total energies of different species, molecular orbitals and electronic excitations

Figure S4. Molecular orbitals of Ti-free HATN molecule calculated with PBE0 Def2-SVP.
Table S2. Total energy and spin contamination deviation of different redox species and spin states of [(Cp₂Ti)₂HATN(Ph)₆] with PBE0/RiJCOSX/Def2/J/Def2-SVP. All states were geometry optimized. All charge blocks are referenced to the first multiplicity.

| Charge | Multiplicity | Energy [a.u.] | Spin Contamination | ΔE [eV] |
|--------|--------------|---------------|--------------------|---------|
| 0      | 1            | -6338.6436    | 3.05               | 0.00    |
| 3      | 1            | -6338.6428    | 1.74               | 0.02    |
| 5      | 1            | -6338.6423    | 0.74               | 0.04    |
| 7      | 1            | -6338.6428    | 0.04               | 0.02    |
| 1      | 2            | -6338.4694    | 2.04               | 0.00    |
| 4      | 2            | -6338.4720    | 0.86               | -0.07   |
| 6      | 2            | -6338.4686    | 0.04               | 0.02    |
| 2      | 1            | -6338.2041    | 2.03               | 0.00    |
| 3      | 1            | -6338.2042    | 1.03               | 0.00    |
| 5      | 1            | -6338.2037    | 0.03               | 0.00    |
| 7      | 1            | -6338.1405    | 0.04               | 1.73    |
Figure S5. Calculated electronic transitions in the neutral complex [(Cp₂Ti)HATN(Ph)] via TD-PBE0. Excitations are compared with experiment (exp. rounded to 25 nm). Molecular orbitals of $S = 1$ and $S = 2$ multiplicity are separated into alpha (a) and beta (b) electrons. Orbitals 354b, 355b and 457a are occupied, orbitals 356b, 358a and 359a are unoccupied. Color scheme of atoms is titanium: red, carbon: brown, nitrogen: blue, hydrogen: white. Orbitals are labelled similar to calculated output.
Table S3. TD-PBE0 excitations and transition dipole moment of \([\text{Cp}_2\text{Ti})_3\text{HATN(Ph)}_6]\) in different spin states.

| Wavelength [nm] | \(T^2\) [a.u.²] | Wavelength [nm] | \(T^2\) [a.u.²] |
|-----------------|-----------------|-----------------|-----------------|
| 2213.5          | 0.11            | 2267.7          | 0.06            |
| 1349.6          | 0.58            | 1339.9          | 0.56            |
| 1193.7          | 3.49            | 1185.2          | 3.42            |
| 974.0           | 2.82            | 986.2           | 2.86            |
| 828.7           | 0.01            | 788.2           | 0.01            |
| 764.2           | 0.01            | 783.4           | 0.02            |
| 763.2           | 0.01            | 686             | 0.00            |
| 660.3           | 0.00            | 650.7           | 0.00            |
| 654.8           | 0.01            | 642.9           | 0.01            |
| 654.7           | 0.00            | 637.6           | 0.00            |
| 630.1           | 0.00            | 625.9           | 0.00            |
| 628.6           | 0.00            | 624.8           | 0.00            |
| 623.2           | 0.00            | 607.5           | 0.00            |
| 599.2           | 0.00            | 590.7           | 0.00            |
| 590.4           | 0.00            | 588.9           | 0.06            |
| 589.5           | 0.00            | 586.9           | 0.00            |
| 583.9           | 0.00            | 585.8           | 0.01            |
| 582.7           | 0.10            | 575.7           | 0.03            |
| 579.5           | 0.00            | 572             | 0.00            |
| 571.4           | 0.00            | 565.8           | 0.00            |
Table S4. TD-PBE0 excitations and transition dipole moment of [(Cp₂Ti)₃HATN(Ph)]⁺ in different spin states.

| Wavelength [nm] | $\text{T}^2$ [a.u.$^2$] | Wavelength [nm] | $\text{T}^2$ [a.u.$^2$] |
|-----------------|----------------------|-----------------|----------------------|
| 3508.1          | 0.49                 | 2316.0          | 0.39                 |
| 1388.6          | 5.98                 | 1281.9          | 0.44                 |
| 993.5           | 0.01                 | 1162.1          | 2.29                 |
| 976.9           | 0.00                 | 1059.3          | 7.78                 |
| 943.0           | 0.00                 | 947.7           | 0.02                 |
| 684.2           | 0.01                 | 863.9           | 0.03                 |
| 681.8           | 0.01                 | 810.3           | 0.01                 |
| 662.3           | 0.00                 | 763.5           | 0.02                 |
| 657.4           | 0.00                 | 722.4           | 0.02                 |
| 656.2           | 0.00                 | 671.3           | 0.00                 |
| 650.1           | 0.00                 | 656.1           | 0.00                 |
| 643.1           | 0.02                 | 655.1           | 0.00                 |
| 635.8           | 0.00                 | 652.0           | 0.01                 |
| 630.1           | 0.00                 | 622.7           | 0.00                 |
| 601.4           | 0.01                 | 619.1           | 0.01                 |
| 600.0           | 0.01                 | 612.2           | 0.00                 |
| 585.3           | 0.00                 | 577.4           | 0.00                 |
| 564.6           | 0.00                 | 571.9           | 0.00                 |
| 563.5           | 0.00                 | 566.6           | 0.00                 |
| 554.6           | 0.00                 | 554.4           | 0.00                 |
Table S5. TD-PBE0 excitations and transition dipole moment of [(Cp_2Ti)_3HATN(Ph)]^2+ in different spin states.

| Wavelength [nm] | T^2 [a.u.^2] | Wavelength [nm] | T^2 [a.u.^2] |
|----------------|-------------|----------------|-------------|
| 2126.3         | 7.33        | 2148.9         | 7.35        |
| 2096.5         | 7.23        | 2129.8         | 7.22        |
| 1208.8         | 0.01        | 1098.1         | 0.01        |
| 1181.5         | 0.00        | 1077.8         | 0.02        |
| 1163.5         | 0.00        | 1072.8         | 0.01        |
| 795.5          | 0.02        | 1065.1         | 0.00        |
| 784.0          | 0.02        | 1052.2         | 0.05        |
| 768.5          | 0.01        | 1029.7         | 0.01        |
| 753.6          | 0.00        | 693.9          | 0.00        |
| 737.6          | 0.00        | 687.4          | 0.00        |
| 724.9          | 0.00        | 686.6          | 0.00        |
| 688.5          | 0.00        | 664.3          | 0.58        |
| 680.9          | 0.00        | 660.2          | 0.41        |
| 680.6          | 0.00        | 654.9          | 0.20        |
| 662.0          | 0.30        | 632.3          | 0.02        |
| 659.0          | 0.23        | 619.7          | 0.01        |
| 654.0          | 0.23        | 613.4          | 0.01        |
| 633.9          | 0.02        | 611.2          | 0.08        |
| 611.0          | 0.21        | 610.4          | 2.50        |
| 610.7          | 2.78        | 608.0          | 2.84        |

Figure S6. Comparison between TD-PBE0 spectra of simplified model complex (Q = 0, S = 1) and the synthesized complex (Q = 0, S = 1).
**Table S6.** Different spin state total energies of CAS(6,7) and NEVPT2 by including all multiplicities with identical weight in one calculation. All charge blocks are referenced to the lowest multiplicity; $Q = 0$, Def2-TZVP/RIJCOSX/Def2/JK.

| Multiplicity | CAS(6,7) Energy [a.u.] | $\Delta E$ [eV] | NEVPT2 Energy [a.u.] | $\Delta E$ [eV] |
|--------------|------------------------|-----------------|----------------------|-----------------|
| 1            | -6546.0119             | 0.00            | -6552.97873          | 0.00            |
| 3            | -6546.0124             | -0.01           | -6552.97914          | 0.00            |
| 5            | -6546.0126             | -0.02           | -6552.97935          | 0.00            |
| 7            | -6546.0046             | 0.20            | -6552.96225          | 0.02            |

**Table S7.** Orbital occupations of different multiplicities for CAS(6,7); $Q = 0$, Def2-TZVP/RIJCOSX/Def2/JK.

| Multiplicity | 180 | 181 | 182 | 183 | 184 | 185 | 186 |
|--------------|-----|-----|-----|-----|-----|-----|-----|
| 1            | 1.68| 1.00| 1.00| 1.00| 0.99| 0.31| 0.01|
| 3            | 1.68| 1.00| 1.00| 1.00| 0.99| 0.31| 0.01|
| 5            | 1.68| 1.00| 1.00| 1.00| 0.99| 0.31| 0.01|
| 7            | 1.00| 1.00| 1.00| 1.00| 1.00| 1.00| 0.00|

**Table S8.** Comparison of population for the relevant orbitals between CAS(6,7) model system and a fully symmetrized CAS(12,13) model system. Both calculation were made with Def2-TZVP/RIJCOSX/Def2/JK and $Q = 0$, $S = 1$. The first two roots have to be equally weighted for the correct ground state.

| CAS(n,m) | Energy [a.u.] | Occupation (relevant orbitals) |
|----------|---------------|--------------------------------|
| 6,7      | -6546.0132    | 1.68 1.00 1.00 1.00 0.99 0.31 |
| 12,13    | -6546.0671    | 1.76 1.00 1.00 1.00 1.00 2.05 |
**SI-4 XYZ files of calculated structures**

The atom positions in the different calculations are given below.

**Table S9. PBE0 RIJCOSX Def2-SVP $S = 1$, $Q = 0$.**

| Atom | $X$ / Å | $Y$ / Å | $Z$ / Å |
|------|---------|---------|---------|
| Ti   | 0.3820  | 4.1318  | 0.0380  |
| N    | 1.5606  | 2.2799  | 0.1218  |
| N    | -1.1113 | 2.5333  | -0.0623 |
| C    | 1.2028  | 4.1635  | 2.3074  |
| C    | -0.4574 | 4.1944  | -2.2044 |
| C    | -0.1860 | 3.9135  | 2.3574  |
| C    | 0.8141  | 3.8085  | -2.2787 |
| C    | -0.8567 | 5.0615  | 1.8625  |
| C    | 1.7754  | 4.7328  | -1.7998 |
| C    | 0.1211  | 6.0043  | 1.4859  |
| C    | 1.0916  | 5.9019  | -1.4035 |
| C    | 1.3999  | 5.4476  | 1.7538  |
| C    | -0.2936 | 5.7056  | -1.6486 |
| C    | 2.9332  | 2.1244  | 0.1519  |
| C    | 0.8319  | 1.1495  | 0.0476  |
| C    | -2.4887 | 2.6371  | -0.1011 |
| C    | -0.6007 | 1.2866  | -0.0331 |
| H    | 1.9882  | 3.4716  | 2.6059  |
| H    | -1.4023 | 3.9639  | -2.4956 |
| H    | -0.6623 | 3.0028  | 2.7174  |
| H    | 1.0293  | 2.8071  | -2.6479 |
| H    | -1.9350 | 5.2001  | 1.8131  |
| H    | 2.8486  | 4.5584  | -1.7639 |
| H    | -0.0803 | 6.9926  | 1.0751  |
| H    | 1.5474  | 6.8008  | -0.9895 |
| H    | 2.3608  | 5.9363  | 1.5924  |
| H    | -1.0899 | 6.4263  | -1.4627 |
| C    | 3.7807  | 3.2308  | 0.3041  |
| C    | 3.5302  | 0.8290  | 0.0401  |
| C    | 1.4191  | -0.1308 | -0.0259 |
| C    | -3.1193 | 3.8828  | -0.2388 |
| C    | -3.3138 | 1.4715  | -0.0188 |
| C    | -1.4117 | 0.1351  | 0.0004  |
| H    | 3.3156  | 4.1975  | 0.4867  |
| C    | 5.1764  | 3.1539  | 0.2711  |
| N    | 2.7701  | -0.3093 | -0.0205 |
| C    | 4.9324  | 0.7684  | -0.0388 |
| C    | 0.5940  | -1.2908 | -0.0282 |
| H    | -2.4858 | 4.7545  | -0.3952 |
| C    | -4.5069 | 4.0559  | -0.2365 |
| N    | -2.7709 | 0.2139  | 0.0083  |
| C    | -4.7049 | 1.6663  | 0.0611  |
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | -0.8147 | -1.1581 | -0.0347 |
| C       | 5.7658  | 1.8847 | 0.0422 |
| Ti      | 3.4049  | -2.4001 | -0.0889 |
| H       | 5.3816  | -0.2051 | -0.2249 |
| N       | 1.2053  | -2.5012 | -0.0764 |
| C       | -5.3222 | 2.9150  | -0.0299 |
| Ti      | -3.7647 | -1.7058 | 0.1487 |
| H       | -5.3258 | 0.7898  | 0.2374 |
| N       | -1.6394 | -2.2351 | 0.0020 |
| C       | 3.2684  | -2.1988 | 2.2793 |
| C       | 4.6071  | -3.0904 | 1.3827 |
| C       | 4.1882  | -4.1107 | 1.4307 |
| C       | 3.0211  | -3.5610 | 2.0010 |
| C       | 3.0272  | -2.3822 | -2.4533 |
| C       | 4.1586  | -1.5665 | -2.2434 |
| C       | 5.1874  | -2.3689 | -1.7076 |
| C       | 4.7002  | -3.6988 | -1.6183 |
| C       | 3.3668  | -3.7084 | -2.0802 |
| C       | 0.3856  | -3.6005 | -0.0720 |
| C       | -3.7039 | -1.5919 | -2.2330 |
| C       | -4.9080 | -0.9705 | -1.8213 |
| C       | -5.7186 | -1.9504 | -1.2131 |
| C       | -5.0256 | -3.1888 | -1.2682 |
| C       | -3.7914 | -2.9659 | -1.9135 |
| C       | -3.2033 | -1.6756 | 2.4730 |
| C       | -4.2072 | -0.6993 | 2.3163 |
| C       | -5.3888 | -1.3441 | 1.8939 |
| C       | -5.1208 | -2.7361 | 1.8224 |
| C       | -3.7714 | -2.9435 | 2.1826 |
| C       | -1.0415 | -3.4676 | -0.0092 |
| H       | 2.5546  | -1.4920 | 2.6980 |
| H       | 5.1027  | -0.9504 | 2.0359 |
| H       | 6.1871  | -3.2093 | 1.0065 |
| H       | 4.3236  | -5.1429 | 1.1072 |
| H       | 2.0857  | -4.0897 | 2.1733 |
| H       | 2.0637  | -2.0489 | -2.8353 |
| H       | 4.2231  | -0.4963 | -2.4345 |
| H       | 6.1882  | -2.0300 | -1.4413 |
| H       | 5.2632  | -4.5613 | -1.2663 |
| H       | 2.7199  | -4.5780 | -2.1692 |
| C       | 0.9174  | -4.9033 | -0.0979 |
| H       | -2.8603 | -1.0952 | -2.7098 |
| H       | -5.1576 | 0.0802  | -1.9536 |
| H       | -6.7072 | -1.7829 | -0.7873 |
| H       | -5.3893 | -4.1470 | -0.8988 |
| H       | -3.0309 | -3.7183 | -2.1151 |
|   | X   | Y   | Z   |
|---|-----|-----|-----|
| H | -2.1736 | -1.4795 | 2.7681 |
| H | -4.0779 | 0.3721 | 2.4641 |
| H | -6.3444 | -0.8606 | 1.6918 |
| H | -5.8384 | -3.5084 | 1.5518 |
| H | -3.2562 | -3.8997 | 2.2514 |
| C | -1.8111 | -4.6463 | 0.0255 |
| H | 2.0017 | -5.0031 | -0.1045 |
| C | 0.1438 | -6.0623 | -0.0644 |
| H | -2.8938 | -4.5316 | 0.0414 |
| C | -1.2726 | -5.9326 | -0.0103 |
| C | 5.9505 | 4.3891 | 0.5463 |
| C | 5.5723 | 5.6139 | -0.0263 |
| C | 7.0263 | 4.3891 | 1.4488 |
| C | 6.2274 | 6.7984 | 0.3048 |
| H | 4.7549 | 5.6362 | -0.7513 |
| C | 7.6819 | 5.5717 | 1.7808 |
| H | 7.3399 | 3.4514 | 1.9119 |
| C | 7.2825 | 6.7833 | 1.2163 |
| H | 5.9076 | 7.7360 | -0.1573 |
| H | 8.5089 | 5.5469 | 2.4952 |
| H | 7.7944 | 7.7092 | 1.4892 |
| C | -5.0461 | 5.4098 | -0.5208 |
| C | -6.0460 | 5.6000 | -1.4883 |
| C | -4.5173 | 6.5442 | 0.1146 |
| C | -6.4876 | 6.8779 | -1.8196 |
| H | -6.4695 | 4.7326 | -1.9983 |
| C | -4.9594 | 7.8246 | -0.2156 |
| H | -3.7601 | 6.4163 | 0.8926 |
| C | -5.9435 | 7.9971 | -1.1888 |
| H | -7.2591 | 7.0043 | -2.5836 |
| H | -4.5334 | 8.6902 | 0.2980 |
| H | -6.2922 | 8.9974 | -1.4578 |
| C | -2.2087 | -7.0877 | -0.0379 |
| C | -2.0411 | -8.1492 | -0.9437 |
| C | -3.3270 | -7.1221 | 0.8131 |
| C | -2.9480 | -9.2052 | -0.9875 |
| H | -1.1873 | -8.1465 | -1.6245 |
| C | -4.2341 | -8.1802 | 0.7716 |
| H | -3.4824 | -6.3143 | 1.5330 |
| C | -4.0476 | -9.2290 | -0.1281 |
| H | -2.7904 | -10.0172 | -1.7025 |
| H | -5.0920 | -8.1838 | 1.4495 |
| H | -4.7551 | -10.0619 | -0.1587 |
| C | 0.8541 | -7.3679 | -0.0478 |
| C | 1.8495 | -7.6469 | -0.9988 |
| C | 0.5811 | -8.3387 | 0.9299 |
| C | 2.5365 | -8.8603 | -0.9860 |
|   |   |   |   |
|---|---|---|---|
| H | 2.0721 | -6.9070 | -1.7722 |
| C | 1.2724 | -9.5472 | 0.9479  |
| H | -0.1834 | -8.1386 | 1.6840  |
| C | 2.2466 | -9.8174 | -0.0144 |
| H | 3.2962 | -9.0639 | -1.7452 |
| H | 1.0435 | -10.2883| 1.7183  |
| H | 2.7787 | -10.7715| -0.0077 |
| C | 7.2135 | 1.6736  | -0.2082 |
| C | 7.9205 | 2.4894  | -1.1059 |
| C | 7.8874 | 0.5867  | 0.3709  |
| C | 9.2432 | 2.2071  | -1.4354 |
| H | 7.4148 | 3.3374  | -1.5718 |
| C | 9.2137 | 0.3081  | 0.0476  |
| H | 7.3597 | -0.0480 | 1.0874  |
| C | 9.8942 | 1.1121  | -0.8657 |
| H | 9.7681 | 2.8451  | -2.1510 |
| H | 9.7183 | -0.5420 | 0.5134  |
| H | 10.9255| 0.8795  | -1.1421 |
| C | -6.7943| 2.9784  | 0.1571  |
| C | -7.3780| 3.9184  | 1.0224  |
| C | -7.6348| 2.0478  | -0.4743 |
| C | -8.7502| 3.9173  | 1.2589  |
| H | -6.7423| 4.6453  | 1.5314  |
| C | -9.0095| 2.0502  | -0.2432 |
| H | -7.2042| 1.3189  | -1.1661 |
| C | -9.5711| 2.9822  | 0.6286  |
| H | -9.1829| 4.6491  | 1.9460  |
| H | -9.6462| 1.3217  | -0.7513 |
| H | -10.6469 | 2.9772 | 0.8227 |
Table S10. PBE0 RIJCOSX Def2-SVP, $S = 2$, $Q = 0$.

| Atom | $X / \text{Å}$ | $Y / \text{Å}$ | $Z / \text{Å}$ |
|------|----------------|----------------|----------------|
| Ti   | 0.3818         | 4.1495         | 0.0479         |
| N    | 1.5660         | 2.2971         | 0.1031         |
| N    | -1.1100        | 2.5619         | -0.0663        |
| C    | 1.2203         | 4.1602         | 2.3158         |
| C    | -0.4699        | 4.4732         | -2.1891        |
| C    | -0.1661        | 3.9049         | 2.3744         |
| C    | 0.7998         | 3.8629         | -2.2813        |
| C    | -0.8450        | 5.0543         | 1.8944         |
| C    | 1.7645         | 4.7777         | -1.7914        |
| C    | 0.1264         | 6.0060         | 1.5225         |
| C    | 1.0848         | 5.9419         | -1.3734        |
| C    | 1.4087         | 5.4512         | 1.7741         |
| C    | -0.3014        | 5.7504         | -1.6132        |
| C    | 2.9272         | 2.1375         | 0.1328         |
| C    | 0.8254         | 1.1625         | 0.0356         |
| C    | -2.4774        | 2.6562         | -0.1040        |
| C    | -0.5885        | 1.3035         | -0.0447        |
| H    | 2.0106         | 3.4680         | 2.6004         |
| H    | -1.4175        | 4.0232         | -2.4804        |
| H    | -0.6356        | 2.9865         | 2.7236         |
| H    | 1.0108         | 2.8650         | -2.6621        |
| H    | -1.9244        | 5.1882         | 1.8521         |
| H    | 2.8377         | 4.6012         | -1.7632        |
| H    | -0.0818        | 6.9977         | 1.1234         |
| H    | 1.5439         | 6.8338         | -0.9480        |
| H    | 2.3667         | 5.9451         | 1.6112         |
| H    | -1.0957        | 6.4690         | -1.4113        |
| C    | 3.7867         | 3.2420         | 0.2822         |
| C    | 3.5251         | 0.8388         | 0.0301         |
| C    | 1.4164         | -0.1221        | -0.0318        |
| C    | -3.1266        | 3.8989         | -0.2272        |
| C    | -3.3024        | 1.4898         | -0.0365        |
| C    | -1.4025        | 0.1537         | -0.0147        |
| H    | 3.3278         | 4.2113         | 0.4672         |
| C    | 5.1782         | 3.1549         | 0.2476         |
| N    | 2.7617         | -0.2973        | -0.0249        |
| C    | 4.9274         | 0.7694         | -0.0481        |
| C    | 0.6008         | -1.2887        | -0.0299        |
| H    | -2.5041        | 4.7804         | -0.3724        |
| C    | -4.5152        | 4.0548         | -0.2226        |
| N    | -2.7468        | 0.2264         | -0.0116        |
| C    | -4.6920        | 1.6641         | 0.0317         |
| C    | -0.8029        | -1.1589        | -0.0427        |
| C    | 5.7658         | 1.8797         | 0.0232         |
| Ti   | 3.4041         | -2.3980        | -0.0801        |
| Element | Value 1  | Value 2  | Value 3 |
|---------|---------|---------|---------|
| H       | 5.3705  | -0.2083 | -0.2269 |
| N       | 1.2176  | -2.5036 | -0.0711 |
| C       | -5.3262 | 2.9066  | -0.0389 |
| Ti      | -3.7532 | -1.6974 | 0.1090  |
| H       | -5.3028 | 0.7763  | 0.1854  |
| N       | -1.6280 | -2.2236 | -0.0072 |
| C       | 3.2653  | -2.1831 | 2.2871  |
| C       | 4.6042  | -1.8955 | 1.9215  |
| C       | 5.1710  | -3.0770 | 1.3977  |
| C       | 4.1885  | -4.0983 | 1.4502  |
| C       | 3.0202  | -3.5472 | 2.0163  |
| C       | 3.0334  | -2.3951 | -2.4461 |
| C       | 4.1634  | -1.5769 | -2.2380 |
| C       | 5.1919  | -2.3753 | -1.6951 |
| C       | 4.7054  | -3.7047 | -1.5984 |
| C       | 3.3729  | -3.7184 | -2.0636 |
| C       | 0.3948  | -3.6008 | -0.0614 |
| C       | -3.6488 | -1.5793 | -2.2669 |
| C       | -4.8590 | -0.9541 | -1.8780 |
| C       | -5.6828 | -1.9313 | -1.2847 |
| C       | -4.9931 | -3.1730 | -1.3287 |
| C       | -3.7477 | -2.9543 | -1.9519 |
| C       | -3.2270 | -1.6734 | 2.4381  |
| C       | -4.2254 | -0.6925 | 2.2685  |
| C       | -5.4024 | -1.3317 | 1.8269  |
| C       | -5.1383 | -2.7249 | 1.7565  |
| C       | -3.7964 | -2.9386 | 2.1393  |
| C       | -1.0300 | -3.4682 | -0.0082 |
| H       | 2.5500  | -1.4749 | 2.7010  |
| H       | 5.0988  | -0.9339 | 2.0397  |
| H       | 6.1868  | -3.1965 | 1.0232  |
| H       | 4.3258  | -5.1321 | 1.1328  |
| H       | 2.0852  | -4.0763 | 2.1896  |
| H       | 2.0706  | -2.0648 | -2.8322 |
| H       | 4.2272  | -0.5081 | -2.4367 |
| H       | 6.1917  | -2.0339 | -1.4288 |
| H       | 5.2682  | -4.5646 | -1.2396 |
| H       | 2.7263  | -4.5888 | -2.1472 |
| C       | 0.9198  | -4.9059 | -0.0742 |
| H       | -2.7972 | -1.0859 | -2.7330 |
| H       | -5.1028 | 0.0974  | -2.0151 |
| H       | -6.6777 | -1.7600 | -0.8754 |
| H       | -5.3668 | -4.1300 | -0.9663 |
| H       | -2.9866 | -3.7091 | -2.1418 |
| H       | -2.2026 | -1.4829 | 2.7543  |
| H       | -4.0938 | 0.3776  | 2.4229  |
| H       | -6.3529 | -0.8442 | 1.6110  |
|   |   |   |   |
|---|---|---|---|
| H | -5.8546 | -3.4942 | 1.4739 |
| H | -3.2861 | -3.8965 | 2.2160 |
| C | -1.8057 | -4.6367 | 0.0250 |
| H | 2.0035  | -5.0120  | -0.0725 |
| C | 0.1384  | -6.0623  | -0.0405 |
| H | -2.8879 | -4.5159  | 0.0316 |
| C | -1.2743 | -5.9300  | 0.00004 |
| C | 5.9627  | 4.3842   | 0.5211 |
| C | 5.5950  | 5.6120   | -0.0515 |
| C | 7.0392  | 4.3744   | 1.4227 |
| C | 6.2617  | 6.7903   | 0.2782 |
| H | 4.7767  | 5.6415   | -0.7751 |
| C | 7.7059  | 5.5509   | 1.7538 |
| H | 7.3446  | 3.4340   | 1.8858 |
| C | 7.3175  | 6.7657   | 1.1887 |
| H | 5.9500  | 7.7307   | -0.1838 |
| H | 8.5332  | 5.5185   | 2.4675 |
| H | 7.8385  | 7.6870   | 1.4602 |
| C | -5.0641 | 5.4098   | -0.4865 |
| C | -6.0634 | 5.6068   | -1.4528 |
| C | -4.5408 | 6.5378   | 0.1643 |
| C | -6.5090 | 6.8871   | -1.7698 |
| H | -6.4822 | 4.7439   | -1.9740 |
| C | -4.9881 | 7.8202   | -0.1504 |
| H | -3.7820 | 6.4028   | 0.9396 |
| C | -5.9703 | 8.0004   | -1.1241 |
| H | -7.2793 | 7.0200   | -2.5338 |
| H | -4.5661 | 8.6813   | 0.3738 |
| H | -6.3220 | 9.0026   | -1.3820 |
| C | -2.2162 | -7.0798  | -0.0298 |
| C | -2.0462 | -8.1476  | -0.9278 |
| C | -3.3431 | -7.1033  | 0.8101 |
| C | -2.9577 | -9.1995  | -0.9731 |
| H | -1.1867 | -8.1531  | -1.6014 |
| C | -4.2555 | -8.1568  | 0.7666 |
| H | -3.5015 | -6.2905  | 1.5238 |
| C | -4.0658 | -9.2125  | -0.1243 |
| H | -2.7972 | -10.0168 | -1.6814 |
| H | -5.1198 | -8.1513  | 1.4362 |
| H | -4.7773 | -10.0419 | -0.1565 |
| C | 0.8442  | -7.3706  | -0.0093 |
| C | 1.8434  | -7.6611  | -0.9524 |
| C | 0.5590  | -8.3325  | 0.9732 |
| C | 2.5231  | -8.8784  | -0.9271 |
| H | 2.0746  | -6.9275  | -1.7293 |
| C | 1.2433  | -9.5448  | 1.0040 |
| H | -0.2106 | -8.1232  | 1.7196 |
|   |       |       |       |
|---|-------|-------|-------|
| C | 2.2218 | -9.8268 | 0.0496 |
| H | 3.2869 | -9.0912 | -1.6797 |
| H | 1.0061 | -10.2789 | 1.7783 |
| H | 2.7482 | -10.7839 | 0.0661 |
| C | 7.2112 | 1.6629 | -0.2319 |
| C | 7.9191 | 2.4744 | -1.1331 |
| C | 7.8832 | 0.5738 | 0.3458 |
| C | 9.2392 | 2.1858 | -1.4674 |
| H | 7.4158 | 3.3241 | -1.5985 |
| C | 9.2066 | 0.2881 | 0.0170 |
| H | 7.3560 | -0.0571 | 1.0661 |
| C | 9.8875 | 1.0882 | -0.8997 |
| H | 9.7641 | 2.8209 | -2.1855 |
| H | 9.7092 | -0.5636 | 0.4820 |
| H | 10.9166 | 0.8505 | -1.1801 |
| C | -6.7981 | 2.9476 | 0.1484 |
| C | -7.3988 | 3.8704 | 1.0211 |
| C | -7.6233 | 2.0041 | -0.4853 |
| C | -8.7693 | 3.8374 | 1.2650 |
| H | -6.7769 | 4.6080 | 1.5320 |
| C | -8.9959 | 1.9729 | -0.2449 |
| H | -7.1816 | 1.2904 | -1.1859 |
| C | -9.5730 | 2.8857 | 0.6369 |
| H | -9.2137 | 4.5557 | 1.9589 |
| H | -9.6192 | 1.2330 | -0.7532 |
| H | -10.6465 | 2.8526 | 0.8401 |
Table S11. PBE0 RIJCOSX Def2-SVP; $S = \frac{1}{2}$, $Q = 1$.

| Atom | $X$ / Å | $Y$ / Å | $Z$ / Å |
|------|---------|---------|---------|
| Ti   | 0.3811  | 4.1413  | 0.0415  |
| N    | 1.5592  | 2.2552  | 0.1416  |
| N    | -1.1116 | 2.5165  | -0.0506 |
| C    | 1.1975  | 4.1800  | 2.3039  |
| C    | -0.4512 | 4.3967  | -2.1995 |
| C    | -0.1937 | 3.9351  | 2.3506  |
| C    | 0.8239  | 3.7890  | -2.2594 |
| C    | -0.8578 | 5.0835  | 1.8479  |
| C    | 1.7791  | 4.7238  | -1.7874 |
| C    | 0.1251  | 6.0193  | 1.4679  |
| C    | 1.0883  | 5.8936  | -1.4080 |
| C    | 1.4012  | 5.4591  | 1.7428  |
| C    | -0.2955 | 5.6886  | -1.6573 |
| C    | 2.9331  | 2.1124  | 0.1705  |
| C    | 0.8392  | 1.1402  | 0.0669  |
| C    | -2.4900 | 2.6282  | -0.0907 |
| C    | -0.6089 | 1.2796  | -0.0094 |
| H    | 1.9788  | 3.4920  | 2.6221  |
| H    | -1.3914 | 3.9382  | -2.5013 |
| H    | -0.6758 | 3.0352  | 2.7301  |
| H    | 1.0471  | 2.7913  | -2.6344 |
| H    | -1.9348 | 5.2327  | 1.8044  |
| H    | 2.8544  | 4.5620  | -1.7574 |
| H    | -0.0706 | 7.0089  | 1.0576  |
| H    | 1.5387  | 6.8020  | -1.0093 |
| H    | 2.3636  | 5.9468  | 1.5872  |
| H    | -1.0941 | 6.4113  | -1.4894 |
| C    | 3.7711  | 3.2273  | 0.3214  |
| C    | 3.5361  | 0.8216  | 0.0565  |
| C    | 1.4308  | -0.1476 | -0.0019 |
| C    | -3.1118 | 3.8770  | -0.2368 |
| C    | -3.3190 | 1.4681  | -0.0031 |
| C    | -1.4215 | 0.1272  | 0.0259  |
| H    | 3.3009  | 4.1912  | 0.5034  |
| C    | 5.1628  | 3.1554  | 0.2878  |
| N    | 2.7820  | -0.3153 | -0.0052 |
| C    | 4.9397  | 0.7648  | -0.0290 |
| C    | 0.6096  | -1.3050 | -0.0086 |
| H    | -2.4752 | 4.7457  | -0.3948 |
| C    | -4.4964 | 4.0528  | -0.2408 |
| N    | -2.7789 | 0.2091  | 0.0340  |
| C    | -4.7102 | 1.6643  | 0.0717  |
| C    | -0.8230 | -1.1703 | 0.0012  |
| C    | 5.7618  | 1.8842  | 0.0486  |
| Ti   | 3.4391  | -2.4179 | -0.1007 |
| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| H       | 5.3931 | -0.2054 | -0.2205 |
| N       | 1.1980 | -2.5108 | -0.0614 |
| C       | -5.3196 | 2.9134 | -0.0249 |
| Ti      | -3.7939 | -1.7137 | 0.1688 |
| H       | -5.3360 | 0.7915 | 0.2482 |
| N       | -1.6220 | -2.2404 | 0.0370 |
| C       | 3.3253 | -2.2306 | 2.2571 |
| C       | 4.6620 | -1.9457 | 1.8803 |
| C       | 5.2159 | -3.1218 | 1.3328 |
| C       | 4.2293 | -4.1404 | 1.3844 |
| C       | 3.0716 | -3.5919 | 1.9724 |
| C       | 3.0172 | -2.3774 | -2.4425 |
| C       | 4.1500 | -1.5578 | -2.2470 |
| C       | 5.1908 | -2.3587 | -1.7357 |
| C       | 4.7120 | -3.6929 | -1.6508 |
| C       | 3.3713 | -3.7061 | -2.0890 |
| C       | 0.3877 | -3.6072 | -0.0583 |
| C       | -3.7008 | -1.5976 | -2.1982 |
| C       | -4.9101 | -0.9743 | -1.8024 |
| C       | -5.7283 | -1.9516 | -1.2025 |
| C       | -5.0378 | -3.1928 | -1.2499 |
| C       | -3.7972 | -2.9735 | -1.8814 |
| C       | -3.2384 | -1.6819 | 2.4793 |
| C       | -4.2426 | -0.7041 | 2.3205 |
| C       | -5.4218 | -1.3473 | 1.8935 |
| C       | -5.1553 | -2.7411 | 1.8255 |
| C       | -3.8088 | -2.9504 | 2.1913 |
| C       | -1.0357 | -3.4740 | 0.0187 |
| H       | 2.6257 | -1.5292 | 2.7086 |
| H       | 5.1673 | -0.9921 | 2.0159 |
| H       | 6.2290 | -3.2434 | 0.9516 |
| H       | 4.3612 | -5.1718 | 1.0572 |
| H       | 2.1420 | -4.1229 | 2.1672 |
| H       | 2.0518 | -2.0485 | -2.8244 |
| H       | 4.2094 | -0.4879 | -2.4416 |
| H       | 6.1963 | -2.0190 | -1.4886 |
| H       | 5.2884 | -4.5563 | -1.3241 |
| H       | 2.7344 | -4.5820 | -2.1868 |
| C       | 0.9248 | -4.9120 | -0.0972 |
| H       | -2.8598 | -1.1063 | -2.6857 |
| H       | -5.1619 | 0.0739 | -1.9484 |
| H       | -6.7240 | -1.7842 | -0.7938 |
| H       | -5.4126 | -4.1507 | -0.8910 |
| H       | -3.0442 | -3.7310 | -2.0912 |
| H       | -2.2155 | -1.4883 | 2.7988 |
| H       | -4.1156 | 0.3657 | 2.4799 |
| H       | -6.3782 | -0.8648 | 1.6931 |
|   |   |   |   |
|---|---|---|---|
| H | -5.8754 | -3.5127 | 1.5600 |
| H | -3.3018 | -3.9093 | 2.2775 |
| C | -1.8155 | -4.6497 | 0.0527 |
| H | 2.0086 | -5.0123 | -0.1148 |
| C | 0.1494 | -6.0603 | -0.0613 |
| H | -2.8974 | -4.5317 | 0.0777 |
| C | -1.2785 | -5.9280 | 0.0038 |
| C | 5.9360  | 4.3903  | 0.5647 |
| C | 5.5611  | 5.6125  | -0.0146 |
| C | 7.0034  | 4.3867  | 1.4764 |
| C | 6.2156  | 6.7962  | 0.3193 |
| H | 4.7536  | 5.6346  | -0.7507 |
| C | 7.6546  | 5.5700  | 1.8139 |
| H | 7.3151  | 3.4497  | 1.9422 |
| C | 7.2606  | 6.7798  | 1.2424 |
| H | 5.9046  | 7.7335  | -0.1486 |
| H | 8.4745  | 5.5473  | 2.5359 |
| H | 7.7715  | 7.7054  | 1.5172 |
| C | -5.0352 | 5.4042  | -0.5362 |
| C | -6.0253 | 5.5824  | -1.5151 |
| C | -4.5136 | 6.5411  | 0.0995 |
| C | -6.4646 | 6.8576  | -1.8594 |
| H | -6.4435 | 4.7120  | -2.0246 |
| C | -4.9567 | 7.8180  | -0.2417 |
| H | -3.7676 | 6.4205  | 0.8895 |
| C | -5.9301 | 7.9804  | -1.2272 |
| H | -7.2282 | 6.9787  | -2.6317 |
| H | -4.5424 | 8.6881  | 0.2730 |
| H | -6.2792 | 8.9781  | -1.5045 |
| C | -2.2094 | -7.0868 | -0.0221 |
| C | -2.0498 | -8.1327 | -0.9466 |
| C | -3.3123 | -7.1321 | 0.8476 |
| C | -2.9587 | -9.1866 | -0.9942 |
| H | -1.2064 | -8.1208 | -1.6403 |
| C | -4.2173 | -8.1916 | 0.8050 |
| H | -3.4561 | -6.3383 | 1.5857 |
| C | -4.0430 | -9.2238 | -0.1163 |
| H | -2.8136 | -9.9875 | -1.7237 |
| H | -5.0615 | -8.2120 | 1.4990 |
| H | -4.7495 | -10.0572 | -0.1487 |
| C | 0.8501  | -7.3705 | -0.0582 |
| C | 1.8334  | -7.6480 | -1.0217 |
| C | 0.5806  | -8.3383 | 0.9226 |
| C | 2.5161  | -8.8635 | -1.0166 |
| H | 2.0472  | -6.9113 | -1.8009 |
| C | 1.2730  | -9.5461 | 0.9350 |
| H | -0.1764 | -8.1394 | 1.6846 |
|   |       |       |       |
|---|-------|-------|-------|
| C | 2.2354| -9.8169| -0.0388|
| H | 3.2644| -9.0720| -1.7853|
| H | 1.0529| -10.2865| 1.7080|
| H | 2.7655| -10.7719| -0.0372|
| C | 7.2103| 1.6881| -0.2046|
| C | 7.9041| 2.5148| -1.1021|
| C | 7.8920| 0.6044| 0.3705|
| C | 9.2272| 2.2426| -1.4380|
| H | 7.3919| 3.3616| -1.5629|
| C | 9.2200| 0.3399| 0.0440|
| H | 7.3747| -0.0344| 1.0910|
| C | 9.8881| 1.1521| -0.8714|
| H | 9.7452| 2.8857| -2.1534|
| H | 9.7367| -0.5032| 0.5087|
| H | 10.9211| 0.9308| -1.1496|
| C | -6.7910| 2.9906| 0.1560|
| C | -7.3635| 3.9338| 1.0246|
| C | -7.6372| 2.0745| -0.4880|
| C | -8.7367| 3.9488| 1.2533|
| H | -6.7225| 4.6506| 1.5411|
| C | -9.0134| 2.0973| -0.2679|
| H | -7.2141| 1.3470| -1.1861|
| C | -9.5655| 3.0313| 0.6079|
| H | -9.1646| 4.6807| 1.9428|
| H | -9.6588| 1.3856| -0.7879|
| H | -10.6429| 3.0437| 0.7913|
Table S12. PBE0 RIJCOSX Def2-SVP, S = 3/2, Q = 1.

| Atom | X / Å | Y / Å | Z / Å |
|------|-------|-------|-------|
| Ti   | 0.3832| 4.1503| 0.0378|
| N    | 1.5568| 2.2659| 0.1436|
| N    | -1.1103| 2.5225| -0.0454|
| C    | 1.2072| 4.2040| 2.3004|
| C    | -0.4575| 4.4042| -2.2026|
| C    | -0.1828| 3.9578| 2.3541|
| C    | 0.8146| 3.7921| -2.2675|
| C    | -0.8502| 5.1016| 1.8453|
| C    | 1.7752| 4.7233| -1.7998|
| C    | 0.1300| 6.0367| 1.4562|
| C    | 1.0906| 5.8972| -1.4206|
| C    | 1.4074| 5.4797| 1.7298|
| C    | -0.2945| 5.6970| -1.6632|
| C    | 2.9300| 2.1192| 0.1705|
| C    | 0.8356| 1.1480| 0.0728|
| C    | -2.4878| 2.6323| -0.0852|
| C    | -0.6061| 1.2857| -0.0108|
| H    | 1.9908| 3.5189| 2.6196|
| H    | -1.4008| 3.9491| -2.5000|
| H    | -0.6622| 3.0591| 2.7398|
| H    | 1.0323| 2.7921| -2.6395|
| H    | -1.9275| 5.2494| 1.8054|
| H    | 2.8500| 4.5568| -1.7729|
| H    | -0.0684| 7.0234| 1.0402|
| H    | 1.5461| 6.8045| -1.0254|
| H    | 2.3687| 5.9675| 1.5676|
| H    | -1.0896| 6.4232| -1.4938|
| C    | 3.7727| 3.2311| 0.3164|
| C    | 3.5301| 0.8288| 0.0572|
| C    | 1.4265| -0.1368| -0.0058|
| C    | -3.1131| 3.8804| -0.2280|
| C    | -3.3148| 1.4722| 0.0002|
| C    | -1.4196| 0.1333| 0.0312|
| H    | 3.3073| 4.1981| 0.4946|
| C    | 5.1648| 3.1526| 0.2810|
| N    | 2.7672| -0.3097| -0.0056|
| C    | 4.9310| 0.7633| -0.0237|
| C    | 0.6022| -1.3045| -0.0050|
| H    | -2.4789| 4.7512| -0.3851|
| C    | -4.4979| 4.0509| -0.2319|
| N    | -2.7684| 0.2119| 0.0359|
| C    | -4.7057| 1.6614| 0.0721|
| C    | -0.8230| -1.1706| -0.0059|
| C    | 5.7596| 1.8799| 0.0489|
| Ti   | 3.4320| -2.4154| -0.0859|
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| H       | 5.3806| -0.2107| -0.2047|
| N       | 1.1966| -2.5011| -0.0608|
| C       | -5.3189| 2.9090| -0.0202|
| Ti      | -3.7920| -1.7143| 0.1591|
| H       | -5.3285| 0.7853| 0.2423|
| N       | -1.6274| -2.2346| 0.0273|
| C       | 3.3008| -2.2196| 2.2726|
| C       | 4.6393| -1.9328| 1.9040|
| C       | 5.1998| -3.1099| 1.3651|
| C       | 4.2151| -4.1301| 1.4128|
| C       | 3.0519| -3.5820| 1.9906|
| C       | 3.0336| -2.3857| -2.4350|
| C       | 4.1643| -1.5656| -2.2307|
| C       | 5.1997| -2.3650| -1.7052|
| C       | 4.7193| -3.6981| -1.6191|
| C       | 3.3833| -3.7126| -2.0715|
| C       | 0.3833| -3.6061| -0.0610|
| C       | -3.6984| -1.5889| -2.2100|
| C       | -4.9071| -0.9663| -1.8116|
| C       | -5.7261| -1.9457| -1.2156|
| C       | -5.0360| -3.1866| -1.2672|
| C       | -3.7950| -2.9655| -1.8977|
| C       | -3.2448| -1.6916| 2.4744|
| C       | -4.2477| -0.7128| 2.3154|
| C       | -5.4258| -1.3540| 1.8817|
| C       | -5.1596| -2.7471| 1.8089|
| C       | -3.8142| -2.9583| 2.1787|
| C       | -1.0376| -3.4740| 0.0091|
| H       | 2.5966| -1.5183| 2.7169|
| H       | 5.1420| -0.9779| 2.0402|
| H       | 6.2158| -3.2306| 0.9916|
| H       | 4.3516| -5.1626| 1.0908|
| H       | 2.1219| -4.1143| 2.1803|
| H       | 2.0725| -2.0587| -2.8287|
| H       | 4.2261| -0.4969| -2.4309|
| H       | 6.2029| -2.0248| -1.4499|
| H       | 5.2917| -4.5604| -1.2823|
| H       | 2.7470| -4.5885| -2.1726|
| C       | 0.9225| -4.9053| -0.0983|
| H       | -2.8573| -1.0964| -2.6960|
| H       | -5.1590| 0.0822| -1.9552|
| H       | -6.7219| -1.7793| -0.8068|
| H       | -5.4112| -4.1457| -0.9119|
| H       | -3.0417| -3.7223| -2.1093|
| H       | -2.2229| -1.4999| 2.7985|
| H       | -4.1210| 0.3562| 2.4810|
| H       | -6.3815| -0.8703| 1.6804|
| Atoms | X   | Y   | Z   |
|-------|-----|-----|-----|
| H     | -5.8789 | -3.5176 | 1.5379 |
| H     | -3.3075 | -3.9176 | 2.2625 |
| C     | -1.8147 | -4.6470 | 0.0418 |
| H     | 2.0066  | -5.0041 | -0.1118 |
| C     | 0.1478  | -6.0591 | -0.0665 |
| H     | -2.8968 | -4.5313 | 0.0653 |
| C     | -1.2750 | -5.9288 | -0.0045 |
| C     | 5.9427  | 4.3867  | 0.5490 |
| C     | 5.5698  | 5.6068  | -0.0358 |
| C     | 7.0129  | 4.3842  | 1.4571 |
| C     | 6.2300  | 6.7900  | 0.2888 |
| H     | 4.7585  | 5.6280  | -0.7678 |
| C     | 7.6697  | 5.5669  | 1.7856 |
| H     | 7.3229  | 3.4487  | 1.9271 |
| C     | 7.2784  | 6.7748  | 1.2080 |
| H     | 5.9212  | 7.7257  | -0.1836 |
| H     | 8.4920  | 5.5454  | 2.5049 |
| H     | 7.936   | 7.7001  | 1.4759 |
| C     | -5.0410 | 5.4023  | -0.5202 |
| C     | -6.0318 | 5.5819  | -1.4981 |
| C     | -4.5232 | 6.5372  | 0.1219 |
| C     | -6.4746 | 6.8575  | -1.8363 |
| H     | -6.4485 | 4.7127  | -2.0107 |
| C     | -4.9700 | 7.8144  | -0.2132 |
| H     | -3.7778 | 6.4150  | 0.9121 |
| C     | -5.9430 | 7.9787  | -1.1988 |
| H     | -7.2379 | 6.9802  | -2.6086 |
| H     | -4.5584 | 8.6833  | 0.3058 |
| H     | -6.2950 | 8.9767  | -1.4713 |
| C     | -2.2071 | -7.0866 | -0.0320 |
| C     | -2.0453 | -8.1341 | -0.9543 |
| C     | -3.3131 | -7.1295 | 0.8339 |
| C     | -2.9542 | -9.1879 | -1.0023 |
| H     | -1.1994 | -8.1238 | -1.6449 |
| C     | -4.2184 | -8.1887 | 0.7906 |
| H     | -3.4597 | -6.3337 | 1.5693 |
| C     | -4.0415 | -9.2229 | -0.1280 |
| H     | -2.8077 | -9.9900 | -1.7303 |
| H     | -5.0651 | -8.2072 | 1.4816 |
| H     | -4.7481 | -10.0562 | -0.1607 |
| C     | 0.8534  | -7.3668 | -0.0625 |
| C     | 1.8374  | -7.6412 | -1.0260 |
| C     | 0.5880  | -8.3350 | 0.9190 |
| C     | 2.5243  | -8.8544 | -1.0208 |
| H     | 2.0503  | -6.9034 | -1.8045 |
| C     | 1.2840  | -9.5408 | 0.9312 |
| H     | -0.1686 | -8.1376 | 1.6817 |
|   |       |       |       |
|---|-------|-------|-------|
| C | 2.2466 | -9.8090 | -0.0432 |
| H | 3.2723 | -9.0611 | -1.7904 |
| H | 1.0662 | -10.2820 | 1.7041 |
| H | 2.7800 | -10.7621 | -0.0414 |
| C | 7.2071 | 1.6757 | -0.2027 |
| C | 7.9042 | 2.4930 | -1.1062 |
| C | 7.8848 | 0.5936 | 0.3803 |
| C | 9.2264 | 2.2136 | -1.4397 |
| H | 7.3955 | 3.3386 | -1.5731 |
| C | 9.2117 | 0.3214 | 0.0555 |
| H | 7.3650 | -0.0382 | 1.1052 |
| C | 9.8831 | 1.1246 | -0.8654 |
| H | 9.7469 | 2.8494 | -2.1599 |
| H | 9.7250 | -0.5204 | 0.5262 |
| H | 10.9153 | 0.8973 | -1.1420 |
| C | -6.7905 | 2.9816 | 0.1611 |
| C | -7.3651 | 3.9209 | 1.0325 |
| C | -7.6342 | 2.0639 | -0.4839 |
| C | -8.7379 | 3.9299 | 1.2637 |
| H | -6.7261 | 4.6395 | 1.5491 |
| C | -9.0100 | 2.0804 | -0.2608 |
| H | -7.2096 | 1.3395 | -1.1844 |
| C | -9.5641 | 3.0099 | 0.6185 |
| H | -9.1674 | 4.6585 | 1.9557 |
| H | -9.6535 | 1.3673 | -0.7812 |
| H | -10.6410 | 3.0169 | 0.8046 |
Table S13. PBE0 RIJCOSX Def2-SVP; \( S = 1, Q = 2 \).

| Atom | \( X / \text{Å} \) | \( Y / \text{Å} \) | \( Z / \text{Å} \) |
|------|-----------------|-----------------|-----------------|
| Ti   | 0.3851          | 4.1889          | 0.0518          |
| N    | 1.5650          | 2.2808          | 0.1416          |
| N    | -1.1192         | 2.5343          | -0.0310         |
| C    | 1.2250          | 4.2238          | 2.3013          |
| C    | -0.4729         | 4.4494          | -2.1741         |
| C    | -0.1661         | 3.9768          | 2.3606          |
| C    | 0.7996          | 3.8357          | -2.2483         |
| C    | -0.8356         | 5.1258          | 1.8654          |
| C    | 1.7634          | 4.7665          | -1.7853         |
| C    | 0.1429          | 6.0631          | 1.4779          |
| C    | 1.0815          | 5.9390          | -1.3980         |
| C    | 1.4223          | 5.5029          | 1.7393          |
| C    | -0.3059         | 5.7396          | -1.6321         |
| C    | 2.9261          | 2.1351          | 0.1671          |
| C    | 0.8340          | 1.1676          | 0.0796          |
| C    | -2.4846         | 2.6441          | -0.0722         |
| C    | -0.6041         | 1.3046          | -0.0005         |
| H    | 2.0096          | 3.5422          | 2.6258          |
| H    | -1.4164         | 4.0007          | -2.4806         |
| H    | -0.6434         | 3.0824          | 2.7593          |
| H    | 1.0159          | 2.8432          | -2.6413         |
| H    | -1.9124         | 5.2815          | 1.8442          |
| H    | 2.8396          | 4.6068          | -1.7779         |
| H    | -0.0565         | 7.0562          | 1.0781          |
| H    | 1.5398          | 6.8483          | -1.0107         |
| H    | 2.3819          | 5.9957          | 1.5818          |
| H    | -1.0976         | 6.4692          | -1.4612         |
| C    | 3.7768          | 3.2475          | 0.3024          |
| C    | 3.5236          | 0.8380          | 0.0700          |
| C    | 1.4283          | -0.1211         | 0.0112          |
| C    | -3.1156         | 3.8955          | -0.2022         |
| C    | -3.3104         | 1.4773          | -0.0090         |
| C    | -1.4222         | 0.1456          | 0.0320          |
| H    | 3.3184          | 4.2182          | 0.4774          |
| C    | 5.1632          | 3.1548          | 0.2709          |
| N    | 2.7500          | -0.2897         | 0.0127          |
| C    | 4.9242          | 0.7570          | -0.0101         |
| C    | 0.5938          | -1.3049         | 0.0079          |
| H    | -2.4854         | 4.7712          | -0.3455         |
| C    | -4.4966         | 4.0527          | -0.2212         |
| N    | -2.7525         | 0.2269          | 0.0287          |
| C    | -4.7051         | 1.6525          | 0.0464          |
| C    | -0.8196         | -1.1716         | 0.0060          |
| C    | 5.7559          | 1.8673          | 0.0437          |
| Ti   | 3.4428          | -2.4250         | -0.0805         |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| H       | 5.3654  | -0.2219 | -0.1831 |
| N       | 1.1924  | -2.4947 | -0.0440 |
| C       | -5.3208 | 2.8950  | -0.0290 |
| Ti      | -3.8076 | -1.7219 | 0.1397  |
| H       | -5.3233 | 0.7705  | 0.1997  |
| N       | -1.6278 | -2.2325 | 0.0403  |
| C       | 3.3220  | -2.2331 | 2.2691  |
| C       | 4.6605  | -1.9472 | 1.8964  |
| C       | 5.2166  | -3.1222 | 1.3508  |
| C       | 4.2307  | -4.1426 | 1.3999  |
| C       | 3.0717  | -3.5965 | 1.9856  |
| C       | 3.0224  | -2.3857 | -2.4151 |
| C       | 4.1527  | -1.5605 | -2.2172 |
| C       | 5.1960  | -2.3570 | -1.7051 |
| C       | 4.7225  | -3.6936 | -1.6225 |
| C       | 3.3831  | -3.7129 | -2.0634 |
| C       | 0.3838  | -3.6008 | -0.0458 |
| C       | -3.6698 | -1.5966 | -2.2177 |
| C       | -4.8864 | -0.9719 | -1.8428 |
| C       | -5.7167 | -1.9490 | -1.2611 |
| C       | -5.0271 | -3.1919 | -1.2983 |
| C       | -3.7757 | -2.9742 | -1.9070 |
| C       | -3.2926 | -1.6979 | 2.4525  |
| C       | -4.2883 | -0.7124 | 2.2781  |
| C       | -5.4636 | -1.3463 | 1.8284  |
| C       | -5.2052 | -2.7418 | 1.7629  |
| C       | -3.8674 | -2.9614 | 2.1533  |
| C       | -1.0409 | -3.4693 | 0.0286  |
| H       | 2.6277  | -1.5392 | 2.7406  |
| H       | 5.1707  | -0.9986 | 2.0475  |
| H       | 6.2330  | -3.2454 | 0.9788  |
| H       | 4.3681  | -5.1756 | 1.0794  |
| H       | 2.1465  | -4.1318 | 2.1898  |
| H       | 2.0625  | -2.0658 | -2.8179 |
| H       | 4.2121  | -0.4936 | -2.4279 |
| H       | 6.2024  | -2.0161 | -1.4631 |
| H       | 5.3050  | -4.5557 | -1.3026 |
| H       | 2.7554  | -4.5940 | -2.1729 |
| C       | 0.9264  | -4.8979 | -0.0851 |
| H       | -2.8276 | -1.1108 | -2.7091 |
| H       | -5.1415 | 0.0729  | -2.0067 |
| H       | -6.7222 | -1.7833 | -0.8763 |
| H       | -5.4140 | -4.1505 | -0.9543 |
| H       | -3.0253 | -3.7350 | -2.1146 |
| H       | -2.2796 | -1.5151 | 2.8085  |
| H       | -4.1615 | 0.3540  | 2.4598  |
| H       | -6.4160 | -0.8594 | 1.6190  |
|  |  |  |  |
|---|---|---|---|
| H | -5.9282 | -3.5084 | 1.4902 |
| H | -3.3730 | -3.9251 | 2.2567 |
| C | -1.8177 | -4.6426 | 0.0628 |
| H | 2.0103 | -4.9963 | -0.1005 |
| C | 0.1535 | -6.0514 | -0.0502 |
| H | -2.9000 | -4.5295 | 0.0832 |
| C | -1.2758 | -5.9221 | 0.0138 |
| C | 5.9550 | 4.3775 | 0.5326 |
| C | 5.5846 | 5.6029 | -0.0445 |
| C | 7.0346 | 4.3577 | 1.4306 |
| C | 6.2623 | 6.7764 | 0.2749 |
| H | 4.7694 | 5.6354 | -0.7718 |
| C | 7.7028 | 5.5335 | 1.7589 |
| H | 7.3422 | 3.4188 | 1.8949 |
| C | 7.3182 | 6.7459 | 1.1860 |
| H | 5.9637 | 7.168 | -0.1943 |
| H | 8.5300 | 5.5032 | 2.4718 |
| H | 7.8463 | 7.6649 | 1.4498 |
| C | -5.0491 | 5.3992 | -0.4981 |
| C | -6.0470 | 5.5746 | -1.4706 |
| C | -4.5287 | 6.5331 | 0.1453 |
| C | -6.4908 | 6.8500 | -1.8062 |
| H | -6.4668 | 4.7069 | -1.9830 |
| C | -4.9830 | 7.8085 | -0.1831 |
| H | -3.7829 | 6.4119 | 0.9354 |
| C | -5.9595 | 7.9703 | -1.1665 |
| H | -7.2561 | 6.9738 | -2.5760 |
| H | -4.5776 | 8.6780 | 0.3390 |
| H | -6.3157 | 8.9678 | -1.4345 |
| C | -2.2010 | -7.0814 | -0.0130 |
| C | -2.0300 | -8.1301 | -0.9334 |
| C | -3.3096 | -7.1236 | 0.8509 |
| C | -2.9371 | -9.1848 | -0.9830 |
| H | -1.1826 | -8.1205 | -1.6219 |
| C | -4.2084 | -8.1875 | 0.8092 |
| H | -3.4593 | -6.3298 | 1.5879 |
| C | -4.0249 | -9.2214 | -0.1091 |
| H | -2.7886 | -9.9870 | -1.7100 |
| H | -5.0539 | -8.2126 | 1.5013 |
| H | -4.7274 | -10.0580 | -0.1409 |
| C | 0.8559 | -7.3576 | -0.0447 |
| C | 1.8472 | -7.6280 | -1.0028 |
| C | 0.5786 | -8.3277 | 0.9327 |
| C | 2.5290 | -8.8434 | -0.9980 |
| H | 2.0652 | -6.8904 | -1.7803 |
| C | 1.2746 | -9.5330 | 0.9467 |
| H | -0.1835 | -8.1338 | 1.6908 |
|    |     |       |       |
|----|-----|-------|-------|
| C  | 2.2420 | -9.7993 | -0.0238 |
| H  | 3.2779 | -9.0529 | -1.7655 |
| H  | 1.0522 | -10.2761 | 1.7161 |
| H  | 2.7723 | -10.7540 | -0.0222 |
| C  | 7.1986 | 1.6596  | -0.2133 |
| C  | 7.8935 | 2.4787  | -1.1181 |
| C  | 7.8715 | 0.5700  | 0.3633  |
| C  | 9.2109 | 2.1904  | -1.4613 |
| H  | 7.3898 | 3.3300  | -1.5798 |
| C  | 9.1955 | 0.2944  | 0.0330  |
| H  | 7.3555 | -0.0586 | 1.0938  |
| C  | 9.8642 | 1.0969  | -0.8914 |
| H  | 9.7311 | 2.8232  | -2.1839 |
| H  | 9.7104 | -0.5471 | 0.5018  |
| H  | 10.8947 | 0.8672  | -1.1716 |
| C  | -6.7906 | 2.9624  | 0.1415  |
| C  | -7.3735 | 3.9029  | 1.0075  |
| C  | -7.6232 | 2.0335  | -0.5038 |
| C  | -8.7463 | 3.8978  | 1.2367  |
| H  | -6.7447 | 4.6304  | 1.5239  |
| C  | -8.9992 | 2.0415  | -0.2868 |
| H  | -7.1925 | 1.3129  | -1.2046 |
| C  | -9.5618 | 2.9686  | 0.5906  |
| H  | -9.1847 | 4.6230  | 1.9263  |
| H  | -9.6375 | 1.3263  | -0.8100 |
| H  | -10.6393 | 2.9677  | 0.7726  |
Table S14. Displacements for model system PBE0 RIJCOSX Def2-TZVP ($Q = 0$, $S = 1$).

| Atom | $X$ / Å | $Y$ / Å | $Z$ / Å |
|------|--------|--------|--------|
| Ti   | -0.0001| 3.4757 | 1.9985 |
| N    | -0.0002| 1.4213 | 2.3664 |
| N    | -0.0003| 2.7814 | 0.0548 |
| C    | -0.0007| 0.7164 | 3.5509 |
| C    | -0.0003| 0.7031 | 1.2217 |
| C    | 0.0003 | 3.4513 | -1.1550|
| C    | -0.0001| 1.4199 | -0.0048|
| C    | -0.0006| 1.3985 | 4.7814 |
| C    | -0.0008| -0.7163| 3.5510 |
| C    | -0.0002| -0.7031| 1.2217 |
| C    | 0.0004 | 4.8549 | -1.1895|
| C    | 0.0002 | 2.7348 | -2.3922|
| C    | 0.0002 | 0.7228 | -1.2154|
| H    | -0.0001| 2.4916 | 4.7789 |
| C    | -0.0010| 0.7027 | 5.9757 |
| N    | 0.0001 | -1.4212| 2.3665 |
| C    | -0.0009| -1.3983| 4.7814 |
| C    | 0.0001 | -1.4199| -0.0048|
| H    | -0.0001| 5.4062 | -0.2456|
| C    | 0.0005 | 5.5378 | -2.3953|
| N    | 0.0000 | 1.3466 | -2.4068|
| C    | 0.0003 | 3.4482 | -3.5999|
| C    | 0.0002 | -0.7228| -1.2154|
| C    | -0.0008| -0.7024| 5.9757 |
| Ti   | 0.0000 | -3.4759| 1.9985 |
| H    | -0.0004| -2.4914| 4.7791 |
| N    | 0.0002 | -2.7813| 0.0548 |
| C    | 0.0006 | 4.8338 | -3.6065|
| Ti   | 0.0000 | 0.0000 | -3.9911|
| H    | -0.0001| 2.8935 | -4.5421|
| N    | -0.0002| -1.3466| -2.4069|
| C    | 0.0003 | -3.4513| -1.1550|
| C    | 0.0001 | -2.7348| -2.3922|
| C    | 0.0002 | -4.8548| -1.1894|
| C    | 0.0004 | -3.4482| -3.5999|
| H    | 0.0003 | -5.4061| -0.2454|
| H    | 0.0006 | -2.8936| -4.5421|
| C    | 0.0004 | -4.8339| -3.6064|
| H    | -0.0006| 1.2496 | 6.9207 |
| H    | -0.0004| -1.2493| 6.9208 |
| H    | 0.0001 | 6.6298 | -2.3965|
| H    | 0.0003 | 5.3723 | -4.5561|
| H    | 0.0007 | -5.3725| -4.5560|
| H    | 0.0006 | -6.6298| -2.3963|
|   |      |      |      |
|---|------|------|------|
| C | 0.0004 | -5.5378 | -2.3952 |
| Cl | -1.9417 | 0.0002 | -5.0555 |
| Cl | 1.9417 | -0.0001 | -5.0556 |
| Cl | -1.9429 | 4.3929 | 2.5540 |
| Cl | 1.9430 | 4.3927 | 2.5533 |
| Cl | -1.9432 | -4.3929 | 2.5537 |
| Cl | 1.9432 | -4.3933 | 2.5535 |
Table S15. Displacements for fully symmetrized model system used for CAS(12,13). PBE0 RIJCOSX Def2-TZVP ($Q = 0, S = 1$).

| Atom | $X$ / Å | $Y$ / Å | $Z$ / Å |
|------|---------|---------|---------|
| Ti   | 0.0000  | 3.4758  | 1.9936  |
| N    | 0.0000  | 1.4212  | 2.3616  |
| N    | 0.0000  | 2.7814  | 0.0500  |
| C    | 0.0000  | 0.7163  | 3.5461  |
| C    | 0.0000  | 0.7031  | 1.2169  |
| C    | 0.0000  | 3.4513  | -1.1598 |
| C    | 0.0000  | 1.4199  | -0.0096 |
| C    | 0.0000  | 1.3984  | 4.7766  |
| C    | 0.0000  | -0.7163 | 3.5461  |
| C    | 0.0000  | -0.7031 | 1.2169  |
| C    | 0.0000  | 4.8548  | -1.1943 |
| C    | 0.0000  | 2.7348  | -2.3970 |
| C    | 0.0000  | 0.7228  | -1.2203 |
| H    | 0.0000  | 2.4915  | 4.7742  |
| C    | 0.0000  | 0.7025  | 5.9709  |
| N    | 0.0000  | -1.4212 | 2.3616  |
| C    | 0.0000  | -1.3984 | 4.7766  |
| C    | 0.0000  | -1.4199 | -0.0096 |
| H    | 0.0000  | 5.4062  | -0.2503 |
| C    | 0.0000  | 5.5378  | -2.4001 |
| N    | 0.0000  | 1.3466  | -2.4117 |
| C    | 0.0000  | 3.4482  | -3.6047 |
| C    | 0.0000  | -0.7228 | -1.2203 |
| C    | 0.0000  | -0.7025 | 5.9709  |
| Ti   | 0.0000  | -3.4758 | 1.9936  |
| H    | 0.0000  | -2.4915 | 4.7742  |
| N    | 0.0000  | -2.7814 | 0.0500  |
| C    | 0.0000  | 4.8339  | -3.6113 |
| Ti   | 0.0000  | 0.0000  | -3.9959 |
| H    | 0.0000  | 2.8936  | -4.5469 |
| N    | 0.0000  | -1.3466 | -2.4117 |
| C    | 0.0000  | -3.4513 | -1.1598 |
| C    | 0.0000  | -2.7348 | -2.3970 |
| C    | 0.0000  | -4.8548 | -1.1943 |
| C    | 0.0000  | -3.4482 | -3.6047 |
| H    | 0.0000  | -5.4062 | -0.2503 |
| H    | 0.0000  | -2.8936 | -4.5469 |
| C    | 0.0000  | -4.8339 | -3.6113 |
| H    | 0.0000  | 1.2494  | 6.9159  |
| H    | 0.0000  | -1.2494 | 6.9159  |
| H    | 0.0000  | 6.6298  | -2.4013 |
| H    | 0.0000  | 5.3724  | -4.5609 |
| H    | 0.0000  | -5.3724 | -4.5609 |
| H    | 0.0000  | -6.6298 | -2.4013 |
| Element | X Coord  | Y Coord  | Z Coord  |
|---------|----------|----------|----------|
| C       | 0.0000   | -5.5378  | -2.4001  |
| Cl      | -1.9417  | 0.0000   | -5.0604  |
| Cl      | 1.9417   | 0.0000   | -5.0604  |
| Cl      | -1.9431  | 4.3930   | 2.5488   |
| Cl      | 1.9431   | 4.3930   | 2.5488   |
| Cl      | -1.9431  | -4.3930  | 2.5488   |
| Cl      | 1.9431   | -4.3930  | 2.5488   |
SI-5 Weighting of configuration state functions for each state involved in electronic excitation and occupation.

Table S16. All CAS(6,7) states involved in NIR electronic excitation with all configuration state functions and their occupation (7 orbitals, \(Q = 0, S = 1\)). The specific state is labeled similar to the specific root in the calculation.

| State | Configuration state function weighting | Occupation | Energy [a.u.] |
|-------|----------------------------------------|------------|---------------|
| 0     | 0.2796                                 | 2210100    | -6546.0132    |
|       | 0.2794                                 | 2012100    |               |
|       | 0.2015                                 | 2111100    |               |
|       | 0.0377                                 | 0210120    |               |
|       | 0.0377                                 | 0012120    |               |
|       | 0.0328                                 | 1210110    |               |
|       | 0.0327                                 | 1012110    |               |
|       | 0.0272                                 | 0111120    |               |
|       | 0.0237                                 | 1111110    |               |
|       | 0.0079                                 | 2120100    |               |
|       | 0.0079                                 | 2102100    |               |
|       | 0.0071                                 | 2021100    |               |
|       | 0.0071                                 | 2201100    |               |
|       | 0.0026                                 | 1210011    |               |
|       | 0.0025                                 | 1012011    |               |
| 1     | 0.1910                                 | 2120100    | -6546.0131    |
|       | 0.1908                                 | 2102100    |               |
|       | 0.1816                                 | 2021100    |               |
|       | 0.1815                                 | 2201100    |               |
|       | 0.0256                                 | 0120120    |               |
|       | 0.0256                                 | 0102120    |               |
|       | 0.0244                                 | 0021120    |               |
|       | 0.0244                                 | 0201120    |               |
|       | 0.0243                                 | 2111100    |               |
|       | 0.0222                                 | 1120110    |               |
|       | 0.0222                                 | 1102110    |               |
|       | 0.0211                                 | 1021110    |               |
|       | 0.0211                                 | 1201110    |               |
|       | 0.0106                                 | 2210100    |               |
|       | 0.0106                                 | 2012100    |               |
|       | 0.0038                                 | 1111110    |               |
|       | 0.0033                                 | 0111120    |               |
| 12    | 0.13265                                | 1120110    | -6545.9205    |
|       | 0.13248                                | 1102110    |               |
|       | 0.12657                                | 1021110    |               |
|       | 0.12654                                | 1201110    |               |
|       | 0.07738                                | 1210110    |               |
|       | 0.0773                                 | 1012110    |               |
| 0.06968        | 1111110 |
| 0.02086        | 212001  |
| 0.02082        | 2102001 |
| 0.0199         | 2021001 |
| 0.01989        | 2201001 |
| 0.0146         | 2120100 |
| 0.01458        | 2102100 |
| 0.01394        | 2021100 |
| 0.01393        | 2201100 |
| 0.01217        | 2210001 |
| 0.01215        | 2012001 |
| 0.01097        | 2111001 |
| 0.00853        | 2210100 |
| 0.00852        | 2021001 |
| 0.00721        | 2111100 |
| 0.0045         | 1120011 |
| 0.00449        | 1102011 |
| 0.00429        | 1021011 |
| 0.00429        | 1201011 |
| 0.00374        | 0120120 |
| 0.00373        | 0102120 |
| 0.00357        | 0021120 |
| 0.00357        | 0201120 |
| 0.00263        | 1210011 |
| 0.00262        | 1012011 |
| **18** 0.12885 | 1120110 | -6545.8660 |
| 0.12868        | 1102110 |
| 0.12293        | 1021110 |
| 0.1229         | 1201110 |
| 0.0763         | 1111110 |
| 0.06998        | 1210110 |
| 0.0699         | 1012110 |
| 0.0174         | 0120120 |
| 0.01737        | 0102120 |
| 0.0166         | 0021120 |
| 0.0166         | 0201120 |
| 0.01177        | 0120201 |
| 0.01175        | 0102201 |
| 0.01123        | 0021201 |
| 0.01122        | 0201201 |
| 0.01045        | 0111120 |
| 0.00942        | 0210120 |
| 0.00941        | 0012120 |
| 0.00871        | 1120011 |
| 0.00869        | 1102011 |
| 0.00831        | 1021011 |
| 0.0083         | 1201011 |
|   |   |   |
|---|---|---|
| 0.00702 | 0111201 |
| 0.00639 | 0210201 |
| 0.00638 | 0012201 |
| 0.00538 | 0120021 |
| 0.00537 | 0102021 |
| 0.00528 | 1111011 |
| 0.00513 | 0021021 |
| 0.00513 | 0201021 |
| 0.00474 | 1210011 |
| 0.00473 | 1012011 |
| 0.00343 | 1111020 |
| 0.00324 | 0111021 |
| 0.00322 | 1120020 |
| 0.00321 | 1102020 |
| 0.00307 | 1021020 |
| 0.00307 | 1201020 |
| 0.00292 | 0210021 |
| 0.00292 | 0012021 |
| 0.10338 | 0210120 | -6545.8185 |
| 0.10327 | 0012120 |
| 0.08669 | 0120120 |
| 0.08657 | 0102120 |
| 0.08291 | 0021120 |
| 0.0829  | 0201120 |
| 0.06153 | 0111120 |
| 0.03671 | 1210110 |
| 0.03667 | 1012110 |
| 0.03068 | 1120110 |
| 0.03064 | 1102110 |
| 0.02934 | 1021110 |
| 0.02933 | 1201110 |
| 0.02191 | 1111110 |
| 0.01524 | 1210011 |
| 0.01523 | 1012011 |
| 0.01271 | 1120011 |
| 0.01269 | 1102011 |
| 0.01216 | 1021011 |
| 0.01215 | 1201011 |
| 0.0121  | 2210100 |
| 0.01208 | 2012100 |
| 0.01016 | 2120100 |
| 0.01015 | 2102100 |
| 0.00972 | 2021100 |
| 0.00972 | 2201100 |
| 0.00904 | 1111011 |
| 0.00721 | 2111100 |
| 0.10848 | 2120001 | -6545.7919 |
| Decimal | Binary  |
|---------|---------|
| 0.10832 | 2102001 |
| 0.1036  | 2021001 |
| 0.10357 | 2201001 |
| 0.08631 | 2210001 |
| 0.08621 | 2012001 |
| 0.06256 | 2111001 |
| 0.01692 | 1120110 |
| 0.0169  | 1102110 |
| 0.01617 | 1021110 |
| 0.01616 | 1201110 |
| 0.01424 | 0120201 |
| 0.01421 | 0102201 |
| 0.0136  | 0021201 |
| 0.01359 | 0201201 |
| 0.01345 | 1210110 |
| 0.01344 | 1012110 |
| 0.01132 | 0210201 |
| 0.01131 | 0012201 |
| 0.0099  | 1111110 |
| 0.00823 | 0111201 |
| 0.00774 | 0120021 |
| 0.00773 | 0102021 |
| 0.00739 | 0021021 |
| 0.00739 | 0201021 |
| 0.00647 | 0120120 |
| 0.00646 | 0102120 |
| 0.00618 | 0021120 |
| 0.00618 | 0201120 |
| 0.00616 | 0210021 |
| 0.00615 | 0012021 |
| 0.00545 | 2120100 |
| 0.00544 | 2102100 |
| 0.00521 | 2201100 |
| 0.00521 | 2021100 |
| 0.00518 | 0210120 |
| 0.00517 | 0012120 |
| 0.00454 | 1120011 |
| 0.00453 | 1102011 |
| 0.00448 | 0111021 |
| 0.00434 | 1021011 |
| 0.00433 | 2210100 |
| 0.00433 | 2012100 |
| 0.00433 | 1201011 |
| 0.00361 | 0111120 |
| 0.00355 | 1210011 |
| 0.00355 | 1012011 |
| 0.00316 | 1111011 |
Table S17. Oscillator strength and transition dipole moments of electronic excitations within CAS(6,7)/NEVPT2 (Q=0, S=1).

| Transition (state0→stateX) | Fosc    | T[^2] [a.u.][^2] |
|---------------------------|---------|-----------------|
| 0→12                      | 0.00388 | 2.36            |
| 0→18                      | 0.05615 | 19.86           |
| 0→27                      | 0.04477 | 9.21            |
| 0→30                      | 0.09020 | 14.35           |

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