Electronic Supplementary Material (ESI) for Dalton Transactions


# Supporrting Inforrmation

# Stabilization of Oxidovanadium(IV) by Organic Radicals

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**Chart S2** Isolated $[(L_1^{R-})(VO^{2+})(L^{R'}{}_{IS}^{\bullet-})]$ complexes.

$[(L_1^{H-})(VO^{2+})(L^{H}{}_{IS}^{\bullet-})]$ **1**

$[(L_1^{H-})(VO^{2+})(L^{t\text{-}Bu}{}_{IS}^{\bullet-})]$ **2**

$[(L_1^{t\text{-}Bu-})(VO^{2+})(L^{H}{}_{IS}^{\bullet-})]$ **3**

$[(L_1^{t\text{-}Bu-})(VO^{2+})(L^{t\text{-}Bu}{}_{IS}^{\bullet-})]$ **4**

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**Chart S3** Electronic states of the de-protonated $L^{R'}H_2$ coordinated to oxidovanadium (IV/V) ions.

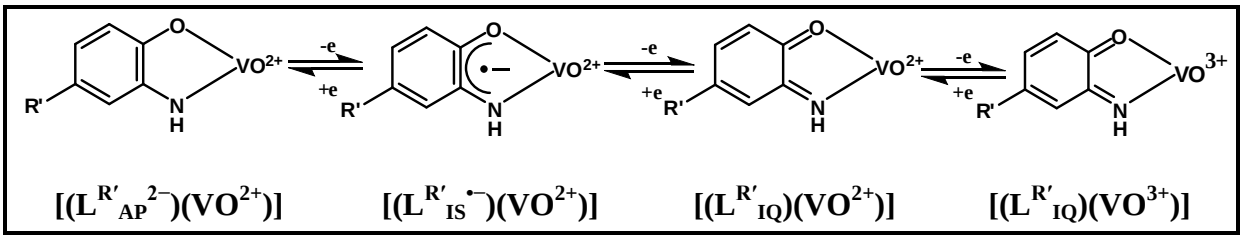
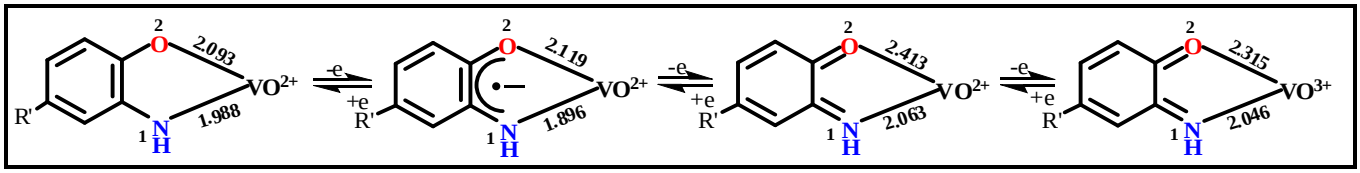
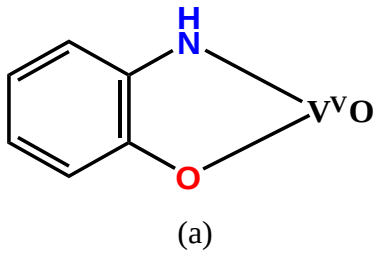
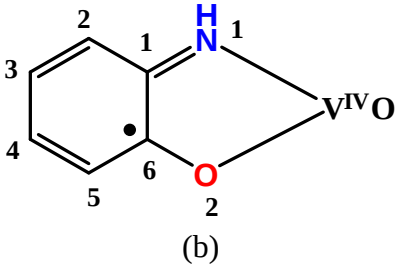



**Chart S4** Calculated average V(1)−N(1) and V(1)−O(2) lengths (Å) of **1** and **2** and their redox series.





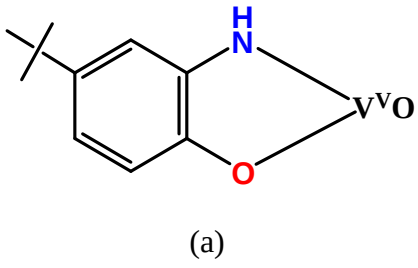

(a)



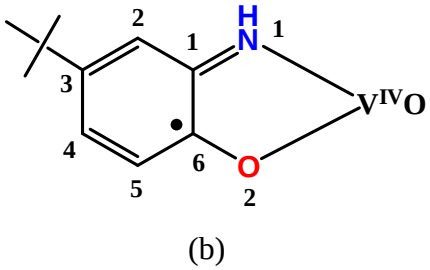

(b)

| | Exp. | Calc. |
|---|---|---|
| N1-C1 | 1.3634(17) | 1.364 |
| C1-C2 | 1.399(3) | 1.409 |
| C2-C3 | 1.360(4) | 1.387 |
| C3-C4 | 1.394(4) | 1.413 |
| C4-C5 | 1.374(4) | 1.387 |
| C5-C6 | 1.392(3) | 1.415 |
| C6-C1 | 1.421(3) | 1.436 |
| O2-C6 | 1.3098(15) | 1.297 |

**Fig. S1** (a) $L^{H}{}_{AP}{}^{2-}$ coordination to $[VO]^{3+}$ ion (Type I state) (b) $L^{H}{}_{IS}{}^{\bullet-}$ coordination to $[VO]^{2+}$ ion (Type III state). Experimental and calculated (in parentheses) bond lengths (Å) of the fragment respectively in **1** and BS(1,1) $M_s = 0$ state of **1**.




(a)




(b)

| | Exp. | Calc. |
|---|---|---|
| N1-C1 | 1.357(3) | 1.363 |
| C1-C2 | 1.403(3) | 1.410 |
| C2-C3 | 1.382(4) | 1.390 |
| C3-C4 | 1.407(4) | 1.424 |
| C4-C5 | 1.373(4) | 1.384 |
| C5-C6 | 1.381(4) | 1.415 |
| C6-C1 | 1.422(3) | 1.432 |
| O2-C6 | 1.311(3) | 1.296 |

**Fig. S2** (a) $L^{t\text{-}Bu}{}_{AP}{}^{2-}$ coordinated to $[VO]^{3+}$ (Type I coordination) (b) $L^{t\text{-}Bu}{}_{IS}{}^{\bullet-}$ coordinated to $[VO]^{2+}$ (Type III coordination). Experimental and calculated bond lengths (Å) of the fragment, respectively, in **2** and BS(1,1) $M_s = 0$ state of **2**.

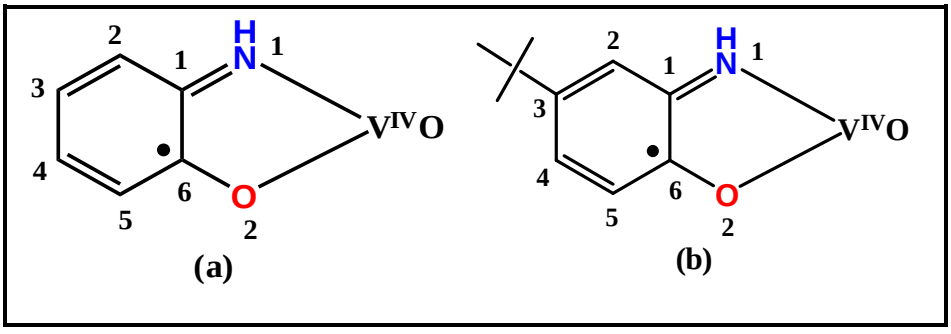
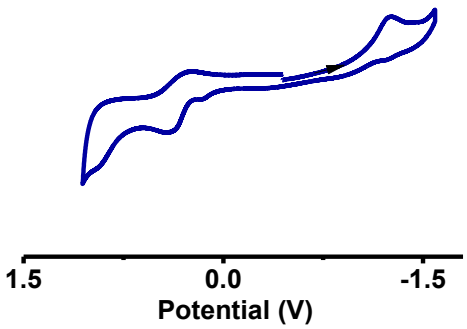
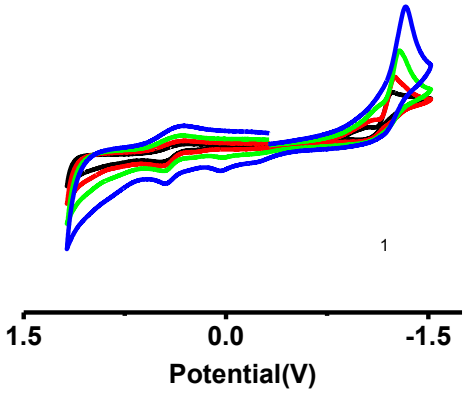


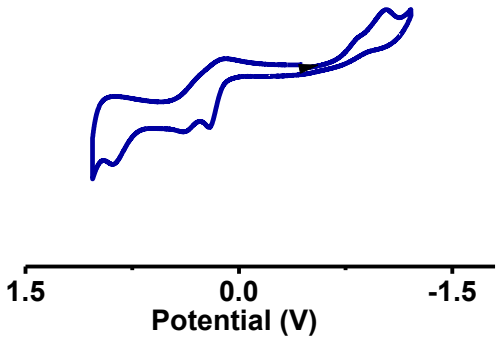

**Fig. S3** (a) Coordination of $L^{H}{}_{IS}{}^{\bullet-}$ to $[VO]^{2+}$ (Type III state) in **3** (bond lengths of the NO-chelate: C(1)−N(1), 1.358(4); C(6)−O(2), 1.314(4); C(1)−C(6), 1.418(5) Å) and (b) Coordination of $L^{t\text{-}Bu}{}_{IS}{}^{\bullet-}$ to $[VO]^{2+}$ (Type III state) in **4** (bond lengths of the NO-chelate: C(1)−N(1), 1.359(3); C(6)−O(2), 1.312(3); C(1)−C(6), 1.412(3) Å).



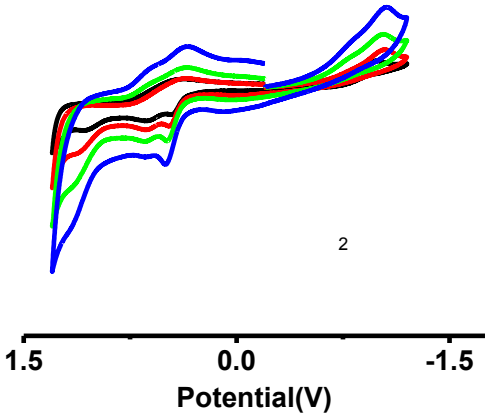

Cyclic voltammogram of **1** in $CH_2Cl_2$ at 298 K. Conditions: 0.2 M $[N(n\text{-}Bu)_4]PF_6$ supporting electrolyte; scan rate, 100 mv $s^{-1}$; platinum working electrode.



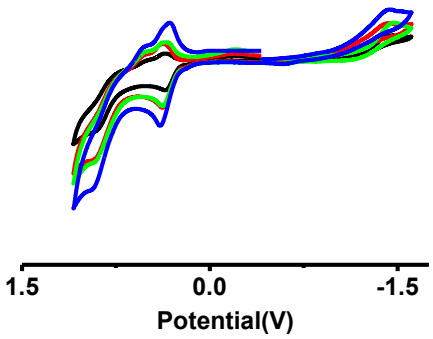

Cyclic voltammograms of **1** in $CH_2Cl_2$ at 298 K. Conditions: 0.2 M $[N(n\text{-}Bu)_4]PF_6$ supporting electrolyte; scan rate, 50, 100, 200, 400 mv $s^{-1}$; platinum working electrode.



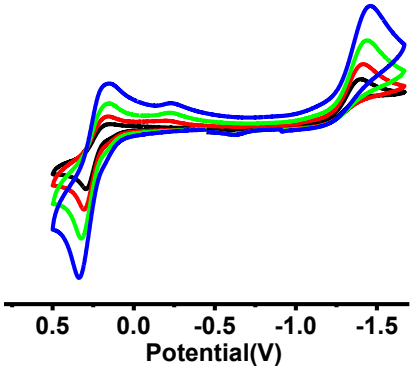

Cyclic voltammogram of **2** in $CH_2Cl_2$ at 298 K. Conditions: 0.2 M $[N(n\text{-}Bu)_4]PF_6$ supporting electrolyte; scan rate, 100 mv $s^{-1}$; platinum working electrode.



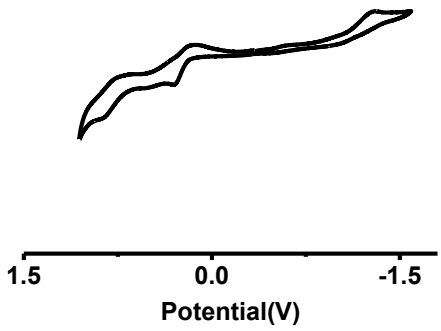

Cyclic voltammograms of **2** in $CH_2Cl_2$ at 298 K. Conditions: 0.2 M $[N(n\text{-}Bu)_4]PF_6$ supporting electrolyte; scan rate, 50, 100, 200, 400 mv $s^{-1}$; platinum working electrode.



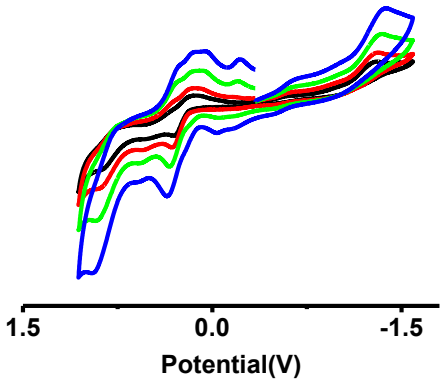

Cyclic voltammograms of **3** in $CH_2Cl_2$ at 298 K. Conditions: 0.2 M $[N(n\text{-}Bu)_4]PF_6$ supporting electrolyte; scan rate, 50, 100, 200, 400 mv $s^{-1}$; platinum working electrode.




Cyclic voltammograms of **3** in $CH_2Cl_2$ at 298 K. Conditions: 0.2 M $[N(n\text{-}Bu)_4]PF_6$ supporting electrolyte; scan rate, 50, 100, 200, 400 mv $s^{-1}$ at first oxidation; platinum working electrode.




Cyclic voltammogram of **4** in $CH_2Cl_2$ at 298 K. Conditions: 0.2 M $[N(n\text{-}Bu)_4]PF_6$ supporting electrolyte; scan rate, 100 mv $s^{-1}$; platinum working electrode.




Cyclic voltammograms of **4** in $CH_2Cl_2$ at 298 K. Conditions: 0.2 M $[N(n\text{-}Bu)_4]PF_6$ supporting electrolyte; scan rate, 50, 100, 200, 400 mv $s^{-1}$; platinum working electrode.

**Fig. S4** Cyclic voltammograms of **1**-**4** complexes in $CH_2Cl_2$ at 298 K.

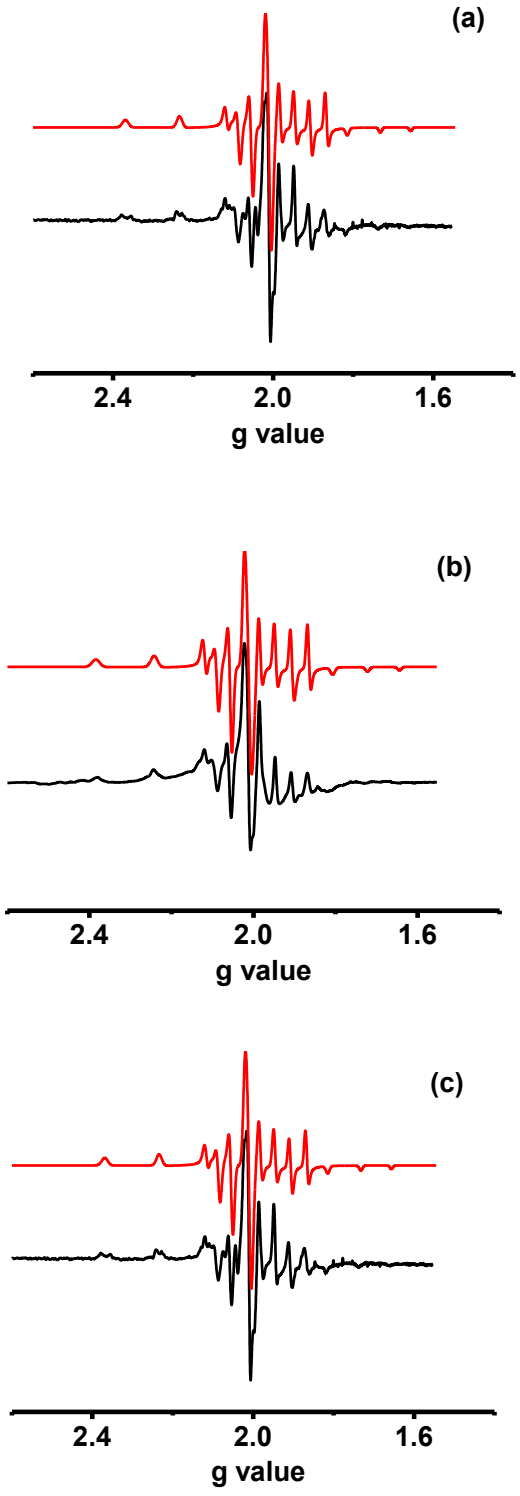



**Fig. S5** X-band EPR spectra of the frozen $CH_2Cl_2$ glasses of (a) $[\mathbf{1}]^+$, (b) $[\mathbf{2}]^+$ and (c) $[\mathbf{3}]^+$ at 78 K (black, experimental; red, simulated).

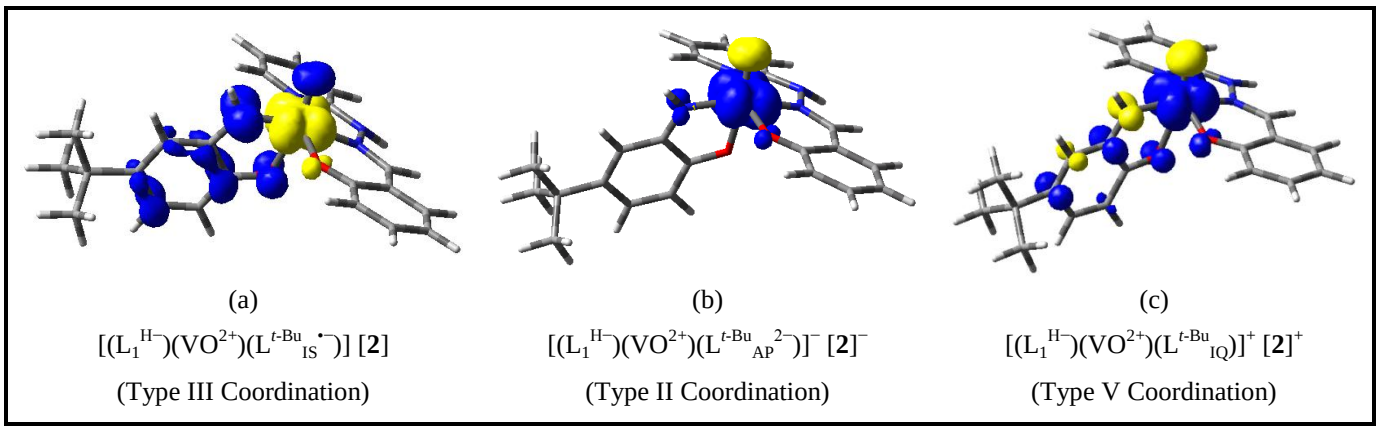



**Fig. S6** Spin density plot of **2**, $[\mathbf{2}]^-$ and $[\mathbf{2}]^+$ **(**blue, α spin; yellow, β spin) and values from Mulliken spin population analyses (spin density, **2:** V -0.77, N1 0.27, O1 0.11, O2 0.12, O3 -0.02, C4 0.11, C6 0.10; $[\mathbf{2}]^-$**:** V 1.05, O1 -0.13, O3 0.02, N1 0.04, C2 0.03; $[\mathbf{2}]^+$**:** V 1.00, O1 -0.15, O2 0.06, O3 0.03, N1 -0.10, C1 0.10, C2 -0.07, C3 0.10, C4 -0.03, C5 0.04).

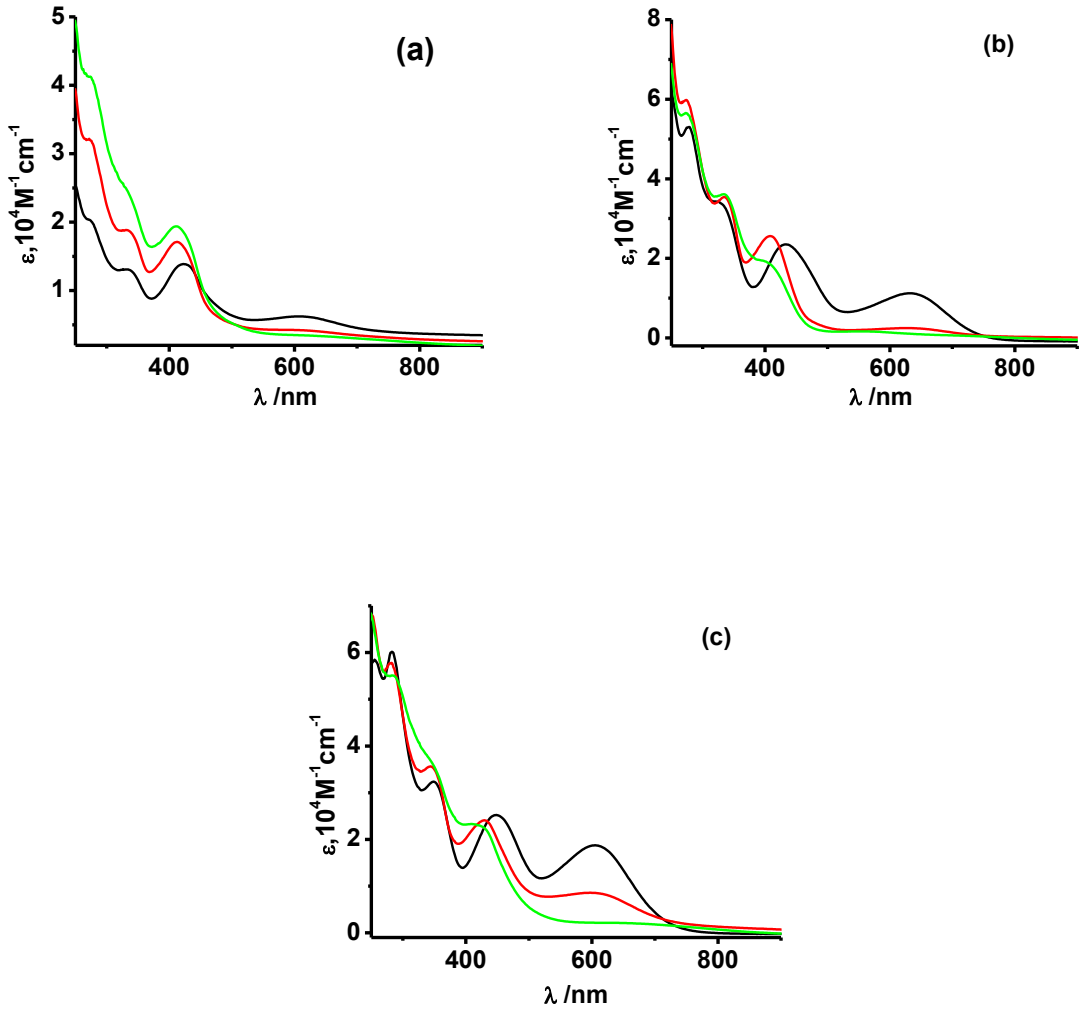



**Fig. S7** Electronic absorption spectra of (a) electrogenerated $[\mathbf{1}]^{2+}$ (green), $[\mathbf{1}]^+$ (red) ions and **1** (black), (b) electrogenerated $[\mathbf{2}]^{2+}$ (green), $[\mathbf{2}]^+$ (red) ions and **2** (black), (c) electrogenerated $[\mathbf{3}]^{2+}$ (green), $[\mathbf{3}]^+$ (red) ions and **3** (black) in $CH_2Cl_2$ at 298 K.

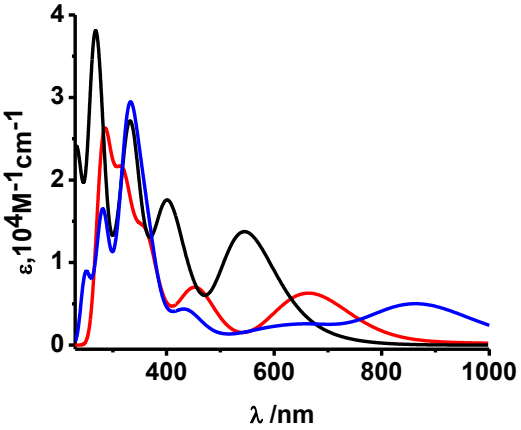



**Fig. S8** Electronic absorption spectra of **2** (black), $[\mathbf{2}]^{+}$ (red) and $[\mathbf{2}]^{2+}$ (blue) obtained from TD-DFT calculations in $CH_2Cl_2$.

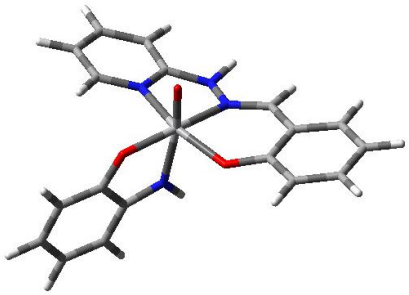


**Fig. S9** Gas phase optimised geometry of $\mathbf{1}^{t\text{-NH}}$.

**Table S1** Selected experimental bond lengths (Å) and angles (°) of **2** and calculated bond parameters of **2**, $[\mathbf{2}]^{+}$, $[\mathbf{2}]^{2+}$ and $[\mathbf{2}]^{-}$ using B3LYP, B3PW91, and PBE1PBE functionals

| | Exp. | Calc. | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | **2** | | | | $[\mathbf{2}]^{+}$ | $[\mathbf{2}]^{2+}$ | $[\mathbf{2}]^{-}$ |
| | **2** | BS(1,1) $M_s = 0^a$ | BS(1,1) $M_s = 0^b$ | BS(1,1) $M_s = 0^c$ | $M_s = 1^a$ | $M_s = 1/2^a$ | $M_s = 0^a$ | $M_s = 1/2^a$ |
| V(1)-O(1) | 1.5968(18) | 1.599 | 1.594 | 1.588 | 1.598 | 1.582 | 1.567 | 1.621 |
| V(1)-O(2) | 2.1505(17) | 2.122 | 2.096 | 2.089 | 2.240 | 2.420 | 2.327 | 2.096 |
| V(1)-O(3) | 1.9244(17) | 1.912 | 1.899 | 1.894 | 1.927 | 1.886 | 1.778 | 1.995 |
| V(1)-N(1) | 1.924(2) | 1.897 | 1.884 | 1.876 | 2.075 | 2.068 | 2.034 | 1.989 |
| V(1)-N(2) | 2.118(2) | 2.144 | 2.126 | 2.119 | 2.181 | 2.133 | 2.100 | 2.222 |
| V(1)-N(4) | 2.1126(18) | 2.156 | 2.144 | 2.138 | 2.095 | 2.083 | 2.097 | 2.139 |
| O(2)-C(6) | 1.311(3) | 1.296 | 1.294 | 1.292 | 1.279 | 1.237 | 1.239 | 1.318 |
| N(1)-C(1) | 1.357(3) | 1.363 | 1.362 | 1.360 | 1.333 | 1.301 | 1.308 | 1.369 |
| O(3)-C(22) | 1.324(3) | 1.303 | 1.299 | 1.297 | 1.304 | 1.321 | 1.329 | 1.287 |
| C(1)-C(2) | 1.403(3) | 1.410 | 1.407 | 1.405 | 1.425 | 1.438 | 1.422 | 1.405 |
| C(2)-C(3) | 1.382(4) | 1.390 | 1.3899 | 1.388 | 1.382 | 1.365 | 1.374 | 1.409 |
| C(3)-C(4) | 1.407(4) | 1.424 | 1.419 | 1.417 | 1.436 | 1.473 | 1.483 | 1.404 |
| C(4)-C(5) | 1.373(4) | 1.384 | 1.384 | 1.382 | 1.377 | 1.355 | 1.354 | 1.403 |
| C(5)-C(6) | 1.381(4) | 1.415 | 1.411 | 1.410 | 1.424 | 1.449 | 1.444 | 1.401 |
| C(6)-C(1) | 1.422(3) | 1.432 | 1.428 | 1.425 | 1.467 | 1.512 | 1.519 | 1.437 |
| N(3)-N(4) | 1.376(3) | 1.377 | 1.366 | 1.362 | 1.380 | 1.377 | 1.372 | 1.381 |
| O(1)-V(1)-O(2) | 168.65(8) | 166.76 | 166.60 | 166.75 | 166.97 | 164.31 | 163.07 | 167.85 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| O(1)-V(1)-N(1) | 95.86(9) | 92.85 | 92.44 | 92.54 | 98.33 | 94.89 | 93.14 | 100.06 |
| O(2)-V(1)-N(1) | 75.86(8) | 76.55 | 76.80 | 76.97 | 74.48 | 70.76 | 72.09 | 77.32 |
| O(1)-V(1)-O(3) | 101.93(9) | 101.73 | 101.47 | 101.57 | 104.06 | 106.57 | 102.90 | 100.09 |
| [a] B3LYP. [b] B3PW91. [c] PBE1PBE. | | | | | | | | |

**Table S2** Selected experimental bond lengths (Å) and angles (deg) of **3** and **4**

| | **3** | **4** | | **3** | **4** |
|---|---|---|---|---|---|
| V(1)-O(1) | 1.601(3) | 1.5985(17) | C(2)-C(3) | 1.357(6) | 1.367(4) |
| V(1)-O(2) | 2.167(3) | 2.1532(17) | C(3)-C(4) | 1.388(6) | 1.410(4) |
| V(1)-O(3) | 1.905(3) | 1.9257(17) | C(4)-C(5) | 1.392(6) | 1.372(4) |
| V(1)-N(1) | 1.906(3) | 1.913(2) | C(5)-C(6) | 1.391(5) | 1.391(3) |
| V(1)-N(2) | 2.128(3) | 2.143(3) | C(6)-C(1) | 1.418(5) | 1.412(3) |
| V(1)-N(4) | 2.096(3) | 2.0992(19) | N(3)-N(4) | 1.373(4) | 1.379(2) |
| O(2)-C(6) | 1.314(4) | 1.312(3) | O(1)-V(1)-O(2) | 170.54(11) | 167.87(8) |
| N(1)-C(1) | 1.358(4) | 1.359(3) | O(1)-V(1)-N(1) | 95.07(14) | 92.19(9) |
| O(3)-C(18/22) | 1.322(4) | 1.319(3) | O(2)-V(1)-N(1) | 75.79(12) | 75.71(7) |
| C(1)-C(2) | 1.401(5) | 1.406(3) | O(1)-V(1)-O(3) | 102.65(13) | 99.77(9) |

**Table S3** Excitation energies (λ/nm), oscillator strengths (f), transition types and dominant contributions of UV-vis/NIR absorption bands of **1**, **2**, [**1**]$^{+}$, [**2**]$^{+}$, [**1**]$^{2+}$ and [**2**]$^{2+}$ obtained from TD-DFT calculations

| $\lambda_{cal}$ | f | $\lambda_{exp}$ | Significant Transitions (>10%) | Dominant Contributions |
|---|---|---|---|---|
| **1** (corresponds to experimental data of **1**-**4** complexes, Table 2) | | | | |
| 662 | 0.012 | | $H_{[AP(67)+dV(25)]} \rightarrow L+1_{[L1(23)+dV(75)]}$ (60)<br>$H_{[AP(67)+dV(25)]} \rightarrow L_{[AP(40)+dV(51)]}$ (15) | LMCT<br>CSS-OSS CT |
| 583 | 0.05 | 608 | $H_{[AP(67)+dV(25)]} \rightarrow L+2_{[dV(80)+L1(18)]}$ (52)<br>$H_{[AP(67)+dV(25)]} \rightarrow L_{[AP(40)+dV(51)]}$ (23) | LMCT<br>CSS-OSS CT |
| 545 | 0.03 | | $H-1_{[L1(93)]} \rightarrow L_{[AP(40)+dV(51)]}$ (23)<br>$H_{[AP(67)+dV(25)]} \rightarrow L+2_{[dV(80)+L1(18)]}$ (19) | LMCT+LLCT<br>LMCT |
| 518 | 0.12 | | $H-1_{[L1(93)]} \rightarrow L_{[AP(40)+dV(51)]}$ (37)<br>$H_{[AP(67)+dV(25)]} \rightarrow L_{[AP(40)+dV(51)]}$ (18)<br>$H_{[AP(67)+dV(25)]} \rightarrow L+2_{[dV(80)+L1(18)]}$ (18) | LMCT+LLCT<br>LMCT<br>LMCT |
| 439 | 0.07 | 424 | $H-1_{[L1(93)]} \rightarrow L+1_{[L1(23)+dV(75)]}$ (82) | LMCT |
| 400 | 0.18 | | $H-2_{[AP(93)]} \rightarrow L_{[AP(40)+dV(51)]}$ (71) | LMCT |
| [**1**]$^{+}$ (corresponds to experimental data of [**1**-**4**]$^{+}$, Table 7) | | | | |
| 726 | 0.04 | | $\alpha\ H-1_{[L1(96)]} \rightarrow L_{[AP(83)+dV(15)]}$ (57)<br>$\alpha\ H-2_{[dV(72)]} \rightarrow L_{[AP(83)+dV(15)]}$ (18) | LLCT<br>MLCT |
| 686 | 0.04 | | $\alpha\ H-2_{[dV(72)]} \rightarrow L_{[AP(83)+dV(15)]}$ (49)<br>$\alpha\ H-1_{[L1(96)]} \rightarrow L_{[AP(83)+dV(15)]}$ (35) | MLCT<br>LLCT |

| | | | | |
|---|---|---|---|---|
| 635 | 0.02 | 610 | α H-2$_{[dV(72)]}$→ L+1$_{[dV(50)+L1(48)]}$ (49)<br>α H-2$_{[dV(72)]}$→ L+2$_{[dV(80)+L1(18)]}$ (18)<br>α H-2$_{[dV(72)]}$→ L+3$_{[L1(54)+dV(46)]}$ (12) | d-d<br>d-d<br>d-d |
| 487 | 0.02 | | α H-4$_{(AP(55)+L1(45))}$→L$_{[AP(83)+dV(15)]}$ (21)<br>α H-3$_{(AP(55)+L1(40))}$→L$_{[AP(83)+dV(15)]}$ (29)<br>β H-2$_{[AP(96)]}$→ L$_{[AP(92)]}$ (31) | ILCT+LLCT<br>ILCT+LLCT<br>ILCT |
| 455 | 0.07 | | α H$_{[L1(95)]}$→ L+1$_{[dV(50)+L1(48)]}$ (40)<br>β H$_{[L1(95)]}$→ L+1$_{[dV(50)+L1(48)]}$ (38) | LMCT+ILCT<br>LMCT+ILCT |
| 413 | 0.01 | 413 | α H$_{[L1(95)]}$→ L+2$_{[dV(80)+L1(18)]}$ (21)<br>β H-4$_{[L1(78)+dV(12)]}$→ L$_{[AP(92)]}$ (64) | LMCT<br>LLCT |
| [**1**]$^{2+}$ (corresponds to experimental data of [**1-4**]$^{2+}$, Table 7) | | | | |
| 856 | 0.09 | | H-1$_{[L1(87)]}$→ L$_{[AP(55)+dV(50)]}$ (78) | LLCT+LMCT |
| 679 | 0.01 | | H-2$_{[AP(98)]}$→ L$_{[AP(55)+dV(50)]}$ (82) | ILCT+LMCT |
| 595 | 0.03 | 640 | H-3$_{[L1(96)]}$→ L$_{[AP(55)+dV(50)]}$ (50)<br>H$_{[L1(92)]}$→ L+2$_{[dV(71)+ L1(25)]}$ (40) | LLCT+LMCT<br>LMCT+ILCT |
| 535 | 0.01 | | H-1$_{[L1(87)]}$→ L+1$_{[AP(45)+dV(50)]}$ (82) | LLCT+LMCT |
| 471 | 0.01 | | H-5$_{[AP(70)+L1(20)]}$→ L$_{[AP(55)+dV(50)]}$ (65)<br>H-4$_{[L1(93)]}$→ L$_{[AP(55)+dV(50)]}$ (25) | ILCT+LMCT<br>LLCT+LMCT |
| 446 | 0.03 | | H-1$_{[L1(87)]}$→ L+2$_{[dV(71)+ L1(25)]}$ (75) | LMCT+ILCT |
| 436 | 0.03 | | H-5$_{[AP(70)+L1(20)]}$→ L$_{[AP(55)+dV(50)]}$ (22)<br>H-4$_{[L1(93)]}$→ L$_{[AP(55)+dV(50)]}$ (62) | ILCT+LMCT<br>LLCT+LMCT |
| 424 | 0.04 | 410 | H-2$_{[AP(98)]}$→ L+1$_{[AP(45)+dV(50)]}$ (83) | ILCT+LMCT |
| **2** (corresponds to experimental data of **1-4** complexes, Table 2) | | | | |
| 597 | 0.06 | 634 | H$_{[AP(67)+dV(25)]}$→ L$_{[AP(41)+dV(50)]}$ (22)<br>H$_{[AP(67)+dV(25)]}$→ L+2$_{[dV(83)]}$ (56) | CSS-OSS CT<br>LMCT |
| 548 | 0.10 | | H$_{[AP(67)+dV(25)]}$→ L$_{[AP(41)+dV(50)]}$ (20)<br>H$_{[AP(67)+dV(25)]}$→ L+2$_{[dV(83)]}$ (24)<br>H-1$_{[L1(93)]}$→ L$_{[AP(41)+dV(50)]}$ (31) | CSS-OSS CT<br>LMCT<br>LMCT |
| 521 | 0.09 | | H-1$_{[L1(93)]}$→ L$_{[AP(41)+dV(50)]}$ (66) | LMCT |
| 436 | 0.07 | 440 | H-1$_{[L1(93)]}$→ L+1$_{[L1(76)+dV(22)]}$ (83) | LMCT |
| 401 | 0.17 | | H-2$_{[AP(93)]}$→ L$_{[AP(41)+dV(50)]}$ (62) | LMCT |
| [**2**]$^{+}$ (corresponds to experimental data of [**1-4**]$^{+}$, Table 7) | | | | |
| 698 | 0.04 | | α H-1$_{[L1(97)]}$→L$_{[AP(89)+dV(10)]}$ (54)<br>α H-2$_{[dV(70)]}$→L$_{[AP(89)+dV(10)]}$ (16) | LLCT<br>MLCT |
| 666 | 0.03 | 650 | α H-2$_{[dV(70)]}$→L$_{[AP(89)+dV(10)]}$ (32)<br>α H-2$_{[dV(70)]}$→L+1$_{[dV(43)+L1(56)]}$ (14)<br>α H-1$_{[L1(97)]}$→L$_{[AP(89)+dV(10)]}$ (39) | MLCT<br>MLCT+d-d<br>LLCT |
| 633 | 0.04 | | α H-2$_{[dV(70)]}$→L$_{[AP(89)+dV(10)]}$ (23)<br>α H-2$_{[dV(70)]}$→L+1$_{[dV(43)+L1(56)]}$ (36)<br>α H-2$_{[dV(70)]}$→L+2$_{[dV(80)]}$ (19) | MLCT<br>d-d +MLCT<br>d-d |

| | | | | |
|---|---|---|---|---|
| 488 | 0.02 | | α H-3$_{[AP(90)]}$→L$_{[AP(89)+dV(10)]}$ (52)<br>β H-2$_{[AP(99)]}$→L$_{[AP(93)]}$ (30) | ILCT<br>ILCT |
| 453 | 0.08 | | α H$_{[L1(95)]}$→ L+1$_{[dV(43)+L1(56)]}$ (40)<br>β H$_{[L1(93)]}$→ L+1$_{[dV(73)+L1(25)]}$ (38) | ILCT+LMCT<br>LMCT |
| [**2**]$^{2+}$ (corresponds to experimental data of [**1-4**]$^{2+}$, Table 7) | | | | |
| 867 | 0.10 | 743$^{sh}$ | H-1$_{[L1(89)]}$→ L$_{[AP(60)+dV(30)]}$ (80) | LLCT+LMCT |
| 678 | 0.04 | | H-2$_{[AP(92)]}$→ L$_{[AP(60)+dV(30)]}$ (79) | ILCT+LMCT |
| 593 | 0.03 | 562 | H-3$_{[L1(96)]}$→ L$_{[AP(60)+dV(30)]}$ (20)<br>H$_{[L1(93)]}$→ L+2$_{[dV(70)+ L1(30)]}$ (72) | LLCT+LMCT<br>LMCT+ILCT |
| 532 | 0.01 | | H-1$_{[L1(89)]}$→ L+1$_{[AP(44)+dV(50)]}$ (77) | LLCT+LMCT |
| 472 | 0.01 | | H-5$_{[AP(75)+L1(23)]}$→ L$_{[AP(60)+dV(30)]}$ (60)<br>H-4$_{[L1(60+AP(37)]}$→ L$_{[AP(55)+dV(50)]}$ (26) | ILCT+LMCT<br>ILCT+LMCT |
| 447 | 0.03 | | H-1$_{[L1(89)]}$→ L+2$_{[dV(70)+L1(30)]}$ (79) | LMCT+ILCT |
| 432 | 0.02 | | H-5$_{[AP(75)+L1(23)]}$→ L$_{[AP(60)+dV(30)]}$ (22)<br>H-4$_{[L1(60+AP(37)]}$→ L$_{[AP(55)+dV(50)]}$ (64) | ILCT+LMCT<br>ILCT+LMCT |
| 423 | 0.03 | 407 | H-2$_{[AP(92)]}$→ L+1$_{[AP(44)+dV(50)]}$ (82) | ILCT+LMCT |

**Table S4** Gas phase optimized coordinates of **1** using B3LYP functionals (S = 0)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 13.342145 | 11.592321 | 7.037984 | 21 | C13 | 14.945964 | 10.114102 | 9.770557 |
| 2 | O1 | 12.819804 | 10.300811 | 6.252653 | 22 | C14 | 15.606279 | 9.414847 | 10.809623 |
| 3 | O2 | 13.812175 | 13.541875 | 7.713036 | 23 | C15 | 16.902498 | 8.963760 | 10.658246 |
| 4 | O3 | 15.095098 | 11.047131 | 7.560996 | 24 | C16 | 17.574884 | 9.214345 | 9.444424 |
| 5 | N1 | 13.718704 | 12.532123 | 5.436286 | 25 | C17 | 16.961014 | 9.902174 | 8.412922 |
| 6 | N2 | 11.366474 | 12.368887 | 7.349448 | 26 | C18 | 15.630470 | 10.374902 | 8.541819 |
| 7 | N3 | 11.601735 | 11.542964 | 9.484373 | 27 | H | 13.645894 | 12.087637 | 4.523992 |
| 8 | N4 | 12.869954 | 11.167284 | 9.098865 | 28 | H | 11.410194 | 11.634044 | 10.475542 |
| 9 | C1 | 14.087963 | 13.845671 | 5.436488 | 29 | H | 14.370141 | 14.227310 | 3.320519 |
| 10 | C2 | 14.392139 | 14.652756 | 4.322069 | 30 | H | 14.969943 | 16.617947 | 3.678529 |
| 11 | C3 | 14.725942 | 15.983450 | 4.525739 | 31 | H | 15.017359 | 17.564868 | 5.969772 |
| 12 | C4 | 14.751877 | 16.519205 | 5.833280 | 32 | H | 14.469247 | 16.155721 | 7.948219 |
| 13 | C5 | 14.447429 | 15.744241 | 6.943332 | 33 | H | 11.120425 | 13.076747 | 5.432769 |
| 14 | C6 | 14.115303 | 14.379274 | 6.770077 | 34 | H | 8.833598 | 14.005914 | 5.844585 |
| 15 | C7 | 10.639914 | 12.991818 | 6.399585 | 35 | H | 7.851736 | 13.769130 | 8.154727 |
| 16 | C8 | 9.377032 | 13.507201 | 6.638827 | 36 | H | 9.171529 | 12.595480 | 9.914405 |
| 17 | C9 | 8.837150 | 13.373583 | 7.926381 | 37 | H | 13.176764 | 10.380387 | 10.974286 |
| 18 | C10 | 9.564847 | 12.729373 | 8.911563 | 38 | H | 15.068783 | 9.233630 | 11.738727 |
| 19 | C11 | 10.838433 | 12.232383 | 8.579334 | 39 | H | 17.397136 | 8.424999 | 11.460275 |
| 20 | C12 | 13.606914 | 10.563408 | 9.983740 | 40 | H | 18.595981 | 8.863628 | 9.315632 |
| | | | | | 41 | H | 17.476126 | 10.104669 | 7.479372 |

**Table S5** Gas phase optimized coordinates of **1** using B3PW91 functionals (S = 0)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 13.362993 | 11.605875 | 7.055303 | 21 | C13 | 14.945805 | 10.111731 | 9.773351 |
| 2 | O1 | 12.841868 | 10.318061 | 6.273778 | 22 | C14 | 15.595728 | 9.398966 | 10.806034 |
| 3 | O2 | 13.822273 | 13.536665 | 7.717915 | 23 | C15 | 16.884169 | 8.932074 | 10.650102 |
| 4 | O3 | 15.100809 | 11.054456 | 7.576827 | 24 | C16 | 17.557020 | 9.182131 | 9.439244 |
| 5 | N1 | 13.723440 | 12.532842 | 5.456561 | 25 | C17 | 16.952073 | 9.884223 | 8.414286 |
| 6 | N2 | 11.400905 | 12.372376 | 7.348428 | 26 | C18 | 15.629893 | 10.371117 | 8.547943 |
| 7 | N3 | 11.642820 | 11.601432 | 9.490088 | 27 | H | 13.647538 | 12.082119 | 4.548759 |
| 8 | N4 | 12.889515 | 11.195621 | 9.105869 | 28 | H | 11.426266 | 11.650687 | 10.477645 |
| 9 | C1 | 14.074685 | 13.849683 | 5.447983 | 29 | H | 14.336404 | 14.231398 | 3.330810 |
| 10 | C2 | 14.358492 | 14.656833 | 4.332721 | 30 | H | 14.903412 | 16.629145 | 3.684399 |
| 11 | C3 | 14.674377 | 15.991640 | 4.534002 | 31 | H | 14.953208 | 17.576047 | 5.973292 |
| 12 | C4 | 14.701720 | 16.526420 | 5.837908 | 32 | H | 14.440733 | 16.160353 | 7.954382 |
| 13 | C5 | 14.416728 | 15.747725 | 6.949627 | 33 | H | 11.157830 | 13.036593 | 5.419211 |
| 14 | C6 | 14.104247 | 14.381661 | 6.777326 | 34 | H | 8.868010 | 13.965783 | 5.807577 |
| 15 | C7 | 10.675608 | 12.971013 | 6.387168 | 35 | H | 7.883477 | 13.771861 | 8.119125 |
| 16 | C8 | 9.411711 | 13.485421 | 6.613189 | 36 | H | 9.203627 | 12.642208 | 9.903659 |
| 17 | C9 | 8.871273 | 13.375987 | 7.900200 | 37 | H | 13.186948 | 10.408470 | 10.981680 |
| 18 | C10 | 9.598625 | 12.756209 | 8.898693 | 38 | H | 15.057004 | 9.218992 | 11.735175 |
| 19 | C11 | 10.872673 | 12.259551 | 8.577655 | 39 | H | 17.372732 | 8.381368 | 11.448155 |
| 20 | C12 | 13.617431 | 10.581683 | 9.989202 | 40 | H | 18.573653 | 8.819165 | 9.306319 |
| | | | | | 41 | H | 17.469320 | 10.086455 | 7.481433 |

**Table S6** Gas phase optimized coordinates of **1**using PBE1PBE functionals (S = 0)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 13.380964 | 11.598800 | 7.058799 | 21 | C13 | 14.946963 | 10.104343 | 9.773405 |
| 2 | O1 | 12.863098 | 10.312099 | 6.284882 | 22 | C14 | 15.587845 | 9.386561 | 10.805216 |
| 3 | O2 | 13.830301 | 13.523740 | 7.722157 | 23 | C15 | 16.873773 | 8.916065 | 10.653846 |
| 4 | O3 | 15.113025 | 11.054645 | 7.586004 | 24 | C16 | 17.551668 | 9.169110 | 9.448431 |
| 5 | N1 | 13.727983 | 12.522865 | 5.465373 | 25 | C17 | 16.954703 | 9.876906 | 8.424961 |
| 6 | N2 | 11.427119 | 12.370660 | 7.342696 | 26 | C18 | 15.635161 | 10.366425 | 8.554200 |
| 7 | N3 | 11.655416 | 11.603093 | 9.482555 | 27 | H | 13.647282 | 12.072594 | 4.558576 |
| 8 | N4 | 12.899235 | 11.195012 | 9.102929 | 28 | H | 11.443845 | 11.669845 | 10.469369 |
| 9 | C1 | 14.058856 | 13.843862 | 5.454993 | 29 | H | 14.294033 | 14.228750 | 3.337694 |
| 10 | C2 | 14.318743 | 14.654431 | 4.339148 | 30 | H | 14.825992 | 16.634034 | 3.687639 |
| 11 | C3 | 14.615097 | 15.992318 | 4.538229 | 31 | H | 14.881895 | 17.577903 | 5.975335 |
| 12 | C4 | 14.645997 | 16.524932 | 5.840910 | 32 | H | 14.410460 | 16.153297 | 7.957814 |
| 13 | C5 | 14.383819 | 15.741772 | 6.953000 | 33 | H | 11.201850 | 13.037091 | 5.414291 |
| 14 | C6 | 14.091328 | 14.372958 | 6.782401 | 34 | H | 8.922442 | 13.991854 | 5.793290 |
| 15 | C7 | 10.714327 | 12.976707 | 6.379911 | 35 | H | 7.928644 | 13.810310 | 8.099774 |
| 16 | C8 | 9.457311 | 13.505478 | 6.600723 | 36 | H | 9.229901 | 12.668826 | 9.888805 |
| 17 | C9 | 8.912299 | 13.403086 | 7.884465 | 37 | H | 13.186811 | 10.407096 | 10.976667 |
| 18 | C10 | 9.628432 | 12.777113 | 8.884909 | 38 | H | 15.043506 | 9.205473 | 11.730576 |
| 19 | C11 | 10.895898 | 12.266862 | 8.568249 | 39 | H | 17.356745 | 8.360454 | 11.451351 |
| 20 | C12 | 13.620556 | 10.579123 | 9.985554 | 40 | H | 18.567386 | 8.803590 | 9.318427 |
| | | | | | 41 | H | 17.476378 | 10.081999 | 7.495495 |

**Table S7** Gas phase optimized coordinates of $[\mathbf{1}]^{+}$ using B3LYP functionals (S = ½)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 13.147840 | 11.557672 | 7.126391 | 21 | C13 | 14.888314 | 10.164280 | 9.719469 |
| 2 | O1 | 12.694162 | 10.258936 | 6.348236 | 22 | C14 | 15.601314 | 9.434057 | 10.702961 |
| 3 | O2 | 13.708975 | 13.816954 | 7.736190 | 23 | C15 | 16.929444 | 9.104570 | 10.517502 |
| 4 | O3 | 14.948311 | 11.290067 | 7.592466 | 24 | C16 | 17.580195 | 9.512386 | 9.337528 |
| 5 | N1 | 13.671757 | 12.598768 | 5.429322 | 25 | C17 | 16.912115 | 10.237514 | 8.361450 |
| 6 | N2 | 11.215440 | 12.396702 | 7.451070 | 26 | C18 | 15.555372 | 10.575776 | 8.526189 |
| 7 | N3 | 11.453455 | 11.405061 | 9.514585 | 27 | H | 13.658107 | 12.123489 | 4.525731 |
| 8 | N4 | 12.739133 | 11.108631 | 9.119750 | 28 | H | 11.200638 | 11.297925 | 10.489933 |
| 9 | C1 | 14.165393 | 13.802491 | 5.424572 | 29 | H | 14.669557 | 14.045712 | 3.306285 |
| 10 | C2 | 14.676820 | 14.520789 | 4.283356 | 30 | H | 15.568560 | 16.326609 | 3.620241 |
| 11 | C3 | 15.170534 | 15.773778 | 4.465645 | 31 | H | 15.602061 | 17.417736 | 5.839244 |
| 12 | C4 | 15.190701 | 16.414677 | 5.773683 | 32 | H | 14.731373 | 16.271992 | 7.867609 |
| 13 | C5 | 14.718916 | 15.802253 | 6.890025 | 33 | H | 10.946771 | 13.242101 | 5.582883 |
| 14 | C6 | 14.175513 | 14.461212 | 6.787103 | 34 | H | 8.616525 | 14.010384 | 6.028299 |
| 15 | C7 | 10.466791 | 13.059367 | 6.537585 | 35 | H | 7.605043 | 13.510943 | 8.281798 |
| 16 | C8 | 9.176781 | 13.480287 | 6.789459 | 36 | H | 8.947969 | 12.262107 | 9.965125 |
| 17 | C9 | 8.617741 | 13.197241 | 8.048253 | 37 | H | 13.118674 | 10.246730 | 10.949999 |
| 18 | C10 | 9.357533 | 12.508870 | 8.991083 | 38 | H | 15.082931 | 9.129725 | 11.609134 |
| 19 | C11 | 10.666322 | 12.116475 | 8.652643 | 39 | H | 17.466101 | 8.538775 | 11.271521 |
| 20 | C12 | 13.526132 | 10.505810 | 9.969107 | 40 | H | 18.625214 | 9.256718 | 9.186519 |
| | | | | | 41 | H | 17.412512 | 10.556468 | 7.453084 |

**Table S8** Gas phase optimized coordinates of $[\mathbf{1}]^{2+}$ using B3LYP functionals (S = 0)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 13.030325 | 11.444686 | 7.009957 | 21 | C13 | 14.931801 | 10.456743 | 9.704421 |
| 2 | O1 | 12.367780 | 10.360358 | 6.092750 | 22 | C14 | 15.775042 | 10.064165 | 10.75969 |
| 3 | O2 | 13.815896 | 13.464020 | 7.792653 | 23 | C15 | 17.079045 | 9.649578 | 10.500532 |
| 4 | O3 | 14.640714 | 10.735604 | 7.365601 | 24 | C16 | 17.552879 | 9.580979 | 9.177235 |
| 5 | N1 | 13.615946 | 12.571223 | 5.389283 | 25 | C17 | 16.734901 | 9.930852 | 8.109205 |
| 6 | N2 | 11.161966 | 12.322539 | 7.391820 | 26 | C18 | 15.436121 | 10.400332 | 8.370105 |
| 7 | N3 | 11.377815 | 11.280608 | 9.426196 | 27 | H | 13.524432 | 12.186911 | 4.446304 |
| 8 | N4 | 12.674358 | 11.068385 | 9.038250 | 28 | H | 11.145764 | 11.197719 | 10.41128 |
| 9 | C1 | 14.173529 | 13.741877 | 5.486188 | 29 | H | 14.594453 | 14.226999 | 3.388699 |
| 10 | C2 | 14.673165 | 14.564490 | 4.418017 | 30 | H | 15.643246 | 16.393309 | 3.959969 |
| 11 | C3 | 15.249192 | 15.752632 | 4.743400 | 31 | H | 15.840105 | 17.182026 | 6.293878 |
| 12 | C4 | 15.369867 | 16.217030 | 6.127908 | 32 | H | 15.005956 | 15.832608 | 8.212223 |
| 13 | C5 | 14.920734 | 15.492111 | 7.185947 | 33 | H | 10.922828 | 13.193003 | 5.519790 |
| 14 | C6 | 14.288500 | 14.220448 | 6.928570 | 34 | H | 8.615576 | 14.012928 | 5.970502 |
| 15 | C7 | 10.441383 | 13.018027 | 6.474209 | 35 | H | 7.566850 | 13.484590 | 8.197562 |
| 16 | C8 | 9.159271 | 13.462568 | 6.729550 | 36 | H | 8.865315 | 12.169758 | 9.872320 |
| 17 | C9 | 8.578091 | 13.160939 | 7.971870 | 37 | H | 13.221072 | 10.726637 | 10.99311 |
| 18 | C10 | 9.293939 | 12.433192 | 8.911082 | 38 | H | 15.399103 | 10.071261 | 11.778907 |
| 19 | C11 | 10.592894 | 12.031076 | 8.578551 | 39 | H | 17.724993 | 9.357509 | 11.321830 |
| 20 | C12 | 13.558380 | 10.772926 | 9.955920 | 40 | H | 18.564858 | 9.238412 | 8.985448 |
| | | | | | 41 | H | 17.078957 | 9.870980 | 7.082285 |

**Table S9** Gas phase optimized coordinates of [**1**]$^{-}$ using B3LYP functionals (S = ½)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 13.323338 | 11.412595 | 6.938019 | 21 | C13 | 14.983038 | 10.138519 | 9.710036 |
| 2 | O1 | 12.662235 | 10.083230 | 6.283753 | 22 | C14 | 15.658813 | 9.591510 | 10.827219 |
| 3 | O2 | 13.786222 | 13.308298 | 7.689710 | 23 | C15 | 16.957966 | 9.126788 | 10.749020 |
| 4 | O3 | 15.147031 | 10.718417 | 7.361206 | 24 | C16 | 17.627852 | 9.209932 | 9.509387 |
| 5 | N1 | 13.724202 | 12.450399 | 5.289788 | 25 | C17 | 17.005939 | 9.741786 | 8.398145 |
| 6 | N2 | 11.312332 | 12.312863 | 7.230858 | 26 | C18 | 15.660520 | 10.229801 | 8.435136 |
| 7 | N3 | 11.593952 | 11.489610 | 9.383013 | 27 | H | 13.829552 | 12.057894 | 4.359548 |
| 8 | N4 | 12.861453 | 11.091735 | 9.003806 | 28 | H | 11.467536 | 11.697036 | 10.368886 |
| 9 | C1 | 14.049071 | 13.776001 | 5.411558 | 29 | H | 14.382083 | 14.339750 | 3.353676 |
| 10 | C2 | 14.356063 | 14.687296 | 4.387680 | 30 | H | 14.857330 | 16.726369 | 3.880045 |
| 11 | C3 | 14.623265 | 16.032861 | 4.687174 | 31 | H | 14.795201 | 17.524440 | 6.239415 |
| 12 | C4 | 14.587821 | 16.479922 | 6.009404 | 32 | H | 14.274569 | 15.911987 | 8.086943 |
| 13 | C5 | 14.290694 | 15.582172 | 7.049283 | 33 | H | 11.074423 | 13.038076 | 5.336136 |
| 14 | C6 | 14.035081 | 14.230288 | 6.778682 | 34 | H | 8.889545 | 14.204628 | 5.850747 |
| 15 | C6 | 10.615868 | 13.005622 | 6.319708 | 35 | H | 7.999972 | 14.049169 | 8.204036 |
| 16 | C8 | 9.417872 | 13.646784 | 6.616864 | 36 | H | 9.290492 | 12.757089 | 9.904135 |
| 17 | C9 | 8.930269 | 13.559506 | 7.926434 | 37 | H | 13.254464 | 10.527596 | 10.941551 |
| 18 | C10 | 9.644784 | 12.847368 | 8.880658 | 38 | H | 15.122870 | 9.541190 | 11.775520 |
| 19 | C11 | 10.849603 | 12.237918 | 8.487666 | 39 | H | 17.452749 | 8.709580 | 11.621970 |
| 20 | C12 | 13.639633 | 10.600055 | 9.915377 | 40 | H | 18.653093 | 8.851696 | 9.427763 |
| | | | | | 41 | H | 17.518248 | 9.814261 | 7.443070 |

**Table S10** Gas phase optimized coordinates of [**1**] using B3LYP functionals (S = 1)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 13.176933 | 11.438365 | 7.020469 | 21 | C13 | 14.941354 | 10.202458 | 9.683957 |
| 2 | O1 | 12.565804 | 10.145249 | 6.308458 | 22 | C14 | 15.663393 | 9.614904 | 10.752514 |
| 3 | O2 | 13.688186 | 13.498310 | 7.732659 | 23 | C15 | 16.978255 | 9.221086 | 10.606473 |
| 4 | O3 | 15.004154 | 10.952847 | 7.384898 | 24 | C16 | 17.612209 | 9.418463 | 9.362948 |
| 5 | N1 | 13.650594 | 12.522112 | 5.310715 | 25 | C16 | 16.939983 | 9.994834 | 8.300750 |
| 6 | N2 | 11.210113 | 12.330404 | 7.322413 | 26 | C18 | 15.585893 | 10.404737 | 8.416022 |
| 7 | N3 | 11.511650 | 11.471277 | 9.452014 | 27 | H | 13.722958 | 12.115019 | 4.381870 |
| 8 | N4 | 12.783293 | 11.112864 | 9.051202 | 28 | H | 11.351778 | 11.586101 | 10.446833 |
| 9 | C1 | 14.113006 | 13.765644 | 5.430919 | 29 | H | 14.617328 | 14.208095 | 3.363984 |
| 10 | C2 | 14.595269 | 14.598603 | 4.379217 | 30 | H | 15.385046 | 16.512460 | 3.850509 |
| 11 | C3 | 15.021266 | 15.879082 | 4.655099 | 31 | H | 15.339868 | 17.404018 | 6.167497 |
| 12 | C4 | 14.995245 | 16.389488 | 5.984993 | 32 | H | 14.532573 | 15.990251 | 8.054972 |
| 13 | C5 | 14.547753 | 15.616331 | 7.035505 | 33 | H | 10.911989 | 13.049734 | 5.422223 |
| 14 | C6 | 14.098129 | 14.282621 | 6.809046 | 34 | H | 8.649409 | 14.018778 | 5.927709 |
| 15 | C7 | 10.462519 | 12.970430 | 6.406429 | 35 | H | 7.748877 | 13.760711 | 8.266815 |
| 16 | C8 | 9.216264 | 13.503721 | 6.694857 | 36 | H | 9.109400 | 12.548186 | 9.964435 |
| 17 | C9 | 8.721102 | 13.357082 | 7.998888 | 37 | H | 13.219043 | 10.471513 | 10.955058 |
| 18 | C10 | 9.472883 | 12.689528 | 8.951242 | 38 | H | 15.155947 | 9.474778 | 11.705434 |
| 19 | C11 | 10.729116 | 12.183363 | 8.569320 | 39 | H | 17.515317 | 8.768804 | 11.434249 |
| 20 | C12 | 13.589957 | 10.602694 | 9.932886 | 40 | H | 18.648459 | 9.114597 | 9.235101 |
| | | | | | 41 | H | 17.424724 | 10.152499 | 7.342439 |

**Table S11** Gas phase optimized coordinates of **2** using B3LYP functionals (S = 0)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 2.197547 | 4.612116 | 4.896821 | 27 | C19 | -0.149604 | -0.523811 | 3.983547 |
| 2 | O1 | 0.856338 | 5.434179 | 5.184568 | 28 | C20 | -0.163896 | 0.213619 | 2.781628 |
| 3 | O2 | 4.176216 | 3.966804 | 4.482458 | 29 | C21 | 0.403992 | 1.472662 | 2.705465 |
| 4 | O3 | 1.568996 | 3.241819 | 3.720316 | 30 | C22 | 1.017442 | 2.066709 | 3.837971 |
| 5 | N1 | 2.825927 | 5.891704 | 3.645384 | 31 | H | 2.250101 | 6.674948 | 3.344928 |
| 6 | N2 | 3.212241 | 5.388580 | 6.619535 | 32 | H | 2.964198 | 2.605297 | 8.205487 |
| 7 | N3 | 2.709937 | 3.356386 | 7.574201 | 33 | H | 4.044595 | 7.530614 | 1.795853 |
| 8 | N4 | 2.156570 | 3.025924 | 6.356832 | 34 | H | 7.685959 | 5.225780 | 1.901212 |
| 9 | C1 | 4.073929 | 5.820545 | 3.100980 | 35 | H | 6.710932 | 3.684173 | 3.552855 |
| 10 | C2 | 4.646607 | 6.704239 | 2.162119 | 36 | H | 8.405231 | 8.689448 | 0.554698 |
| 11 | C3 | 5.947888 | 6.507100 | 1.712911 | 37 | H | 8.627132 | 7.268074 | 1.585282 |
| 12 | C4 | 6.668100 | 5.398038 | 2.241264 | 38 | H | 7.673714 | 8.638418 | 2.171806 |
| 13 | C5 | 6.134261 | 4.521848 | 3.171193 | 39 | H | 4.790803 | 8.211727 | -0.240969 |
| 14 | C6 | 4.805927 | 4.705227 | 3.623563 | 40 | H | 6.230218 | 9.205193 | -0.500364 |
| 15 | C7 | 6.624197 | 7.423859 | 0.678086 | 41 | H | 5.424978 | 9.222551 | 1.074279 |
| 16 | C8 | 7.908666 | 8.038169 | 1.285093 | 42 | H | 6.103396 | 6.166028 | -1.039067 |
| 17 | C9 | 5.708200 | 8.579457 | 0.232695 | 43 | H | 7.678943 | 5.775881 | -0.335768 |
| 18 | C10 | 6.998061 | 6.598921 | -0.577168 | 44 | H | 7.493552 | 7.234549 | -1.322074 |
| 19 | C11 | 3.749060 | 6.623490 | 6.689237 | 45 | H | 3.637459 | 7.225337 | 5.795760 |
| 20 | C12 | 4.414311 | 7.090256 | 7.810582 | 46 | H | 4.834207 | 8.089512 | 7.817522 |
| 21 | C13 | 4.534093 | 6.235759 | 8.916426 | 47 | H | 5.053309 | 6.563273 | 9.812423 |
| 22 | C14 | 3.983557 | 4.967139 | 8.865534 | 48 | H | 4.046070 | 4.285209 | 9.707804 |
| 23 | C15 | 3.320167 | 4.577247 | 7.687585 | 49 | H | 1.650321 | 1.183607 | 7.118417 |
| 24 | C16 | 1.631160 | 1.841838 | 6.243036 | 50 | H | 0.466590 | -0.521242 | 6.038457 |
| 25 | C17 | 1.025858 | 1.320637 | 5.059005 | 51 | H | -0.597015 | -1.511745 | 4.028431 |
| 26 | C18 | 0.442606 | 0.030989 | 5.100623 | 52 | H | -0.627355 | -0.214817 | 1.896220 |
| | | | | | 53 | H | 0.402312 | 2.041737 | 1.781318 |

**Table S12** Gas phase optimized coordinates of **2** using B3PW91functionals (S = 0)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 2.214093 | 4.586436 | 4.877000 | 27 | C19 | -0.182908 | -0.514399 | 4.013871 |
| 2 | O1 | 0.879029 | 5.407381 | 5.167709 | 28 | C20 | -0.199005 | 0.216296 | 2.810696 |
| 3 | O2 | 4.169136 | 3.952267 | 4.461277 | 29 | C21 | 0.382708 | 1.466441 | 2.722765 |
| 4 | O3 | 1.574427 | 3.221773 | 3.720358 | 30 | C22 | 1.011685 | 2.057292 | 3.845163 |
| 5 | N1 | 2.827451 | 5.866938 | 3.637270 | 31 | H | 2.246209 | 6.647521 | 3.343958 |
| 6 | N2 | 3.220745 | 5.374569 | 6.575727 | 32 | H | 2.972620 | 2.609135 | 8.193763 |
| 7 | N3 | 2.768205 | 3.343293 | 7.527662 | 33 | H | 4.046106 | 7.527456 | 1.803389 |
| 8 | N4 | 2.186320 | 3.015638 | 6.336318 | 34 | H | 7.691679 | 5.235094 | 1.915341 |
| 9 | C1 | 4.076162 | 5.808994 | 3.096720 | 35 | H | 6.712417 | 3.679738 | 3.549939 |
| 10 | C2 | 4.647983 | 6.699784 | 2.169508 | 36 | H | 8.400479 | 8.701009 | 0.596909 |
| 11 | C3 | 5.951877 | 6.509265 | 1.727457 | 37 | H | 8.622726 | 7.271288 | 1.616221 |
| 12 | C4 | 6.670677 | 5.402440 | 2.250947 | 38 | H | 7.663023 | 8.633785 | 2.211389 |
| 13 | C5 | 6.134706 | 4.518541 | 3.171333 | 39 | H | 4.799196 | 8.215841 | -0.214388 |
| 14 | C6 | 4.806163 | 4.695811 | 3.614492 | 40 | H | 6.236601 | 9.216036 | -0.459756 |
| 15 | C7 | 6.627720 | 7.431710 | 0.705490 | 41 | H | 5.425018 | 9.219600 | 1.112024 |
| 16 | C8 | 7.902967 | 8.042169 | 1.320166 | 42 | H | 6.114684 | 6.184767 | -1.015084 |
| 17 | C9 | 5.713279 | 8.583232 | 0.266644 | 43 | H | 7.689740 | 5.796421 | -0.309332 |
| 18 | C10 | 7.006535 | 6.618558 | -0.548434 | 44 | H | 7.502286 | 7.260147 | -1.288343 |
| 19 | C11 | 3.735576 | 6.615343 | 6.637208 | 45 | H | 3.608366 | 7.211200 | 5.741262 |
| 20 | C12 | 4.396893 | 7.097912 | 7.752131 | 46 | H | 4.799881 | 8.104385 | 7.752316 |
| 21 | C13 | 4.535622 | 6.251693 | 8.859170 | 47 | H | 5.052782 | 6.591895 | 9.752036 |
| 22 | C14 | 4.008261 | 4.974966 | 8.816409 | 48 | H | 4.087706 | 4.297764 | 9.661446 |
| 23 | C15 | 3.348289 | 4.570863 | 7.644007 | 49 | H | 1.678562 | 1.181437 | 7.113956 |
| 24 | C16 | 1.649692 | 1.836909 | 6.236397 | 50 | H | 0.453030 | -0.510665 | 6.061629 |
| 25 | C17 | 1.022901 | 1.317775 | 5.066290 | 51 | H | -0.641978 | -1.496854 | 4.067919 |
| 26 | C18 | 0.426304 | 0.037786 | 5.121152 | 52 | H | -0.675865 | -0.210465 | 1.931204 |
| | | | | | 53 | H | 0.379253 | 2.030808 | 1.795315 |

**Table S13** Gas phase optimized coordinates of $[\mathbf{2}]^{+}$ using B3LYP functionals (S = ½)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 2.228445 | 4.672467 | 5.167373 | 27 | C19 | 0.054547 | -0.318748 | 3.689933 |
| 2 | O1 | 0.866704 | 5.451115 | 5.369289 | 28 | C20 | 0.250114 | 0.447736 | 2.524955 |
| 3 | O2 | 4.520919 | 4.078474 | 4.668741 | 29 | C21 | 0.869299 | 1.687729 | 2.575816 |
| 4 | O3 | 1.920620 | 3.391720 | 3.817822 | 30 | C22 | 1.311762 | 2.218802 | 3.803670 |
| 5 | N1 | 2.996436 | 6.013452 | 3.793259 | 31 | H | 2.403068 | 6.768617 | 3.447173 |
| 6 | N2 | 3.236111 | 5.374125 | 6.912183 | 32 | H | 2.570537 | 2.613218 | 8.454780 |
| 7 | N3 | 2.526058 | 3.359127 | 7.770422 | 33 | H | 4.035801 | 7.531080 | 1.788595 |
| 8 | N4 | 2.095508 | 3.072341 | 6.493945 | 34 | H | 7.657674 | 5.175153 | 1.676240 |
| 9 | C1 | 4.150496 | 5.893257 | 3.205293 | 35 | H | 6.887598 | 3.715090 | 3.494595 |
| 10 | C2 | 4.662061 | 6.720527 | 2.145154 | 36 | H | 8.267292 | 8.509580 | 0.131453 |
| 11 | C3 | 5.889958 | 6.474854 | 1.600980 | 37 | H | 8.567247 | 7.158725 | 1.225477 |
| 12 | C4 | 6.686300 | 5.351929 | 2.125677 | 38 | H | 7.678964 | 8.581416 | 1.801629 |
| 13 | C5 | 6.279716 | 4.535278 | 3.127571 | 39 | H | 4.600099 | 8.069902 | -0.358233 |
| 14 | C6 | 4.984675 | 4.751367 | 3.740570 | 40 | H | 6.031540 | 9.004481 | -0.792078 |
| 15 | C7 | 6.489065 | 7.303005 | 0.464871 | 41 | H | 5.359786 | 9.153872 | 0.832415 |
| 16 | C8 | 7.830582 | 7.918073 | 0.943113 | 42 | H | 5.812953 | 5.933132 | -1.116483 |
| 17 | C9 | 5.557641 | 8.445084 | 0.020164 | 43 | H | 7.441814 | 5.560811 | -0.522660 |
| 18 | C10 | 6.746305 | 6.375005 | -0.751429 | 44 | H | 7.185625 | 6.960119 | -1.566368 |
| 19 | C11 | 3.814186 | 6.587841 | 7.070597 | 45 | H | 3.830766 | 7.215802 | 6.186962 |
| 20 | C12 | 4.350268 | 7.012046 | 8.269861 | 46 | H | 4.805704 | 7.992133 | 8.349104 |
| 21 | C13 | 4.281377 | 6.143715 | 9.373518 | 47 | H | 4.690385 | 6.443187 | 10.333531 |
| 22 | C14 | 3.682510 | 4.905308 | 9.239412 | 48 | H | 3.600768 | 4.220123 | 10.076847 |
| 23 | C15 | 3.161522 | 4.551298 | 7.980442 | 49 | H | 1.478878 | 1.204660 | 7.101761 |
| 24 | C16 | 1.571297 | 1.899610 | 6.262666 | 50 | H | 0.348680 | -0.400868 | 5.812915 |
| 25 | C17 | 1.114932 | 1.446574 | 4.989452 | 51 | H | -0.430821 | -1.287259 | 3.633787 |
| 26 | C18 | 0.488682 | 0.177732 | 4.902794 | 52 | H | -0.088623 | 0.062351 | 1.567285 |
| | | | | | 53 | H | 1.024187 | 2.278855 | 1.679176 |

**Table S14** Gas phase optimized coordinates of $[\mathbf{2}]^{2+}$ using B3LYP functionals (S = 0)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 2.084154 | 4.825204 | 5.206456 | 27 | C19 | 0.640105 | -0.345032 | 3.463460 |
| 2 | O1 | 0.893263 | 5.785983 | 5.545895 | 28 | C20 | 0.331423 | 0.584082 | 2.455164 |
| 3 | O2 | 4.165291 | 3.994963 | 4.57662 | 29 | C21 | 0.554820 | 1.944884 | 2.644723 |
| 4 | O3 | 1.351458 | 3.673991 | 4.049798 | 30 | C22 | 1.133689 | 2.378054 | 3.846199 |
| 5 | N1 | 2.894299 | 6.121302 | 3.864345 | 31 | H | 2.368473 | 6.954215 | 3.594031 |
| 6 | N2 | 3.148784 | 5.462386 | 6.901582 | 32 | H | 2.582651 | 2.683639 | 8.428964 |
| 7 | N3 | 2.468900 | 3.451398 | 7.774587 | 33 | H | 4.076196 | 7.631451 | 1.908008 |
| 8 | N4 | 2.094331 | 3.163726 | 6.485849 | 34 | H | 7.412989 | 4.880718 | 1.630671 |
| 9 | C1 | 4.023352 | 5.921292 | 3.233842 | 35 | H | 6.487216 | 3.403886 | 3.368155 |
| 10 | C2 | 4.600714 | 6.735460 | 2.219789 | 36 | H | 8.362016 | 8.189612 | 0.256640 |
| 11 | C3 | 5.793613 | 6.372452 | 1.641228 | 37 | H | 8.524708 | 6.783945 | 1.307609 |
| 12 | C4 | 6.468003 | 5.133200 | 2.098321 | 38 | H | 7.785713 | 8.275157 | 1.930020 |
| 13 | C5 | 5.975580 | 4.306926 | 3.052575 | 39 | H | 4.671525 | 8.165852 | -0.248785 |
| 14 | C6 | 4.723750 | 4.650382 | 3.685137 | 40 | H | 6.193603 | 8.957238 | -0.648223 |
| 15 | C7 | 6.467254 | 7.175668 | 0.545205 | 41 | H | 5.541582 | 9.122875 | 0.979305 |
| 16 | C8 | 7.870192 | 7.623742 | 1.054215 | 42 | H | 5.670533 | 5.929149 | -1.091051 |
| 17 | C9 | 5.661605 | 8.423579 | 0.144150 | 43 | H | 7.260718 | 5.383367 | -0.516366 |
| 18 | C10 | 6.639120 | 6.264127 | -0.706146 | 44 | H | 7.132969 | 6.845466 | -1.491231 |
| 19 | C11 | 3.715984 | 6.690818 | 7.030408 | 45 | H | 3.684559 | 7.325098 | 6.153293 |
| 20 | C12 | 4.287389 | 7.117155 | 8.211802 | 46 | H | 4.728661 | 8.105021 | 8.274616 |
| 21 | C13 | 4.259655 | 6.256203 | 9.321870 | 47 | H | 4.691340 | 6.566931 | 10.268109 |
| 22 | C14 | 3.665292 | 5.009141 | 9.213129 | 48 | H | 3.611306 | 4.329744 | 10.057256 |
| 23 | C15 | 3.115417 | 4.648098 | 7.976069 | 49 | H | 2.042204 | 1.157255 | 6.936869 |
| 24 | C16 | 1.888864 | 1.913650 | 6.164688 | 50 | H | 1.370383 | -0.625833 | 5.468864 |
| 25 | C17 | 1.436847 | 1.454413 | 4.886279 | 51 | H | 0.445428 | -1.400514 | 3.305733 |
| 26 | C18 | 1.171084 | 0.088248 | 4.674685 | 52 | H | -0.099232 | 0.240132 | 1.519986 |
| | | | | | 53 | H | 0.308226 | 2.675105 | 1.881594 |

**Table S15** Gas phase optimized coordinates of $[\mathbf{2}]^{-}$ using B3LYP functionals (S = ½)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 1.974407 | 4.684707 | 4.884558 | 27 | C19 | 0.017947 | -0.635625 | 3.983483 |
| 2 | O1 | 0.635353 | 5.441354 | 5.398246 | 28 | C20 | -0.205190 | 0.111907 | 2.807166 |
| 3 | O2 | 3.914160 | 3.999812 | 4.479538 | 29 | C21 | 0.184116 | 1.432955 | 2.718349 |
| 4 | O3 | 1.166213 | 3.346342 | 3.645507 | 30 | C22 | 0.824109 | 2.115369 | 3.801636 |
| 5 | N1 | 2.640045 | 6.014761 | 3.563250 | 31 | H | 2.075176 | 6.726527 | 3.110651 |
| 6 | N2 | 3.142496 | 5.519581 | 6.580463 | 32 | H | 3.108365 | 2.668153 | 8.035128 |
| 7 | N3 | 2.705883 | 3.436133 | 7.506815 | 33 | H | 4.018923 | 7.548856 | 1.748801 |
| 8 | N4 | 2.095606 | 3.097492 | 6.314259 | 34 | H | 7.622837 | 5.193505 | 2.111980 |
| 9 | C1 | 3.918653 | 5.883951 | 3.089839 | 35 | H | 6.476513 | 3.702938 | 3.723456 |
| 10 | C2 | 4.578281 | 6.715515 | 2.168510 | 36 | H | 8.465593 | 8.638167 | 0.730112 |
| 11 | C3 | 5.918662 | 6.490752 | 1.796103 | 37 | H | 8.605416 | 7.220253 | 1.788637 |
| 12 | C3 | 6.586779 | 5.400253 | 2.376283 | 38 | H | 7.644815 | 8.609724 | 2.308207 |
| 13 | C4 | 5.948027 | 4.552575 | 3.293986 | 39 | H | 4.886917 | 8.191371 | -0.235573 |
| 14 | C5 | 4.611098 | 4.760329 | 3.658067 | 40 | H | 6.353739 | 9.166669 | -0.437264 |
| 15 | C6 | 6.657046 | 7.389075 | 0.783808 | 41 | H | 5.465020 | 9.205296 | 1.097258 |
| 16 | C7 | 7.919424 | 7.999103 | 1.439804 | 42 | H | 6.206402 | 6.121585 | -0.940552 |
| 17 | C8 | 5.785594 | 8.554125 | 0.275823 | 43 | H | 7.737178 | 5.721170 | -0.154191 |
| 18 | C9 | 7.085132 | 6.551219 | -0.445386 | 44 | H | 7.625735 | 7.167919 | -1.178980 |
| 19 | C10 | 3.732671 | 6.721981 | 6.618673 | 45 | H | 3.526914 | 7.348654 | 5.756326 |
| 20 | C11 | 4.557902 | 7.121977 | 7.664296 | 46 | H | 5.023300 | 8.102000 | 7.651765 |
| 21 | C12 | 4.775494 | 6.221610 | 8.714234 | 47 | H | 5.417458 | 6.490831 | 9.549466 |
| 22 | C13 | 4.172118 | 4.971395 | 8.684694 | 48 | H | 4.318015 | 4.252097 | 9.486232 |
| 23 | C14 | 3.358929 | 4.654124 | 7.582270 | 49 | H | 1.856045 | 1.172708 | 6.995725 |
| 24 | C15 | 1.691902 | 1.875259 | 6.167490 | 50 | H | 0.823533 | -0.572837 | 5.968218 |
| 25 | C16 | 1.046200 | 1.340721 | 5.002674 | 51 | H | -0.287973 | -1.676366 | 4.047626 |
| 26 | C18 | 0.637360 | -0.013698 | 5.050822 | 52 | H | -0.689491 | -0.360940 | 1.954006 |
| | | | | | 53 | H | 0.021171 | 2.011687 | 1.813721 |

**Table S16** Gas phase optimized coordinates of **2** using B3LYP functionals (S = 1)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V1 | 2.071507 | 4.728552 | 5.089588 | 27 | C19 | 0.174750 | -0.445143 | 3.719732 |
| 2 | O1 | 0.731240 | 5.494814 | 5.501470 | 28 | C20 | 0.111044 | 0.364166 | 2.567293 |
| 3 | O2 | 4.174106 | 4.086809 | 4.657554 | 29 | C21 | 0.555971 | 1.673317 | 2.586916 |
| 4 | O3 | 1.503786 | 3.493021 | 3.724391 | 30 | C22 | 1.088399 | 2.257271 | 3.766353 |
| 5 | N1 | 2.809888 | 6.119178 | 3.738045 | 31 | H | 2.248681 | 6.852842 | 3.313362 |
| 6 | N2 | 3.161124 | 5.488428 | 6.819817 | 32 | H | 2.929732 | 2.608625 | 8.231550 |
| 7 | N3 | 2.642752 | 3.390627 | 7.653205 | 33 | H | 4.027319 | 7.545363 | 1.773686 |
| 8 | N4 | 2.120210 | 3.101701 | 6.408601 | 34 | H | 7.584974 | 5.107599 | 1.890581 |
| 9 | C1 | 4.013570 | 5.929816 | 3.197559 | 35 | H | 6.606585 | 3.694633 | 3.654971 |
| 10 | C2 | 4.608154 | 6.718068 | 2.169509 | 36 | H | 8.368254 | 8.458708 | 0.337744 |
| 11 | C3 | 5.876579 | 6.444777 | 1.693340 | 37 | H | 8.574551 | 7.092716 | 1.443209 |
| 12 | C4 | 6.588411 | 5.333250 | 2.259046 | 38 | H | 7.689194 | 8.529374 | 1.976561 |
| 13 | C5 | 6.054763 | 4.536643 | 3.247194 | 39 | H | 4.717595 | 8.076635 | -0.321962 |
| 14 | C6 | 4.749327 | 4.790194 | 3.756289 | 40 | H | 6.184756 | 8.994101 | -0.684702 |
| 15 | C7 | 6.549045 | 7.272906 | 0.586740 | 41 | H | 5.432554 | 9.137698 | 0.909472 |
| 16 | C8 | 7.874057 | 7.870091 | 1.120622 | 42 | H | 5.928262 | 5.933487 | -1.033841 |
| 17 | C9 | 5.663052 | 8.435031 | 0.100463 | 43 | H | 7.513786 | 5.529344 | -0.359688 |
| 18 | C10 | 6.851932 | 6.359846 | -0.626474 | 44 | H | 7.342302 | 6.935000 | -1.421860 |
| 19 | C11 | 3.703838 | 6.710089 | 6.961886 | 45 | H | 3.584126 | 7.366207 | 6.106213 |
| 20 | C12 | 4.379322 | 7.102707 | 8.106710 | 46 | H | 4.807720 | 8.096024 | 8.177167 |
| 21 | C13 | 4.489355 | 6.180159 | 9.157378 | 47 | H | 5.011005 | 6.447552 | 10.071902 |
| 22 | C14 | 3.926490 | 4.921120 | 9.031696 | 48 | H | 3.984294 | 4.190919 | 9.833043 |
| 23 | C15 | 3.261636 | 4.608574 | 7.831465 | 49 | H | 1.767535 | 1.161810 | 6.990296 |
| 24 | C16 | 1.697531 | 1.894735 | 6.179301 | 50 | H | 0.754566 | -0.517104 | 5.781824 |
| 25 | C17 | 1.152087 | 1.430802 | 4.939848 | 51 | H | -0.176159 | -1.471991 | 3.693292 |
| 26 | C18 | 0.692900 | 0.091458 | 4.881222 | 52 | H | -0.293089 | -0.046893 | 1.645186 |
| | | | | | 53 | H | 0.512643 | 2.299361 | 1.701250 |

**Table S17** Gas phase optimized coordinates of **5** using B3LYP functionals (S = 0)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V | 13.327363 | 11.578844 | 6.977299 | 25 | C | 17.089308 | 10.607303 | 8.626128 |
| 2 | O | 12.871824 | 10.178437 | 6.315492 | 26 | C | 15.697123 | 10.863286 | 8.671063 |
| 3 | O | 13.434122 | 13.445103 | 7.480321 | 27 | H | 13.559671 | 11.821274 | 4.471497 |
| 4 | O | 15.065812 | 11.126567 | 7.556747 | 28 | H | 11.272000 | 11.711468 | 10.382939 |
| 5 | N | 13.596815 | 12.363586 | 5.330922 | 29 | H | 15.736592 | 13.493395 | 4.037937 |
| 6 | N | 11.175056 | 11.990450 | 7.179771 | 30 | H | 15.509992 | 15.851141 | 3.699110 |
| 7 | N | 11.511685 | 11.532251 | 9.413966 | 31 | H | 13.846543 | 16.738659 | 5.093418 |
| 8 | N | 12.830856 | 11.315599 | 9.103841 | 32 | H | 15.160560 | 15.258732 | 7.440584 |
| 9 | C | 13.894123 | 13.775976 | 5.168022 | 33 | H | 10.838195 | 12.313214 | 5.179732 |
| 10 | C | 15.390188 | 14.047276 | 4.919450 | 34 | H | 8.422733 | 12.923586 | 5.473796 |
| 11 | C | 15.653315 | 15.560841 | 4.747913 | 35 | H | 7.468444 | 12.891783 | 7.807212 |
| 12 | C | 14.737520 | 16.423220 | 5.655397 | 36 | H | 8.940667 | 12.229920 | 9.706399 |
| 13 | C | 14.287253 | 15.640562 | 6.897060 | 37 | H | 13.239322 | 11.036127 | 11.100272 |
| 14 | C | 13.411968 | 14.433750 | 6.501347 | 38 | H | 15.292078 | 10.501278 | 12.062908 |
| 15 | C | 10.368080 | 12.321081 | 6.155841 | 39 | H | 17.729729 | 10.063175 | 11.934223 |
| 16 | C | 9.033520 | 12.655591 | 6.328397 | 40 | H | 18.868802 | 10.133880 | 9.713493 |
| 17 | C | 8.508656 | 12.635136 | 7.628381 | 41 | H | 17.573629 | 10.640343 | 7.655381 |
| 18 | C | 9.320543 | 12.275496 | 8.690340 | 42 | H | 13.737191 | 16.282611 | 7.595140 |
| 19 | C | 10.663781 | 11.951957 | 8.419945 | 43 | H | 15.253532 | 17.346629 | 5.944419 |
| 20 | C | 13.643373 | 11.063766 | 10.081939 | 44 | H | 16.706553 | 15.762664 | 4.979699 |
| 21 | C | 15.048750 | 10.817927 | 9.943074 | 45 | H | 15.947844 | 13.652208 | 5.775948 |
| 22 | C | 15.804381 | 10.529517 | 11.102851 | 46 | H | 12.375338 | 14.792340 | 6.340084 |
| 23 | C | 17.163428 | 10.284627 | 11.035014 | 47 | H | 13.326750 | 14.176438 | 4.310763 |
| 24 | C | 17.800691 | 10.325849 | 9.780402 | | | | | |

**Table S18** Gas phase optimized coordinates of $\mathbf{1}^{t\text{-NH}}$ using B3LYP functionals (S = 0)

| S. No. | Symbol | X | Y | Z | S. No. | Symbol | X | Y | Z |
|---|---|---|---|---|---|---|---|---|---|
| 1 | V | 13.515517 | 11.765475 | 7.181452 | 21 | C | 16.995761 | 8.692787 | 10.409279 |
| 2 | O | 13.033188 | 10.374663 | 6.551424 | 22 | C | 17.651994 | 9.017575 | 9.204063 |
| 3 | O | 15.302161 | 11.284880 | 7.650817 | 23 | C | 17.077530 | 9.874871 | 8.282375 |
| 4 | N | 11.514598 | 12.431897 | 7.543665 | 24 | C | 15.801242 | 10.444003 | 8.516730 |
| 5 | N | 11.971006 | 11.952195 | 9.747322 | 25 | H | 11.618486 | 11.566191 | 10.618185 |
| 6 | N | 13.142831 | 11.404999 | 9.257134 | 26 | H | 13.620196 | 14.111861 | 3.311139 |
| 7 | C | 13.829692 | 13.960090 | 5.448946 | 27 | H | 14.105531 | 16.570119 | 3.294662 |
| 8 | C | 13.822210 | 14.657112 | 4.228594 | 28 | H | 14.582376 | 17.757417 | 5.420899 |
| 9 | C | 14.095601 | 16.017438 | 4.229707 | 29 | H | 14.578754 | 16.553722 | 7.583966 |
| 10 | C | 14.368734 | 16.691528 | 5.443986 | 30 | H | 11.121937 | 12.874737 | 5.573330 |
| 11 | C | 14.368208 | 16.025325 | 6.656618 | 31 | H | 8.742637 | 13.556616 | 5.998303 |
| 12 | C | 14.092391 | 14.630228 | 6.692494 | 32 | H | 7.877033 | 13.440900 | 8.360770 |
| 13 | C | 10.687357 | 12.850590 | 6.565535 | 33 | H | 9.402721 | 12.657881 | 10.173433 |
| 14 | C | 9.375205 | 13.223577 | 6.813150 | 34 | H | 13.469906 | 10.479124 | 11.066016 |
| 15 | C | 8.899803 | 13.157958 | 8.129571 | 35 | H | 15.234287 | 9.008268 | 11.592628 |
| 16 | C | 9.740044 | 12.723726 | 9.143697 | 36 | H | 17.460765 | 8.021819 | 11.124656 |
| 17 | C | 11.053244 | 12.364017 | 8.803169 | 37 | H | 18.629006 | 8.589174 | 8.994352 |
| 18 | C | 13.859318 | 10.675699 | 10.061011 | 38 | H | 17.580434 | 10.134946 | 7.356554 |
| 19 | C | 15.132283 | 10.110902 | 9.737558 | 39 | N | 14.030002 | 13.796552 | 7.739793 |
| 20 | C | 15.755163 | 9.242171 | 10.665878 | 40 | H | 14.234308 | 14.238107 | 8.634658 |
| | | | | | 41 | O | 13.595962 | 12.662589 | 5.548037 |