

Ni(II)-polypyridyl complexes as potential DNA binders

Priya Sahni^{a‡}, Rahat Gupta^{a‡}, Debakanta Tripathy^b, Soumya Lipsa Rath^{*c} and Amlan K. Pal^{*a}

^aDepartment of Chemistry, Indian Institute of Technology Jammu, Nagrota Bypass Road, Jammu and Kashmir – 181221, India

^bDepartment of Chemistry, School of Advanced Sciences, VIT-AP University, Amaravati, Andhra Pradesh-522237, India

^cDepartment of Biotechnology, National Institute of Technology, Warangal, Telengana-506004, India

‡Equal contribution

Supporting Information

Table of Content

Materials, methods and instrumentation.....	2 – 3
Synthesis of complexes 1 – 3	3 – 5
Characterization of complexes 1 – 3 (NMR Studies).....	6
X-ray diffraction studies.....	6 – 9
Computational details.....	9 – 13
Molecular docking and non-bonding interactions.....	13 – 15
Optimized atomic coordinates.....	16 – 22
References.....	23

Materials, methods and instrumentation

^1H , and ^{13}C NMR spectra were recorded with 500 MHz JEOL spectrometer (500 and 126 for ^1H , and ^{13}C respectively) in the deuterated solvents as mentioned in the experimental section. The following abbreviations have been used for multiplicity assignments: “s” for singlet, “d” for doublet, “t” for triplet, “m” for multiplet, and “br” for broad. Chemical shifts are reported in parts per million (ppm) relative to respective residual solvent protons and coupling constants (J) are reported in Hertz (Hz). Chromatography was performed on columns with an i.d. of 25-30 mm on silica gel (Silica gel, 100-200 μm). The progress of the reactions and the elution of the products were followed by TLC (silica gel on plastic sheets, 250 μm with indicator F-254). Compounds were visualized under UV light.

High-resolution mass spectra were recorded by Xevo, G2-XS QT. Elemental analyses were recorded by UNICUBE®

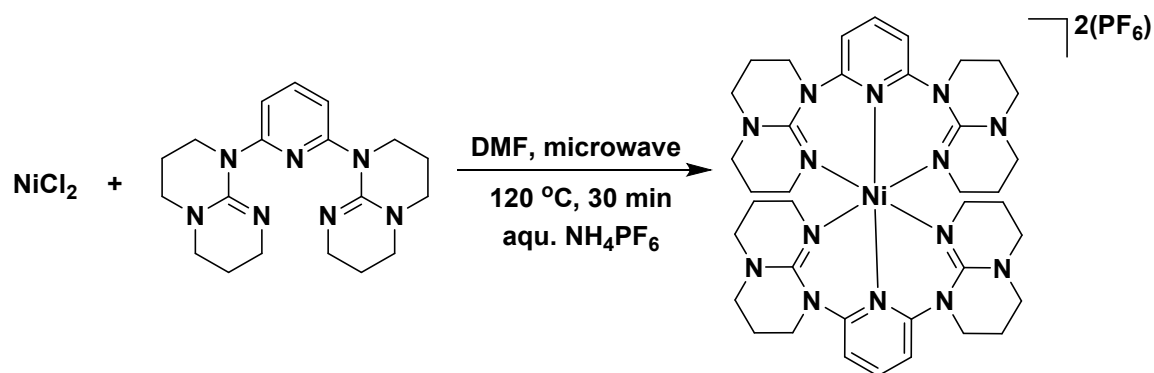
Photophysical measurements. All photophysical measurements were carried out in deaerated acetonitrile at r.t. in septa-sealed quartz cells. UV-vis spectroscopy (UV) was completed at room temperature using a Cary 5000 UV-vis spectrophotometer. All samples were prepared in HPLC grade MeCN, with varying concentrations in the order of 10^{-5} - 10^{-6} μM . Molar absorptivity determination was verified by linear least-squares fit of values obtained from at least four independent solutions at varying concentrations.

Electrochemical measurements. Cyclic voltammetry (CV) measurements were performed on an Electrochemical Analyzer potentiostat model 620E from CH Instruments at a sweep rate of 100 mV/s. Differential pulse voltammetry (DPV) was conducted with an increment potential of 0.004 V and a pulse amplitude, width and period of 50 mV, 0.05 s and 0.5 s, respectively. Solutions

for CV and DPV were prepared in *N,N'*-DMF and degassed by bubbling nitrogen through the solutions for about 6 min prior to scanning. Tetra(*n*-butyl)ammoniumhexafluorophosphate (TBAPF₆; *ca.* 0.1 M in MeCN) was used as the supporting electrolyte. Glassy carbon, platinum and silver electrodes were used as the working, counter and reference electrodes, respectively. Ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as an internal reference with respect to a saturated calomel electrode (0.38 V vs SCE)¹ and the redox potentials were calibrated to this.

Experimental uncertainties are as follows: absorption maxima, ±2 nm; molar absorption coefficient, 10%; redox potentials, ± 10 mV.

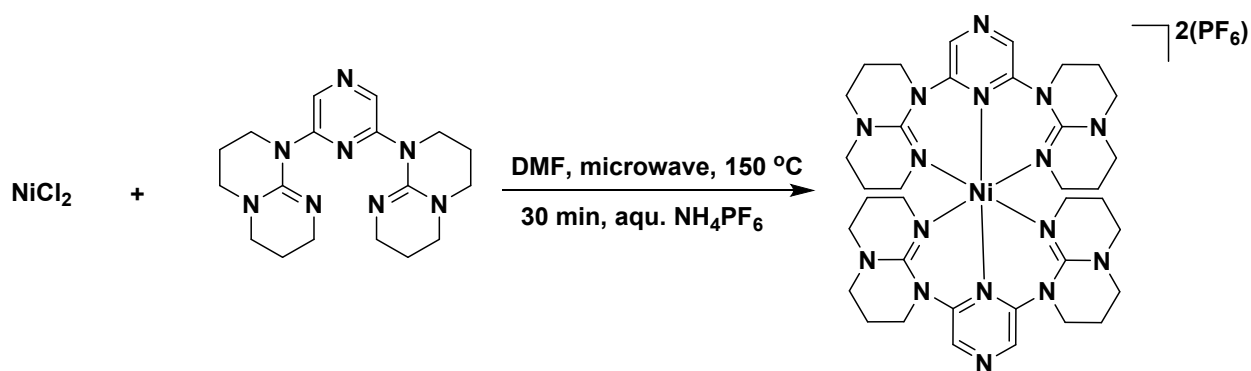
Synthesis of bis[(2,6-bis(2,3,4,6,7,8-hexahydro-1*H*-pyrimido[1,2-*a*]pyrimidin-1-yl)pyridine)]Ni(II) hexafluorophosphate (**1**)



A microwave vial equipped with a magnetic stir bar was charged with NiCl₂ (50 mg, 0.38 mmol, 1 equiv.) in 12 mL DMF to get a green colour suspension. The resulting suspension was sonicated for 5 minutes to get a clear green-colour solution. To the solution **L1** (300 mg, 0.85 mmol, 2.2 equiv.) was added to get brown colour solution. The reaction mixture was left to stir at 180 °C for 30 minutes to obtain a clear light brown solution. The resulting reaction mixture was concentrated under reduced pressure to give a brown solid residue. The chloride salt was metathesized to the PF₆ salt by addition of an aliquot of saturated aqueous KPF₆ solution to the methanolic solution of the compound. The resulting beige solid was collected by filtration, washed with water (3 x 20 mL) and dried under vacuum. Crude yield: 317 mg. Crystals suitable for X-ray diffraction study were grown by vapour diffusion of diethylether into an acetonitrile solution of

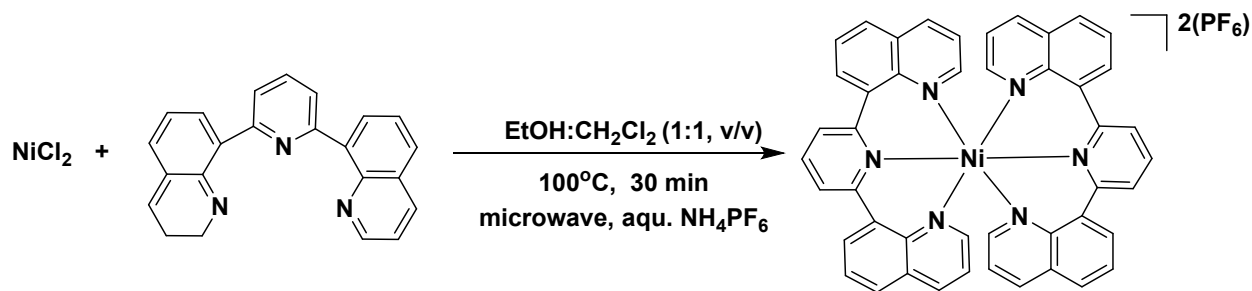
the title compound. The magenta colour crystals were formed after 12 h (yield = 225 mg, 56.0%). M.P. – 254 °C (dec.). Rf: 0.25 (7:1, v/v acetonitrile/aliquot of KNO₃ saturated water on silica) ¹H NMR (500 MHz, DMSO-d₆) δ (ppm): due to the paramagnetic nature of the product, only a few broad peaks at 52.92, 26.49, 15.70, 14.89, 8.71, 5.76, -1.34, -2.77, -6.40 ppm were observed. ESI+ MS: [M+2MeCN+Na]⁺ Calculated: (C₄₂H₆₀N₁₆NaNi) 869.44; Found: 869.15 (~ 6%). **Anal. Calcd** for C₃₈H₅₄N₁₄NiP₂F₁₂·4H₂O (MW 1127.612): C, 40.48; H, 5.54; N, 17.39, **Found:** C, 40.91; H, 4.91; N, 17.15.

Synthesis of bis[(2,6-bis(2,3,4,6,7,8-hexahydro-1*H*-pyrimido[1,2-*a*]pyrimidin-1-yl)pyrazine)Ni(II) hexafluorophosphate (**2**)



Complex **2** was synthesized following the similar procedure as that of complex **1**, however, ligand **L2** was used instead of ligand **L1**. Crude yield: 324 mg, Purified Yield = 274 mg, 68%. M.P. – 260 °C (dec.). Rf: 0.22 (7:1, v/v acetonitrile/aliquot of KNO₃ saturated water on silica). ¹H NMR (500 MHz, DMSO-d₆) δ (ppm): due to the paramagnetic nature of the product, only a few broad peaks at 60.95, 25.33, 16.18, 8.54, 5.40, -1.42, -3.53 ppm were observed. ESI+ MS: [M-2PF₆]²⁺ Calculated: (C₃₆H₅₂N₁₆Ni) 383.19; Found: 383.18 (~ 21%), [M-PF₆]⁺ Calculated: (C₃₆H₅₂N₁₆F₆PNi) 911.35; Found: 911.39 (< 1%). **Anal. Calcd** for C₃₆H₅₂N₁₆NiP₂F₁₂·4MeCN (MW 1221.7347): C, 43.26; H, 5.28; N, 22.93 **Found:** C, 43.48; H, 5.32; N, 22.34.

Synthesis of bis[2,6-di(quinolin-8-yl)pyridine]Ni(II) hexafluorophosphate (**3**)



A microwave vial equipped with a magnetic stir bar was charged with NiCl_2 (100 mg, 0.77 mmol, 1 equiv.) in 15 mL $\text{EtOH}:\text{CH}_2\text{Cl}_2$ (1:1, v/v) to get a pale yellow suspension. The resulting suspension was sonicated for 10 minutes to get a clear yellow solution. To this solution BQP (514 mg, 1.54 mmol, 2 equiv.) was added while the colour immediately changed to greenish-yellow. The reaction mixture was left to stir at 100°C for 30 minutes to obtain a dark yellow solution after which time it was concentrated under reduced pressure to ~ 5 mL to give a pale orange suspension. The chloride salt was metathesized to the PF_6 salt by addition of an aliquot of saturated aqueous KPF_6 solution to the suspension. The resulting pale orange solid was then filtered out, washed with water (3 x 20 mL) and dried under vacuum. Crude yield: 723 mg. Crystals suitable for X-ray diffraction study were grown by vapour diffusion of diethylether into an acetonitrile solution of the title compound. The pale orange crystals were formed after 12 h (yield = 562 mg, 72%). M.P. – 180°C (dec.). Rf: 0.32 (7:1, v/v acetonitrile/aliquot of KNO_3 saturated water on silica). ^1H NMR (500 MHz, CD_3CN) δ (ppm): 46.82 (1H), 43.06 (1H), 31.68 (2H), 22.07 (1H), 14.49 (2H), 11.27 (2H), 6.76 (2H), 2.09 (3H). ^{13}C NMR (125 MHz, CD_3CN) δ (ppm): 207.42, 139.63, 79.14, 78.88, 78.62, 66.21 and 30.83 (some peaks are missing due to paramagnetic nature of the complex). HR ESI+ MS: $[\text{M}-\text{PF}_6]^+$ Calculated: ($\text{C}_{46}\text{H}_{30}\text{N}_6\text{F}_6\text{PNi}$) 869.1527; Found: 869.1589 (70%). **Anal. Calcd** for $\text{C}_{46}\text{H}_{30}\text{N}_6\text{NiP}_2\text{F}_{12}\cdot 2\text{H}_2\text{O}$ (MW 1015.3924): C, 52.55; H, 3.26; N, 7.99 **Found**: C, 52.99; H, 3.20; N, 8.16.

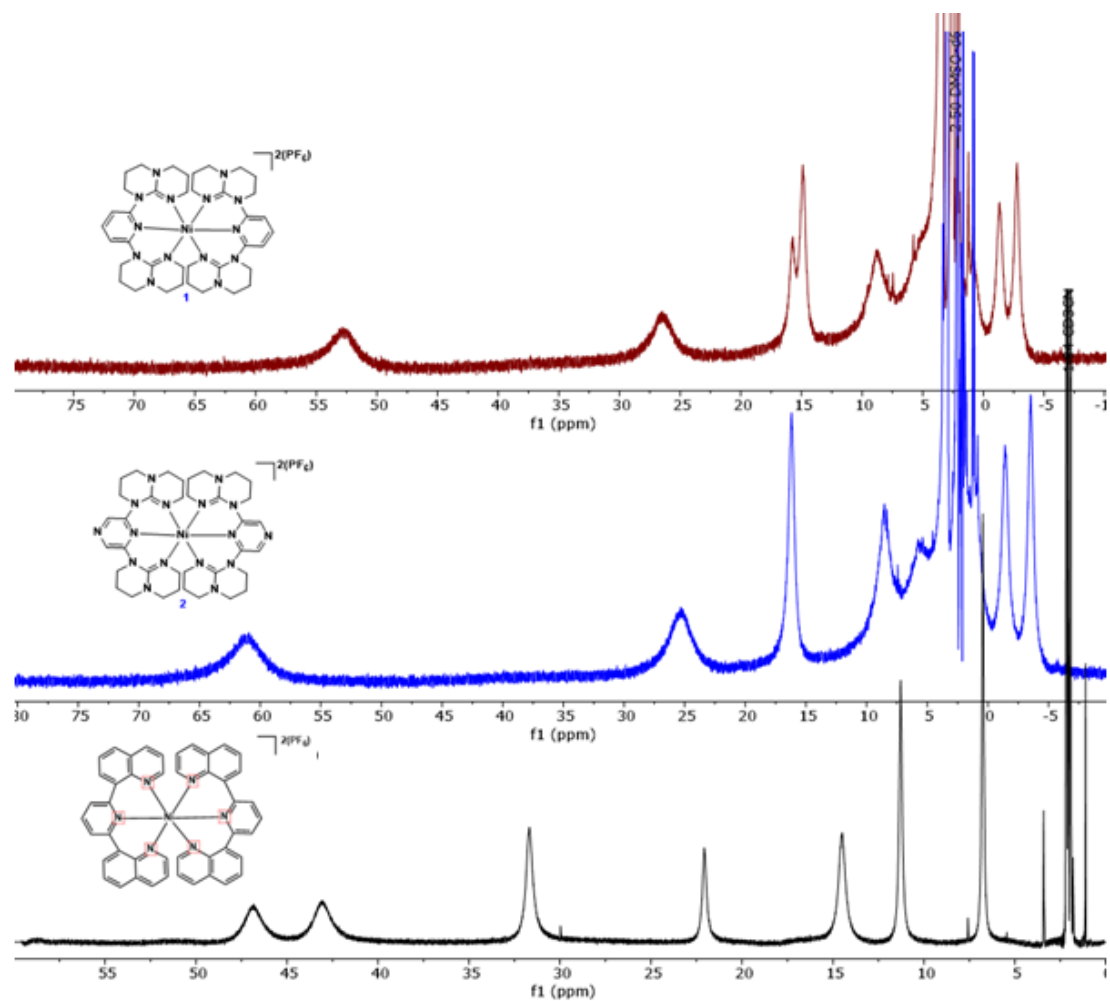


Figure S1. Stacked ¹H NMR spectra of **1**, **2** in DMSO-d₆ and **3** in CD₃CN at room temperature in 500 MHz.

X-ray diffraction studies

X-ray crystallographic data were collected from a single crystal sample, which was mounted on a loop fiber. Data were collected using a Bruker diffractometer equipped with a Bruker APEX-II CCD detector, a Kappa goniometer and a Mo-K_α source ($\lambda = 0.71073 \text{ \AA}$) at 150(2) K for **1** and 100(2) K for **2** and **3**. The crystal-to-detector distance was 4.0 cm, and the data collection was carried out in 1024 x 1024 pixel mode. The initial unit cell parameters were determined by a least-

squares fit of the angular setting of strong reflections, collected by a 180.0 degree scan in 180 frames over three different parts of the reciprocal space.

The diffraction quality of the crystals were checked, revealing in some cases poor diffraction with a large amount of diffuse scattering, signaling extensive crystal disorder. Data collection, cell refinement and data reduction were done using APEX2² and SAINT.³ Absorption corrections were applied using SADABS.⁴ Structures were solved by direct methods using SHELXS2012 and refined on F^2 by full-matrix least squares using SHELXL2012.⁵ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropic on calculated positions using a riding model. For complex **1**, atom C18 in the hpp moiety was found to be disordered over two positions. This positional disorder was taken into account for modelling with a 1:1 occupancy of the same atom. The minor positional disorders associated with the P and F atoms in PF₆ anions or C and N atoms of the cosolvated acetonitrile molecules either in **1**, **2** or **3** were not taken into account for modelling.

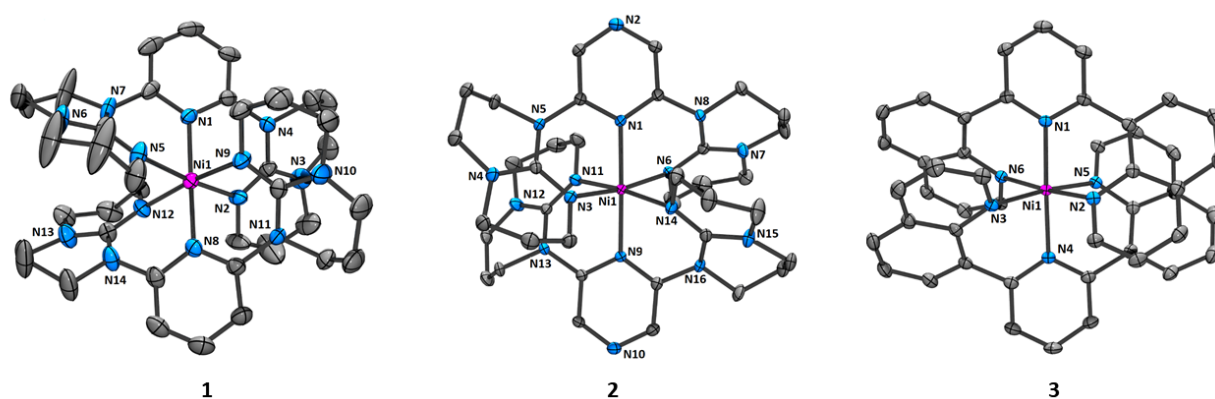


Figure S2. ORTEP view of complexes **1-3**. Hydrogen atoms anions and cocrystallized acetonitrile molecules are not shown for clarity. Ellipsoids correspond to a 50% probability level.

Table S1. Crystallographic data of complexes **1-3**.

compound	1	2	3
CCDC number	2237517	2237518	2237519
empirical formula	C ₃₈ H ₅₄ N ₁₄ F ₁₂ P ₂ Ni·C ₂ H ₃ N	C ₃₆ H ₅₂ N ₁₆ F ₁₂ P ₂ Ni·C ₂ H ₃ N	C ₄₆ H ₃₀ N ₆ F ₁₂ P ₂ Ni·2(C ₂ H ₃ N)
fw	1096.65	1098.64	1097.52
cryst syst	Orthorhombic	Orthorhombic	Orthorhombic
space group	Pna2(1)	Pna2(1)	Pbca
a [Å]	23.7720(14)	23.253(4)	12.757(5)
b [Å]	14.0221(8)	14.073(3)	15.419(6)
c [Å]	13.8462(9)	13.729(3)	46.854(16)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	90	90	90
vol [Å] ³	4615.4(5)	4492.9(15)	9216(6)
Z	4	4	8
ρ (calc) [Mg/m ³]	1.578	1.624	1.582
μ [cm ⁻¹]	0.589	0.607	0.587
F(000)	2272	2272	4464
cryst	magenta, block	brown, block	orange, block
cryst size [mm ³]	0.20 × 0.18 × 0.14	0.16 × 0.12 × 0.10	0.16 × 0.12 × 0.12
θ range	2.067 – 28.324°	2.072 – 28.318°	2.117 – 28.415°
reflns collected	59351	125442	193545
indep reflns (R _{int})	11414 (4.29)	11137 (7.13)	11490 (11.40)
max/min transm	0.746 / 0.640	0.706 / 0.648	0.732 / 0.571
data/restraints/para	10897 / 4 / 653	10706 / 1 / 633	9569 / 0 / 661
ms			
final R indices	R1 = 0.0479,	R1 = 0.0288,	R1 = 0.0447,
[I > 2σ(I)]	wR2 = 0.1241	wR2 = 0.0756	wR2 = 0.1139
R indices	R1 = 0.0499,	R1 = 0.0302,	R1 = 0.0555,
(all data)	wR2 = 0.1257	wR2 = 0.0761	wR2 = 0.1204

^aR1(F) based on observed reflections with I>2σ(I) for **2**; wR(F²) and GoF(F²) based on all data for all compounds.

Complex	Bond Length			Angle		
		Obs. (X-ray)	Calc. (DFT)		Obs. (X-ray)	Calc. (DFT)
Complex 1	Ni1-N1	2.057(3)	2.13236	N2-Ni1-N5	172.96(17)	169.649
	Ni1-N2	2.072(4)	2.13234	N9-Ni1-N12	172.66(15)	169.646
	Ni1-N5	2.073(4)	2.14364	N1-Ni1-N2	87.08(14)	85.978
	Ni1-N8	2.054(3)	2.13655	N1-Ni1-N5	86.03(16)	83.733
	Ni1-N9	2.073(4)	2.13647	N8-Ni1-N9	86.73(14)	85.977
	Ni1-N12	2.090(4)	2.14367	N8-Ni1-N12	86.03(14)	83.730
	Complex 2	Ni1-N1	2.0426(18)	2.13584	N3-Ni1-N6	171.83(8)
Ni1-N3		2.081(2)	2.13583	N11-Ni1-N14	172.87(8)	169.325
Ni1-N6		2.086(2)	2.14643	N1-Ni1-N3	86.45(8)	85.863
Ni1-N9		2.0501(18)	2.12354	N1-Ni1-N6	85.50(8)	83.509
Ni1-N11		2.072(2)	2.12345	N9-Ni1-N11	87.83(8)	85.866
Ni1-N14		2.073(2)	2.14647	N9-Ni1-N14	85.29(8)	83.511
Complex 3	Ni1-N1	2.0614(16)	2.16609	N2-Ni1-N6	175.27(6)	173.719
	Ni1-N2	2.0993(17)	2.16612	N3-Ni1-N5	173.91(6)	173.727
	Ni1-N3	2.1150(17)	2.16617	N1-Ni1-N2	88.07(6)	86.864
	Ni1-N4	2.0660(17)	2.16616	N1-Ni1-N6	87.34(6)	86.863
	Ni1-N5	2.1336(17)	2.11858	N3-Ni1-N4	86.82(7)	86.859
	Ni1-N6	2.1089(17)	2.11848	N4-Ni1-N4	87.26(7)	86.860

Table S2. Comparison of bond distances and angles in **2**.

Computational details

All calculations were performed using Gaussian 16 revision C.01 suite of programs employing the DFT method, the Becke three-parameter hybrid functional, Lee-Yang-Parr's gradient-corrected correlation functional (B3LYP), singlet ground state geometry optimizations for complex **1**, **2** and **3** were carried out at the R(B3LYP) whereas triplet optimization were carried out by using U(B3LYP) in MeCN. The basis set used for C, H, N, F atoms are 6-31g(d,p) along with SBKJC VDZ ECP for Ni(IV) ion. Vertical electronic excitations based on the (R)B3LYP- and (U)B3LYP-optimized geometries were also computed for the complexes mentioned (not shown here due to space limitation), using the TD-DFT formalism in solvents like acetonitrile and chloroform using conductor-like polarizable continuum model (CPCM).

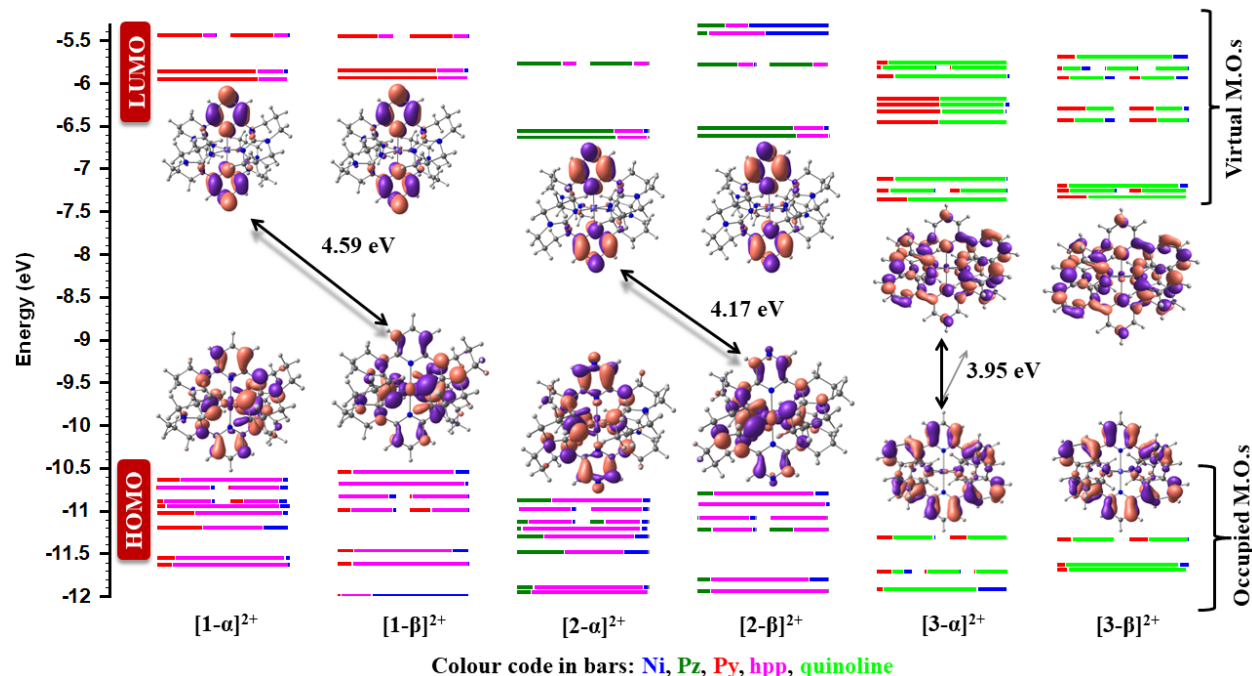


Figure S3. Calculated frontier M.O. energies of the modeled complexes **1**, **2** and **3** obtained from DFT(B3LYP/SBKJC VDZ ECP [Ni] 6-31G** [C,H,N,F] with CPCM (CH₃CN) and 0.05 eV of threshold of degeneracy.

Table S3. Electrochemical data for **L1**, **L2**, **L3**, **1** - **3**.

Compound	$E_{1/2}(\text{ox})^a / \text{V}$		$E_{1/2}(\text{red})^a / \text{V}$		$\Delta E_{1/2} / \text{V}$	
L1 (dgpy) ^b	1.11 (308)	0.77 (irr) ^c	----		----	
L2 (dgpz) ^b	1.14 (189)	0.77 (irr) ^c	-1.99 (irr) ^c		2.76	
L3 (BQP)	----	1.67 (irr) ^c	-2.11 (irr) ^c	-2.32 (irr) ^c	3.78	
1	1.53 (irr) ^c	0.71 (100)	-0.97 (310)	-2.12 (irr) ^c		1.72
2	1.69 (110)	0.92 (100)	-0.89 (254)	-1.73 (irr) ^c	-2.35 (310) ^c	1.81
3	1.84 (122)	1.13 (irr) ^c	-1.12 (irr) ^c	-2.04 (irr) ^c	-2.34 (irr) ^c	2.58
[Ni(3-Pytpy) ₂] ²⁺ , R1 ^d	1.73 (irr) ^c		-1.18 (71)	-1.39 (98)	-1.93 (138)	2.91
[Ni(ⁱ Bu ₃ tpy)(Mes)] ⁺ , R2 ^e	1.46		-1.22 (66)	-1.78(67)	-2.54 (irr) ^c	2.68
[Ni(tpy)(Mes)] ⁺ , R3 ^e	1.29		-1.11 (61)	-1.62(60)	-2.4 (irr) ^c	2.4
[Ni(toltpy)(Mes)] ⁺ , R4 ^e	1.28		-1.09 (64)	-1.63(63)	-2.42 (irr) ^c	2.37
[Ni(Cltpy)(Mes)] ⁺ , R5 ^e	1.47		-1.02 (64)	-1.59(63)	-2.42 (irr) ^c	2.49
[Ni(4,4',4''-Butpy)(CF ₃) ₂], R6 ^f	0.68 (irr) ^c		-1.34 (~100)	-1.61 (~100)	-1.82 (irr) ^c	2.02

^aPotentials are in volts vs. SCE for acetonitrile solutions, 0.1 M in [*n*-Bu₄N]PF₆, recorded at 25 ± 1 °C at a sweep rate of 100 mVs⁻¹ for cyclic voltammetry. The difference between cathodic and anodic peak potentials ($\Delta E_{1/2}$ in mV) is given in parentheses. ^bFrom ref ⁶., ^cIrreversible; oxidation potential is given for anodic wave, while reduction potential is given for cathodic wave. ^dFrom ref ⁷. ^eFrom ref ⁸. ^fFrom ref ⁹. (redox potentials for **R2-R6** has been calibrated vs SCE, $\Delta E_{1/2}$ for R7 was calculated by eye-estimation in absence of a tabulated data).

DFT Calculations:

Table S4. UV-vis absorption data of **L1-L3**, **1-3** and some benchmark complexes

Compound	λ_{\max} , nm ($\epsilon \times 10^3$, M ⁻¹ cm ⁻¹)
L1 (dgyy)^a	228 (29.0), 311 (12.8)
L2 (dgpz)^a	224 (26.9), 340 (14.1)
L3 (BQP)	213 (72.9), 227 (70.8), 295 sh (18.9), 307 (20.2)
1	224 (55.36), 258 sh (26.27), 309 (16.68)
2	225 (59.86), 263 sh (25.99), 344 (17.86)
3	204 (131.0), 229 sh (65.74), 321 sh (25.25), 332 (28.14), 354 sh (14.58)
[Ni(3-Pytpy)₂]²⁺, R1^b	249(23), 284(48), 315(17), 327(17), 341(15)
[Ni(Bu₃tpy)(Mes)]⁺, R2^c	324(17.4), 335(21.4), 399(2.7), 448(2.8), 487 sh(1.5)
[Ni(tpy)(Mes)]⁺, R3^c	324(14.1), 337(18.4), 401(2.3), 452(2.4), 487 sh(1.1)
[Ni(toltpy)(Mes)]⁺, R4^c	337(20.3), 420(2.2), 458(2.3), 505 sh (1.1)
[Ni(Cltpy)(Mes)]⁺, R5^c	323(16.8), 332(20.3), 392(2.7), 457(2.8), 480 sh (1.6)

^adata in dry acetonitrile at room temperature. ^aFrom ref ⁶. ^bFrom ref ⁷. ^cFrom ref ⁸.

Table S5. Selected Transitions from TD-DFT calculations of [**1**]²⁺ in the Triplet Ground State (b3lyp/SBKJC-VDZ[Ni]6-31G**[C,H,N], CPCM (CH₃CN)).

state	λ /nm	λ /nm ($\epsilon \times 10^3$ M ⁻¹ cm ⁻¹) [expt.]	f	Major transition(s)	character
90	238	224 (55.36)	0.3648	H-9(A)->L+2(A) (19%), H-8(A)->L+3(A) (26%), H-7(B)->L+2(B) (15%), H-6(B)->L+3(B) (21%)	HPP(π) to Py(π^*)
72	250	258 sh (26.27)	0.2804	H-6(A)->L+3(A) (15%), H-5(B)->L+2(B) (20%), H-4(B)->L+3(B) (10%)	HPP(π) to Py(π^*)
13	314	309 (16.68)	0.0816	H-3(A)->L+1(A) (11%), H-2(A)->L (A) (10%), H-1(A)->L (A) (11%), H (B)->L+1(B) (35%)	HPP(π) to Py(π^*)

Table S6. Selected Transitions from TD-DFT calculations of [2]²⁺ in the Triplet Ground State (b3lyp/SBKJC-VDZ[Ni]6-31G**[C,H,N], CPCM (CH₃CN)).

state	λ/nm	λ/nm ($\epsilon \times 10^3$ $\text{M}^{-1}\text{cm}^{-1}$) [expt.]	f	Major transition(s)	character
100	238	225 (59.86)	0.1104	H-7(A)->L+2(A) (16%), H-10(B)->L+3(B) (10%)	HPP(π) to Pz(π^*) (major) + Pz(π) to Pz(π^*) (minor)
76	259	263 sh (25.99)	0.1491	H-4(A)->L+3(A) (12%), H-4(B)->L+2(B) (16%)	HPP(π) to Pz(π^*)
29	324	344 (17.86)	0.1584	H-6(A)->L (A) (29%), H-3(A)->L+1(A) (27%), H-5(B)->L (B) (12%)	HPP(π) to Pz(π^*) (major) + Pz(π) to Pz(π^*) (minor)

Table S7. Selected Transitions from TD-DFT calculations of [3]²⁺ in the Triplet Ground State (b3lyp/SBKJC-VDZ[Ni]6-31G**[C,H,N], CPCM (CH₃CN)).

state	λ/nm	λ/nm ($\epsilon \times 10^3$ $\text{M}^{-1}\text{cm}^{-1}$) [expt.]	f	Major transition(s)	character
----	----	204 (131.0)	----	----	----
----	----	229 sh (65.74)	----	----	----
56	299	321 sh (25.25)	0.2324	H-7(A)->L (A) (27%), H-6(A)->L+2(A) (14%), H-5(B)->L (B) (23%), H-4(B)->L+2(B) (16%)	quinoline(π) to quinoline(π^*)
18	355	332 (28.14)	0.4646	H (A)->L+1(A) (18%), H-1(B)->L (B) (39%), H (B)->L+1(B) (11%)	quinoline(π) to quinoline(π^*)
11	368	354 sh (14.58)	0.2746	H-2(A)->L (A) (25%), H-1(A)->L (A) (56%)	quinoline(π) to quinoline(π^*) (major) + Py(π) to quinoline(π^*) (minor) + Ni($d\pi$) to quinoline(π^*) (minor)

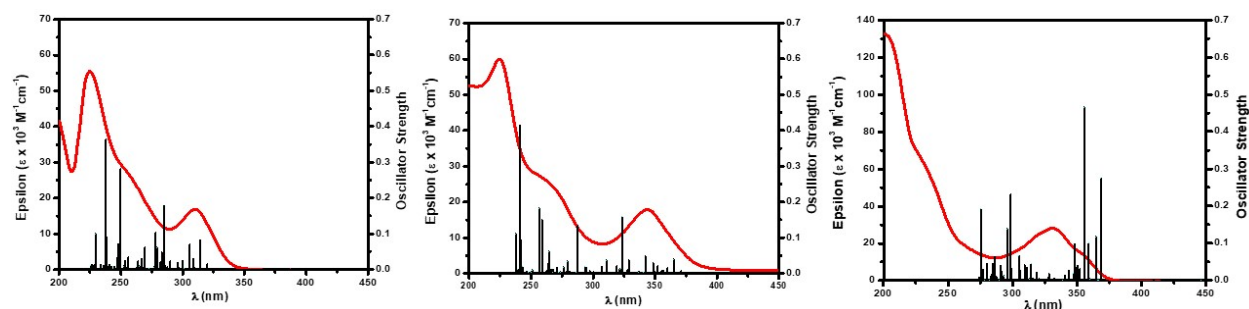


Figure S4. Overlay of experimental (curved line) absorption spectra and TD-DFT calculated oscillator strengths (black bars) at different wavelengths of **1**, **2** and **3** at ambient temperature in acetonitrile.

Table S8. List of non-bonded interactions between DNA and complex [**1**]²⁺

<----- ATOM 1 -----> <----- ATOM 2 ----->

Atom no	Atom name	Res name	Res no	Chain	Atom no	Atom name	Res name	Res no	Chain	Distance	
1	24	C36	UNK	1	---	76	O4'	DC	23	B	3.706
2	24	C36	UNK	1	---	75	C4'	DC	23	B	3.426
3	25	C37	UNK	1	---	74	C5'	DC	23	B	3.171
4	24	C36	UNK	1	---	74	C5'	DC	23	B	2.879
5	6	N13	UNK	1	---	74	C5'	DC	23	B	3.652
6	25	C37	UNK	1	---	71	OP1	DC	23	B	3.347
7	25	C37	UNK	1	---	70	P	DC	23	B	3.841
8	25	C37	UNK	1	---	56	O3'	DG	22	B	3.485
9	25	C37	UNK	1	---	55	C3'	DG	22	B	3.854
10	26	C38	UNK	1	---	54	O4'	DG	22	B	3.711
11	25	C37	UNK	1	---	54	O4'	DG	22	B	3.399
12	26	C38	UNK	1	---	53	C4'	DG	22	B	3.360
13	25	C37	UNK	1	---	53	C4'	DG	22	B	3.008
14	26	C38	UNK	1	---	52	C5'	DG	22	B	3.782
15	16	C28	UNK	1	---	90	OP1	DT	7	A	3.155
16	15	C27	UNK	1	---	90	OP1	DT	7	A	3.616
17	16	C28	UNK	1	---	89	P	DT	7	A	3.856
18	15	C27	UNK	1	---	89	P	DT	7	A	3.750
19	16	C28	UNK	1	---	35	O3'	DA	6	A	3.487
20	15	C27	UNK	1	---	35	O3'	DA	6	A	2.999
21	14	C26	UNK	1	---	35	O3'	DA	6	A	3.293
22	15	C27	UNK	1	---	34	C3'	DA	6	A	3.537
23	14	C26	UNK	1	---	34	C3'	DA	6	A	3.569
24	15	C27	UNK	1	---	32	C4'	DA	6	A	3.800

25	14	C26	UNK	1	---	32	C4'	DA	6	A	3.205
26	15	C27	UNK	1	---	31	C5'	DA	6	A	3.879
27	14	C26	UNK	1	---	31	C5'	DA	6	A	3.142

Table S9. List of non-bonded interactions between DNA and complex [2]²⁺

<----- A T O M 1 -----> <----- A T O M 2 ----->

<----- A T O M 1 ----->					<----- A T O M 2 ----->						
Atom no	Atom name	Res name	Res no	Chain	Atom no	Atom name	Res name	Res no	Chain	Distance	
1	24	C34	UNK	1	---	87	C7	DT	7	A	3.806
2	25	C35	UNK	1	---	85	O4	DT	7	A	3.789
3	24	C34	UNK	1	---	85	O4	DT	7	A	3.386
4	24	C34	UNK	1	---	61	N7	DA	6	A	3.485
5	23	C33	UNK	1	---	61	N7	DA	6	A	2.879
6	23	C33	UNK	1	---	60	C8	DA	6	A	3.405
7	22	C32	UNK	1	---	36	C2'	DA	5	A	3.712
8	21	C31	UNK	1	---	30	O5'	DA	5	A	3.873
9	21	C31	UNK	1	---	29	OP2	DA	5	A	3.245
10	20	C30	UNK	1	---	29	OP2	DA	5	A	2.824

Table S10. List of non-bonded interactions between DNA and complex [3]²⁺

<----- A T O M 1 -----> <----- A T O M 2 ----->

<----- A T O M 1 ----->					<----- A T O M 2 ----->							
Atom no	Atom name	Res name	Res no	Chain	Atom no	Atom name	Res name	Res no	Chain	Distance		
1	12	C32	UNK	1	X	---	116	O4'	DG	24	B	3.545
2	15	C35	UNK	1	X	---	114	C5'	DG	24	B	3.897
3	14	C34	UNK	1	X	---	114	C5'	DG	24	B	3.160
4	12	C32	UNK	1	X	---	40	O2	DC	23	B	3.493
5	11	C31	UNK	1	X	---	40	O2	DC	23	B	2.864
6	10	C30	UNK	1	X	---	40	O2	DC	23	B	3.258
7	12	C32	UNK	1	X	---	37	C1'	DC	23	B	3.866
8	11	C31	UNK	1	X	---	37	C1'	DC	23	B	3.866
9	10	C30	UNK	1	X	---	37	C1'	DC	23	B	3.788
10	9	C29	UNK	1	X	---	37	C1'	DC	23	B	3.804
11	15	C35	UNK	1	X	---	35	O3'	DC	23	B	3.367
12	14	C34	UNK	1	X	---	35	O3'	DC	23	B	3.354

13	13	C33 UNK	1	X	---	35	O3' DC	23	B	3.791
14	17	C37 UNK	1	X	---	33	O4' DC	23	B	3.773
15	10	C30 UNK	1	X	---	33	O4' DC	23	B	3.889
16	9	C29 UNK	1	X	---	33	O4' DC	23	B	3.490
17	8	C28 UNK	1	X	---	33	O4' DC	23	B	3.504
18	7	C27 UNK	1	X	---	33	O4' DC	23	B	3.289
19	17	C37 UNK	1	X	---	32	C4' DC	23	B	3.514
20	9	C29 UNK	1	X	---	32	C4' DC	23	B	3.731
21	8	C28 UNK	1	X	---	32	C4' DC	23	B	3.823
22	1	N3 UNK	1	X	---	32	C4' DC	23	B	3.712
23	7	C27 UNK	1	X	---	66	N3 DG	22	B	3.118
24	6	C26 UNK	1	X	---	66	N3 DG	22	B	3.347
25	11	C31 UNK	1	X	---	65	N2 DG	22	B	3.734
26	10	C30 UNK	1	X	---	65	N2 DG	22	B	3.119
27	7	C27 UNK	1	X	---	65	N2 DG	22	B	3.509
28	7	C27 UNK	1	X	---	64	C2 DG	22	B	3.734
29	6	C26 UNK	1	X	---	56	C1' DG	22	B	3.583
30	7	C27 UNK	1	X	---	52	O4' DG	22	B	3.795
31	6	C26 UNK	1	X	---	52	O4' DG	22	B	2.896
32	5	C25 UNK	1	X	---	52	O4' DG	22	B	3.604
33	6	C26 UNK	1	X	---	51	C4' DG	22	B	3.599
34	24	C44 UNK	1	X	---	69	OP1 DA	6	A	3.197
35	23	C43 UNK	1	X	---	69	OP1 DA	6	A	2.807
36	22	C42 UNK	1	X	---	69	OP1 DA	6	A	3.798
37	24	C44 UNK	1	X	---	68	P DA	6	A	3.708
38	23	C43 UNK	1	X	---	68	P DA	6	A	3.665
39	25	C45 UNK	1	X	---	97	O3' DA	5	A	3.449
40	24	C44 UNK	1	X	---	97	O3' DA	5	A	2.943
41	23	C43 UNK	1	X	---	97	O3' DA	5	A	3.333
42	25	C45 UNK	1	X	---	94	C4' DA	5	A	3.566
43	7	C27 UNK	1	X	---	151	N2 DG	4	A	3.646
44	6	C26 UNK	1	X	---	151	N2 DG	4	A	3.508

Table S11. Optimized atomic coordinates obtained from DFT calculations of [1]²⁺

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	28	0	0.054174	0.000006	-0.000113
2	7	0	1.497263	-0.369594	-1.525835
3	7	0	1.497189	0.369420	1.525708
4	7	0	-1.423449	0.013944	-1.553053
5	7	0	0.045860	-2.116026	0.295154
6	7	0	0.045941	2.115977	-0.295208
7	7	0	-1.423541	-0.013877	1.552789
8	7	0	3.490467	1.435341	2.227256
9	7	0	-2.296417	-2.076240	0.867785
10	7	0	-3.604062	0.618801	-2.214469
11	7	0	2.369182	-2.140345	-0.276373
12	7	0	-2.296286	2.076327	-0.868071
13	7	0	-3.604119	-0.618807	2.214385
14	7	0	3.490834	-1.435254	-2.226897
15	7	0	2.369261	2.140125	0.276324
16	6	0	4.369867	3.397802	0.950907
17	1	0	5.327987	3.810104	0.628687
18	1	0	3.753100	4.228090	1.302102
19	6	0	1.260365	4.188777	-0.362301
20	1	0	2.161879	4.744453	-0.160476
21	6	0	-4.750578	-2.084794	0.640574
22	1	0	-5.619422	-2.729870	0.501639
23	1	0	-5.085885	-2.018580	2.773276
24	1	0	-4.701924	-1.391483	-0.203777
25	6	0	-1.028594	-4.125514	1.045598
26	1	0	-1.891540	-4.627729	1.448531
27	6	0	-1.056682	-2.760508	0.739031
28	6	0	-1.056567	2.760523	-0.739073
29	6	0	3.657745	0.511726	3.359412
30	1	0	4.223324	1.036755	4.130648
31	1	0	4.252581	-0.359129	3.055504
32	6	0	-1.028443	4.125587	-1.045466
33	1	0	-1.891420	4.627852	-1.448288
34	6	0	2.425755	1.265220	1.382270
35	6	0	1.191273	2.811421	-0.121026
36	6	0	-1.534307	-1.184980	-2.388603
37	1	0	-2.013043	-1.989841	-1.818472
38	1	0	-0.523700	-1.521595	-2.619068
39	6	0	3.666744	-2.669310	0.184269
40	1	0	3.498899	-3.299887	1.053446
41	1	0	4.274340	-1.821553	0.518968
42	6	0	-4.750471	2.084667	-0.640509
43	1	0	-5.619344	2.729708	-0.501594

44	1	0	-4.701890	1.391308	0.203771
45	6	0	2.425849	-1.265346	-1.382223
46	6	0	4.600129	-2.392387	-2.069098
47	1	0	5.512937	-1.817893	-1.867145
48	1	0	4.748534	-2.903149	-3.024121
49	6	0	3.666891	2.669001	-0.184226
50	1	0	3.499165	3.299515	-1.053468
51	1	0	4.274477	1.821192	-0.518812
52	6	0	-1.533822	1.184794	2.388803
53	1	0	-2.011645	1.990298	1.818819
54	1	0	-0.523035	1.520533	2.619783
55	6	0	1.260153	-4.188901	0.362247
56	1	0	2.161620	-4.744620	0.160322
57	6	0	1.191127	-2.811531	0.120942
58	6	0	-3.711662	0.428348	3.243671
59	1	0	-4.248795	-0.001246	4.094719
60	1	0	-4.320319	1.256740	2.860232
61	6	0	-4.856800	1.330505	-1.950047
62	1	0	-5.661526	0.589399	-1.916824
63	1	0	-5.085702	2.018765	-2.773205
64	6	0	-2.420146	0.847023	-1.556536
65	6	0	0.140371	4.839454	-0.842923
66	1	0	0.173120	5.900592	-1.055299
67	6	0	-3.711491	-0.427724	-3.244414
68	1	0	-4.247815	0.002620	-4.095617
69	1	0	-4.320898	-1.255933	-2.861794
70	6	0	-2.420254	-0.846929	1.556382
71	6	0	-3.495732	2.930987	-0.709576
72	1	0	-3.360429	3.524239	0.195595
73	1	0	-3.605455	3.623101	-1.551795
74	6	0	0.140181	-4.839471	0.843023
75	1	0	0.172865	-5.900593	1.055498
76	6	0	1.498323	-0.489546	2.715660
77	1	0	1.915219	-1.464268	2.438986
78	1	0	0.460676	-0.669320	2.996724
79	6	0	-2.336661	0.920459	3.656306
80	1	0	-2.432034	1.825710	4.258607
81	1	0	-1.833421	0.166729	4.268743
82	6	0	3.658578	-0.510986	-3.358433
83	1	0	4.252663	0.360042	-3.053536
84	1	0	4.225087	-1.035262	-4.129489
85	6	0	2.294571	0.085608	3.878460
86	1	0	1.783196	0.952529	4.306538
87	1	0	2.405561	-0.656879	4.671083
88	6	0	1.498385	0.489319	-2.715857
89	1	0	0.460751	0.668362	-2.997410
90	1	0	1.914441	1.464341	-2.438995
91	6	0	4.369795	-3.398096	-0.950829
92	1	0	5.327868	-3.810445	-0.628518

93	1	0	3.753046	-4.228365	-1.302091
94	6	0	-3.495800	-2.931035	0.709803
95	1	0	-3.360614	-3.524618	-0.195169
96	6	0	-2.336513	-0.920432	-3.656470
97	1	0	-2.432039	-1.825667	-4.258768
98	1	0	-1.832688	-0.166956	-4.268736
99	6	0	4.600056	2.392108	2.069201
100	1	0	5.512673	1.817329	1.867163
101	1	0	4.748740	2.902885	3.024163
102	6	0	-4.856940	-1.330477	1.950016
103	6	0	2.295562	-0.085328	-3.878279
104	1	0	1.784805	-0.952423	-4.306742
105	1	0	2.406710	0.657290	-4.670757
106	1	0	-5.661581	-0.589295	1.916676
107	1	0	-3.605368	-3.622812	1.552320

Table S12. Optimized atomic coordinates obtained from DFT calculations of $[2]^{2+}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	28	0	0.057583	0.000015	-0.000074
2	7	0	1.508695	-0.407034	-1.513483
3	7	0	1.508650	0.406894	1.513402
4	7	0	-1.425152	-0.011654	-1.552017
5	7	0	0.043174	-2.097037	0.333945
6	7	0	0.043123	2.097006	-0.333935
7	7	0	-1.425252	0.011703	1.551821
8	7	0	3.498364	1.492126	2.196510
9	7	0	-2.292725	-2.077851	0.937322
10	7	0	-3.595318	0.589858	-2.252174
11	7	0	2.363537	-2.179781	-0.250888
12	7	0	-2.292710	2.077864	-0.937557
13	7	0	-3.595376	-0.589958	2.252073
14	7	0	3.498757	-1.491869	-2.196121
15	7	0	2.363487	2.179683	0.250905
16	6	0	4.320146	3.494286	0.939018
17	1	0	5.267530	3.935984	0.624630
18	1	0	3.675280	4.305973	1.283275
19	6	0	1.186627	4.187713	-0.424803
20	1	0	2.065933	4.790921	-0.245884
21	6	0	-4.749619	-2.132002	0.754997
22	1	0	-5.611482	-2.793773	0.657848
23	1	0	-5.048205	-1.985730	2.888917
24	1	0	-4.727092	-1.472531	-0.117270
25	6	0	-0.981632	-4.110911	1.087635
26	1	0	-1.824216	-4.650839	1.492009

27	6	0	-1.052821	-2.739256	0.789034
28	6	0	-1.052857	2.739252	-0.789024
29	6	0	3.681956	0.569378	3.327917
30	1	0	4.259055	1.094316	4.090069
31	1	0	4.271098	-0.301718	3.015067
32	6	0	-0.981647	4.110943	-1.087515
33	1	0	-1.824253	4.650885	-1.491848
34	6	0	2.431440	1.309270	1.361778
35	6	0	1.175364	2.808003	-0.159846
36	6	0	-1.535158	-1.232503	-2.357368
37	1	0	-2.021252	-2.020232	-1.769553
38	1	0	-0.524039	-1.577396	-2.572947
39	6	0	3.650146	-2.746528	0.202508
40	1	0	3.470722	-3.372378	1.072933
41	1	0	4.282116	-1.915451	0.532695
42	6	0	-4.749668	2.131702	-0.754954
43	1	0	-5.611599	2.793365	-0.657813
44	1	0	-4.727178	1.472085	0.117198
45	6	0	2.431563	-1.309299	-1.361685
46	6	0	4.571903	-2.494840	-2.058731
47	1	0	5.508201	-1.955648	-1.870629
48	1	0	4.684052	-3.008161	-3.017259
49	6	0	3.650110	2.746338	-0.202551
50	1	0	3.470688	3.372177	-1.072984
51	1	0	4.282007	1.915208	-0.532758
52	6	0	-1.534941	1.232412	2.357424
53	1	0	-2.020430	2.020543	1.769642
54	1	0	-0.523724	1.576790	2.573379
55	6	0	1.186630	-4.187762	0.424875
56	1	0	2.065911	-4.791000	0.245934
57	6	0	1.175393	-2.808051	0.159877
58	6	0	-3.702715	0.490302	3.247882
59	1	0	-4.233055	0.085061	4.114652
60	1	0	-4.317610	1.302269	2.840692
61	6	0	-4.843089	1.328214	-2.035310
62	1	0	-5.657203	0.598704	-1.987053
63	1	0	-5.047956	1.985871	-2.888917
64	6	0	-2.418378	0.826349	-1.589772
65	7	0	0.123318	4.817388	-0.895151
66	6	0	-3.702489	-0.489920	-3.248526
67	1	0	-4.232235	-0.084129	-4.115415
68	1	0	-4.317888	-1.301828	-2.841995
69	6	0	-2.418439	-0.826327	1.589643
70	6	0	-3.482747	2.958256	-0.832214
71	1	0	-3.355291	3.579357	0.055101
72	1	0	-3.561494	3.620991	-1.700548
73	7	0	0.123331	-4.817387	0.895287
74	6	0	1.516047	-0.437107	2.715446
75	1	0	1.926627	-1.416883	2.447312

76	1	0	0.479851	-0.607654	3.008016
77	6	0	-2.327949	1.000681	3.637065
78	1	0	-2.423660	1.922852	4.212910
79	1	0	-1.817165	0.267757	4.268132
80	6	0	3.682696	-0.568474	-3.326920
81	1	0	4.270931	0.302891	-3.013103
82	1	0	4.260822	-1.092592	-4.088847
83	6	0	2.324853	0.146192	3.865502
84	1	0	1.818596	1.015782	4.294133
85	1	0	2.444086	-0.591705	4.661098
86	6	0	1.515874	0.436765	-2.715697
87	1	0	0.479650	0.606313	-3.008744
88	1	0	1.925398	1.416964	-2.447516
89	6	0	4.320051	-3.494524	-0.939109
90	1	0	5.267391	-3.936348	-0.624760
91	1	0	3.675076	-4.306130	-1.283345
92	6	0	-3.482658	-2.958391	0.832511
93	1	0	-3.355271	-3.579888	-0.054536
94	6	0	-2.327699	-1.000605	-3.637270
95	1	0	-2.423434	-1.922737	-4.213173
96	1	0	-1.816534	-0.267789	-4.268153
97	6	0	4.571918	2.494603	2.058636
98	1	0	5.507948	1.955010	1.870309
99	1	0	4.684567	3.007966	3.017074
100	6	0	-4.843203	-1.328286	2.035188
101	6	0	2.325711	-0.145949	-3.865339
102	1	0	1.820206	-1.015776	-4.294372
103	1	0	2.445019	0.592106	-4.660783
104	1	0	-5.657242	-0.598711	1.986688
105	1	0	-3.561243	-3.620738	1.701162

Table S13. Optimized atomic coordinates obtained from DFT calculations of $[3]^{2+}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	1.466666	-0.118552	1.589649
2	6	0	1.540110	0.865398	2.475045
3	1	0	0.651952	1.474978	2.581384
4	6	0	2.690407	1.153764	3.226945
5	1	0	2.673152	1.954665	3.953357
6	6	0	3.830346	0.433680	2.969909
7	1	0	4.760841	0.662597	3.476007
8	6	0	3.795035	-0.629812	2.037465
9	6	0	2.543812	-0.941966	1.418616
10	6	0	2.430692	-2.129482	0.627305
11	6	0	3.608215	-2.794567	0.306998

12	1	0	3.567677	-3.658316	-0.343180
13	6	0	4.864296	-2.411350	0.814855
14	1	0	5.745656	-2.970665	0.529447
15	6	0	4.952084	-1.378949	1.713000
16	1	0	5.896293	-1.120798	2.176622
17	6	0	1.136550	-2.802201	0.298293
18	6	0	1.135565	-4.203392	0.354964
19	1	0	2.016434	-4.730888	0.686692
20	6	0	-0.000136	-4.908745	0.000282
21	1	0	-0.000163	-5.991508	0.000338
22	6	0	-1.135796	-4.203375	-0.354489
23	1	0	-2.016684	-4.730864	-0.686183
24	6	0	-1.136718	-2.802178	-0.297972
25	7	0	-1.466672	-0.118591	-1.589567
26	6	0	-1.540006	0.865269	-2.475072
27	1	0	-0.651841	1.474851	-2.581344
28	6	0	-2.690203	1.153544	-3.227159
29	1	0	-2.672858	1.954371	-3.953651
30	6	0	-3.830168	0.433476	-2.970200
31	1	0	-4.760597	0.662326	-3.476451
32	6	0	-3.794974	-0.629920	-2.037641
33	6	0	-2.543833	-0.942000	-1.418589
34	6	0	-2.430807	-2.129445	-0.627155
35	6	0	-3.608369	-2.794516	-0.306959
36	1	0	-3.567908	-3.658223	0.343280
37	6	0	-4.864385	-2.411355	-0.815016
38	1	0	-5.745776	-2.970662	-0.529687
39	6	0	-4.952061	-1.379035	-1.713264
40	1	0	-5.896206	-1.120939	-2.177047
41	7	0	-1.466687	0.118695	1.589719
42	6	0	-1.540127	-0.865142	2.475240
43	1	0	-0.651977	-1.474726	2.581633
44	6	0	-2.690417	-1.153406	3.227191
45	1	0	-2.673159	-1.954213	3.953707
46	6	0	-3.830350	-0.433336	2.970087
47	1	0	-4.760838	-0.662174	3.476234
48	6	0	-3.795045	0.630041	2.037511
49	6	0	-2.543834	0.942088	1.418588
50	6	0	-2.430704	2.129516	0.627147
51	6	0	-3.608204	2.794636	0.306843
52	1	0	-3.567634	3.658351	-0.343382
53	6	0	-4.864285	2.411498	0.814760
54	1	0	-5.745636	2.970822	0.529338
55	6	0	-4.952082	1.379176	1.712995
56	1	0	-5.896283	1.121103	2.176677
57	6	0	-1.136562	2.802194	0.298083
58	6	0	-1.135578	4.203387	0.354676
59	1	0	-2.016469	4.730887	0.686349
60	6	0	0.000129	4.908717	-0.000031

61	1	0	0.000165	5.991479	-0.000021
62	6	0	1.135789	4.203322	-0.354751
63	1	0	2.016704	4.730781	-0.686427
64	6	0	1.136695	2.802128	-0.298178
65	7	0	1.466655	0.118491	-1.589623
66	6	0	1.540028	-0.865416	-2.475073
67	1	0	0.651849	-1.474969	-2.581395
68	6	0	2.690279	-1.153787	-3.227042
69	1	0	2.672964	-1.954653	-3.953491
70	6	0	3.830247	-0.433739	-2.970036
71	1	0	4.760710	-0.662651	-3.476197
72	6	0	3.795013	0.629719	-2.037550
73	6	0	2.543835	0.941864	-1.418604
74	6	0	2.430782	2.129368	-0.627263
75	6	0	3.608328	2.794464	-0.307063
76	1	0	3.567825	3.658229	0.343098
77	6	0	4.864371	2.411241	-0.815002
78	1	0	5.745752	2.970559	-0.529664
79	6	0	4.952092	1.378838	-1.713152
80	1	0	5.896262	1.120691	-2.176854
81	28	0	-0.000004	-0.000066	0.000061
82	7	0	0.000046	2.118515	-0.000047
83	7	0	-0.000071	-2.118546	0.000138

References

1. N. G. Connelly and W. E. Geiger, *Chemical Reviews*, 1996, **96**, 877-910.
2. *APEX2 (2013); Bruker Molecular Analysis Research Tool*. Bruker AXS Inc., Madison, WI 53719-1173.
3. SAINT (2013) V8.34A; Integration Software for Single Crystal Data. Bruker AXS Inc., Madison, WI 53719-1173.
4. Sheldrick, G. M. (1996). *SADABS*, Bruker Area Detector Absorption Corrections. Bruker AXS Inc., Madison, WI 53719-1173.
5. *SHELXTL (2012) version 6.14*; Bruker Analytical X-ray Systems Inc., Madison, WI 53719-1173.
6. A. K. Pal and G. S. Hanan, *Dalton Transactions*, 2014, **43**, 11811-11814.
7. A. K. Pal, B. Laramée-Milette and G. S. Hanan, *Inorganica Chimica Acta*, 2014, **418**, 15-22.
8. C. Hamacher, N. Hurkes, A. Kaiser, A. Klein and A. Schüren, *Inorganic Chemistry*, 2009, **48**, 9947-9951.
9. C.-P. Zhang, H. Wang, A. Klein, C. Biewer, K. Stirnat, Y. Yamaguchi, L. Xu, V. Gomez-Benitez and D. A. Vicic, *Journal of the American Chemical Society*, 2013, **135**, 8141-8144.