

1,5-Diarylbiguanides and their Nickel(II) Complexes.

David A McMorran*, C John McAdam, Holly van der Salm and Keith C Gordon

Department of Chemistry, University of Otago,

PO Box 56, Dunedin, New Zealand

Supplementary Information

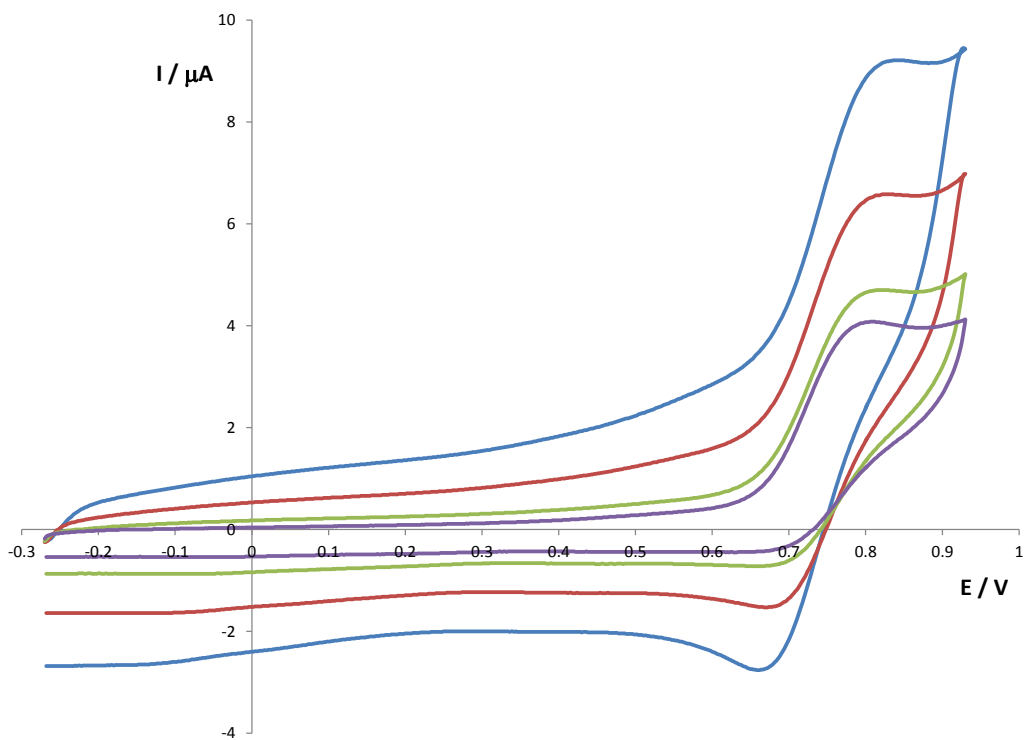
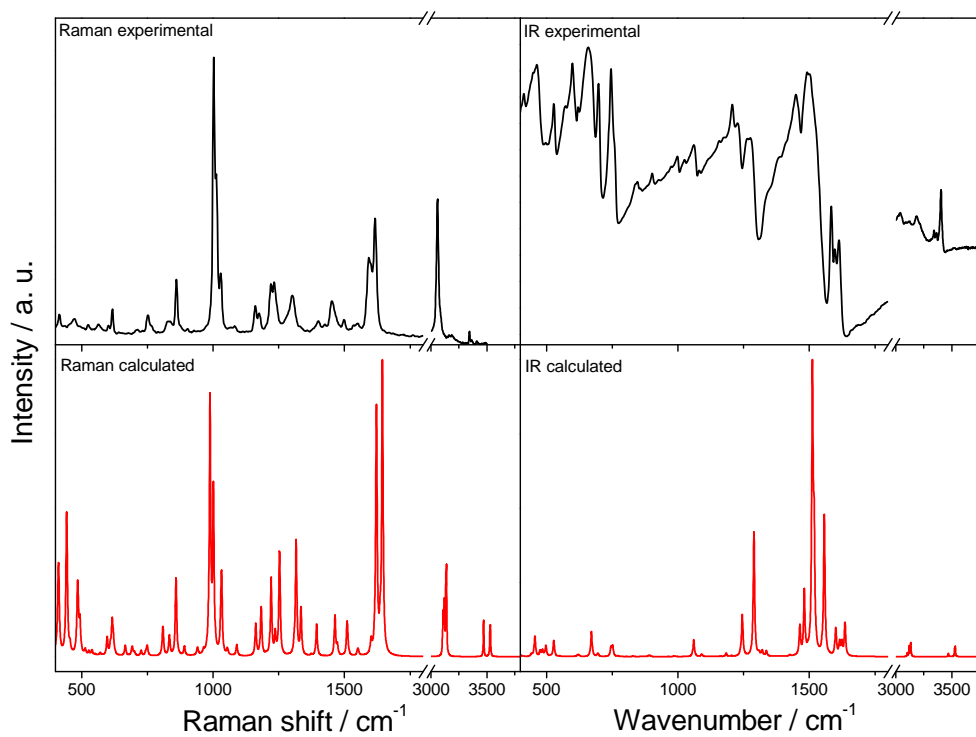
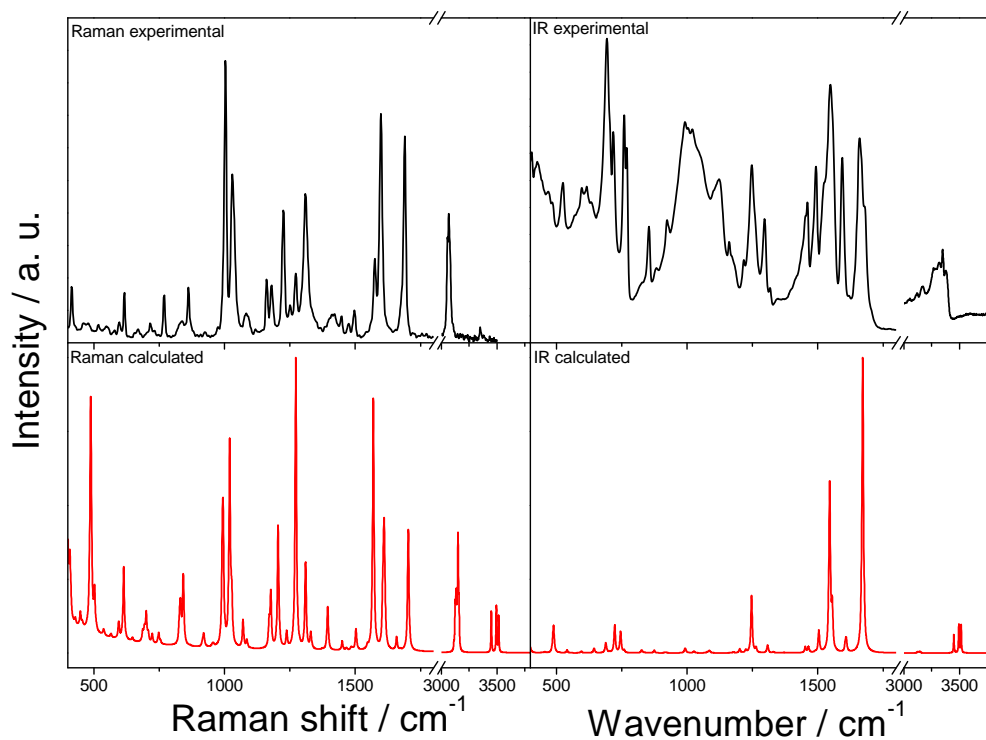


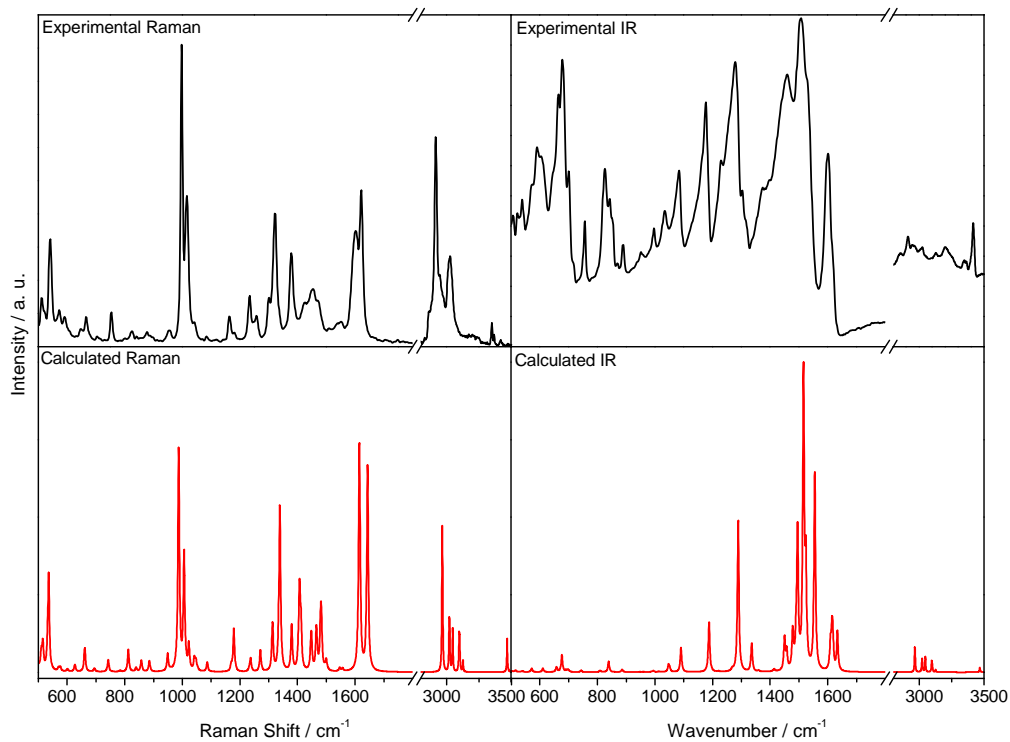
Fig. S1 Cyclic voltammograms of $[\text{Ni}(\text{HL1})_2](\text{BF}_4)_2$ at 100, 200, 500 & 1000 mVs^{-1} ($\sim 1 \times 10^{-3}$ M in DMF, 0.1 M Bu_4NPF_6 , referenced to $[\text{Fc}^*]^{+/0} = 0.00$ V).



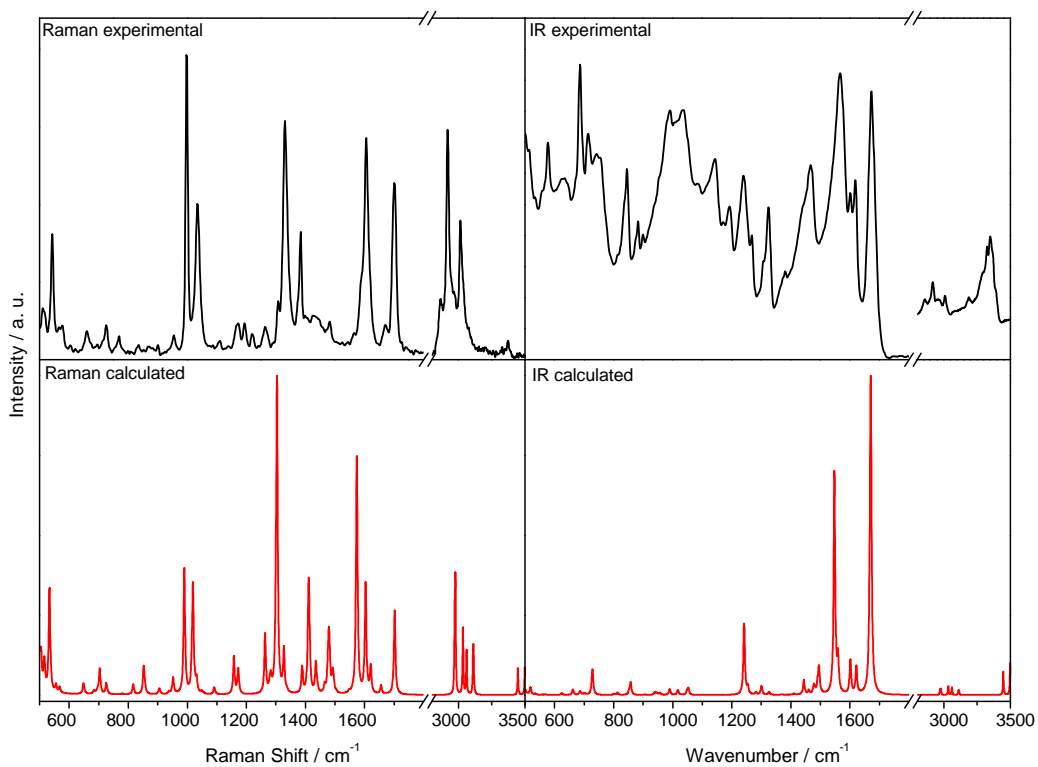
S2. Experimental and calculated Raman and IR spectra for [Ni(L1)₂]



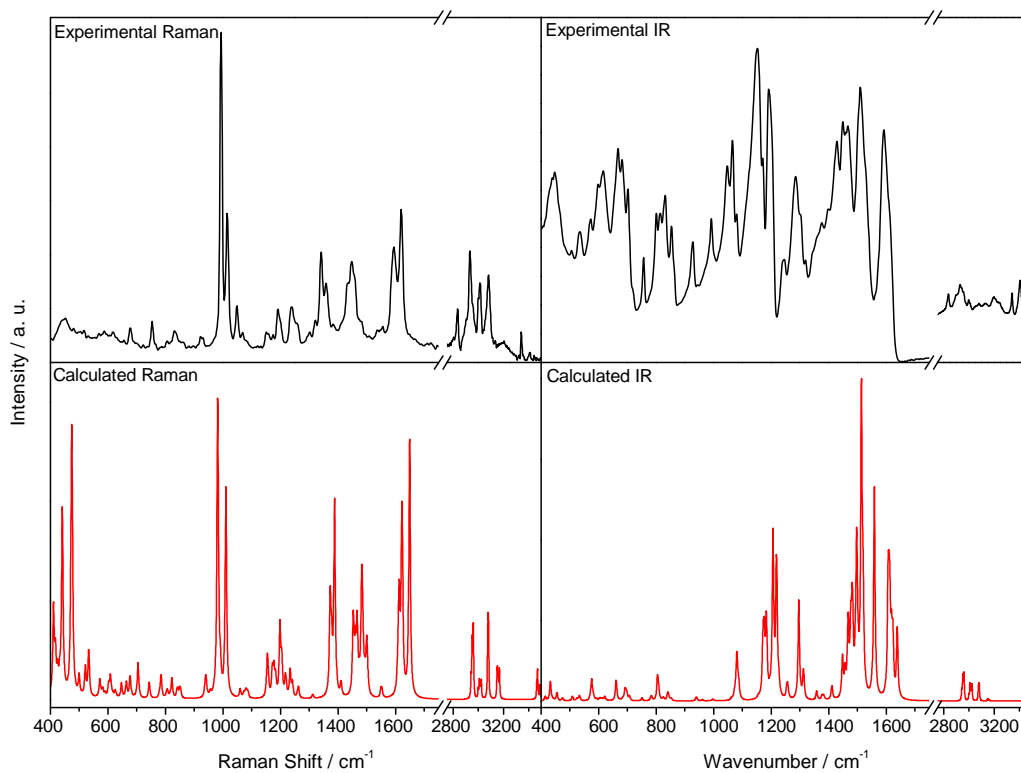
S3. Experimental and calculated Raman and IR spectra for [Ni(HL1)₂](BF₄)₂



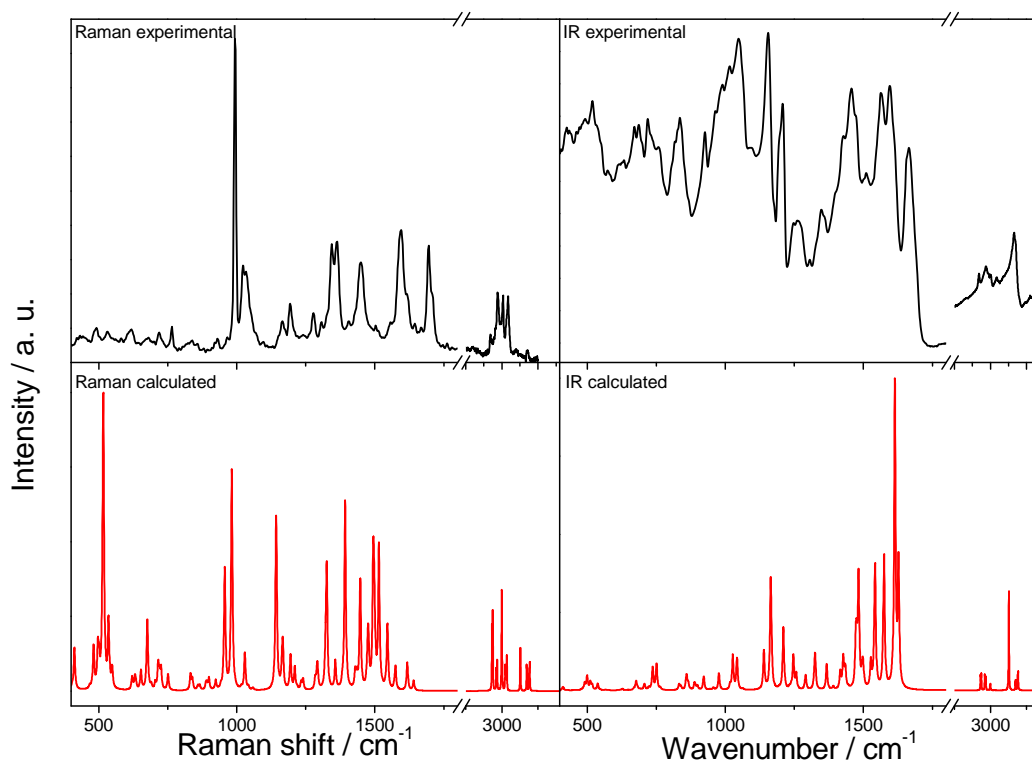
S4. Experimental and calculated Raman and IR spectra for [Ni(L2)₂]



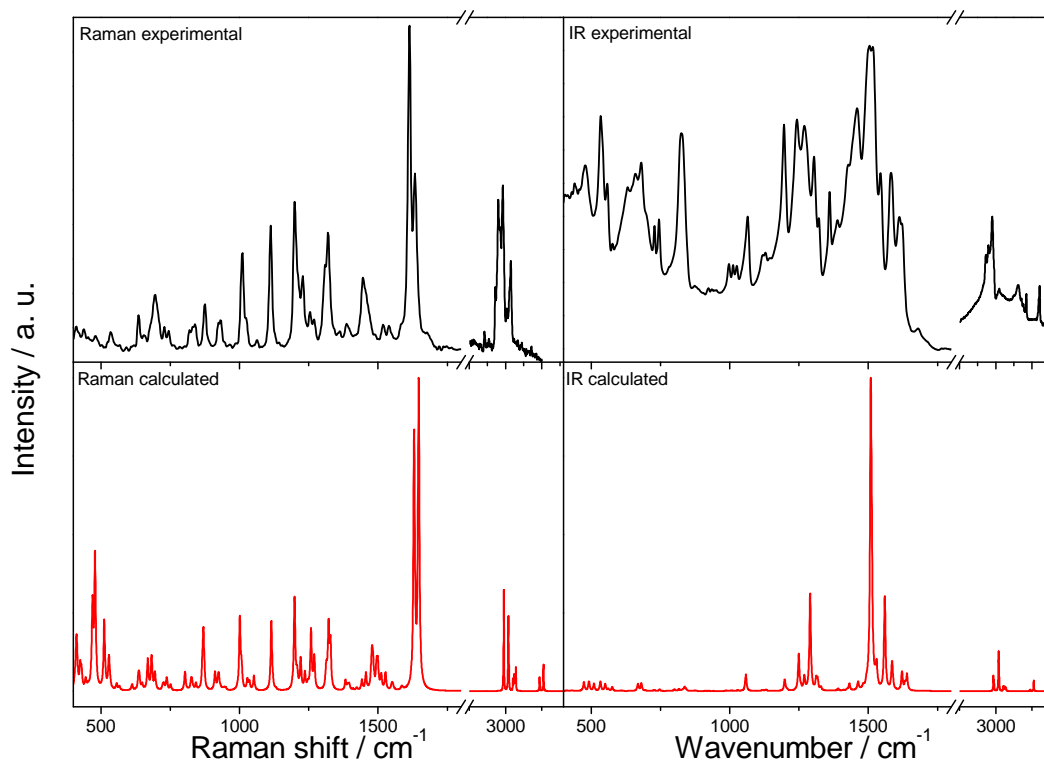
S5. Experimental and calculated Raman and IR spectra for [Ni(HL2)₂](BF₄)₂



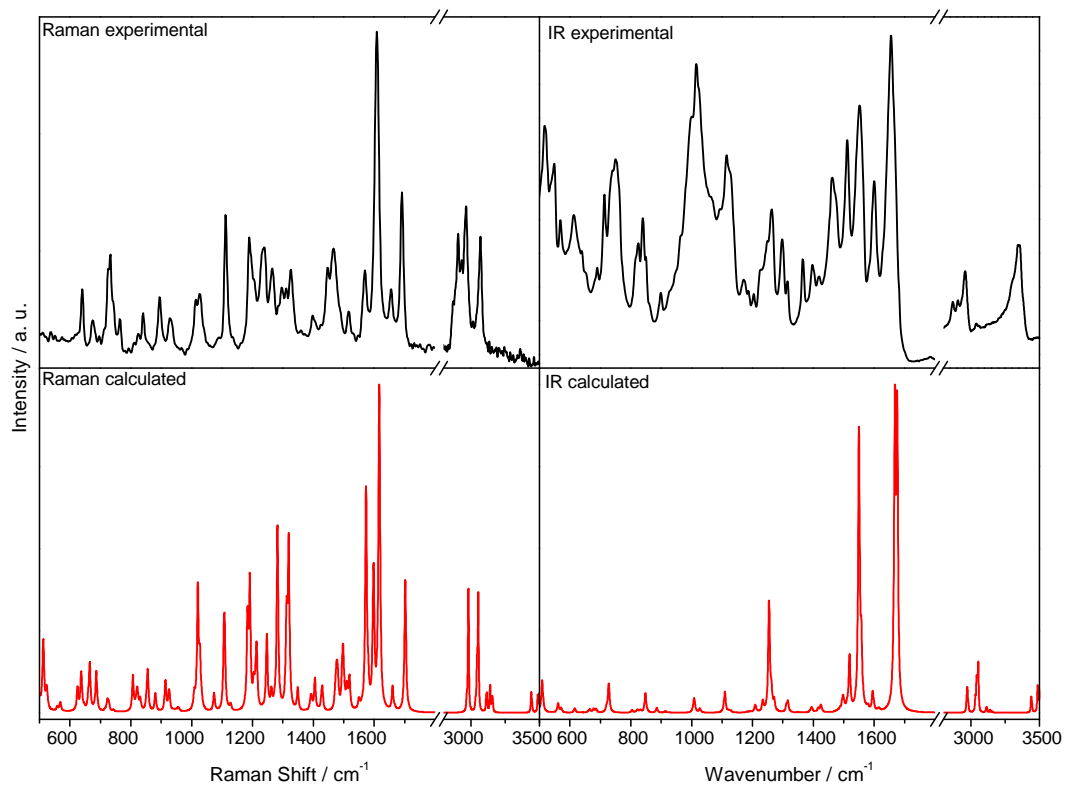
S6. Experimental and calculated Raman and IR spectra for $[\text{Ni}(\text{L3})_2]$



S7. Experimental and calculated Raman and IR spectra for $[\text{Ni}(\text{HL3})_2](\text{BF}_4)_2$



S8. Experimental and calculated Raman and IR spectra for [Ni(L4)₂]



S9. Experimental and calculated Raman and IR spectra for [Ni(HL4)₂](BF₄)₂

Table S1 MADS

Complex	MAD / cm⁻¹
[Ni(HL1) ₂](BF ₄) ₂	11
[Ni(HL2) ₂](BF ₄) ₂	10
[Ni(HL3) ₂](BF ₄) ₂	12
[Ni(HL4) ₂](BF ₄) ₂	10
[Ni(L1) ₂]	10
[Ni(L2) ₂]	13
[Ni(L3) ₂]	13
[Ni(L4) ₂]	7

Table S2 Calculated single point energy values / hartrees

Compound	Energy in vacuo	Energy in water
[Ni(HL1) ₂](BF ₄) ₂	-1801.50994872	-1801.71113514
[Ni(L1) ₂]	-1800.77850250	-1800.80035065
[Ni(HL2) ₂](BF ₄) ₂	-2116.06332921	-2116.25513549
[Ni(L2) ₂]	-2115.32095201	-2115.34183996
[Ni(HL3) ₂](BF ₄) ₂	-2717.68516588	-2717.87428853
[Ni(L3) ₂]	-2716.94718770	-2716.98144196
[Ni(HL4) ₂](BF ₄) ₂	-2430.52644673	-2430.71614991
[Ni(L4) ₂]	-2429.78664136	-2429.80854907

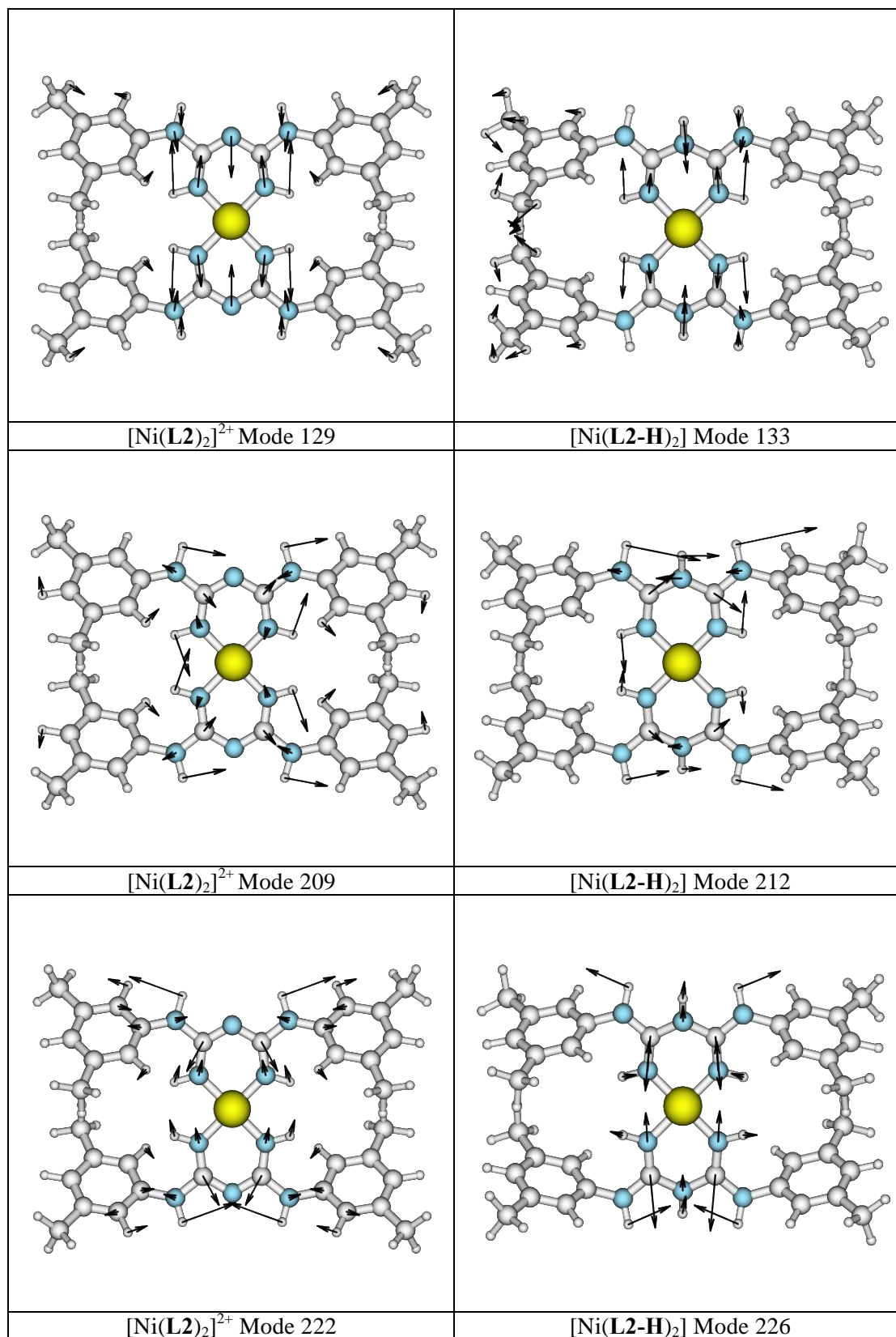
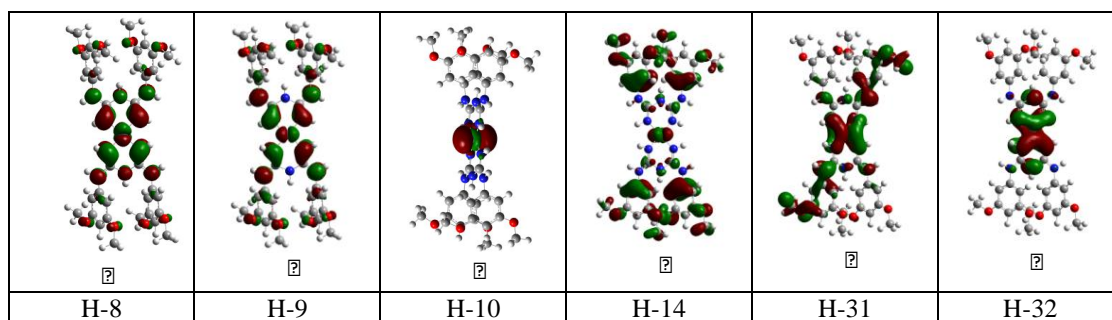


Figure S10 Selected corresponding vibrational modes for [Ni(HL2)₂]²⁺ and [Ni(L2)₂].

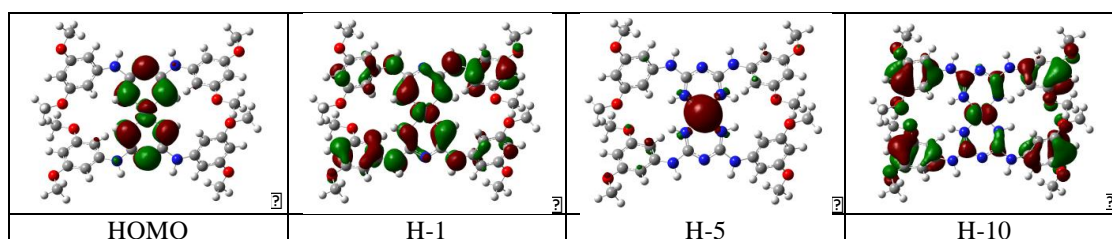
Table S3: Predicted transitions assigned to the relevant absorption band.

Compound	Wavelength / nm	Major MO configuration (%)
[Ni(HL1)](BF ₄) ₂	579	H-9→LUMO (76), H-8→LUMO (20)
	569	H-9→LUMO (23), H-8→LUMO (48)
	533	H-15→LUMO (19), H-10→LUMO (53), HOMO→LUMO (19)
[Ni(L1)]	575	H-14→LUMO (14), HOMO→LUMO (70)
	536	H-5→LUMO (51), H-4→LUMO (36)
	502	H-7→LUMO (25), H-1→LUMO (57)
[Ni(HL2)](BF ₄) ₂	581	H-10→LUMO (72), H-8→LUMO (23)
	572	H-10→LUMO (28), H-8→LUMO (51)
	538	H-14→LUMO (18), H-9→LUMO (54)
[Ni(L2)]	569	HOMO→LUMO (70), HOMO→L+6 (10)
	532	H-5→LUMO (87), H-5→L+6 (13)
	498	H-8→LUMO (18), H-1→LUMO (55)
[Ni(HL3)](BF ₄) ₂	641	H-10→LUMO (85), H-8→LUMO (12)
	635	H-32→LUMO (10), H-10→LUMO (16), H-8→LUMO (61)
	585	H-31→LUMO (13), H-14→LUMO (13), H-9→LUMO (62)
[Ni(L3)]	566	HOMO→LUMO (69)
	528	H-5→LUMO (82)
	492	H-10→LUMO (23), H-1→LUMO (51)
[Ni(HL4)](BF ₄) ₂	699	H-8→LUMO (43), H-4→LUMO (27)
	649	H-9→LUMO (100)
	635	H-10→LUMO (59), HOMO→LUMO (14)
[Ni(L4)]	575	H-12→LUMO (14), HOMO→LUMO (71)
	539	H-5→LUMO (89), H-5→L+6 (10)
	504	H-7→LUMO (30), H-1→LUMO (51)

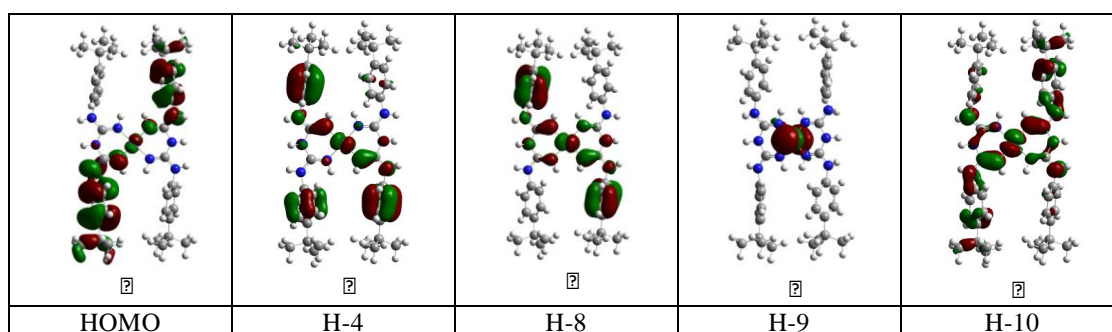
$[\text{Ni}(\text{L3})_2](\text{BF}_4)_2$



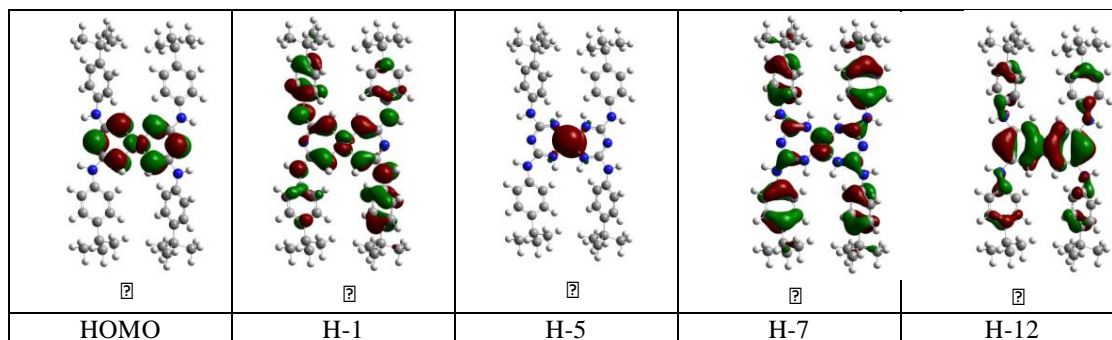
$[\text{Ni}(\text{L3-H})_2]$



$[\text{Ni}(\text{L4})_2](\text{BF}_4)_2$

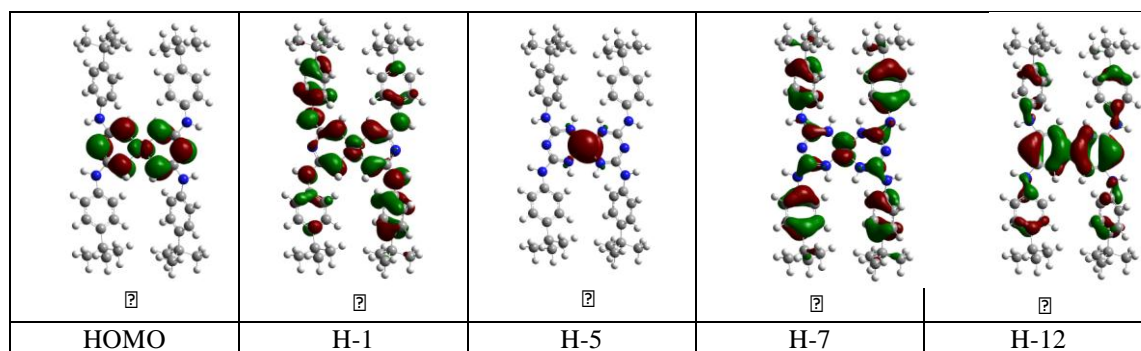
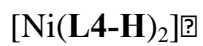
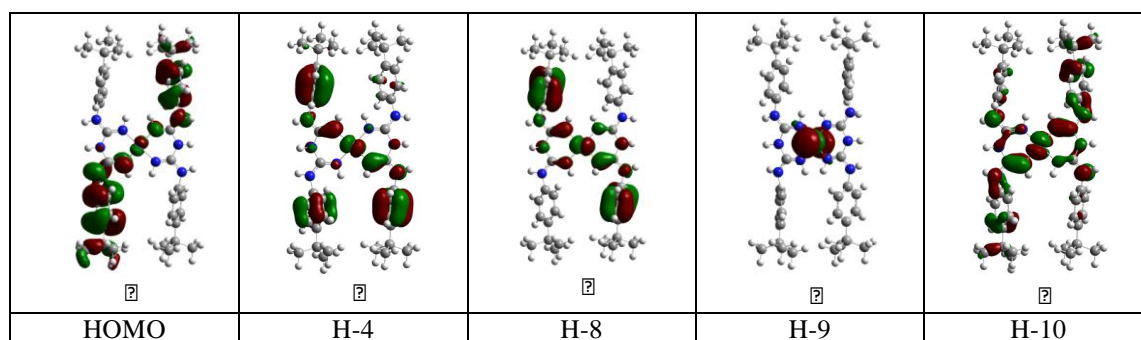
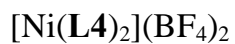
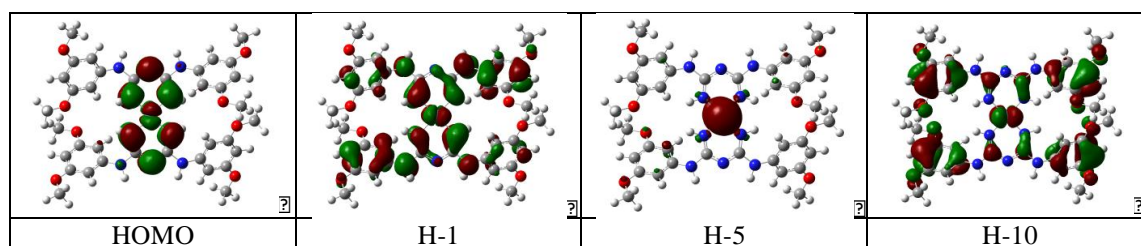
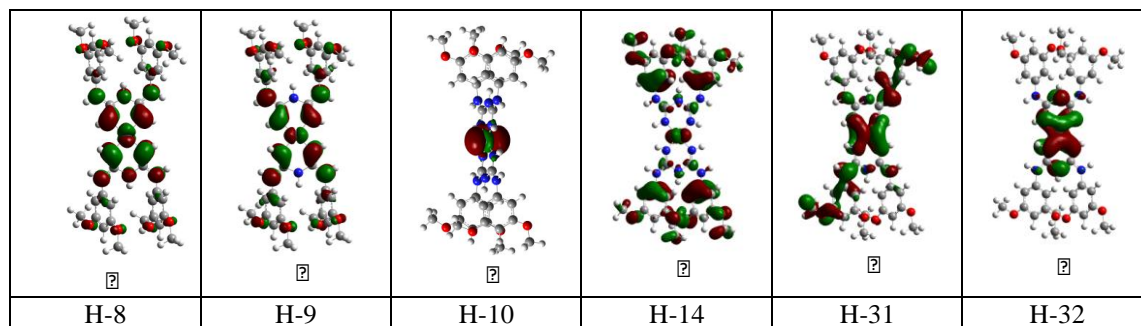
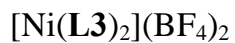


$[\text{Ni}(\text{L4-H})_2]$



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Figure S11 Molecular orbitals involved in predicted electronic transitions for $[\text{Ni}(\text{HL1})_2](\text{BF}_4)_2$, $[\text{Ni}(\text{L1})_2]$, $[\text{Ni}(\text{HL2})_2](\text{BF}_4)_2$ and $[\text{Ni}(\text{L2})_2]$.



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Figure S12 Molecular orbitals involved in predicted electronic transitions for $[\text{Ni}(\text{HL3})_2](\text{BF}_4)_2$, $[\text{Ni}(\text{L3})_2]$, $[\text{Ni}(\text{HL4})_2](\text{BF}_4)_2$ and $[\text{Ni}(\text{L4})_2]$.