Electronic Supplementary Material (ESI) for Dalton Transactions.
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Supporting Information

Enhanced Catalytic Activity and Magnetization of Encapsulated Nickel Schiff-Base Complexes in Zeolite-Y: A correlation with the Adopted Non-Planar Geometry

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Physical Measurements

X-ray diffraction analysis has been performed on a Shimadzu XD-D1 powder X-ray diffractometer using Cu Kα radiation (λ = 1.542 Å) in the 2θ range 8–50° with the scanning rate of 2°/min. The SEM – EDX analysis is carried out with Zeiss EVO 40 at an accelerated voltage of 5–20 kV, with gold coating. X-ray photoelectron spectroscopy (XPS) was performed using a commercial Omicron EA 125 spectrometer equipped with an Mg Kα X-ray source (1253.6 eV). The spectra were recorded for neat and encapsulated complexes taken in pellet form after neutralization for X-ray photoelectron spectroscopic (XPS) analysis. High resolution XPS traces were deconvoluted using the Gaussian and Lorentzian statistical analysis by Origin-7 software. The IR spectra have been recorded in the range (450–4000) cm^{-1} by using an ABB FTIR spectrometer using a DRIFT accessory. The IR spectra of the complexes have been recorded after mixing them thoroughly with KBr . The electronic spectra in the solid state are recorded using a Shimadzu UV- 2100 spectrophotometer with a diffuse reflectance attachment, which is outfitted with an integrating sphere of 60 mm inner diameter, using $BaSO_4$ as reference material. The temperature dependent magnetic studies have been carried out by using SQUID magnetometer Quantum Design MPMS XL Ever Cool, FC measurement in the field strength of 1000 Oe and temperature range of 5K to 300K. Shimadzu GC-2014 gas chromatography machine has been used for the catalytic activity studies of the complexes in both the states.

Theoretical Methods

All Density Functional (DFT) studies presented are done using GAUSSIAN 09 suite of *ab initio* quantum chemistry programs.[1] The structural optimizations used the hybrid B3PW91[2, 3] exchange and correlation functional with the double-zeta 6-31++G** basis set for all atoms and consequently the same methodology is used for the vibrational frequency calculations to ascertain the stable isomers. We have also studied all the complexes using B3LYP /6-31++G** as well and these are incorporated in the Supporting information. Symmetry constraints are not imposed and default self-consistency and geometry convergence criteria are used for all studies. The electron density plots for frontier molecular orbitals, of the complexes in both singlet and triplet states are shown in the Supporting Information. The molecular orbitals are defined with respect to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as HOMO-n (H-n) and LUMO+n (L+n). We have studied both the singlet and triplet spin states of the Ni-complexes, and the optical spectra for all the complexes are calculated using time dependent density functional (TD-DFT) methods. SWizard software[4, 5] are used to analyze the transition energies and oscillator strengths for electronic excitations calculated (first 50 singlet or triplet excited states of the different complexes were calculated). In our theoretical studies, the geometrical relaxations of encapsulated Ni-complexes are started with an initial triplet structure, as switching of spin states during optimizations are not permissible. Triplet to triplet transitions are only considered for the triplet complexes, though pure d-d transitions are hard to identify due to strongly hybridized nature of the metal d-orbitals with ligand p orbitals. In the studies of encapsulation, we have modelled only a portion Zeolite-Y supercage as shown in Figure 5 and all the unsatisfied valancies of Si atoms are terminated using H atoms. The experimental structure of the zeolite supercage was taken without changes, and not relaxed, however the positions of the hydrogen atoms were optimized. In case of the studies with zeolite supercage with the complex encapsulated, only the complex inside the supercage was optimized and lowest energy structure was obtained.

EDX data

Figure (S1-S3)

(S1)

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Spectrum: s1_1


Element     Series    unn. C norm. C Atom. C Error

                     [wt.-%] [wt.-%] [at.-%]    [%]

-------------------------------------------------

Silicon    K-series    13.54   16.18   10.09   0.6

Aluminium  K-series     6.03    7.21    4.68   0.3

Sodium     K-series     4.73    5.65    4.31   0.3

Carbon     K-series     5.86    7.00   10.21   0.7

Nickel     K-series     0.50    0.59    0.18   0.0

Nitrogen   K-series     6.03    7.20    9.01   0.9

Oxygen     K-series    47.00   56.17   61.52   5.2

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            Total:     83.68  100.00  100.00
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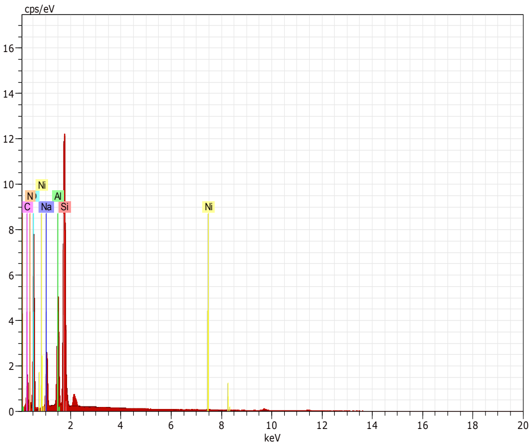

(S2)

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Spectrum: s3_1

Element     Series    unn. C norm. C Atom. C Error

                     [wt.-%] [wt.-%] [at.-%]    [%]

-------------------------------------------------

Silicon    K-series     4.07    4.07    2.29   0.2

Aluminium  K-series     5.39    5.39    3.15   0.3

Sodium     K-series     1.50    1.50    1.03   0.1

Carbon     K-series    14.92   14.92   19.62   5.0

Nickel     K-series     0.47    0.47    0.13   0.0

Nitrogen   K-series     7.65    7.65    8.62   2.9

Oxygen     K-series    65.99   65.99   65.15  20.4
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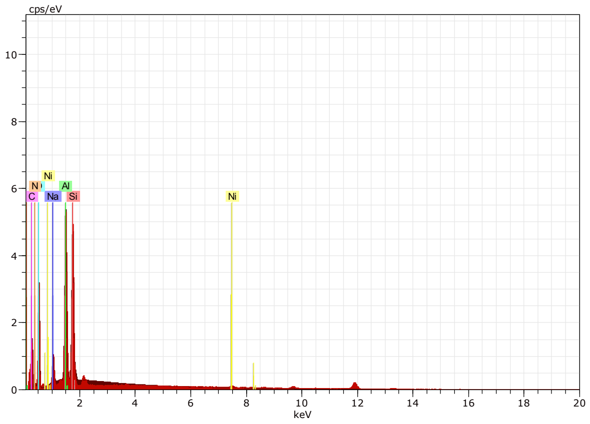

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          Total:  100.00  100.00  100.00
```

(S3)

```
Spectrum: s7_1


Element    Series   unn. C norm. C Atom. C Error

                    [wt.-%] [wt.-%] [at.-%]   [%]

------------------------------------------------

Silicon   K-series   12.47   13.67    8.21   0.6

Aluminium K-series    5.65    6.19    3.87   0.3

Sodium    K-series    4.83    5.29    3.88   0.3

Carbon    K-series   11.48   12.58   17.66   1.3

Nickel    K-series    0.47    0.52    0.15   0.0

Nitrogen  K-series    7.07    7.75    9.33   1.0

Oxygen    K-series   49.27   53.99   56.90   5.4

------------------------------------------------

            Total:   91.25  100.00  100.00
```

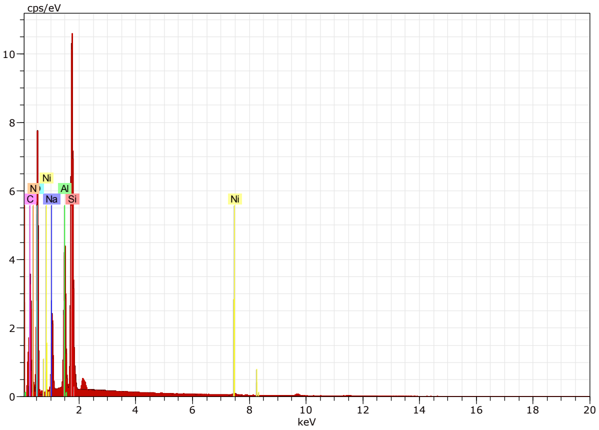


Figure S1-S3. EDX data of (a) ENiL1, (b) ENiL2 and (c) ENiL3 complexes.

Figure S4

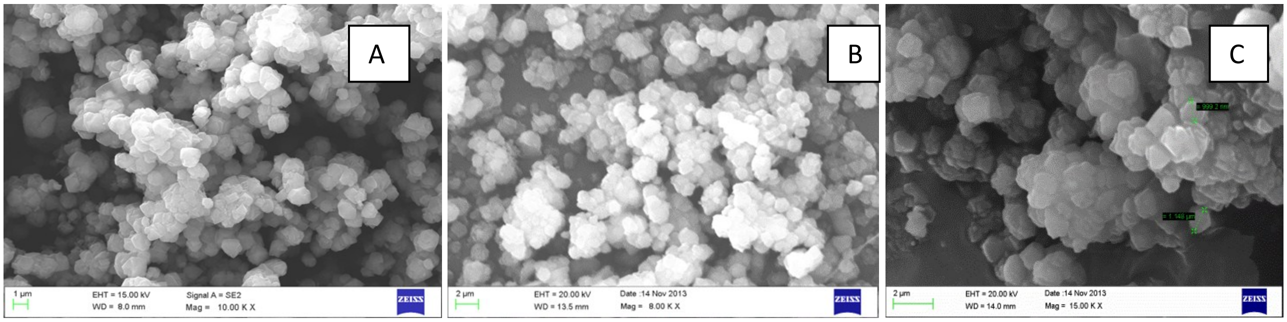


Figure S4. SEM images of pure (A) zeolite Y and (B) ENiL1, (C) ENiL3 after Soxhlet extraction.

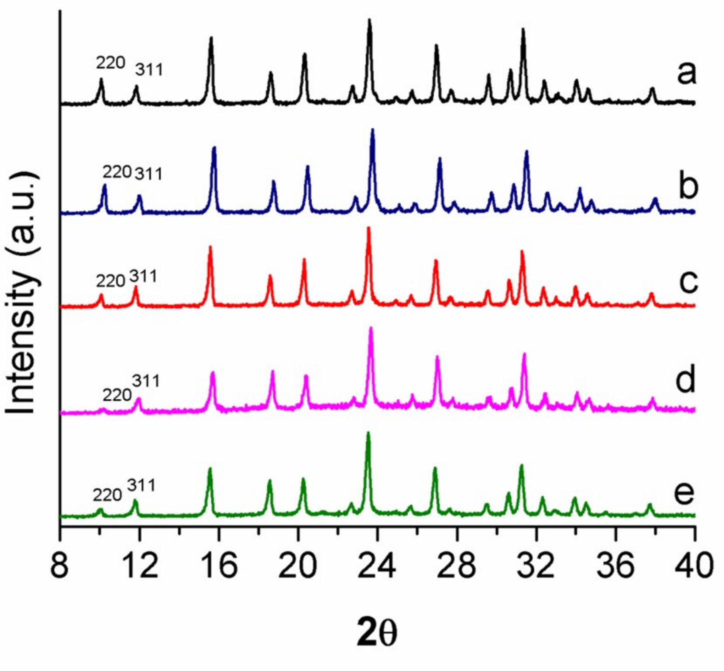
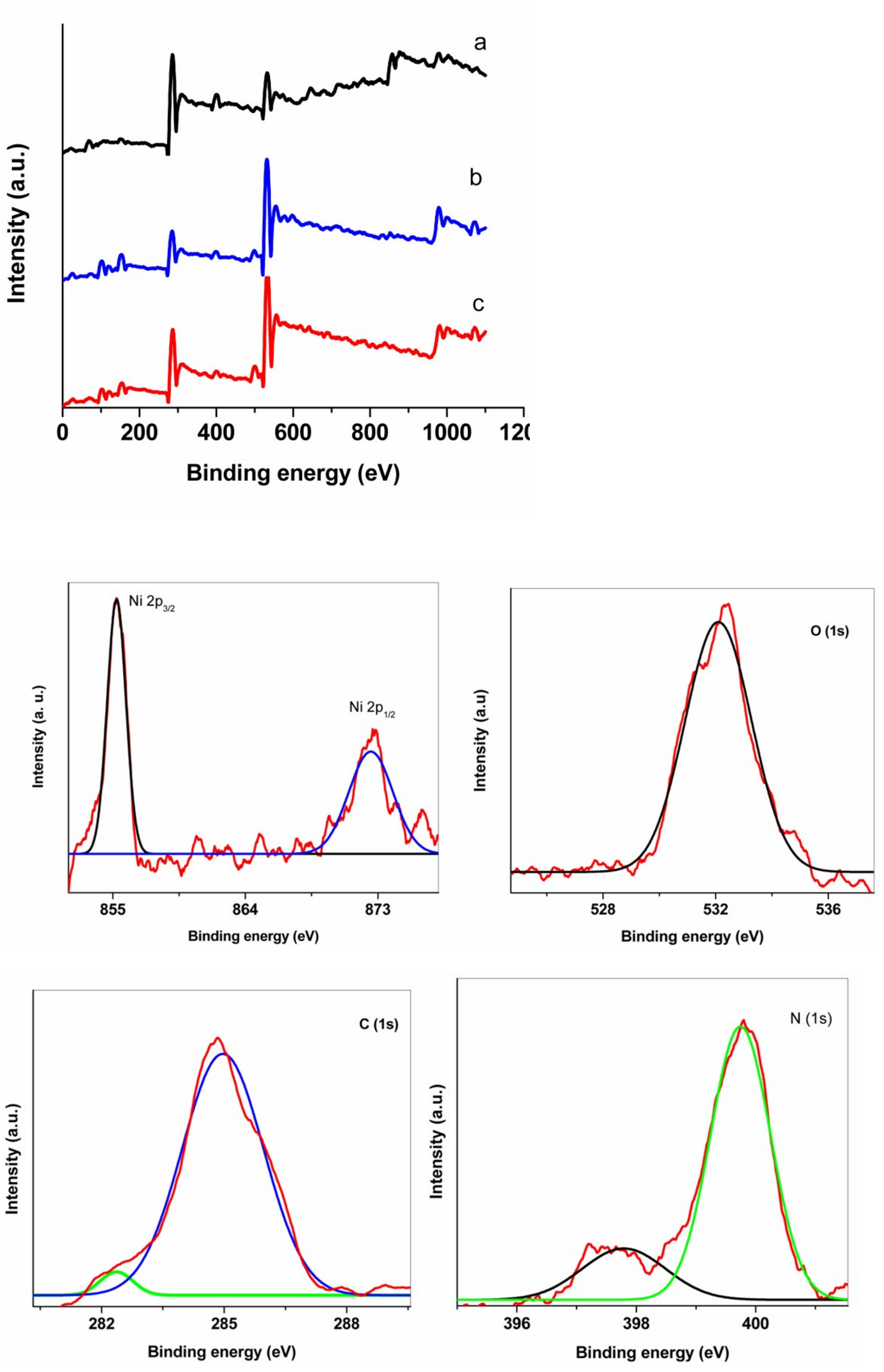


Figure S5. XRD pattern of (a) pure zeolite Y, (b) Nickel exchanged Y, (c) ENiL1, (d) ENiL2 and (e) ENiL3 complexes.

Figure S6



a
b
c
Intensity (a.u.)
0
200
400
600
800
1000
12(
Binding energy (eV)
Ni $2p_{3/2}$
Ni $2p_{1/2}$
Intensity (a. u.)
855
864
873
Binding energy (eV)
O (1s)
Intensity (a.u)
528
532
536
Binding energy (eV)
C (1s)
Intensity (a.u.)
282
285
288
Binding energy (eV)
N (1s)
Intensity (a.u.)
396
398
400
Binding energy (eV)

Figure S6. XPS survey spectra of neat (NiL1) and encapsulated complexes (ENiL1 and ENiL3) and high resolution XPS spectra of Ni $2p_{3/2}$ and $2p_{1/2}$ peaks, O (1s), C (1s) and N(1s) for NiL1.

Figure S7

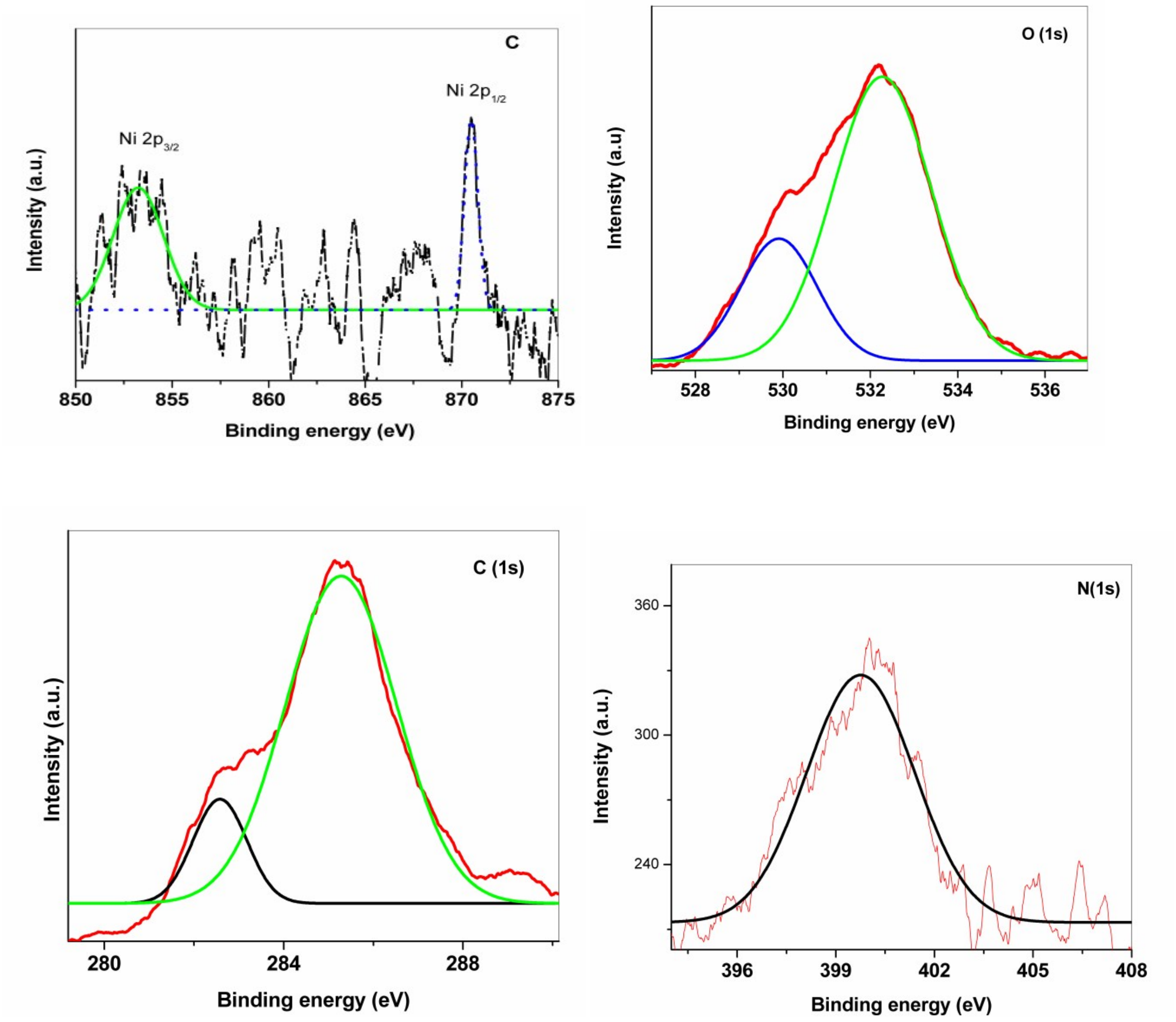


Figure S7. High resolution XPS spectra of nickel (2p) for Ni $2p_{3/2}$ and $2p_{1/2}$ peaks, O (1s), C (1s) and N(1s) for ENiL1.

Figure S8

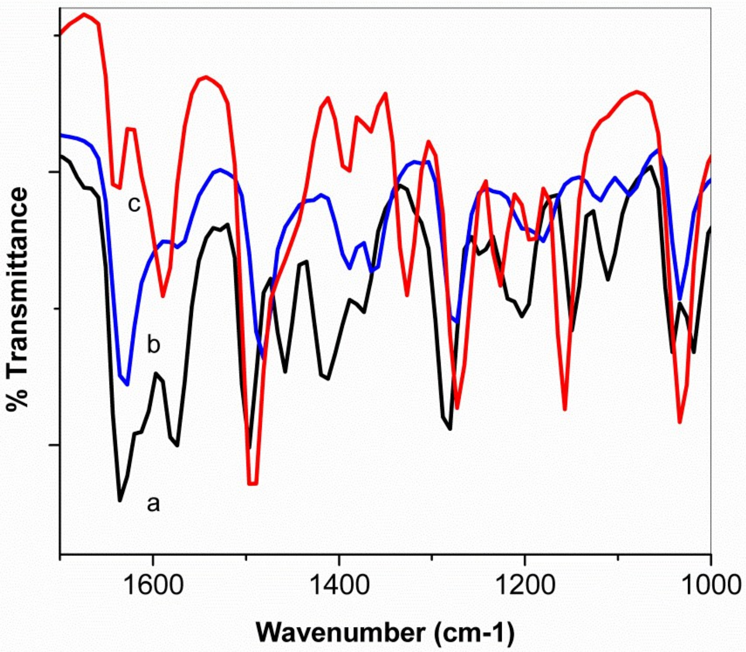


Figure S8. FTIR data of (a) L1, (b) L2 and (c) L3 ligand.

Figure S9

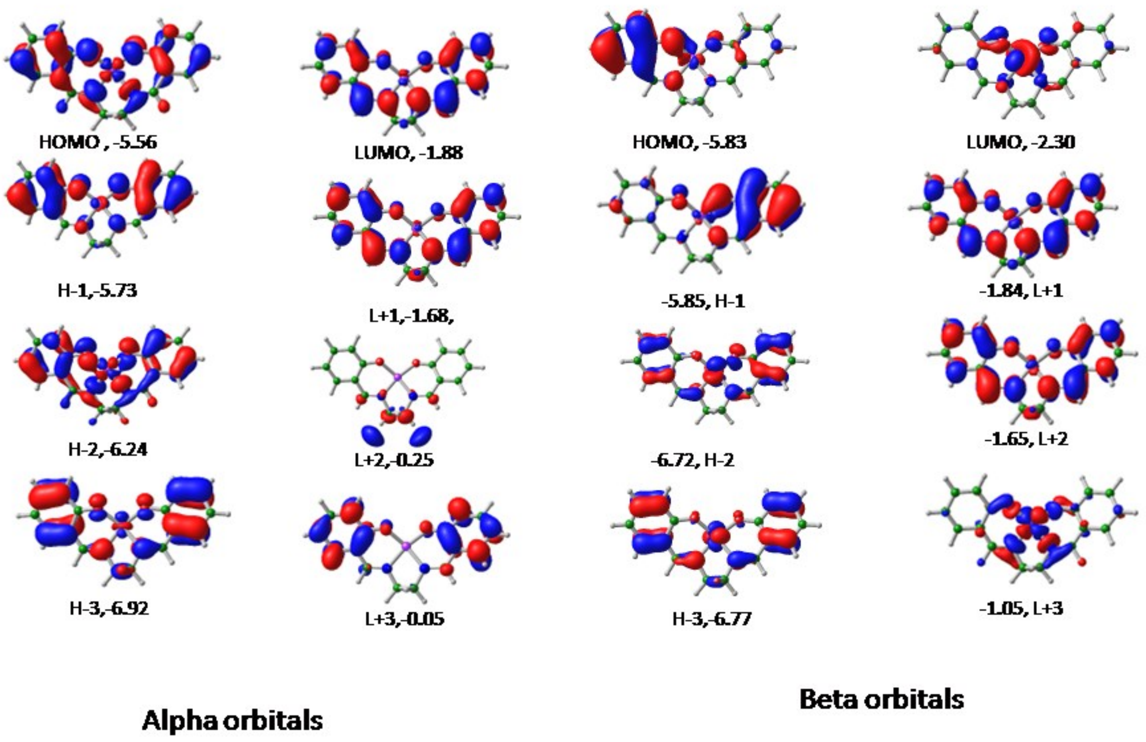


Figure S9. Molecular orbitals for NiL1 in encapsulated & extracted (triplet) state. Orbitals are marked with respect to the HOMO and LUMO and energies in eV are in the parentheses.

Figure S10

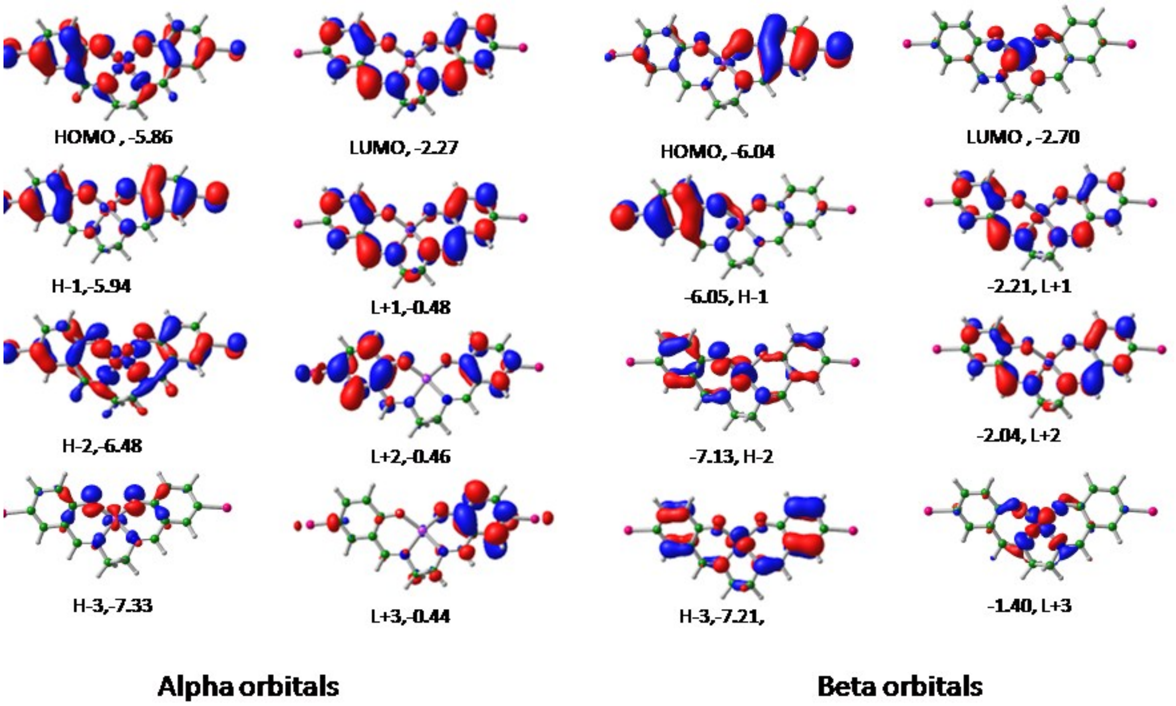


Figure S10. Molecular orbitals for NiL2 in encapsulated & extracted (triplet) state. Orbitals are marked with respect to the HOMO and LUMO and energies in eV are in the parentheses.

Figure S 11

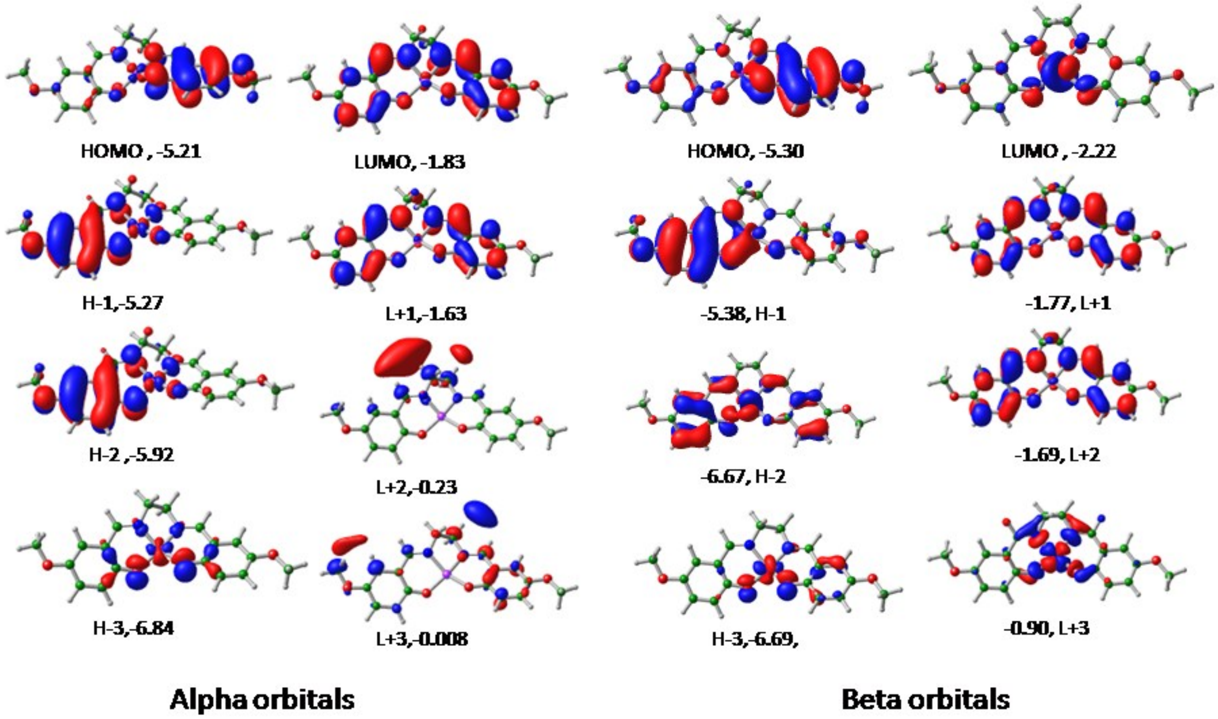


Figure S11. Molecular orbitals for NiL3 in encapsulated & extracted (triplet) state. Orbitals are marked with respect to the HOMO and LUMO and energies in eV are in the parentheses.

References:

1. M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, J. Montgomery Jr, T. Vreven, K. Kudin and J. Burant, *There is no corresponding record for this reference*.
2. A. D. Becke, *The Journal of Chemical Physics*, 1993, 98, 5648.
3. A. D. Becke, *Physical Review A*, 1988, 38, 3098.
4. S. H. Lee, S. I. Gorelsky and G. I. Nikonov, *Organometallics*, 2013, 32, 6599.
5. J. P. Holland, P. J. Barnard, S. R. Bayly, J. R. Dilworth and J. C. Green, *Inorganica Chimica Acta*, 2009, 362, 402.