Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

An Insight into the Catalytic Activity of Palladium Schiff-Base Complexes towards Heck Coupling Reaction: Routes via Encapsulation in Zeolite-Y

Susheela Kumari[a], Bidisa Das[b], and Saumi Ray*[a]

[a]Birla Institute of Technology and Science, Pilani, Rajasthan 333031, India.

[b]Technical Research Center, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India.

Physical Measurements

The XRD patterns between 8-50° have been observed by using a powder X-ray diffractometer (RIGAKU MINIFLEX II) with a Cu Kα X-ray source ($\lambda = 1.542$ Å) at a scanning step of 2° min^{-1}. The FESEM-EDX analysis has been carried out by using a Zeiss EVO 40 instrument with an accelerated voltage of 5–20 kV and samples are coated with gold coating. Nitrogen sorption isotherms have been recorded on a Quantachrome instruments with a volumetric adsorption setup at -196 °C. For all encapsulated systems, the Brunauer–Emmett–Teller (BET) surface area and pore volume have been calculated. To know the thermal stability of the catalysts, thermogravimetric (TGA) analysis in nitrogen atmosphere from 25 to 800° C have been performed on a TGA-60, SHIMADZU apparatus with a heating rate of 10 °C min^{-1}. FT-IR measurements have been carried out by using an ABB FTIR spectrometer in the range of 450–4000 cm^{-1} with a DRIFT accessory. X-ray photoelectron spectroscopic measurement (XPS) is carried out on a commercial Omicron EA 125 spectrometer with an Mg Kα X-ray source (1253.6 eV). Samples are kept in a vacuum oven overnight before XPS analysis and used in form of pellets after neutralization. High-resolution XPS spectra for elements are deconvoluted using the Gaussian and Lorentzian statistical analysis by Origin-9 software. The solution UV-vis spectra have been recorded by using Shimadzu UV-2100 spectrophotometer. The solid-state UV-vis spectra measured on a Shimadzu UV-2450 spectrophotometer in the reflectance mode by using barium sulfate as a reference. UV-vis spectrophotometer is equipped with an integrating sphere of 60 mm inner diameter and Kubelka–Munk analysis is performed on the reflectance data. The KM factor, F(R), is given by $F(R) = (1- R)^2 /2R = k/s$ where R is the diffuse reflectance of the sample as compared to $BaSO_4$, k is the molar absorption coefficient, and s is the scattering coefficient of the sample. GC chromatographic experiments are carried out on a Shimadzu GC-2014 by using a FID detector for the catalysis study of neat and encapsulated palladium (II) Schiff-base complexes.

Theoretical studies

The electronic structure calculations based on Density Functional Theory (DFT) using GAUSSIAN 09 suite of programs[1] were used to study and analyse the structural and optical properties of the PdL-OH complex in neat and zeolite encapsulated states. For structural optimizations we used the hybrid B3PW91[2, 3] exchange and correlation functional with the double-zeta 6-31G** basis set for all atoms except Palladium (Pd) for which LanL2DZ basis-set along with effective core potential was found to be appropriate. All positive vibrational frequencies confirm the stabilities of the Pd-complexes where no symmetry constraints were imposed.

For encapsulated PdL-OH complex within zeolite pore, only a portion Zeolite-Y supercage was modelled as shown in Figure 8d in the main manuscript and all the under coordinated Si atoms were terminated by Hydrogen atoms. During the study of encapsulated complexes, the experimental structure of the zeolite supercage was kept fixed, only the positions of the terminal hydrogen atoms were allowed to relax. The PdL-OH complex was studied both in the singlet, neat and triplet, encapsulated states and the absorption spectra are calculated using time dependent density functional (TD-DFT) methods. In this case we used B3PW91/6-31++G** for all atoms and Lan2DZ basis-set and ECP for Pd atom on B3PW91/6-31G** optimized structures. The structure of triplet PdL-OH complex within zeolite pore was optimized keeping zeolite framework rigid and energy was calculated. In case of the encapsulated PdL-OH complex, the TD-DFT optical spectra are calculated without the zeolite supercage, *i.e.* after extracting the encapsulated triplet PdL-OH complex and keeping it rigid. Similar strategy was used for our earlier studies as well, which approximately models the real experiments by taking into account the interactions arising due to the confinement within a pore.[4-6] The transitions in the TD-DFT spectra are understood in terms of the transitions between the molecular orbitals of the PdL-OH complex in neat or encapsulated states. The plots for frontier molecular orbitals of the Pd-complexes in both singlet and triplet states are shown in the Supporting Information to understand their nature. The molecular orbitals are marked 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).

Experimental section

Materials

The zeolite -NaY, 2-hydroxy-5-hydroxy benzaldehyde, 2-hydroxy-5-bromo benzaldehyde,2-hydroxy-5-methyl benzaldehyde,1,3- phenylenediamine, styrene and bromobenzene are purchased from Sigma-Aldrich, India. Palladium acetate is purchased from TCI chemicals, India. All the solvents like methanol, ethanol, acetone, acetonitrile and ether are purchased from S.D. fine, India.

Synthesis of ligands and free state Pd (II)–Schiff base complexes[7]

The Pd (II)–Schiff base complexes are synthesized according to the literature report. An ethanolic solution of 1,3-Phenylenediamine and salicylaldehyde or its derivatives is stirred at 70 °C for 4 h. After the end of the reaction, the solid product is filtered, washed with ethanol and finally dried at room temperature (Scheme S1).

A mixture of ligand and palladium acetate is stirred 80 °C for 3 h in a 1:1 ligand−metal mole ratio.The solid Pd (II)–Schiff base complexes washed with ethanol and finally dried in vacuum. All three Pd (II)–Schiff base complexes are prepared using the same procedure Scheme S2 is given.

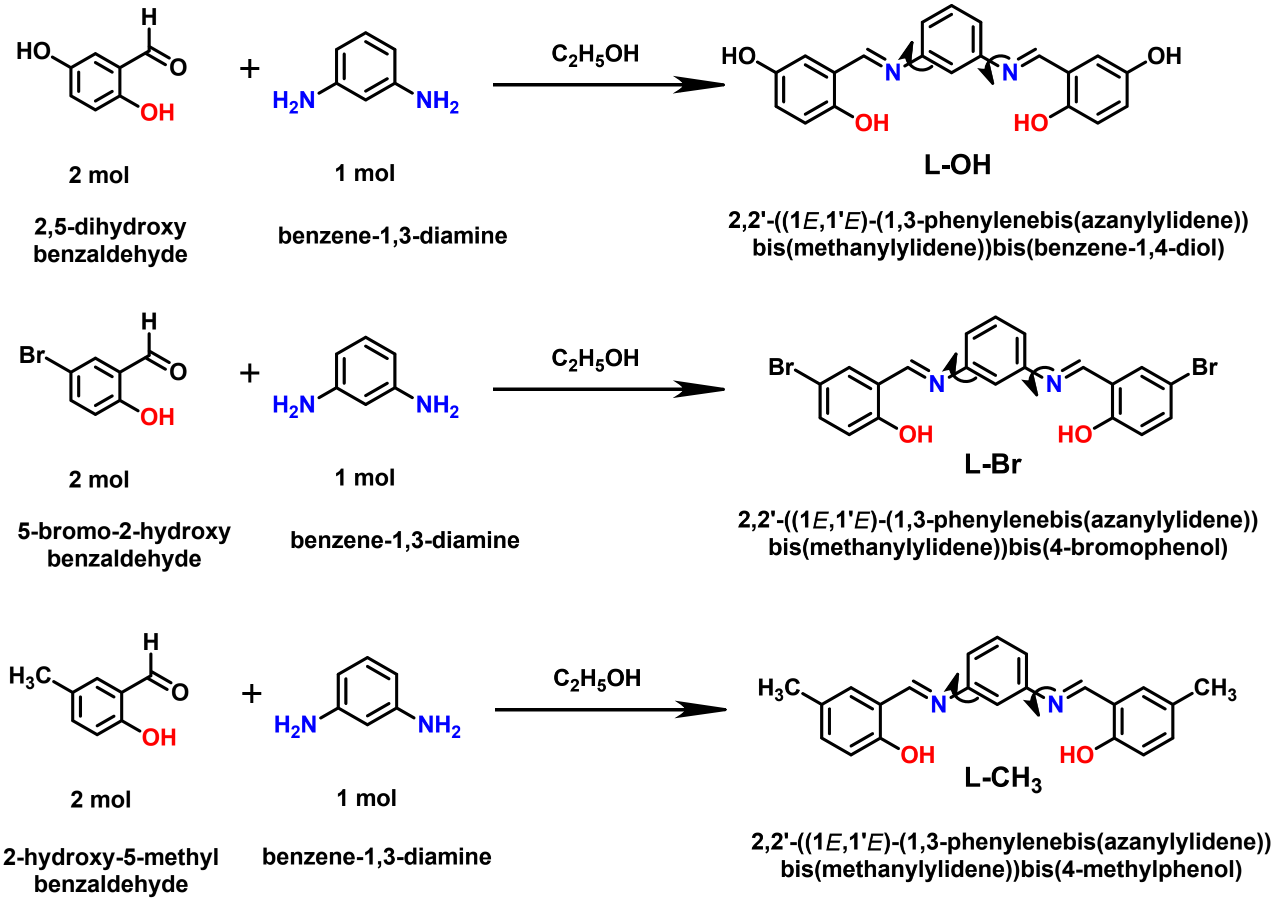
Preparation of Pd(II) exchanged zeolite -Y[8, 9]

A mixture of 10 g of the zeolite –NaY and 0.224 g of palladium(II) acetate solution in water are stirred at room temperature for 24 h.The slurry is filtered, washed repeatedly with distilledwater, and finally dried for 12 h in an oven at 150 °C to obtain Pd(II) -exchanged NaY as a light brown powder.

Synthesis of encapsulated Pd(II)−Schiff base complexes in zeolite Y[8, 10]

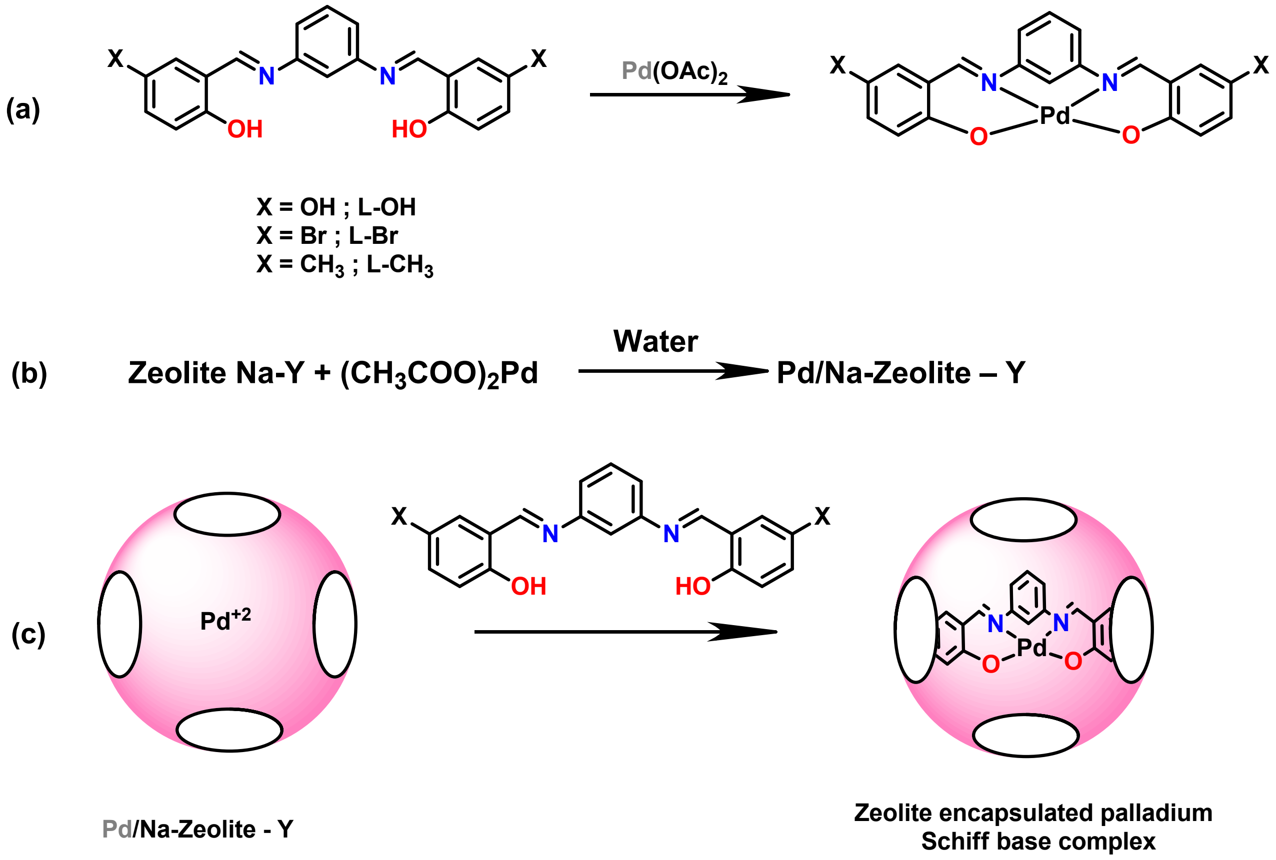
Ligands L-OH, L-Br, and L-CH_3 are flexible in nature; thus, one of the methods of encapsulation of metal complex inside the supercage of zeolite Y could be possible via the "flexible ligand" approach. The Pd(II) - exchanged NaY are treated with stoichiometric excess amount of the ligand (L-OH, L-Br, and L-CH_3 in each respective reaction). The reaction mixture is allowed to react at 150−200°C for 24 h under constant stirring to synthesize the complex inside the supercage of zeolite Y. On heating, the solid reaction mass is changed colour from pale yellow to dark brown. The resultant product is recovered and purified by the Soxhlet extraction using the sequence of different solvents such as acetone, methanol, and diethyl ether to remove unreacted and surface species. The recovered product is further dried in a muffle furnace for 10−12 h at 150 °C. The product is further treated with 0.01 M NaCl solution at room temperature for 12 h to remove the unreacted palladium metal ions. The resultant solid is then filtered, washed with distilled water until the filtrate is negative for the chloride ion test.

Scheme S1:



Scheme S1: Synthesis of Schiff base Ligand L-OH, L-Br and L-CH_3

Scheme S2:



Scheme S2 : (a) Synthesis of Palladium Schiff base Complexes, (b) Synthesis of palladium exchanged zeolite-Y and (c) synthesis of zeolite encapsulated palladium Schiff base complexes via flexible ligand synthesis method.

Catalytic reaction

To carry out the Heck coupling reaction, 0.70 mmol% of catalyst, 10ml DMF as a solvent, 5mmol of bromobenzene, 10 mmol of styrene and 1.06 g Na2CO3 as a base is added and the whole reaction mixture is refluxed for 20 h at 140 °C under constant stirring. The reaction is monitored by Gas chromatography (GC). After the completion of the reaction, the catalyst is extracted by filtration and washed with solvents and the supernatant solution of the reaction mixture is collected after centrifugation. The reaction mixture is then analyzed by FID-GC using n-heptane as the internal standard. For the recycling experiments, the solid catalyst is separated by centrifugation from the reaction mixture, washed thoroughly with the organic solvents (DMF and DCM) and water and then again has participated in a new catalytic cycle under the same reaction conditions.

X-ray Diffraction (XRD) studies

The powder X-ray diffraction patterns of zeolite-Y, Pd-exchanged zeolite-Y and all encapsulated Pd(II) Schiff-base complexes are presented in Figure S1. Similar X-ray diffraction patterns have been found for all the systems, indicated that the host framework does not show any considerable structural changes during ion exchange reaction and even after the encapsulation of Pd(II) Schiff-base complex inside the cavity.

Figure S1:

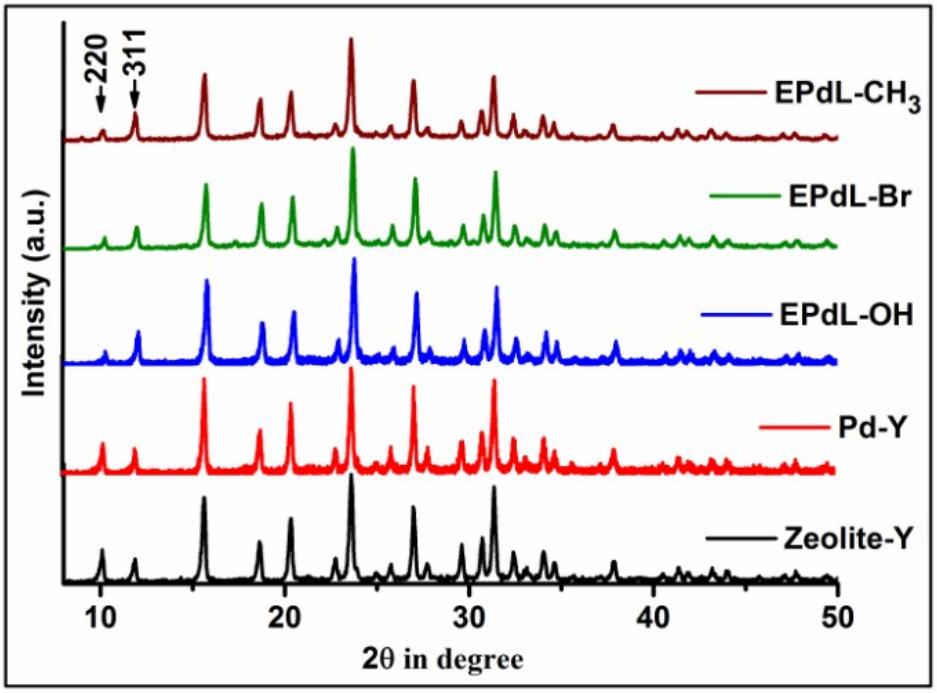


Figure S1: XRD patterns of parent zeolite-Y, Pd-exchanged zeolite -Y, EPdL-OH, EPdL-Br and EPdL-CH_3.

Figure S2:

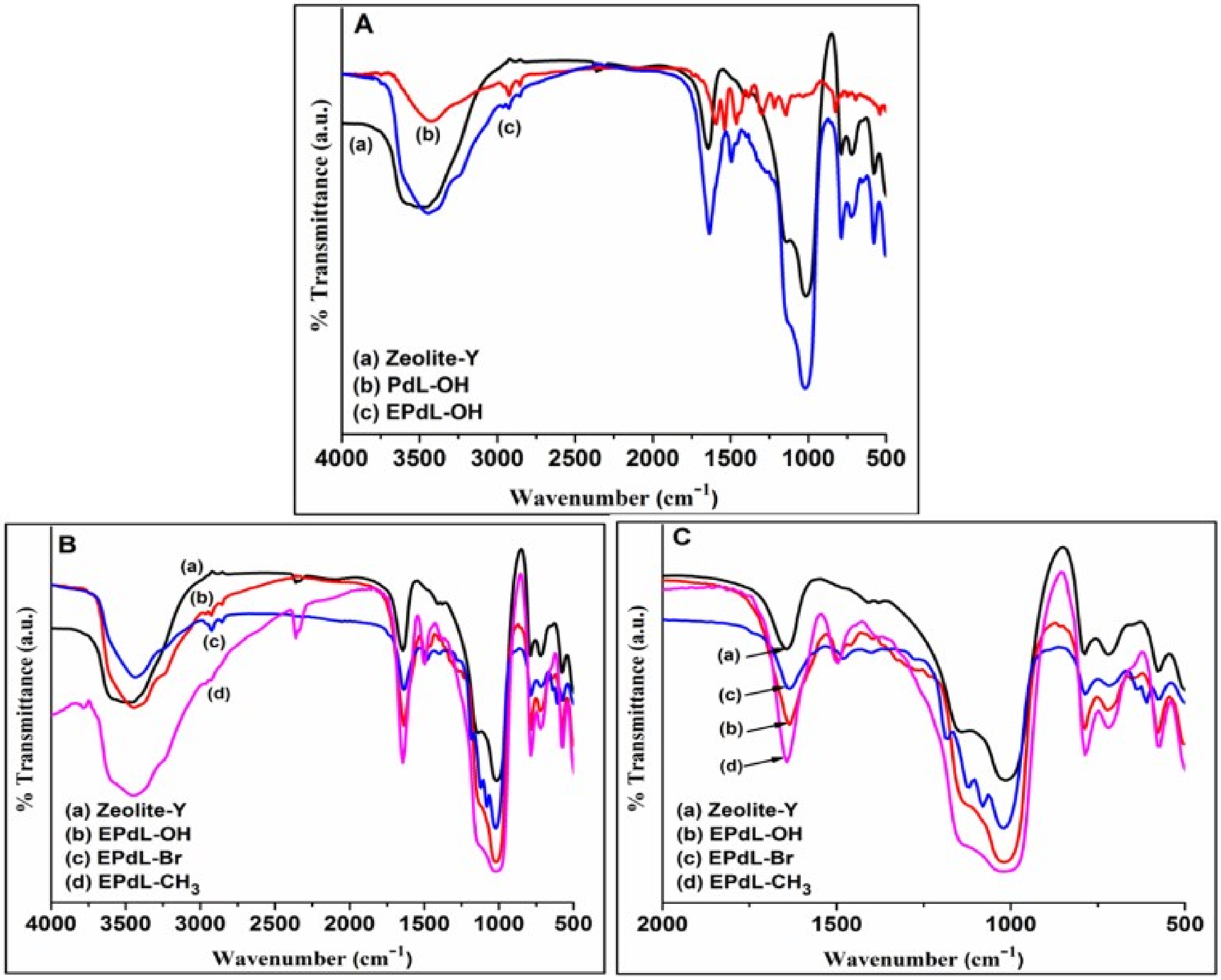


Figure S2: FTIR spectra of (A) parent zeolite-Y, PdL-OH and EPdL-OH, (B) zeolite-Y, EPdL-OH, EPdL-Br and EPdL-CH_3 and (C) Enlarged view of FTIR spectra in the range of 500 cm^{-1} to 2000 cm^{-1} for (a) parent zeolite-Y, (b) EPdL-OH, (c) EPdL-Br and (d) EPdL-CH_3.

Table S1. FTIR data of neat and encapsulated complexes.

S. No	Samples	C=N stretching	C=C stretching	ν_{C-H} deformation	C-O stretching
1	**PdL-OH**	1593	1539, 1462	1385	1296
2	**EPdL-OH**	1636	1497, 1458	1396	1292
3	**PdL-Br**	1609	1516, 1450	1373	1277
4	**EPdL-Br**	1636	1481, 1444	1396	1265
5	**PdL-CH_3**	1609	1528, 1481	1373	1257
6	**EPdL-CH_3**	1643	1520, 1497	1381	1233

Figure S3:

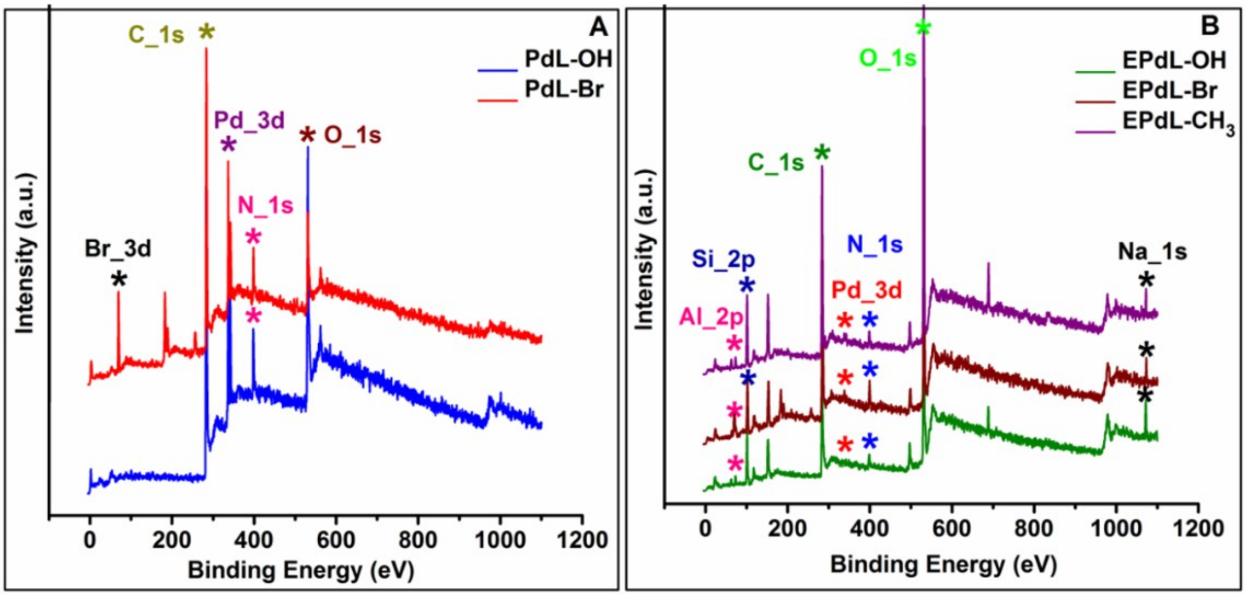


Figure S3: XPS survey spectra for neat and encapsulated complexes (A) PdL-OH and PdL-Br, and (B) EPdL-OH, EPdL-Br and EPdL-CH_3.

Figure S4:

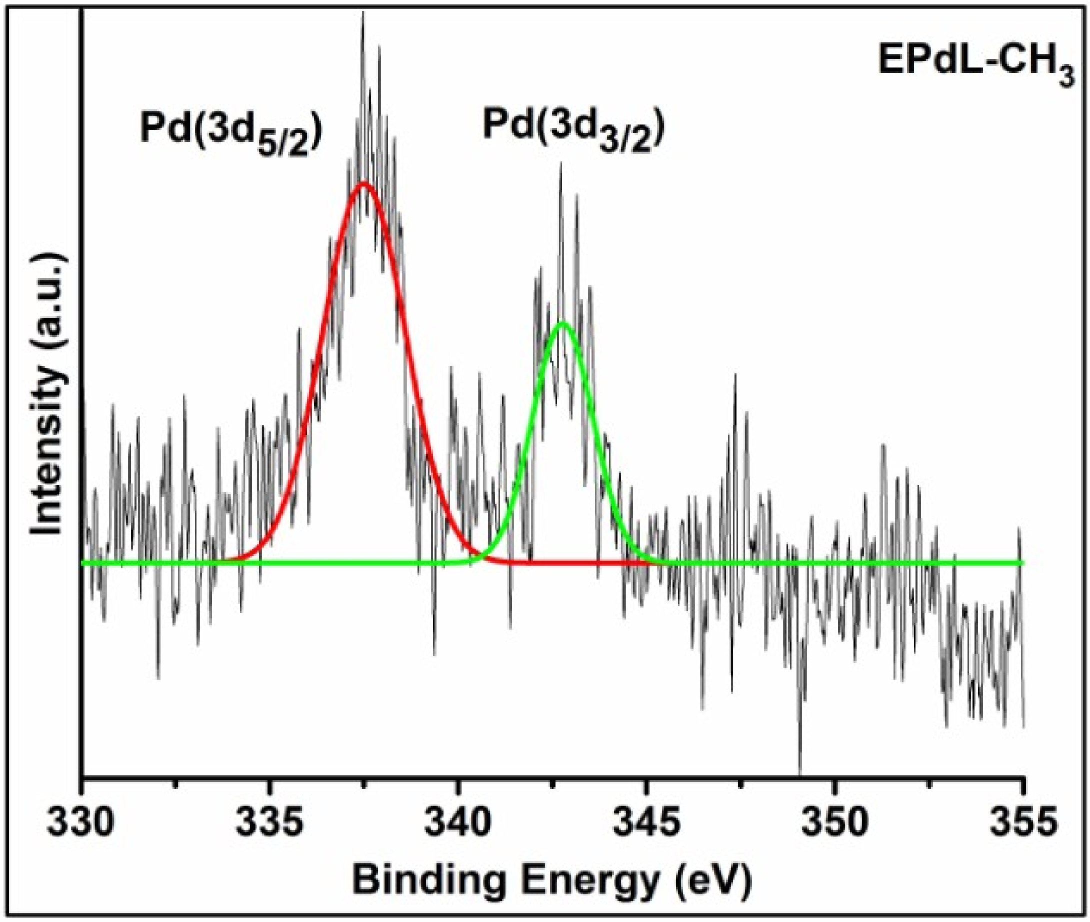


Figure S4: High-resolution XPS signals of Pd (3d) for EPdL-CH$_3$ complex.

Figure S5:

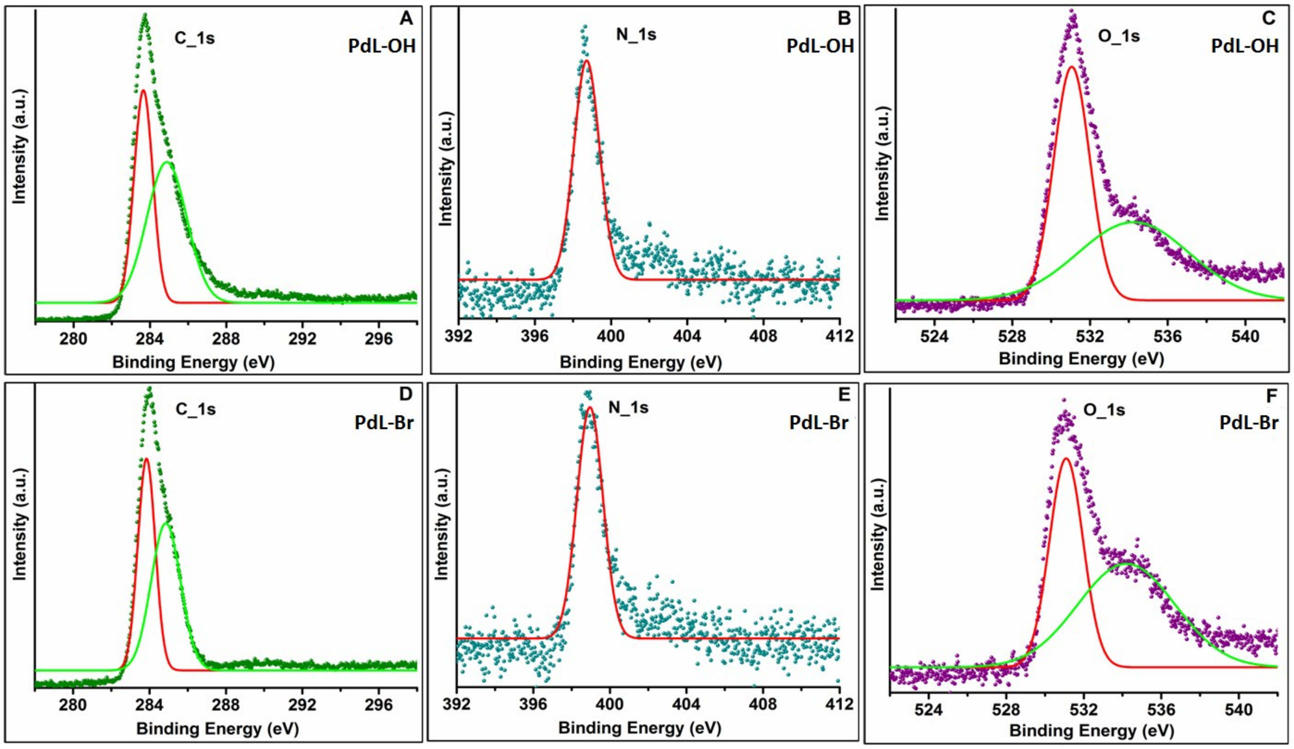


Figure S5: High-resolution XPS spectra of C (1s), N (1s), and O (1s) for PdL-OH and PdL-Br complex.

Figure S6:

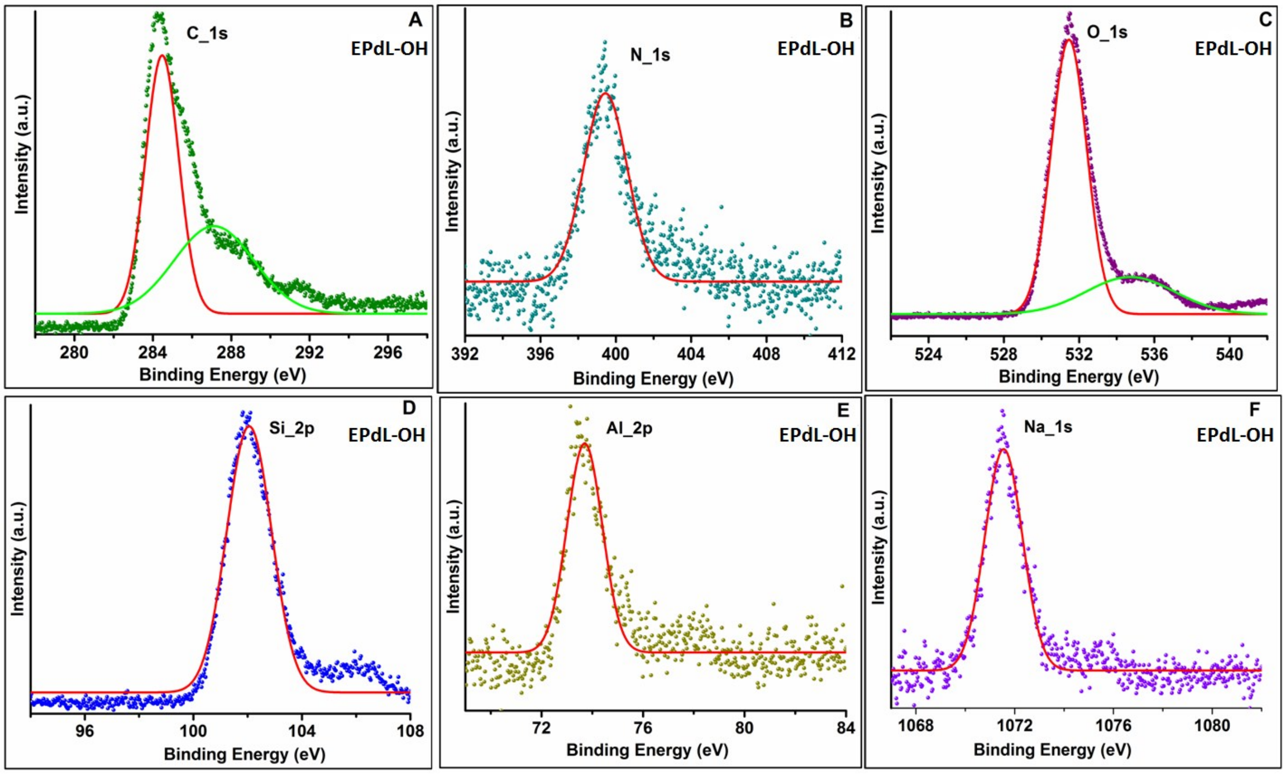


Figure S6: High-resolution XPS spectra of C (1s), N (1s), O (1s), Si (2p), Al (2p) and Na (1s) for EPdL-OH complex.

Figure S7:

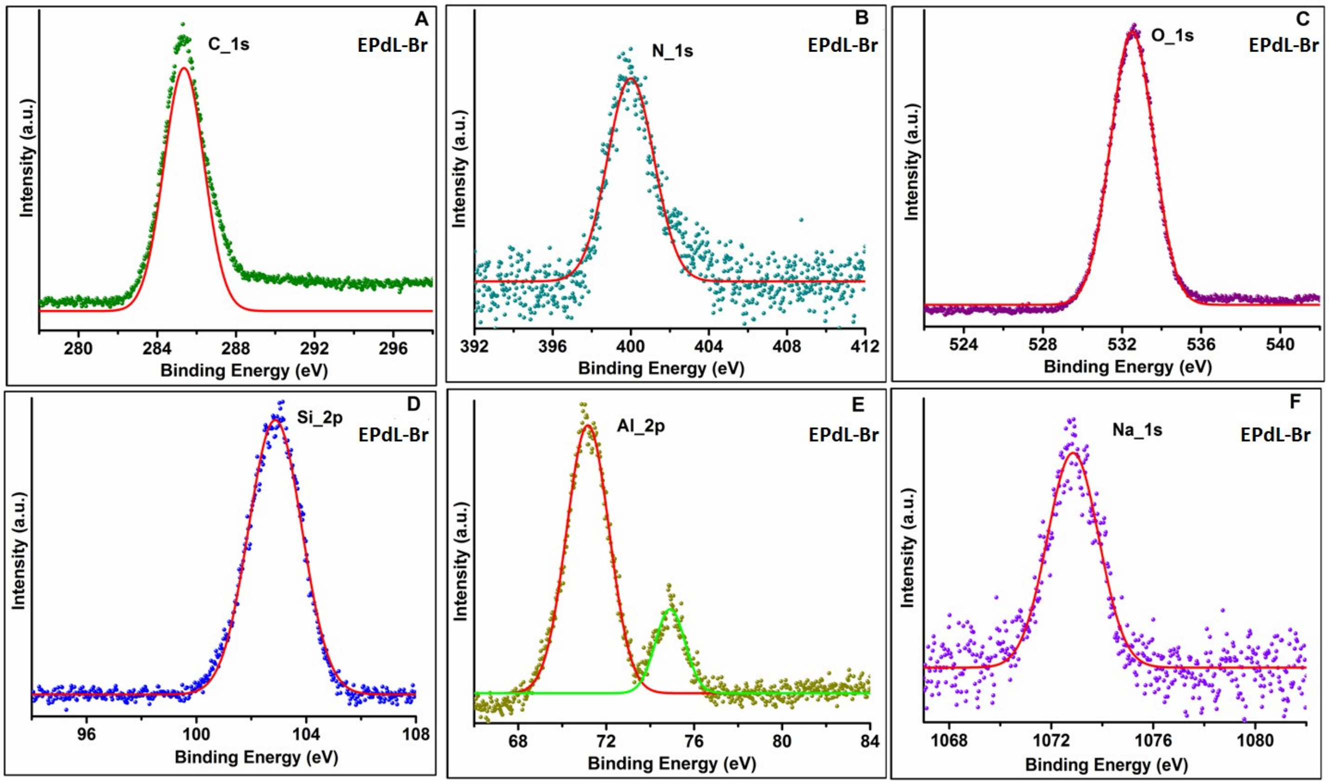


Figure S7: High-resolution XPS spectra of C (1s), N (1s), O (1s), Si (2p), Al (2p) and Na (1s) for EPdL-Br complex.

Figure S8:

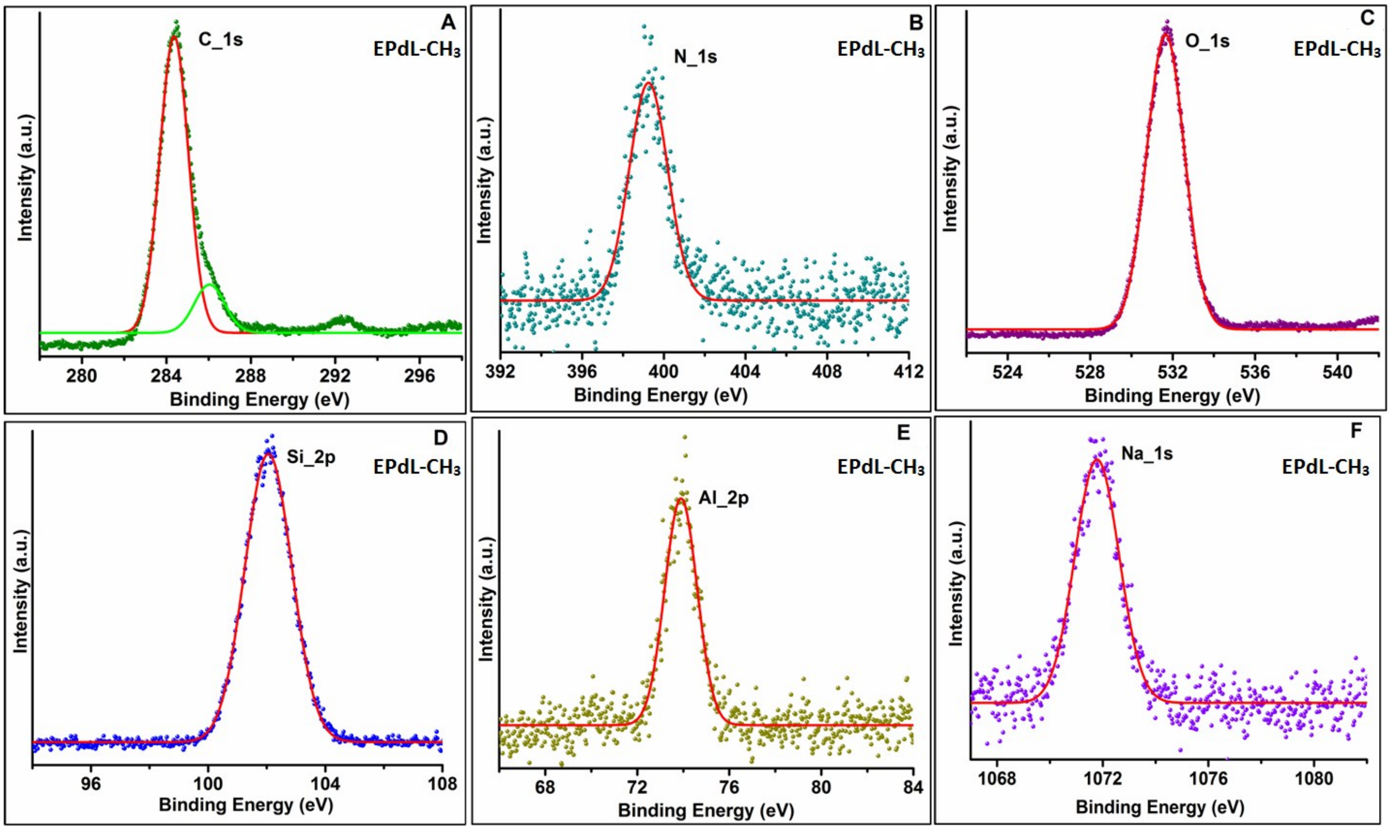


Figure S8: High-resolution XPS spectra of C (1s), N (1s), O (1s), Si (2p), Al (2p) and Na (1s) for EPdL-CH_3 complex.

Table S2. Important structural parameters and HOMO, LUMO energies of neat PdL-OH, PdL-Br and PdL-CH_3 complexes obtained from DFT studies.

S. No	Bond distances / angles	PdL-OH, Neat singlet	PdL-Br, Neat , singlet	PdL-CH_3, Neat, singlet
1	**Pd-O (Å)**	2.00	2.01	2.01
2	**Pd-N (Å)**	2.19	2.19	2.19
3	**O-C (Å)**	1.29	1.29	1.29
4	**N-C (Å)**	1.30	1.29	1.30

5	**<O-Pd-N**	85.9	85.9	85.9
6	**End to end distance(Å)**	13.74	14.76	14.06
7	**<C-Pd-C**	170.9	170.8	170.8
8	**HOMO,**	-5.24	-5.78	-5.38
	LUMO (eV)	-2.62	-2.98	-2.58

Figure S9:

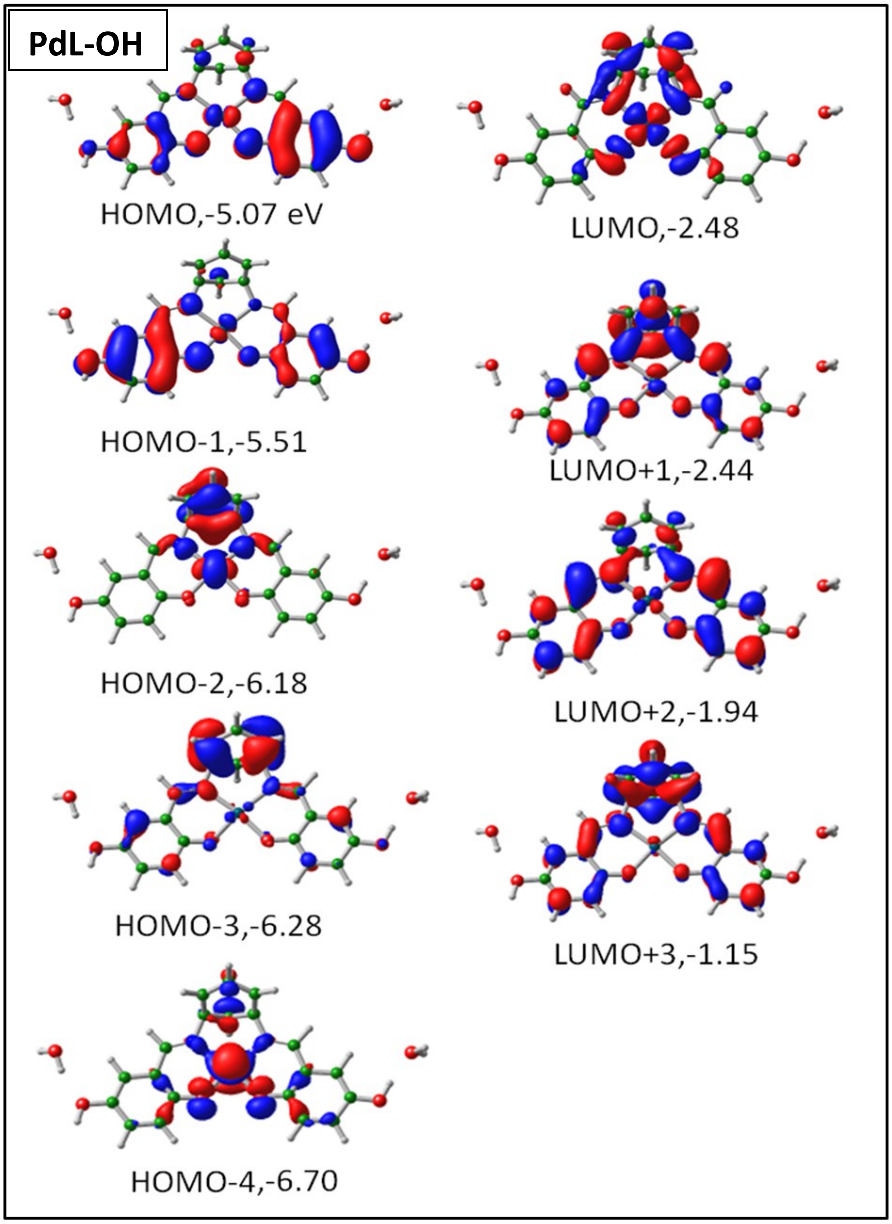


Figure S9: The frontier molecular orbitals of singlet, PdL-OH complex are shown.

Figure S10:

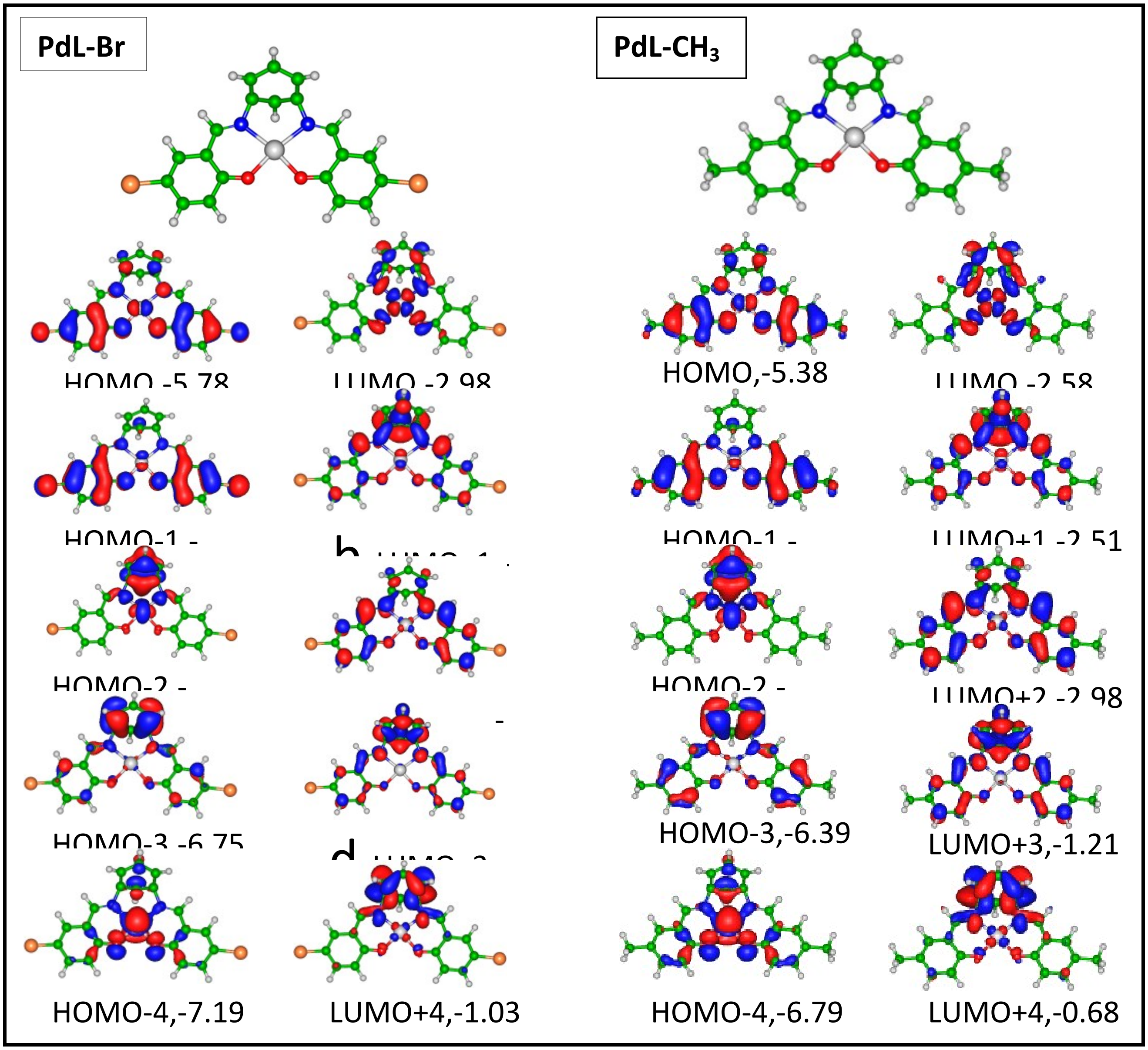


Figure S10: The frontier molecular orbitals for PdL-Br and PdL-CH_3.

Figure S11:

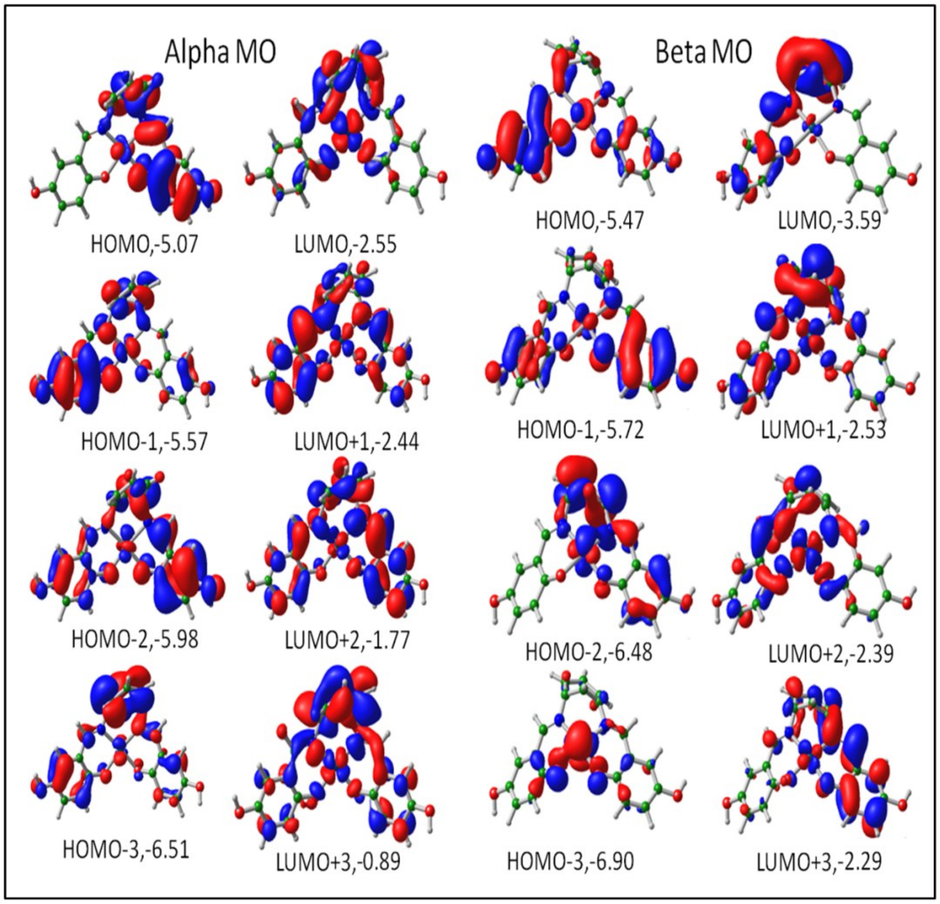


Figure S11: The frontier molecular orbitals of triplet, encapsulated and extracted PdL-OH complex are shown.

Figure S12:

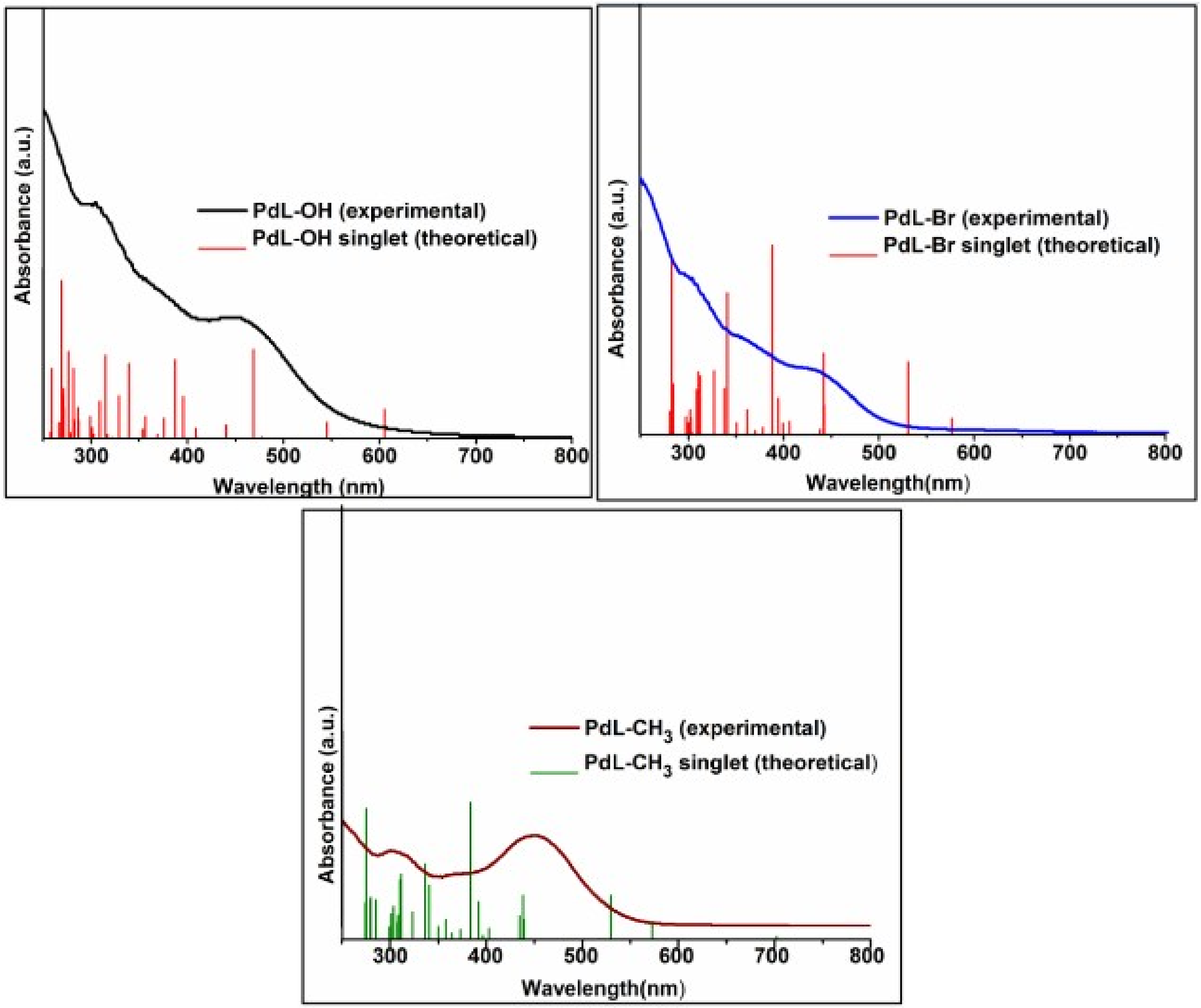


Figure S12: Experimental and TD-DFT spectra for PdL-OH, PdL-Br and PdL-CH$_3$ in neat, singlet state.

Figure S13:

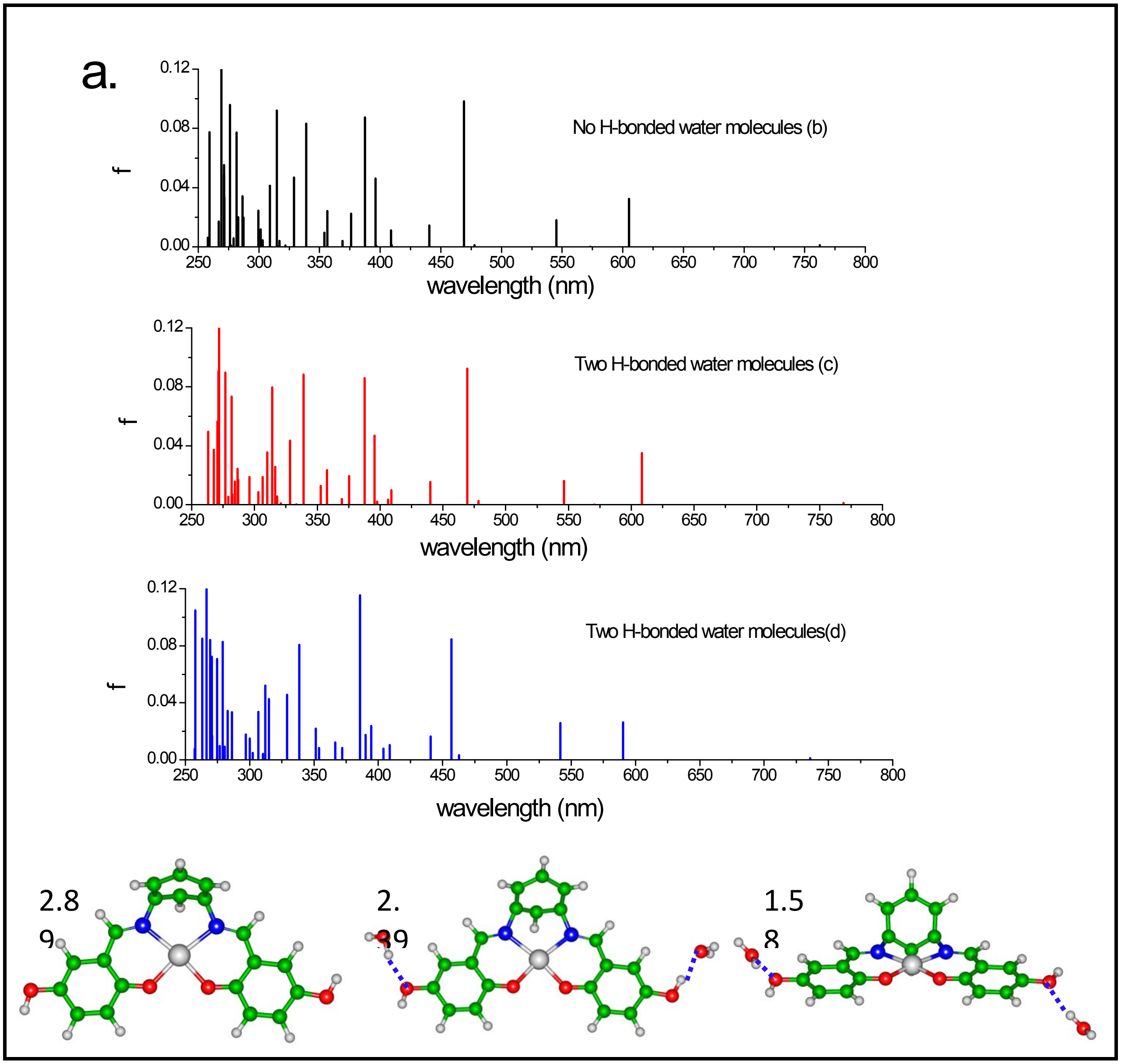
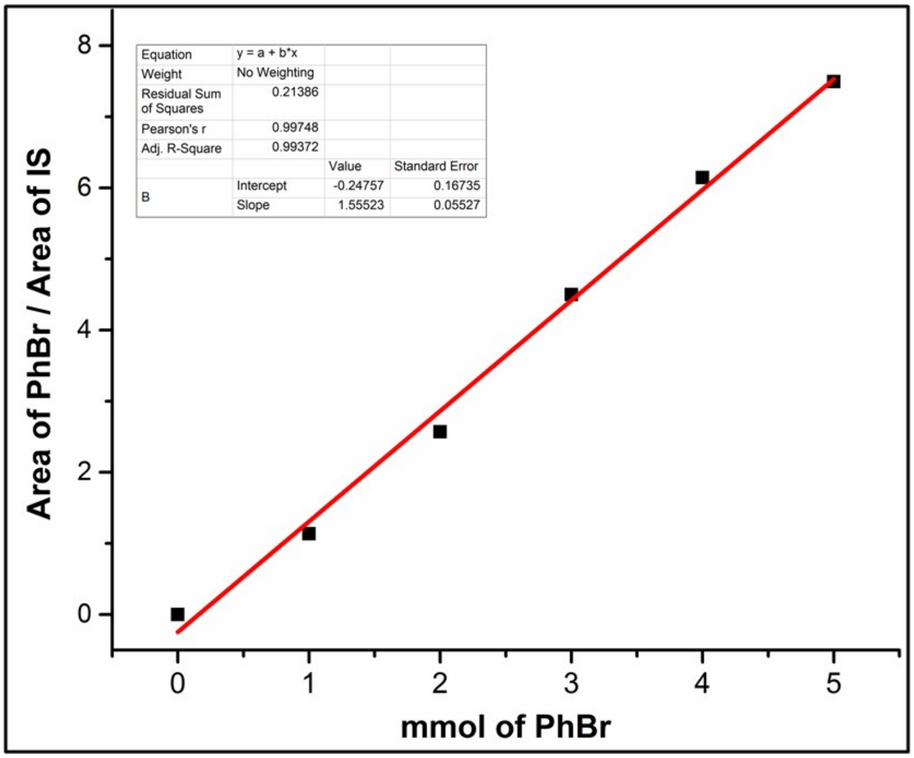


Figure S13: (a) The comparative TD-DFT spectra are shown for neat and water bound singlet PdL-OH complexes. The structures of the singlet complexes studied are given below (b) no water (c) two water molecules hydrogen bonded to Pd complex (c) two water molecules hydrogen bonded to Pd complex in different configuration.

Figure S14:



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.21386		
Pearson's r	0.99748		
Adj. R-Square	0.99372		
		Value	Standard Error
B	Intercept	-0.24757	0.16735
	Slope	1.55523	0.05527

Figure S14: Calibration curve of bromobenzene.

Figure S15:

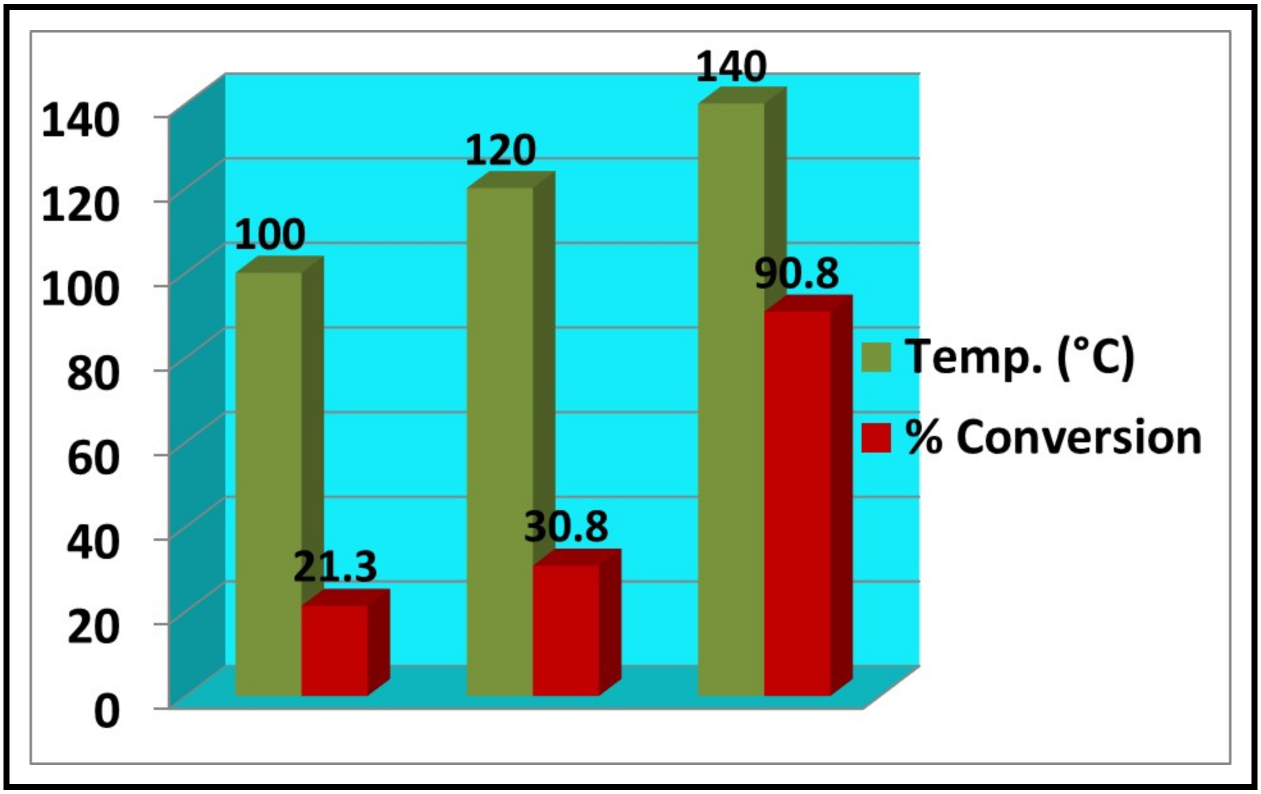


Figure S15: % Conversion of bromobenzene for Heck reaction with respect to temperature.

Figure S16:

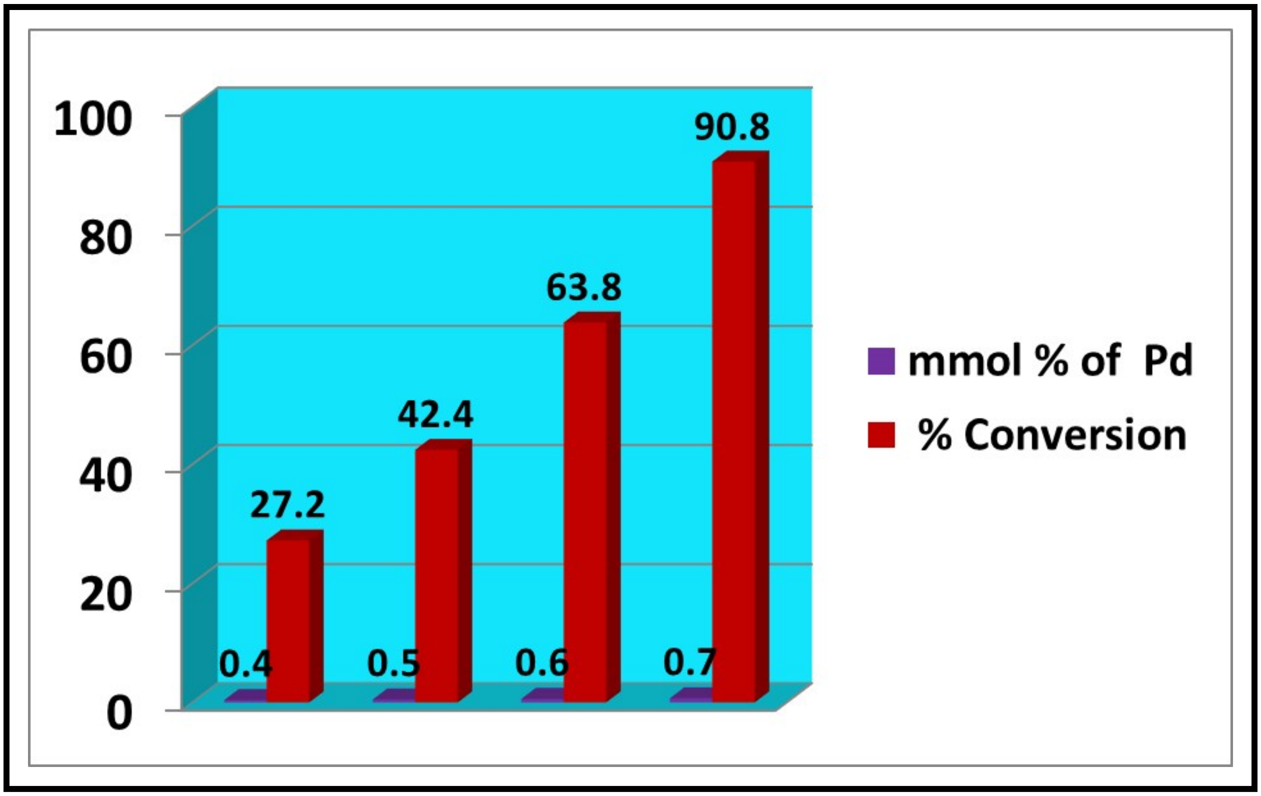


Figure S16: % Conversion of bromobenzene for Heck reaction with respect to amount of catalyst.

Figure S17:

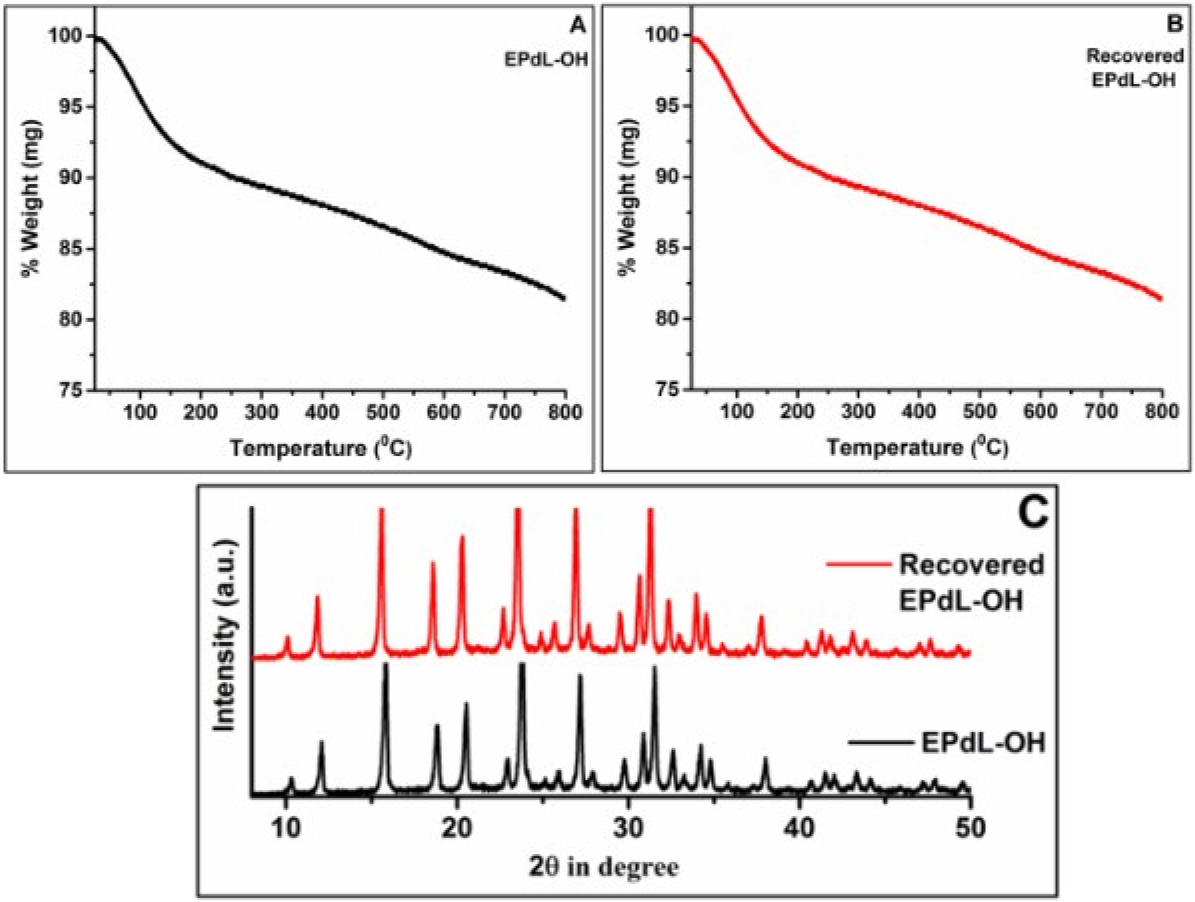


Figure S17: Thermo gravimetric analysis (TGA) results for (A) EPdL-OH, (B) Recovered catalyst EPdL-OH and (C) XRD patterns for EPdL-OH and recovered EPdL-OH.

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**, 5648-5652.
3. A. D. Becke, *Physical Review A*, 1988, **38**, 3098-3100.
4. A. Choudhary, B. Das and S. Ray, *Dalton Trans.*, 2015, **44**, 3753-3763.
5. A. Choudhary, B. Das and S. Ray, *Dalton Transactions*, 2016, **45**, 18967-18976.
6. S. Kumari, K. Maddipoti, B. Das and S. Ray, *Inorg. Chem.*, 2019.
7. A. P. Andrade, L. M. Arantes, J. Y. Kadooca, R. L. Carvalho, A. de Fatima and A. A. Sabino, *ChemistrySelect*, 2016, **1**, 886-890.

8. A. Choudhary, S. Kumari and S. Ray, *ACS Omega*, 2017, **2**, 6636-6645.
9. L. Becker and H. Förster, *Applied Catalysis B: Environmental*, 1998, **17**, 43-49.
10. S. Ernst, E. Fuchs and X. Yang, *Microporous Mesoporous Mater.*, 2000, **35**, 137-142.