Supporting Information

Highly Efficient Post-Synthetically Modified UiO-66 for the Extraction of Pd(II) from Aqueous Solution: Experimental and Theoretical studies

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Determination of Pd(II) concentration using UV-vis spectroscopy

The colorimetric determination of Pd(II) was done using Thorin indicator as chromogenic agent, which tends to form 1:1 violet complex with divalent palladium which shows λ_{max} around 540 nm. 1 mL of 0.05 % (w/V) thorin indicator was used for the studies. pH of the solution to be analysed was maintained at 3.7 using sodium acetate-acetic acid buffer. A series of solutions ranging from 1 ppm to 10 ppm was prepared from a standard Pd(II) stock solution of concentration 1 g/L. The calibration was done with these standard solutions which yielded a linear calibration plot. The value of molar extinction coefficient, obtained from the slope of calibration plot was found to be 6598.04 L mol^{-1} cm^{-1}. Similar procedure for palladium(II) determination was reported in literature.[1]

EXAFS STUDIES

The EXAFS measurements for the synthesized Si@-UiO-66-AO with U(VI) were performed in transmission mode at the scanning XAS beamline (BL-09) of the Indus-2 Synchrotron Source (2.5 GeV, 200 mA) at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.[2-3] The energy range of beamline operation is 4 to 30 keV. The beamline optics consist of a Rh/Pt coated collimating meridional cylindrical mirror followed by a Si(111) (2d = 6.2709 Å) based double crystal monochromator (DCM). The second crystal of the DCM is a sagittal cylindrical crystal used for horizontal focusing. Two ionization chambers (with a length of 300 mm) were used as detectors. The absorption coefficient 'μ' was obtained using the following relation:

$$\mu(E) \propto I_0/I_t$$

Here, I_0 is the incident X-ray intensity and It is the measured transmission intensity.

The EXAFS function χ(E) was obtained from μ(E) using the below equation:

$$(E)=(E)-\mu_0(E)/\Delta\mu_0(E_0)$$

Here, E_0 is the absorption edge energy, μ(E) is the experimentally measured absorption co-efficient, $\Delta\mu_0(E_0)$ is the edge step and $\mu_0(E)$ is a smooth background curve that is fit to the data to remove the bare atom background. The goodness of the fit was measured by R-factor, which is given by:

$$R = \frac{\sum_{i=min}^{max} [R_e(\chi_d(r_i) - \chi_t(r_i))^2 + I_m(\chi_d(r_i) - \chi_t(r_i))^2]}{\sum_{i=min}^{max} [R_e(\chi_d(r_i))^2 + \sum_{i=min}^{max} [I_m(\chi_d(r_i))^2}$$

Pd(II) adsorbed MOFs were prepared by equilibrating ~20-30 mg of MOFs in Pd(II) (pH = 5) for 3h followed by centrifugation. Then resultant MOF powderswere collected and utilized for EXAFS analysis. The effects of sample concentration, thickness, detector solid angle, filter thickness, slit position etc., are taken care of by normalizing the data to the unit edge step. In addition, absorption due to lower-energy edges by the atoms of interest, absorption from other elements, absorption from the ion chamber and air path between the chambers slowly vary with energy and add to the background. To account for these factors, a cubic spline was used to fit the data above the edge using the ATHENA software package[4].

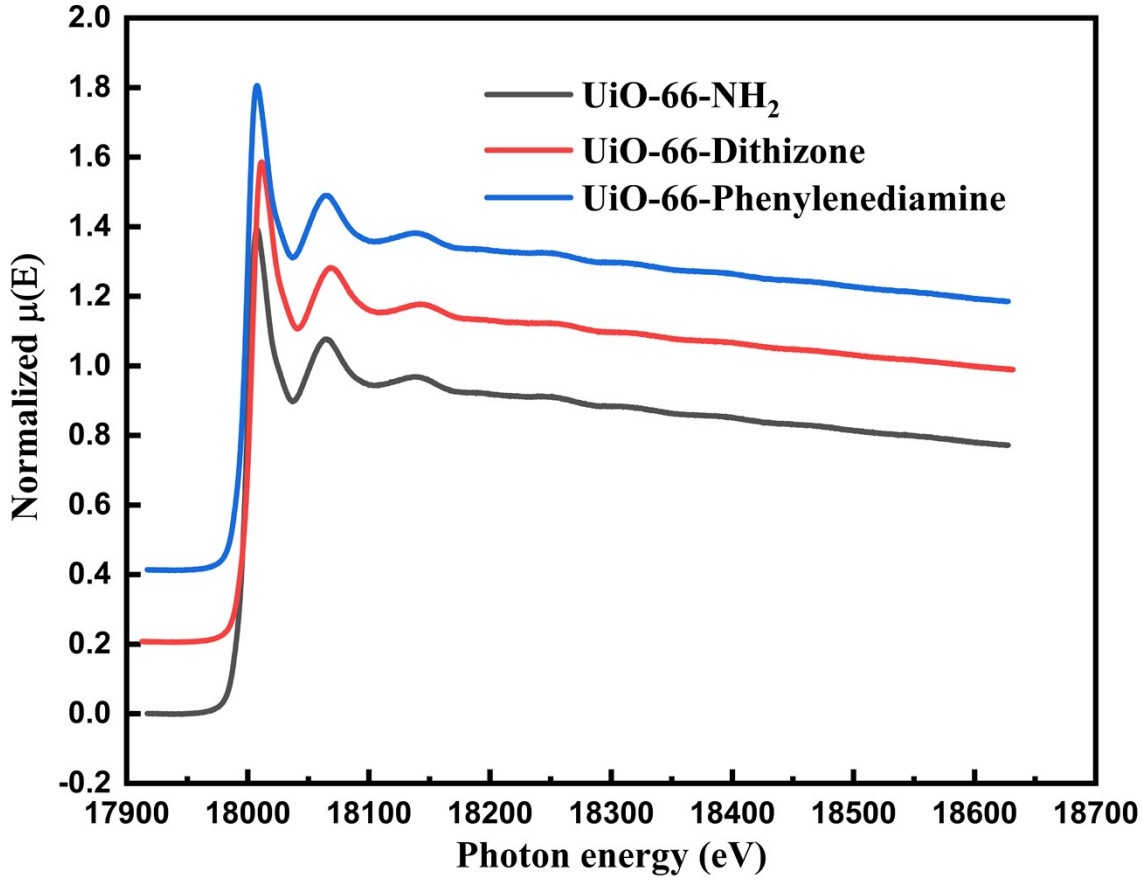


Fig. S1 Normalized EXAFS spectra for UiO-66-NH_2, UiO-66-Dithizone and UiO-66-Phenylenediamine at Zr-K edge. The plots are provided with constant offset of 0.2 units.

SEM Analysis

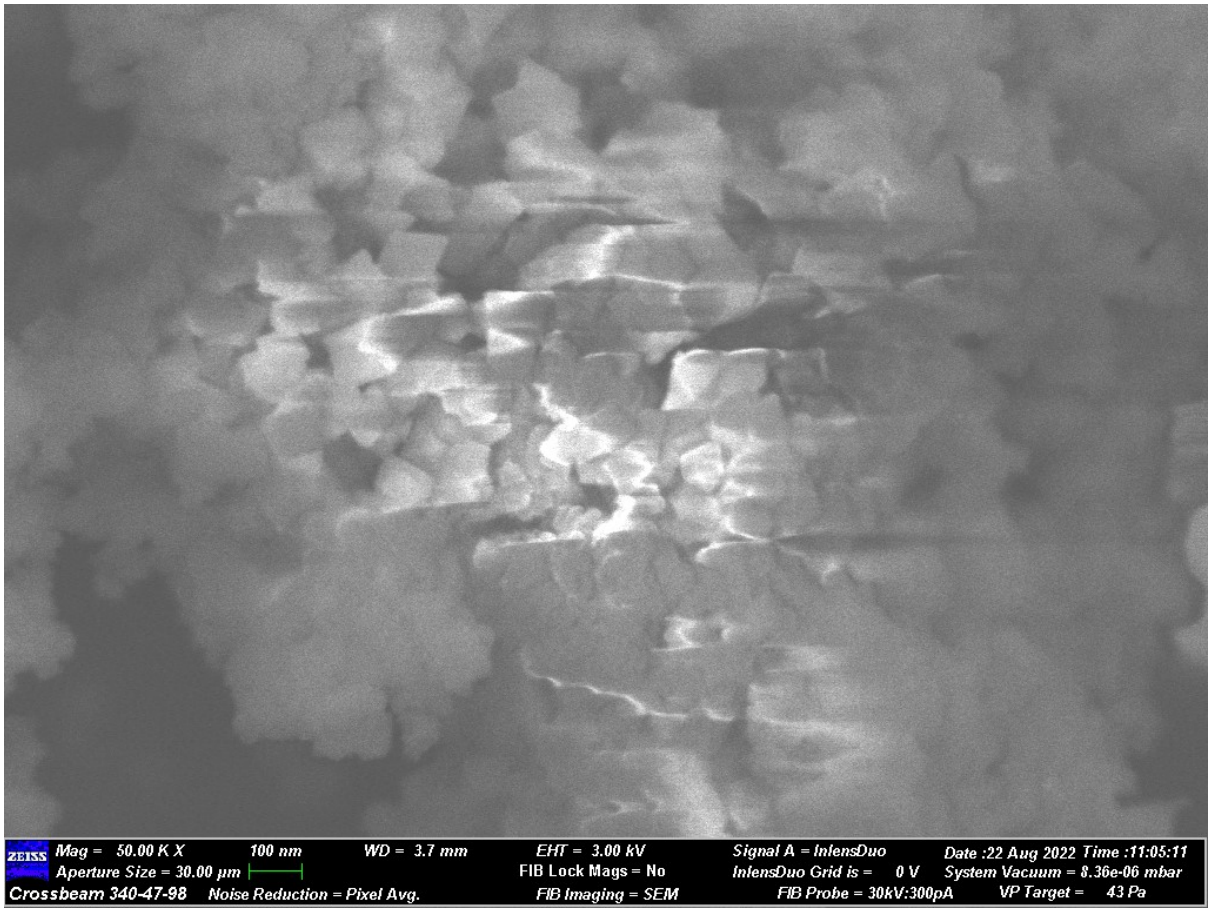


Fig. S2 SEM image of UiO-66-NH_2

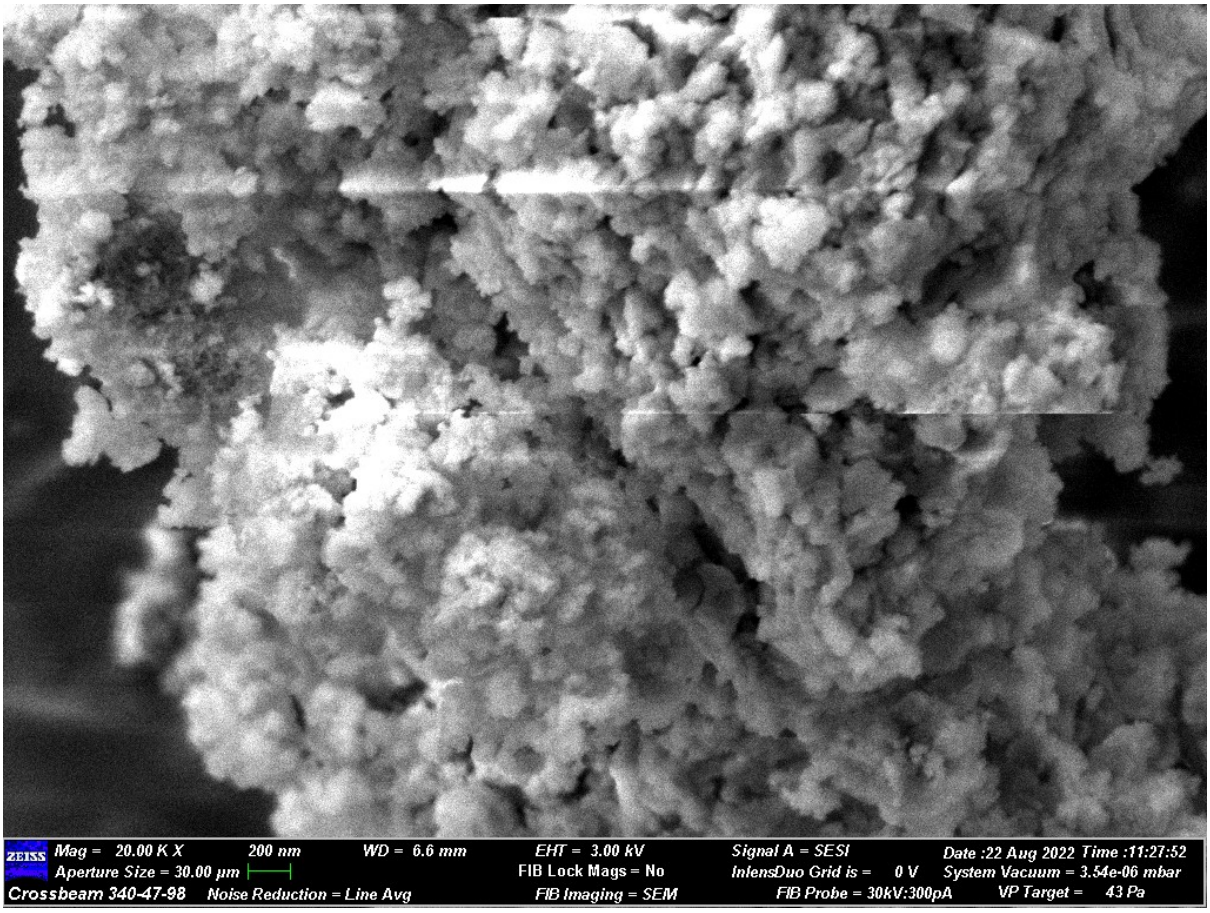


Fig. S3 SEM image of UiO-66-Phenylenediamine

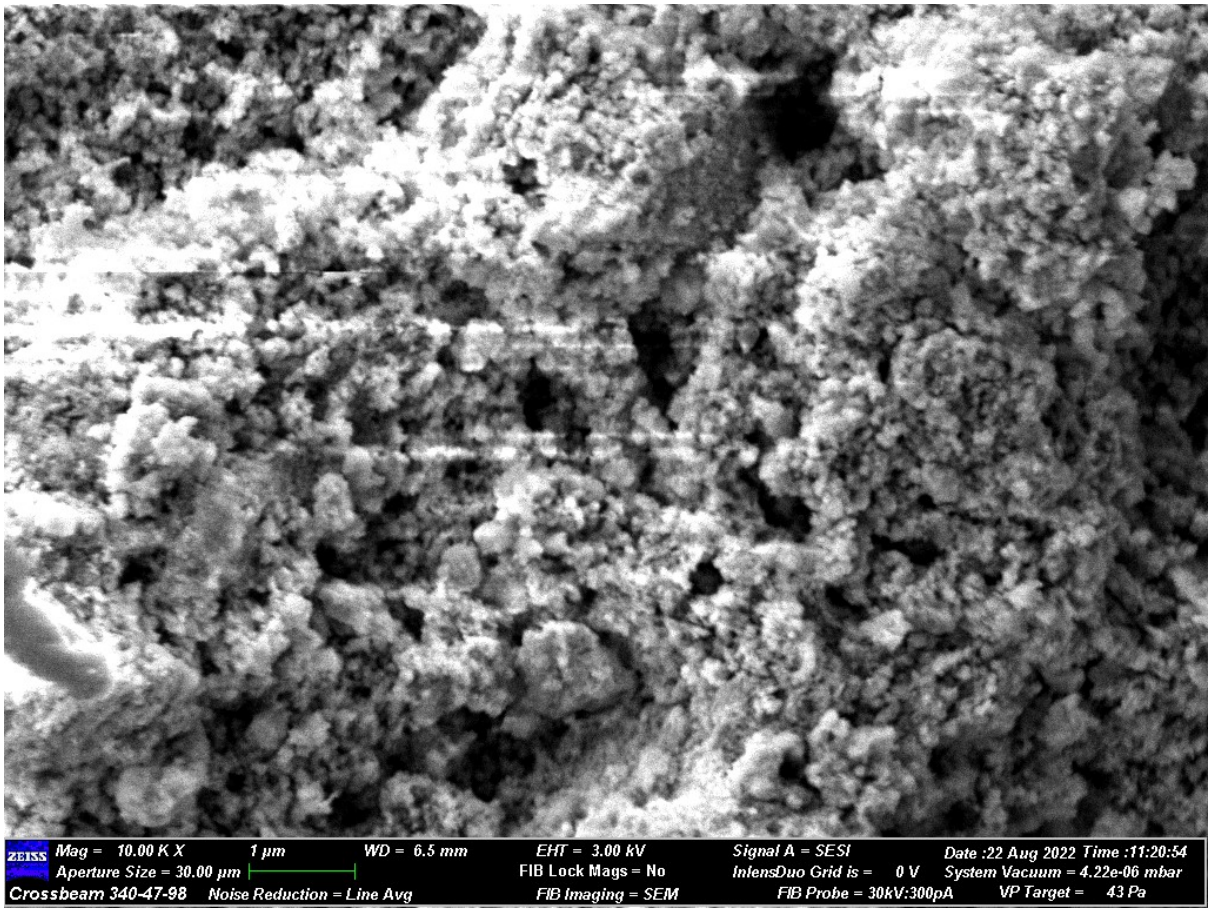


Fig. S4 SEM image of UiO-66-Dithizone

Pd(II) sorption kinetic studies

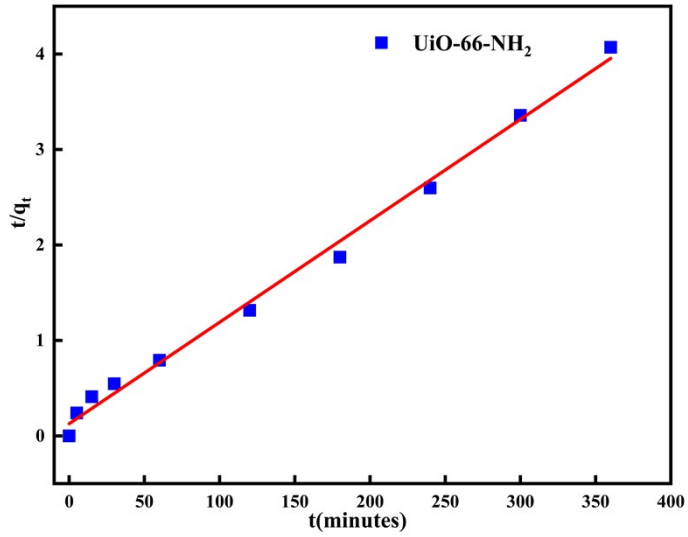


Fig. S5 Contact time *vs* t/q_t plot for UiO-66-NH_2;$m_{sorbent}$=10 mg, t= 0 to 360 min, $V_{solution}$= 3 mL, C_o= 1000 mg L^{-1}, T = 25°C±1.

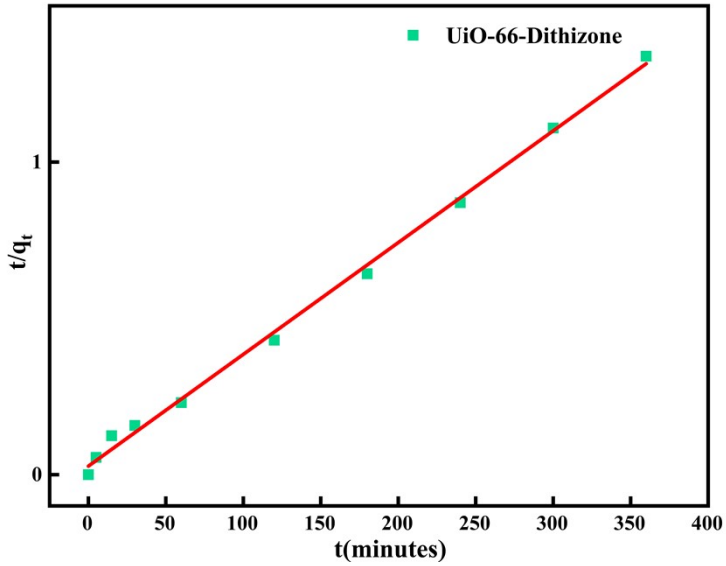


Fig. S6 Contact time *vs* t/q_t plot for UiO-66-Dithizone;$m_{sorbent}$=10 mg, t= 0 to 360 min, $V_{solution}$= 3 mL, C_o= 1000 mg L^{-1}, T = 25°C±1.

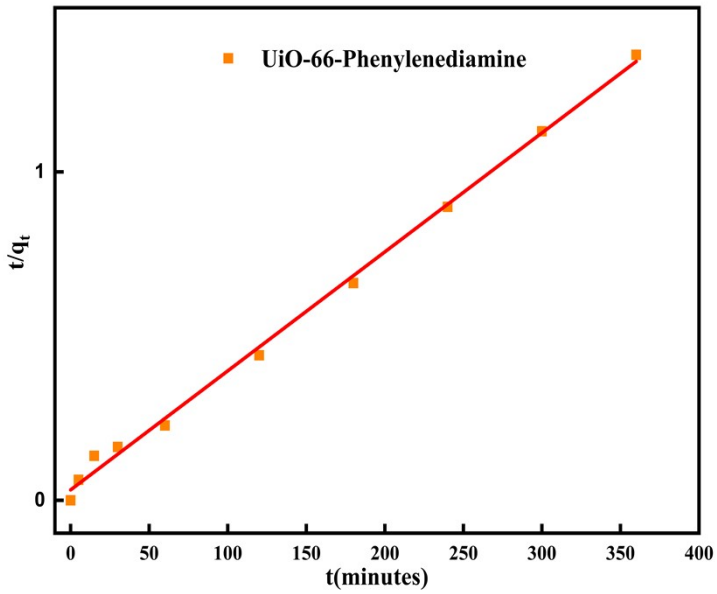
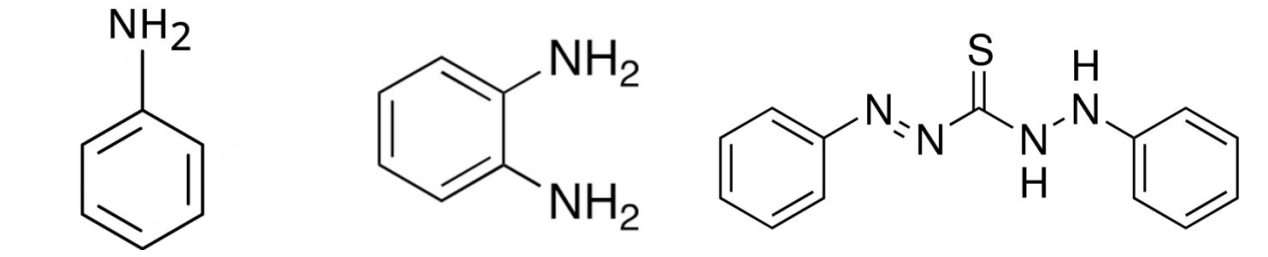


Fig. S7 Contact time *vs* t/q_t plot for UiO-66-Phenylenediamine;$m_{sorbent}$=10 mg, t= 0 to 360 min, $V_{solution}$= 3 mL, C_o= 1000 mg L^{-1}, T = 25°C±1.

DFT Studies



a ***b*** ***c***

Fig. S8 Chemical structures for the ligands **(*a*)**aniline**(*b*)** dithizone **(*c*)**o-phenylenediamine employed in computational studies.

Coordinates of Optimized Geometries of Ligands:

Aniline

C -1.39066693000986 -0.00996324596291 -4.31421914542241

C	-2.49580776196835	-0.43302547247378	-3.57033154042262
C	-0.25536014199058	0.44520437359766	-3.63779752926976
H	-3.39105004205523	-0.79359175812714	-4.07982816837974
H	0.61864217893161	0.77803020940055	-4.20029344976855
C	-2.47164915448969	-0.40306742092135	-2.17726504884205
C	-0.22067779705210	0.47927889636166	-2.24502870850891
H	-3.34352082378131	-0.73264116396404	-1.60731869044994
H	0.67134136344712	0.84144015522043	-1.72854903140634
C	-1.33079453159863	0.05419106521033	-1.49264068247539
H	-1.41343274131114	-0.03606596891516	-5.40360775397702
N	-1.32519324259010	0.14647445532507	-0.09871718317594
H	-0.40448915597278	0.13937663168545	0.33041115725535
H	-1.97198785955895	-0.47564075643675	0.37723160884334

Dithizone

C	-2.31413975588219	6.31822837102753	4.98237673193831
S	-1.71219836330261	7.65894565208168	5.76157901775378

N	-1.93701234375742	5.02374796498377	5.40288470967172
N	-3.15643650721380	6.35580400999873	3.92427185004263
C	-7.12892196501964	7.34983692901850	2.91811698356981
C	-5.82247069542273	6.97538056111774	3.23674934148793
C	-7.40819807798825	8.62878858614613	2.43375774053431
H	-5.61791298540075	5.98623510632727	3.64536721826085
H	-8.43134945586154	8.91523758804783	2.19043127913039
C	-4.77559681745901	7.89122167572180	3.06139094047014
C	-6.36023867323891	9.54160390606075	2.26934040432652
H	-6.56375416092374	10.54681645981695	1.89771412277155
C	-5.05151263665690	9.17956350139925	2.57274236316099
H	-4.23274660085996	9.88731566845418	2.43085834737538
H	-7.93771736974135	6.63204557406352	3.06277217575602
C	-0.94882083955045	1.15202884901869	6.44128531022610
C	-1.25342806527078	2.47938321870307	6.16814863424713
C	-0.99515119760706	0.18814184823065	5.42291044191781
H	-1.21950807698635	3.24681935397404	6.94064169853015
H	-0.75360854163470	-0.85144068967230	5.64846498543303
C	-1.60842173983101	2.84927969107562	4.85648664653849

C	-1.34463583642136	0.55636456197044	4.12104880286512
H	-1.37688659092681	-0.19277888087151	3.32937385601302
C	-1.64719872900734	1.88611401147318	3.83545960291880
H	-1.91767941452899	2.20698535172716	2.82876539764908
H	-0.67018251982488	0.85734768842958	7.45399950765247
N	-3.42833622635071	7.55557273966166	3.30114823098767
N	-1.94030960543100	4.16357228865856	4.46676942929676
H	-2.85465127907943	8.28238954422103	3.76068208005495
H	-3.16865479481985	5.50529563713375	3.34844892841858

o-Phenylenediamine

C	-0.04359327553559	0.17317029802529	-0.45083806891161
C	-0.10058577479362	1.56912574514193	-0.48929460626868
C	-0.07313552577819	1.62155848621916	1.92597875518350
C	-0.00550784537738	-0.51103417434287	0.76761921262580
N	0.09068144439213	-1.91380854712041	0.85335541605659
H	-0.04233954396933	-0.40120648528958	-1.38064566177600
H	-0.13321418954835	2.08316376961567	-1.45029729986534
H	-0.51508104579162	-2.30113938124978	1.57916171615439
H	-0.08174947994985	-2.37963725667789	-0.03506198040873

C	-0.12845148824264	2.29454683308873	0.70227484872667
H	-0.18281830196504	3.38339202949043	0.68542265012442
H	-0.07380790231409	2.18544266328981	2.86218854020246
C	0.00160544485994	0.22652405128468	1.97597598234051
N	0.02065167099549	-0.49462948414706	3.18594772055700
H	0.18587558351404	0.09567524803545	3.99851390566531
H	0.68976855450411	-1.26646174336355	3.16772512259368

Coordinates of Optimized Geometries of Pd^{2+} species:

$Pd(H_2O)_4^{2+}$

Pd	-7.26958064239857	2.43741337081494	1.67401984090149
O	-6.75530517594401	1.01139575140183	3.06227128848576
H	-6.12014026227511	1.27819720589549	3.76285738842186
H	-7.51828032331525	0.58733997259433	3.51496348217683
O	-8.72397714880216	3.14607360185025	2.94207493412663
H	-8.49930993887170	3.93388070873127	3.48461442438392
H	-9.58683966253141	3.33412729170957	2.50964196922995
O	-7.87635766636605	3.77415231460203	0.23540358108027
H	-7.94824025344174	3.39606003107551	-0.66945824477548
H	-7.36420474718689	4.60892761055212	0.15610786008986

O	-5.89548340267317	1.65160388067512	0.36247762237003
H	-4.96906276059526	1.96906027500156	0.44260935236882
H	-5.86027956759867	0.66903891809597	0.34785488814006

$PdCl_2 \cdot 2H_2O$

Pd	-7.32068878665965	2.58517698513532	1.62537858569010
O	-6.06083280397300	3.94128930312553	2.72209549879149
H	-6.63627999988580	4.56829094102239	3.20061642332838
H	-5.82627426768215	3.23902872135855	3.38833444280174
O	-7.88317072466154	3.91374586416997	0.02927348342803
H	-8.47753648190838	3.22685300755147	-0.37934292158258
H	-7.12388894400791	3.99207573508403	-0.57952000710306
Cl	-6.75334510969938	1.19509144583257	3.31611208958799
Cl	-8.61845442752215	1.14782489572012	0.45802855805788

Coordinates of Optimized Geometries of Pd-Ligand Complexes:

Pd-aniline

Pd	-7.29871761304105	2.47291741896870	1.90035942607071
O	-8.97958732024931	3.59718413701526	2.60309934976945
H	-8.90265145809518	4.56883680973480	2.50771564372288
H	-9.82841630682391	3.35409510575052	2.17988247235744

O	-7.92280725313092	2.85958664386055	-0.13752923360465
H	-8.15628575110333	2.13327441608611	-0.74683138721032
H	-7.51083325637348	3.56286374840552	-0.67538901309729
O	-5.47678537853367	1.45094297658180	1.40466027474965
H	-5.56430248431978	0.50490568088994	1.17221326035418
H	-4.88442374595570	1.85258357476987	0.73786992231390
C	-7.19641660814880	-2.00205716941417	4.79274829403156
C	-8.35310596718286	-1.20381868011194	4.77373242068006
C	-5.93721519305079	-1.44881342469901	4.50830789621391
H	-9.32149766500351	-1.64069918066549	5.01630969211502
H	-5.04416006173737	-2.07175882147397	4.55484521428978
C	-8.25994089503301	0.14542273827553	4.46453709478521
C	-5.82593194758431	-0.10073955545990	4.19327463370072
H	-9.14888122486835	0.77917633661218	4.46794102802791
H	-4.85006422088789	0.34942507727581	4.00186484723683
C	-6.99253037353332	0.69000992688526	4.17716609361841
H	-7.27592741933122	-3.05969226452929	5.04594750551693
N	-6.89034625017561	2.07899089168574	3.87074656988259
H	-5.94786069997180	2.44783714890070	4.05720498569371

H	-7.58395951986436	2.64117972865543	4.38395342178119

Pd-Dithizone

C	-2.93912410514487	3.63648461910164	3.00201088047104
S	-4.33769689533779	2.76953506507719	2.54807640670844
N	-2.17582445811787	3.36147424874903	4.10027598829846
N	-2.49928345253111	4.70901535748186	2.30248603387462
C	-4.71111531580669	8.27005080003418	1.87488081297008
C	-3.94333281395318	7.11563743764287	2.03997905524507
C	-5.37579682583233	8.51881280279467	0.67339264226513
H	-3.45104397785591	6.91284470306670	2.99079022823322
H	-5.97782840940253	9.41933789621950	0.55338912985110
C	-3.83573890641376	6.20353925273535	0.98460664972352
C	-5.26758816319632	7.59781123947840	-0.37379253718358
H	-5.78679456320137	7.77644726360202	-1.31607493966015
C	-4.49685903411717	6.44776267187788	-0.22778747649299
H	-4.40381356115964	5.73534010081582	-1.04970187289306
H	-4.79694616352026	8.97416716938554	2.70343395973084
C	0.19305459387267	2.21406730729732	7.24579515335466
C	-0.48885666120101	2.45441093578440	6.06246306540080

C	-0.47524619637556	1.64930799147428	8.34329243319909
H	0.01096936107297	2.87847855193830	5.19359229872831
H	0.06702377445565	1.46634710405823	9.27178925810630
C	-1.84842975131791	2.09893474465790	5.96505410685919
C	-1.82712877790087	1.31692074747721	8.24927954553018
H	-2.34816722351170	0.88389317349564	9.10282730551677
C	-2.51968195869767	1.52067703884793	7.05789608190672
H	-3.57730627962992	1.28785812674950	6.97232625304550
H	1.25379189602356	2.45588496507712	7.31785888068952
N	-3.02386588133960	5.04279306786055	1.07329461952283
N	-2.56524000946587	2.31828117880514	4.77480719905830
H	-3.41365758245687	4.21477019278581	0.61316163659018
H	-1.58833408204754	5.09812682569653	2.54436996951295
Pd	-3.99306251246729	1.08576018813234	4.05816175161405
Cl	-3.42784848092782	-0.76283963992579	5.32828761070773
Cl	-5.67621687549403	-0.07589820027559	3.05184493551466

Pd-Phenylenediamine

C	-0.04925977819517	0.13413836667468	-0.43782399248260
C	-0.06341014710328	1.52831729001118	-0.47826074267494

C	-0.09260020154969	1.60302331847458	1.93926301228408
C	-0.05681615145509	-0.52837634554208	0.79127383089557
N	-0.04355051588761	-1.98270298758746	0.88118312531884
H	-0.03246362194963	-0.44736934432537	-1.36124461543359
H	-0.05734830412844	2.04195717487818	-1.43963358128237
H	-0.86048178271497	-2.40759955484839	0.42884738264474
H	0.78528416916354	-2.39321975224974	0.43739044946698
C	-0.08531749660894	2.26282039591383	0.71036558998620
H	-0.09657356504071	3.35236704302150	0.68098178138433
H	-0.10915950796612	2.16860931995269	2.87251476171778
C	-0.07803391481495	0.20745187202244	1.98197993441534
N	-0.08355080384504	-0.52355943290316	3.24227992538089
H	-0.91481070705869	-0.31960603034584	3.80783310028083
H	0.73082795281452	-0.30191543391440	3.82550247063174
Pd	-0.05371386266865	-2.57026747341154	2.87578832173157
Cl	-0.01832190818986	-4.75531463201168	2.20634941972240
Cl	-0.07172601580121	-2.94718747880944	5.13005217201217

References:

1. S. P. Sangal and A. K. Dey, Microdetermination of palladium (II) using 1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonate (thoron) as a colorimetric reagent, *Microchemical Journal*, 1963, **7**, 257-262.

2. S. Basu, C. Nayak, A. K. Yadav, A. Agrawal, A. K. Poswal, D. Bhattacharyya, S. N. Jha andN. K. Sahoo, A comprehensive facility for EXAFS measurements at the INDUS-2 synchrotron source at RRCAT, Indore, India. *J Phys Conf Ser*.**2014**,493 (1), 012032, DOI: 10.1088/1742-6596/493/1/012032.

3. A. K. Poswal, A. Agrawal, A. K. Yadav, C. Nayak, S. Basu, S. R. Kane, C. K. Garg, D. Bhattachryya, S. N. Jha andN. K. Sahoo, Commissioning and first results of scanning type EXAFS beamline (BL-09) at INDUS-2 synchrotron source. *AIP Conf Pro.***2014**,1591 (1), 649-651, DOI: 10.1063/1.4872706.

4. B. Ravel and M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.***2005**,12 (4), 537-541, DOI: 10.1107/S0909049505012719.