Pd(II) Complexes of *Meso*-Tetraaryl Triphyrin(2.1.1)s: Synthesis and Studies

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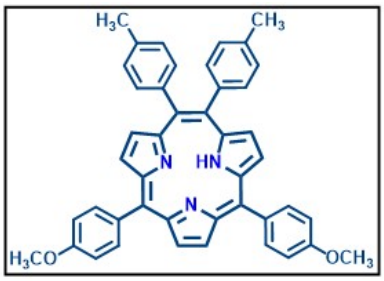
General Experimental section

Materials and Methods. All chemicals and reagents were purchased from Sigma-Aldrich or Merck and used as received without further purification in analytical grade. The required *meso*-tetra(aryl) triphyrin(2.1.1)[1] derivatives **1a–1c** were synthesized following our recently reported procedure. Column chromatography was carried out using basic alumina and silica gel (60–120 mesh). The ^{1}H, ^{13}C, and 2D NMR spectra (δ in ppm) were recorded on 400 and 500 MHz Bruker spectrometers using $CDCl_3$ as the deuterated solvent. The operating frequencies for ^{13}C nuclei were 100.06 MHz and 125.77 MHz for the 400 and 500 MHz instruments, respectively. Tetramethylsilane (TMS, $Si(CH_3)_4$) was used as the internal standard for both ^{1}H and $^{13}C\{^{1}H\}$ NMR measurements. Structural assignments were further supported by 2D NMR experiments, including COSY and NOESY, particularly for complex **1c.Pd(II)**. UV–Vis–NIR absorption spectra were recorded on a Cary series spectrophotometer. Stock solutions for UV–Vis measurements (10^{-5} M) were prepared in HPLC-grade chloroform. Electrochemical measurements were performed in dry dichloromethane containing 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. Cyclic voltammetry experiments were conducted using a BAS electrochemical workstation equipped with a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). Half-wave potentials were determined from differential pulse voltammetry (DPV) as well as by averaging the anodic and cathodic peak potentials. High-resolution mass spectra were recorded using a Q-TOF micro mass spectrometer.

X-ray crystal structure analysis. Single brown-colored crystals of **1b.Pd(II)** were obtained as supplied. A suitable crystal was selected and mounted on a Bruker APEX-II CCD diffractometer. Diffraction data were collected at 150 K using graphite-monochromated Cu

Kα radiation (λ = 1.54184 Å) employing the ω-scan technique. The crystal temperature was maintained at a constant 150.15 K throughout the data collection. The structure was solved using the dual-space method with the solve program implemented in the Olex2 (v1.5) package, which was also used as the graphical interface. The structural model was refined using refine within Olex2 through full-matrix least-squares minimization on F^2.[2,3] Crystallographic data for compound **1b.Pd(II)** have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 2536465) and can be obtained free of charge from the CCDC.

Computational Details. For all the calculations Gaussian 16 program package was used.[4] The density functional theory (DFT) method with the B3LYP/6-31G(d,p) and LANL2DZ basis set was used to optimize the structures of **1a.Pd(II)-1c.Pd(II)** in S_0 state.[5-7] All the computations were performed using the self-consistent reaction field (SCRF) under the polarisable continuum model (PCM) in the toluene media. The electronic absorption spectra as well as the oscillator strengths were thoroughly examined using TD-DFT with PCM model based on the optimized structures in the S_0 state.[8]

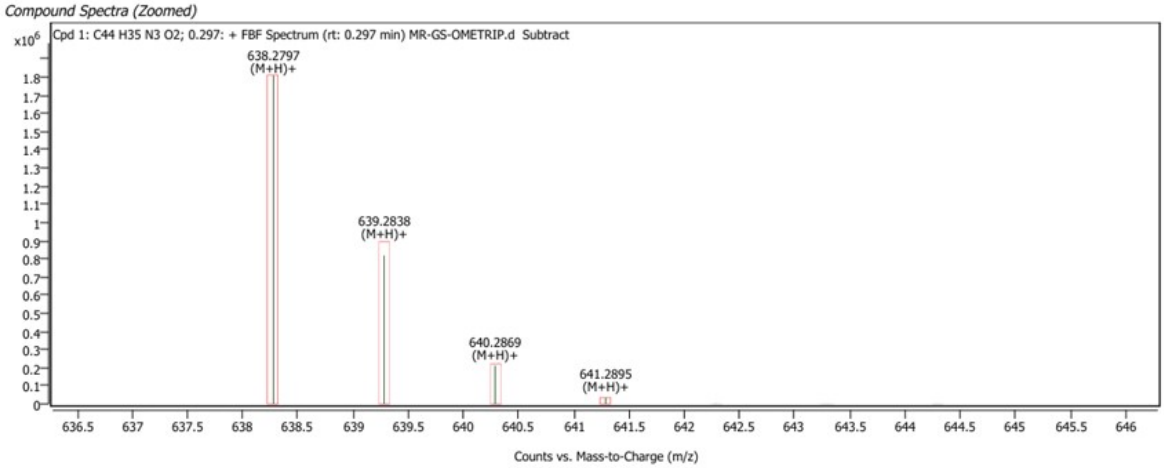


Compound Details

Cpd. 1: C44 H35 N3 O2

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C44 H35 N3 O2	638.2797	638.279744255072	-0.159890412191999	-0.250897857607922	98.15

Compound Spectra (Zoomed)



MassHunter Qual 10.0
(End of Report)

Figure S1. HR mass spectrum of the compound **1c**

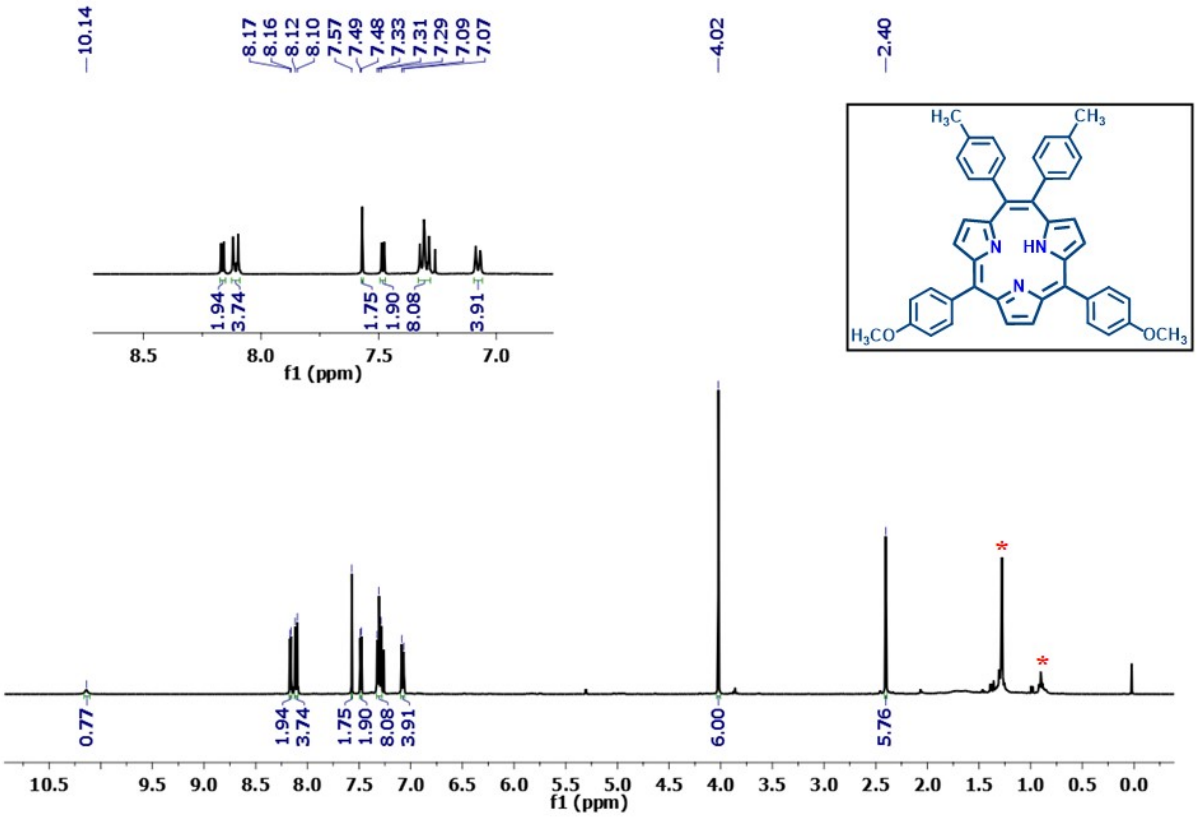


Figure S2. ^{1}H NMR spectrum of the compound **1c** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

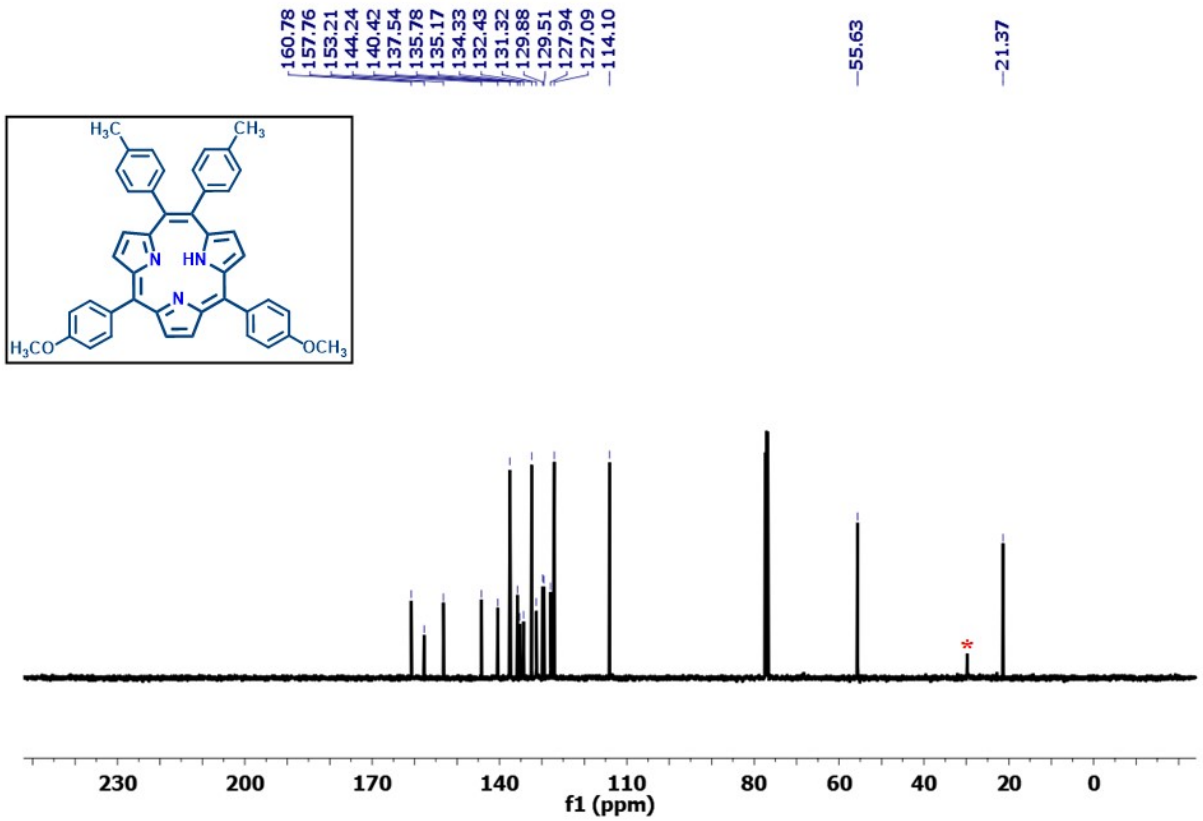
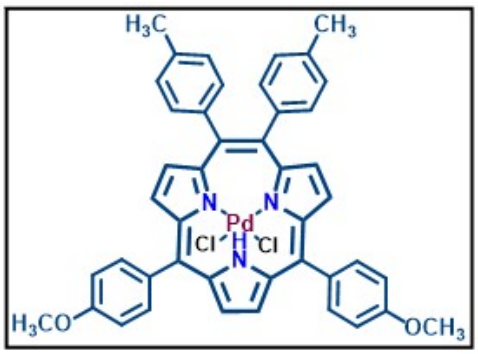


Figure S3. $^{13}C\{1H\}$ NMR spectrum of the compound **1c** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

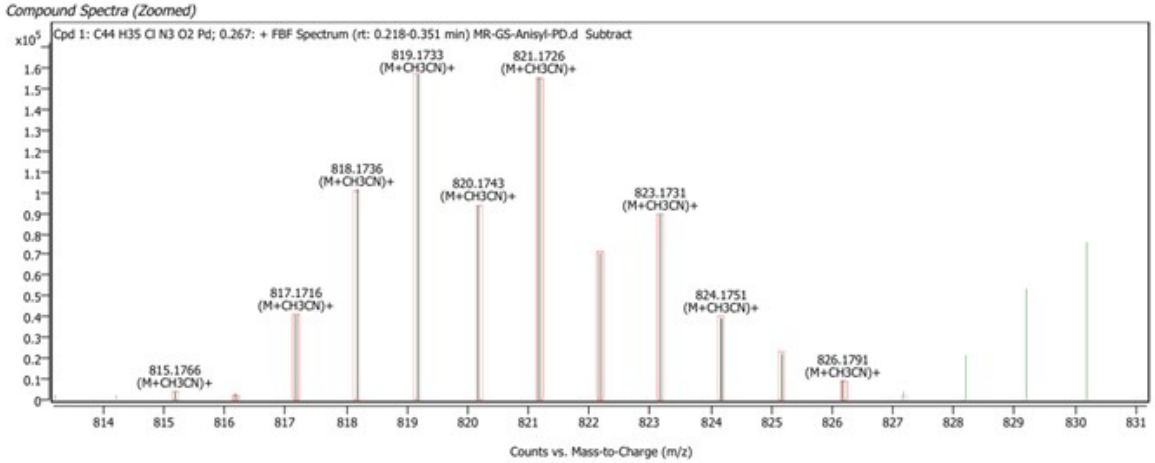


Compound Details

Cpd. 1: C44 H35 Cl N3 O2 Pd

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C44 H35 Cl N3 O2 Pd	819.1733	819.173283206022	0.595253715459876	0.768915229042989	94.21

Compound Spectra (Zoomed)



MassHunter Qual 10.0
(End of Report)

Figure S4. HR mass spectrum of the compound **1c.Pd(II)**

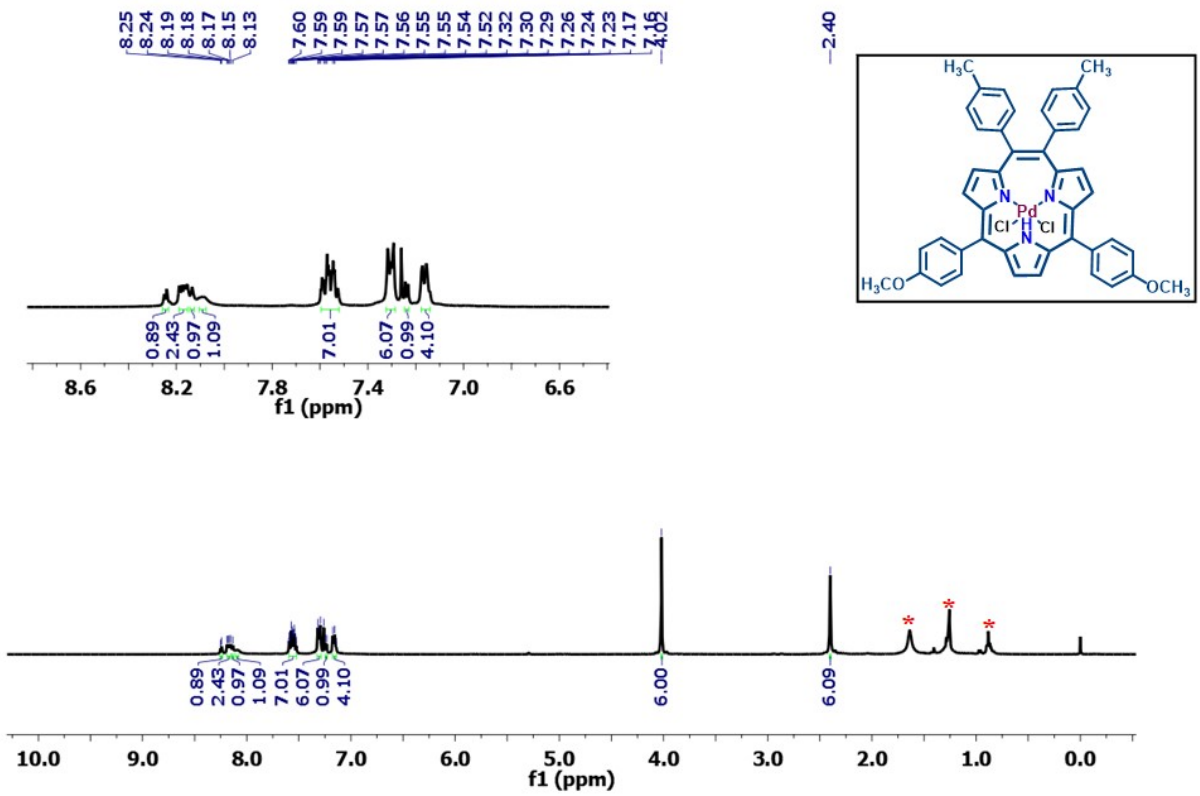


Figure S5. ^{1}H NMR spectrum of the compound **1c.Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

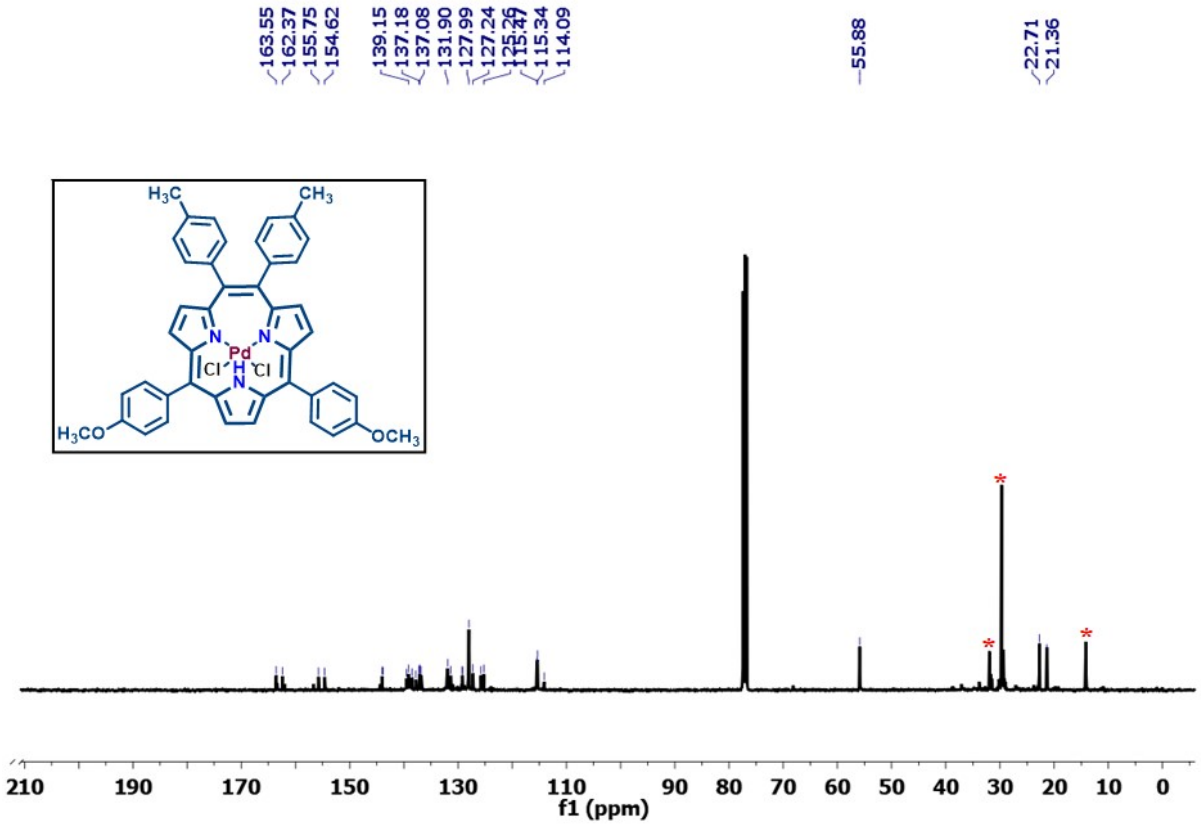
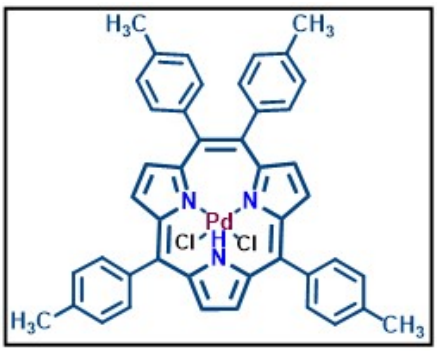


Figure S6. $^{13}C\{1H\}$ NMR spectrum of the compound **1c.Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents



Compound Details

Cpd. 1: C44 H35 Cl N3 Pd

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C44 H35 Cl N3 Pd	787.1841	787.184105733664	1.1528650627497	1.55339664813428	91.73

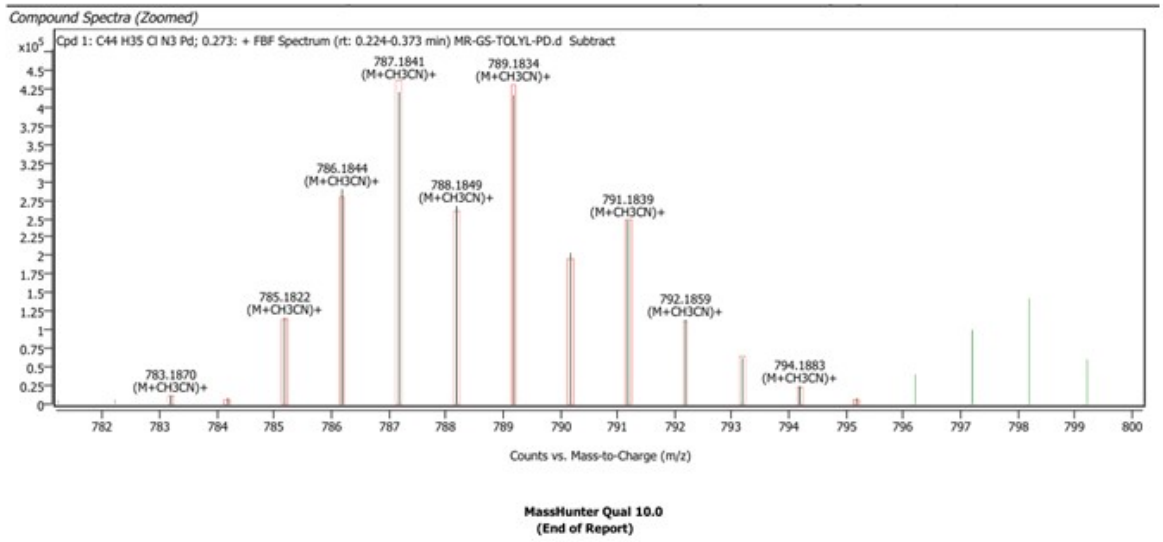


Figure S7. HR mass spectrum of the compound **1b.Pd(II)**

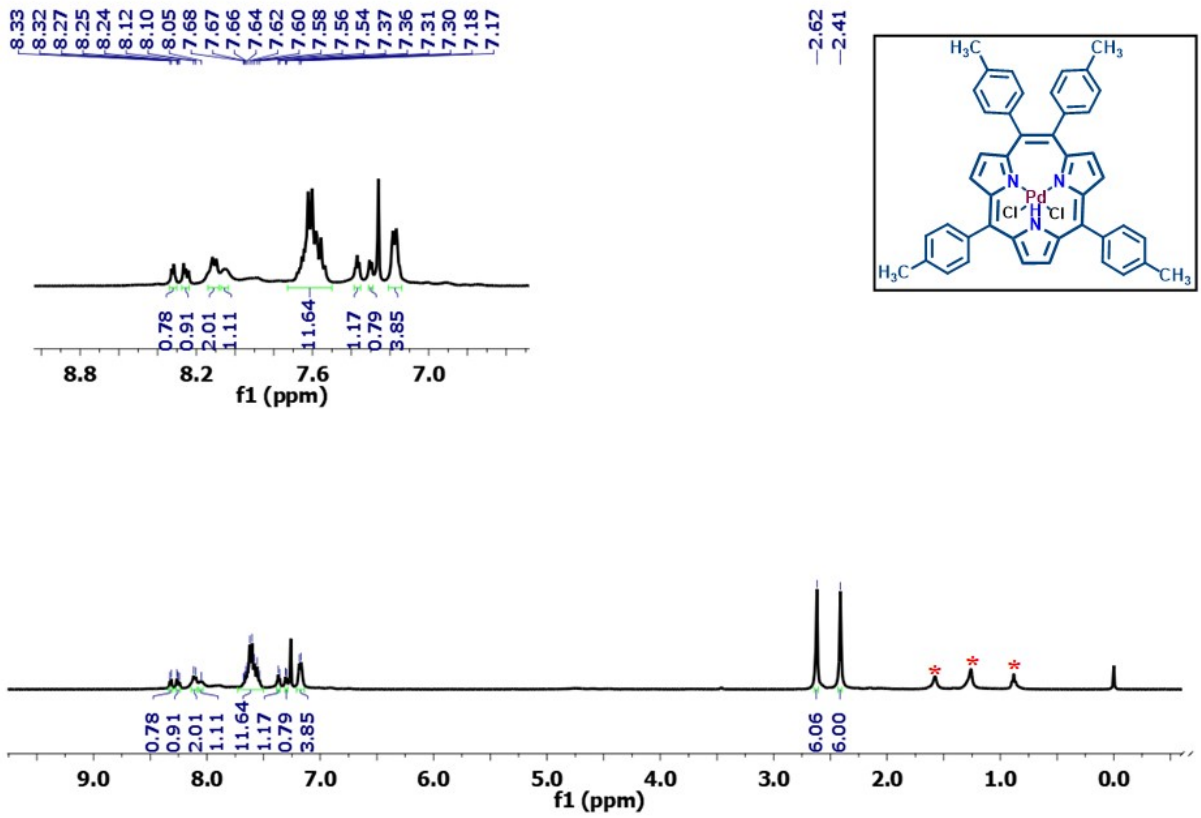


Figure S8. ^{1}H NMR spectrum of the compound **1b.Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

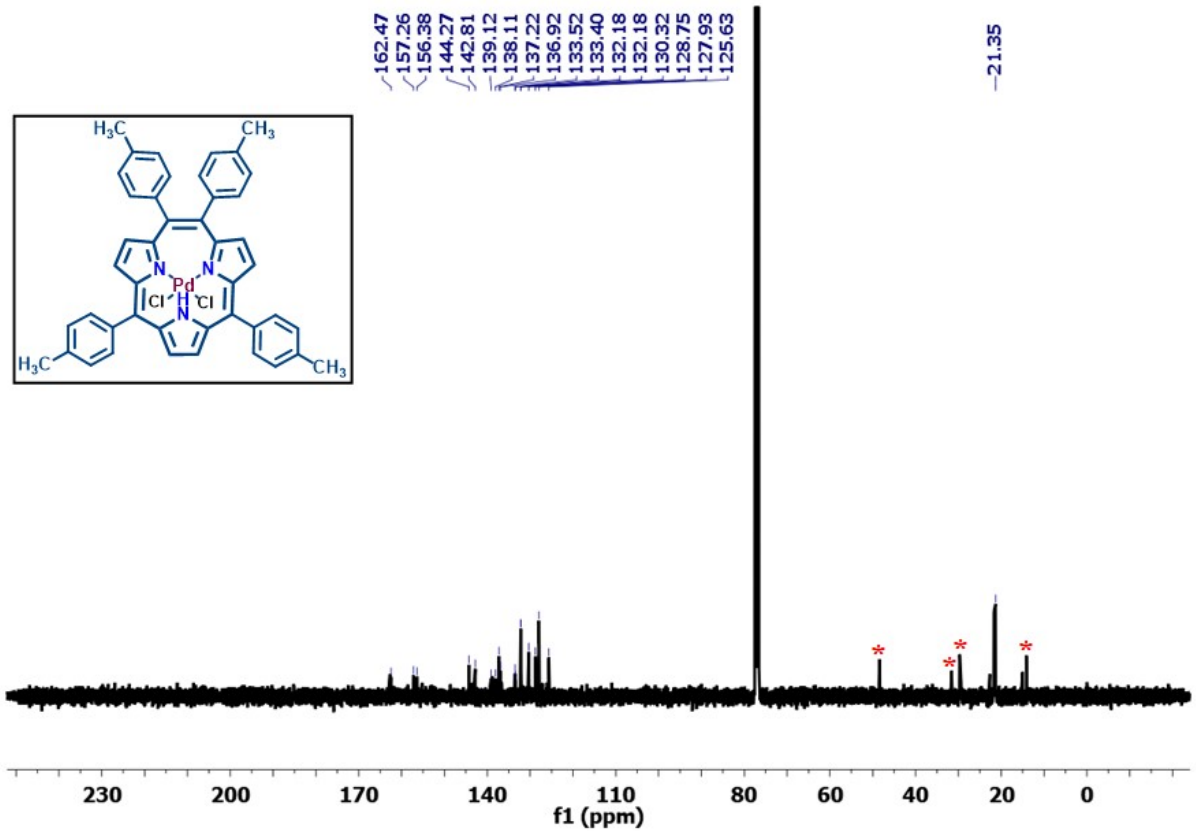
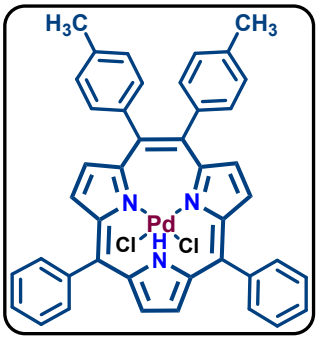


Figure S9. $^{13}C\{1H\}$ NMR spectrum of the compound **1b.Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents

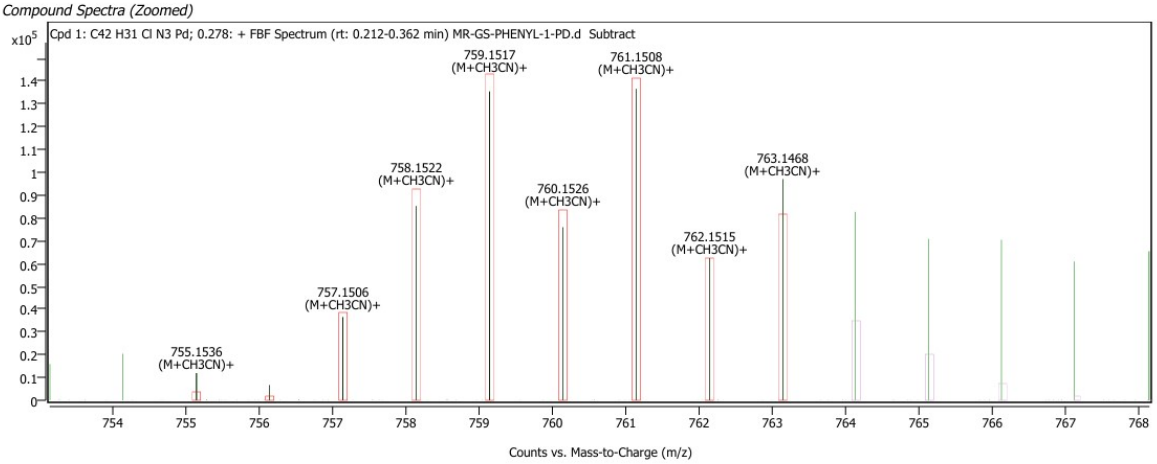


Compound Details

Cpd. 1: C42 H31 Cl N3 Pd

Formula	m/z	Observed M/Z	Difference Da	Difference PPM	Score
C42 H31 Cl N3 Pd	761.1508	761.150793151296	-0.678555769013656	-0.950190196309325	80.42

Compound Spectra (Zoomed)



MassHunter Qual 10.0
(End of Report)

Figure S10. HR mass spectrum of the compound **1a.Pd(II)**

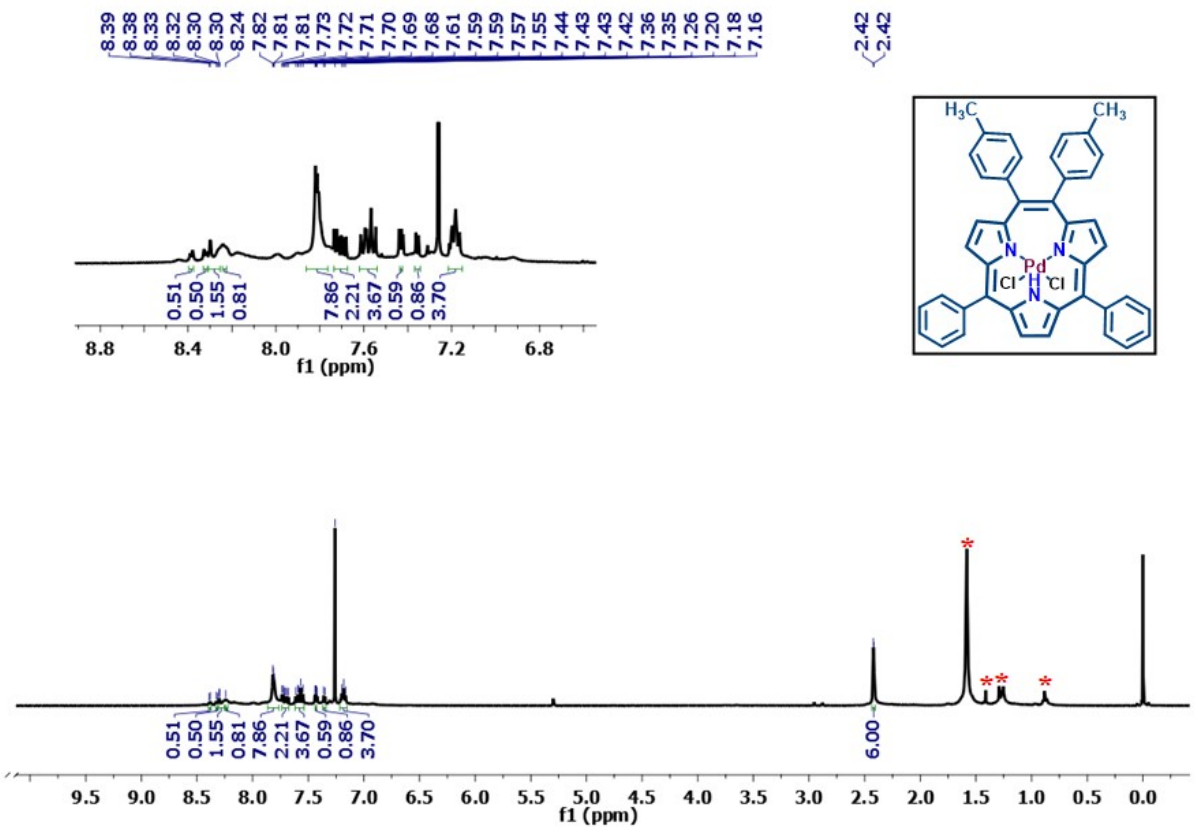


Figure S11. ^{1}H NMR spectrum of the compound **1a.Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

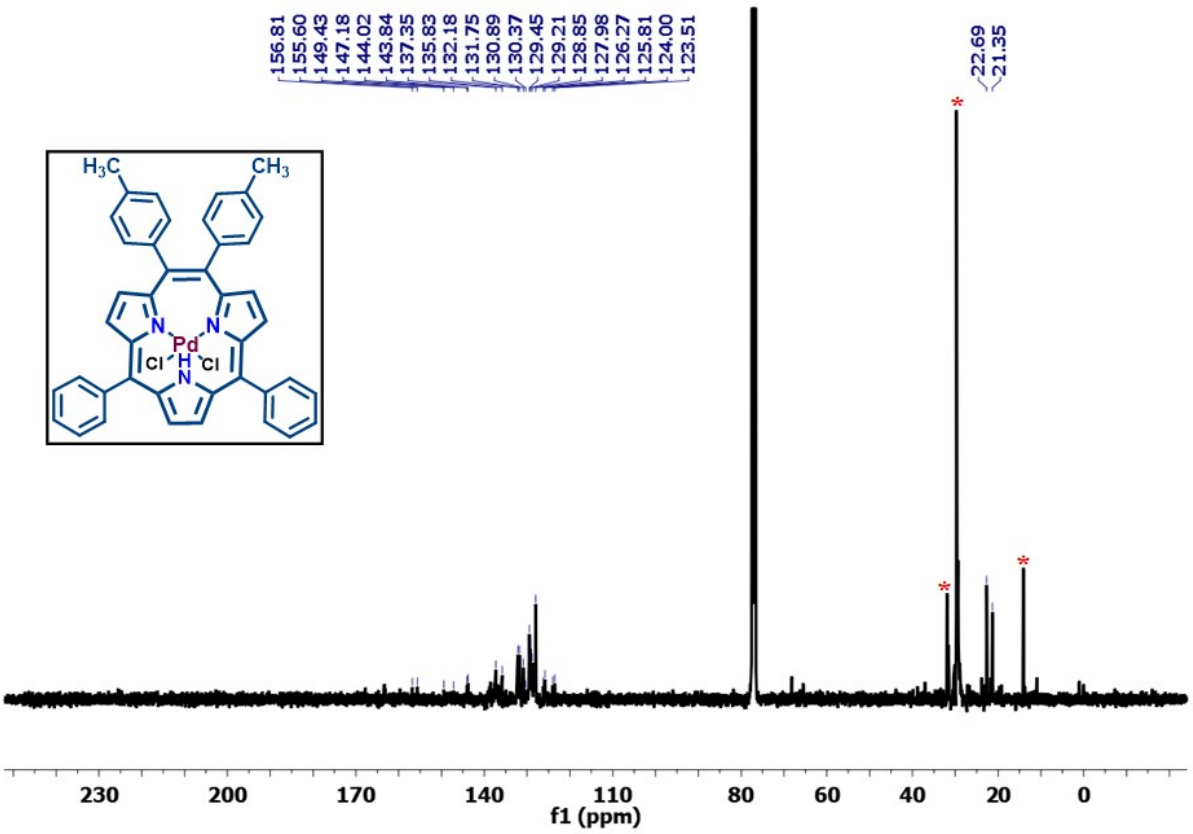


Figure S12. $^{13}C\{1H\}$ NMR spectrum of the compound **1a.Pd(II)** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

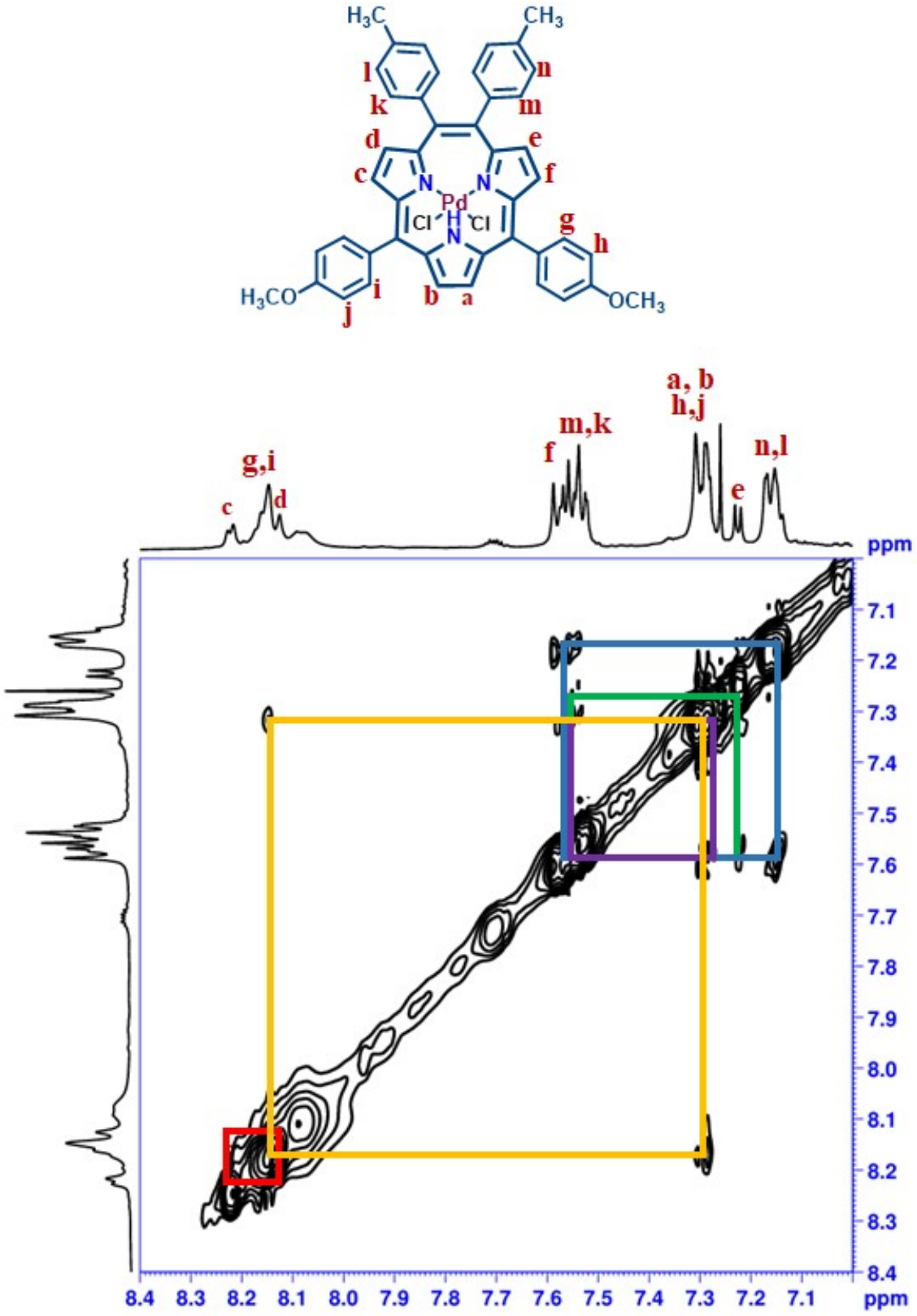


Figure S13. Partial ^{1}H-^{1}H COSY spectrum of compound **1c.Pd(II)** recorded in $CDCl_3$ at room temperature on 400 MHz instrument.

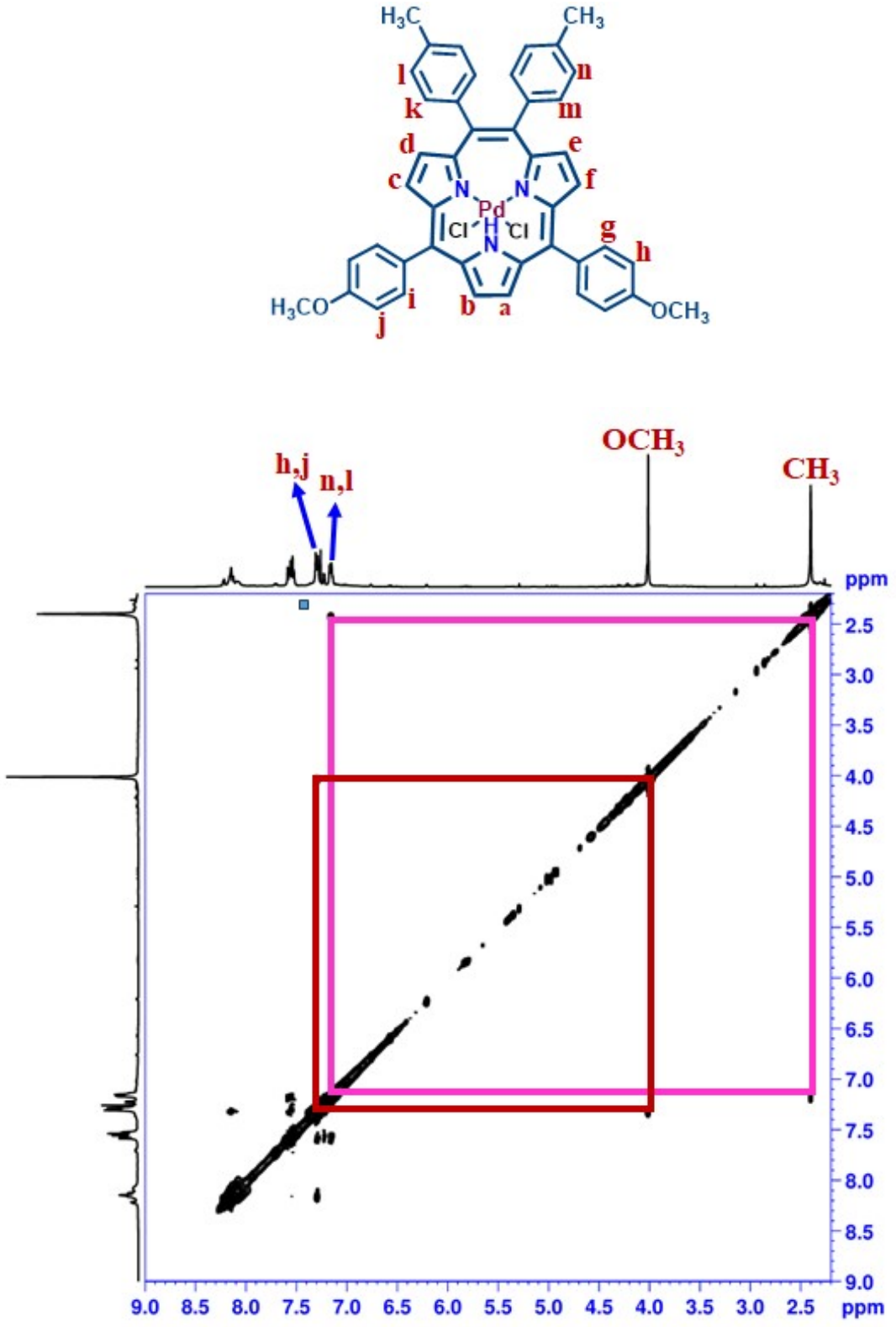


Figure S14. ^{1}H-^{1}H NOESY spectrum of compound **1c.Pd(II)** recorded in $CDCl_3$ at room temperature on 400 MHz instrument.

Table S1. Crystal data and data collection parameters for compound **1b.Pd(II).**

Empirical formula	$C_{44}H_{35}Cl_2N_3Pd$
Formula weight	783.109
Temperature/K	150.15
Crystal system	monoclinic
Space group	$P2_1/m$
a/Å	8.6766(4)
b/Å	25.1706(8)
c/Å	9.7595(3)
α/°	90
β/°	91.352(3)
γ/°	90
Volume/Å^3	2130.83(14)
Z	2
ρ_{calc}g/cm^3	1.221
μ/mm^{-1}	0.592
F(000)	799.0
Crystal size/mm^3	0.1 × 0.05 × 0.01
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.18 to 50
Index ranges	$-9 \leq h \leq 12$, $-35 \leq k \leq 36$, $-13 \leq l \leq 13$
Reflections collected	43347
Independent reflections	3850 [R_{int} = 0.1273, R_{sigma} = 0.0939]
Data/restraints/parameters	3850/0/231
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0806, wR_2 = 0.2030
Final R indexes [all data]	R_1 = 0.0905, wR_2 = 0.2120
Largest diff. peak/hole / e Å^{-3}	2.43/-1.10

Table S2. Selected bond lengths for compound **1b.Pd(II).**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd00	Cl1[1]	2.299(2)	C00A	C00F	1.348(9)
Pd00	Cl1	2.299(2)	C00B	C00B[1]	1.365(12)
Pd00	N005[1]	2.027(5)	C00C	C00C[1]	1.383(12)
Pd00	N005	2.027(5)	C00D	C00F	1.452(8)
N003	C007[1]	1.368(7)	C00E	C00H	1.390(9)
N003	C007	1.368(7)	C00E	C00I	1.391(9)
N005	C006	1.343(7)	C00G	C00M	1.373(9)
N005	C00D	1.374(7)	C00G	C00N	1.371(9)
C006	C00A	1.440(9)	C00G	C00Q	1.514(9)
C006	C00C	1.453(8)	C00H	C00O	1.387(10)
C007	C009	1.433(8)	C00I	C00K	1.391(9)
C007	C00B	1.395(8)	C00J	C00M	1.381(9)
C008	C00C	1.482(8)	C00K	C00L	1.386(11)
C008	C00J	1.374(9)	C00L	C00O	1.392(11)
C008	C00R	1.404(9)	C00L	C00S	1.502(10)
C009	C00D	1.386(8)	C00N	C00R	1.366(9)
C009	C00E	1.463(8)			

Table S3. Selected bond angles for compound **1b.Pd(II)**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1[1]	Pd00	Cl1	94.39(12)	C008	C00C	C006	112.8(5)
N005	Pd00	Cl1	175.30(14)	C00C[1]	C00C	C006	128.5(3)
N005[1]	Pd00	Cl1	89.83(14)	C00C[1]	C00C	C008	118.5(3)
N005[1]	Pd00	Cl1[1]	175.30(14)	C009	C00D	N005	123.7(5)
N005	Pd00	Cl1[1]	89.83(14)	C00F	C00D	N005	106.7(5)
N005	Pd00	N005[1]	85.9(2)	C00F	C00D	C009	129.3(5)
C007	N003	C007[1]	109.3(7)	C00H	C00E	C009	121.2(6)
C006	N005	Pd00[1]	119.4(4)	C00I	C00E	C009	120.4(6)
C00D	N005	Pd00[1]	128.6(4)	C00I	C00E	C00H	118.3(6)
C00D	N005	C006	109.6(5)	C00D	C00F	C00A	107.5(5)
C00A	C006	N005	108.2(5)	C00N	C00G	C00M	117.8(6)
C00C	C006	N005	127.1(6)	C00Q	C00G	C00M	120.3(6)
C00C	C006	C00A	124.8(5)	C00Q	C00G	C00N	121.9(6)
C009	C007	N003[1]	119.1(5)	C00O	C00H	C00E	120.2(7)
C00B	C007	N003[1]	107.1(5)	C00K	C00I	C00E	121.4(6)
C00B	C007	C009	133.0(6)	C00M	C00J	C008	120.6(6)
C00J	C008	C00C	120.4(5)	C00L	C00K	C00I	120.4(7)
C00R	C008	C00C	122.2(6)	C00O	C00L	C00K	118.1(6)
C00R	C008	C00J	117.2(6)	C00S	C00L	C00K	120.7(8)
C00D	C009	C007	118.6(5)	C00S	C00L	C00O	121.2(8)
C00E	C009	C007	118.8(5)	C00J	C00M	C00G	121.9(6)
C00E	C009	C00D	122.6(5)	C00R	C00N	C00G	121.3(6)
C00F	C00A	C006	107.7(5)	C00L	C00O	C00H	121.7(7)
C00B[1]	C00B	C007	108.1(4)	C00N	C00R	C008	121.2(6)

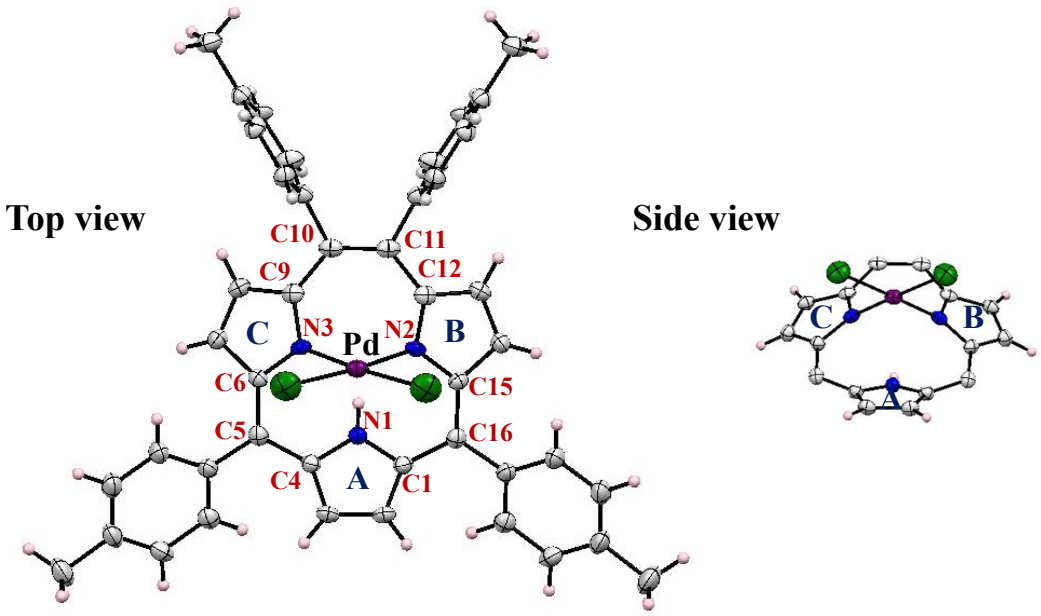


Figure S15. The ORTEP diagram of compound **1b.Pd(II)** at 50% probability level. (a) Top view; (b) Side view. The *meso*-aryl substituents in side view are omitted for clarity.

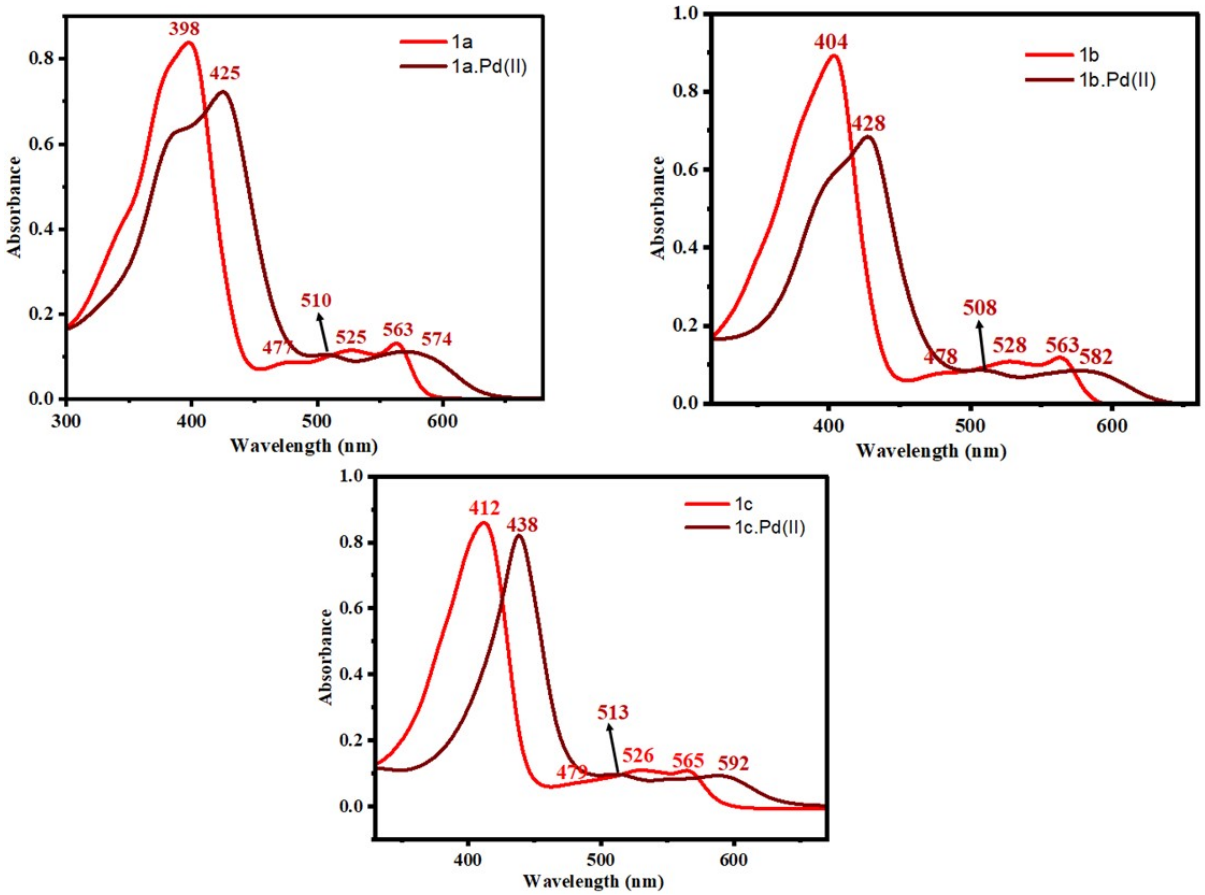


Figure S16. Absorption spectra of compounds **1a-c** and **1a.Pd(II)-1c.Pd(II)** (10^{-5} M) recorded in chloroform at rt.

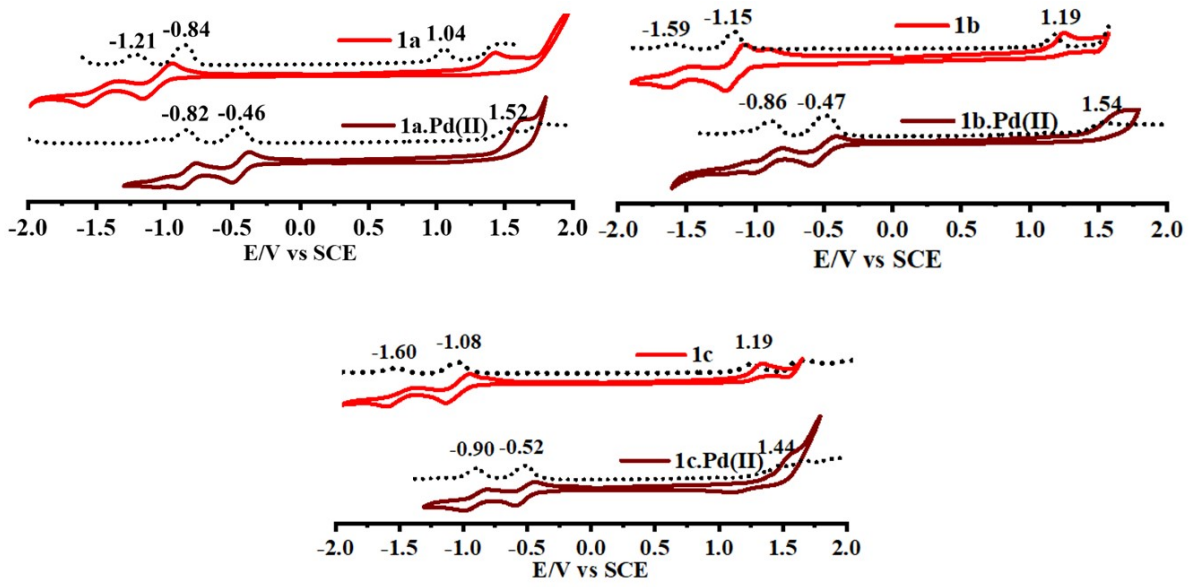


Figure S17. Comparison of cyclic voltammograms (red and brown coloured solid line) with their differential pulse voltammogram (dotted black line) of compounds **1a-c** and **1a.Pd(II)-1c.Pd(II)** recorded in dry CH_2Cl_2 with 0.1 M TBAP as the supporting electrolyte and a saturated calomel electrode (SCE) as the reference electrode at a scan rate of 50 mVs^{-1}. A saturated calomel electrode (SCE) was employed as the reference electrode, glassy carbon as the working electrode, and platinum wire as the auxiliary electrode. (Note that polarographic convention has been followed for plotting CV starting at 0 V). All the potentials were calibrated using ferrocene as an external standard, taking E1/2 (Fc/Fc+) = 0.42 V versus SCE.

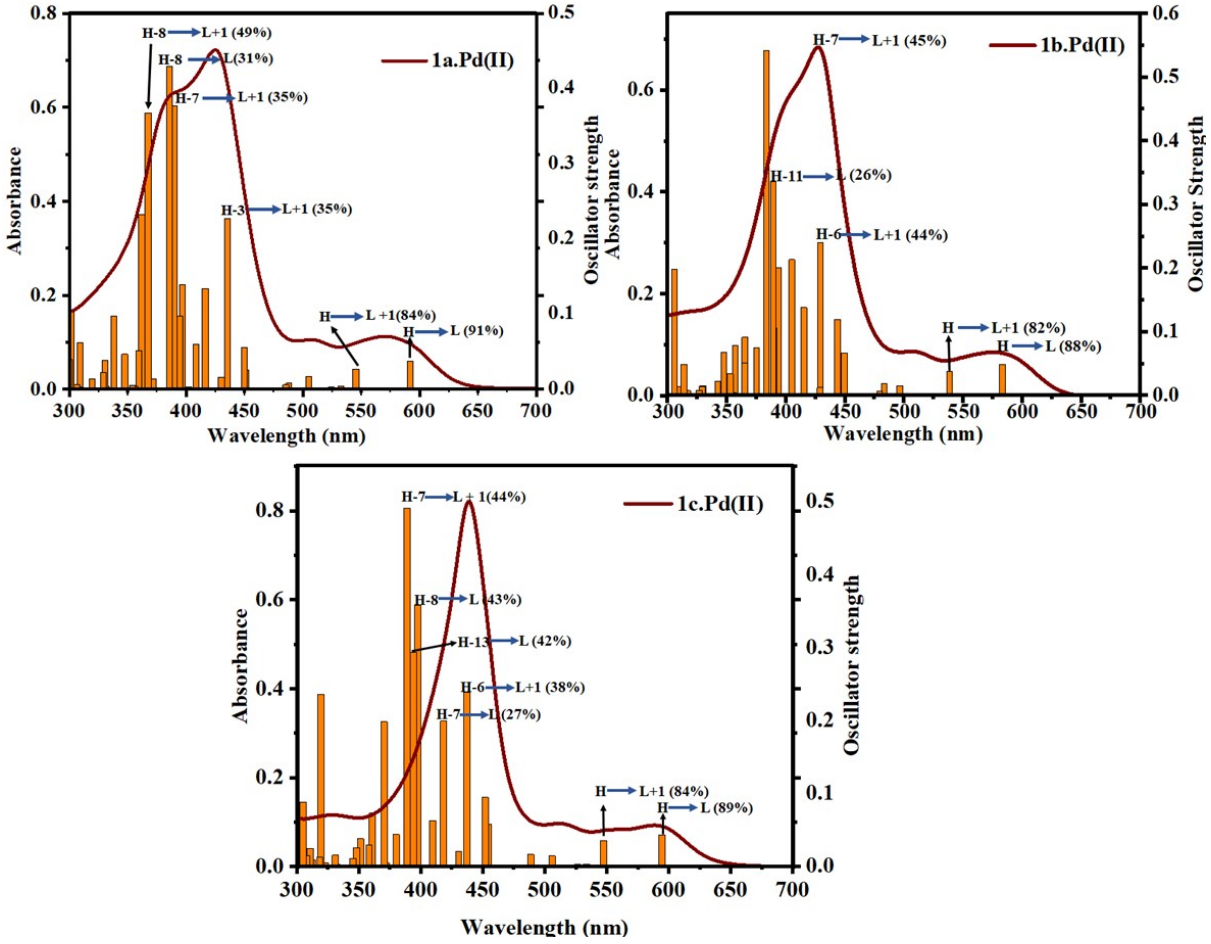


Figure S18. Calculated excitations (orange vertical lines) and experimental absorption spectrum (brown line) for compounds **1a.Pd(II)-1c.Pd(II)** .

Table S4. S_0 optimized geometry of dyad **1a.Pd(II)** at B3LYP/6-31G (d,p) and LANL2DZ level of theory.

Sum of imaginary frequencies= 0

Total Energy (Hartree) = -2830.220176

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Pd	1.262433	-0.61143	0	H	-2.36453	3.860797	-1.45
Cl	2.790045	-0.93789	1.686682	N	-0.17091	-0.22948	1.380607
N	-0.92112	-2.40379	0	C	-0.55941	1.038239	1.595816
H	-1.40034	-1.66605	0	C	-0.4905	-3.06714	1.115058
N	-0.17091	-0.22948	-1.38061	C	-0.35892	3.465797	1.399485
C	-0.55941	1.038239	-1.59582	C	-0.56024	-2.4101	2.38869
C	-0.4905	-3.06714	-1.11506	C	-1.16036	1.107155	2.90217
C	-0.35892	3.465797	-1.39949	H	-1.485	1.891173	3.329189
C	-0.56024	-2.4101	-2.38869	C	0.138877	-4.23456	0.682123
C	-1.16036	1.107155	-2.90217	H	0.503843	-4.9116	1.240206
H	-1.485	1.891173	-3.32919	C	-0.41137	2.164758	0.692192
C	0.138877	-4.23456	-0.68212	C	-0.5961	-1.02525	2.416378
H	0.503843	-4.9116	-1.24021	C	-0.62924	-3.22485	3.601913
C	-0.41137	2.164758	-0.69219	C	-1.17964	-0.14189	3.410616
C	-0.5961	-1.02525	-2.41638	H	-1.51426	-0.39644	4.262289
C	-0.62924	-3.22485	-3.60191	C	-0.24923	5.837921	2.892102
C	-1.17964	-0.14189	-3.41062	C	-0.02534	-2.81082	4.782414
H	-1.51426	-0.39644	-4.26229	H	0.407082	-1.96578	4.821705
C	-0.24923	5.837921	-2.8921	C	-1.23464	-4.47761	3.574225

C	-0.02534	-2.81082	-4.78241	H	-1.64642	-4.77803	2.77229
H	0.407082	-1.96578	-4.82171	C	0.844311	3.981959	1.817317
C	-1.23464	-4.47761	-3.57423	H	1.650649	3.523757	1.612278
H	-1.64642	-4.77803	-2.77229	C	-1.25018	-5.29768	4.696834
C	0.844311	3.981959	-1.81732	H	-1.6725	-6.14802	4.655252
H	1.650649	3.523757	-1.61228	C	-0.65313	-4.88299	5.877335
C	-1.25018	-5.29768	-4.69683	C	0.88998	5.160732	2.537196
H	-1.6725	-6.14802	-4.65525	H	1.735081	5.512613	2.792426
C	-0.65313	-4.88299	-5.87734	C	-1.45118	5.328313	2.476787
C	0.88998	5.160732	-2.5372	H	-2.25431	5.781189	2.707652
H	1.735081	5.512613	-2.79243	C	-0.05249	-3.62682	5.902506
C	-1.45118	5.328313	-2.47679	H	0.349362	-3.32173	6.707512
H	-2.25431	5.781189	-2.70765	C	-0.15748	7.12138	3.69001
C	-0.05249	-3.62682	-5.90251	H	0.069057	7.863018	3.089666
H	0.349362	-3.32173	-6.70751	H	-1.01978	7.301608	4.11937
C	-0.15748	7.12138	-3.69001	H	0.536859	7.031938	4.374776
H	0.069057	7.863018	-3.08967	C	-1.51832	4.181008	1.739288
H	-1.01978	7.301608	-4.11937	H	-2.36453	3.860797	1.450003
H	0.536859	7.031938	-4.37478	Cl	2.790045	-0.93789	-1.68668
C	-1.51832	4.181008	-1.73929	H	-0.65381	-5.51014	6.744276
H	-0.65381	-5.51014	-6.74428				

Table S5 . S_0 optimized geometry of dyad **1b.Pd(II)** at B3LYP/6-31G (d,p) and LANL2DZ level of theory.

Sum of imaginary frequencies= 0

Total Energy (Hartree) = -2908.800054

Atom	X	Y	Z	Atom	X	Y	Z
Pd	-1.29151	-0.36072	0	H	0.578792	-5.01057	7.895967
Cl	-2.82285	-0.66924	-1.68668	H	1.299372	-6.16635	7.055697
N	0.870873	-2.17856	0	N	0.146207	0.004406	-1.38061
H	1.358717	-1.44649	0	C	0.549552	1.26748	-1.59582
N	0.146207	0.004406	1.380607	C	0.43251	-2.83681	-1.11506
C	0.549552	1.26748	1.595816	C	0.377536	3.697221	-1.39949
C	0.43251	-2.83681	1.115058	C	0.50995	-2.18064	-2.38869
C	0.377536	3.697221	1.399485	C	1.151266	1.329345	-2.90217
C	0.50995	-2.18064	2.38869	H	1.485072	2.109503	-3.32919
C	1.151266	1.329345	2.90217	C	-0.21051	-3.99677	-0.68212
H	1.485072	2.109503	3.329189	H	-0.58339	-4.66948	-1.24021
C	-0.21051	-3.99677	0.682123	C	0.41473	2.395657	-0.69219
H	-0.58339	-4.66948	1.240206	C	0.562042	-0.7963	-2.41638
C	0.41473	2.395657	0.692192	C	0.56939	-2.99614	-3.60191
C	0.562042	-0.7963	2.416378	C	1.155895	0.080165	-3.41062
C	0.56939	-2.99614	3.601913	H	1.487515	-0.1783	-4.26229
C	1.155895	0.080165	3.410616	C	0.295664	6.070468	-2.8921
H	1.487515	-0.1783	4.262289	C	-0.02961	-2.57505	-4.78241
C	0.295664	6.070468	2.892102	H	-0.4521	-1.725	-4.82171
C	-0.02961	-2.57505	4.782414	C	1.160059	-4.25591	-3.57423

H	-0.4521	-1.725	4.821705	H	1.568287	-4.56114	-2.77229
C	1.160059	-4.25591	3.574225	C	-0.81956	4.227456	-1.81732
H	1.568287	-4.56114	2.77229	H	-1.63122	3.778739	-1.61228
C	-0.81956	4.227456	1.817317	C	1.165985	-5.0761	-4.69683
H	-1.63122	3.778739	1.612278	H	1.578308	-5.93133	-4.65525
C	1.165985	-5.0761	4.696834	C	0.573839	-4.65444	-5.87734
H	1.578308	-5.93133	4.655252	C	-0.85141	5.406683	-2.5372
C	0.573839	-4.65444	5.877335	H	-1.69232	5.768448	-2.79243
C	-0.85141	5.406683	2.537196	C	1.491554	5.546803	-2.47679
H	-1.69232	5.768448	2.792426	H	2.299945	5.990231	-2.70765
C	1.491554	5.546803	2.476787	C	-0.01204	-3.39131	-5.90251
H	2.299945	5.990231	2.707652	H	-0.41028	-3.08154	-6.70751
C	-0.01204	-3.39131	5.902506	C	0.218966	7.354915	-3.69001
H	-0.41028	-3.08154	6.707512	H	0.001143	8.099158	-3.08967
C	0.218966	7.354915	3.69001	H	1.083325	7.52502	-4.11937
H	0.001143	8.099158	3.089666	H	-0.47637	7.27362	-4.37478
H	1.083325	7.52502	4.11937	C	1.545237	4.39879	-1.73929
H	-0.47637	7.27362	4.374776	H	2.387641	4.068679	-1.45
C	1.545237	4.39879	1.739288	C	0.535026	-5.55371	-7.08049
H	2.387641	4.068679	1.450003	H	-0.29789	-6.06961	-7.07687
C	0.535026	-5.55371	7.08049	H	0.578792	-5.01057	-7.89597
H	-0.29789	-6.06961	7.076865	H	1.299372	-6.16635	-7.0557
Cl	-2.82285	-0.66924	1.686682				

Table S6. S_0 optimized geometry of dyad **1c.Pd(II)** at B3LYP/6-31G (d,p) and LANL2DZ level of theory.

Sum of imaginary frequencies= 0

Total Energy (Hartree) = -3059.253070

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
Pd	-0.10078	-0.00042	1.38118	C	3.895825	1.39279	-0.43466
Cl	-0.35067	1.686689	2.922698	C	-1.9814	2.391159	-0.35283
N	-1.9962	0.00248	-0.71353	C	1.503674	2.899189	-1.12163
H	-1.28239	0.001355	-1.22773	H	2.271816	3.325002	-1.48365
N	0.209563	-1.38155	-0.06885	C	-3.77274	0.687401	0.433371
C	1.456765	-1.59872	-0.51795	H	-4.43055	1.24652	0.830501
C	-2.63978	-1.11157	-0.25145	C	2.59267	0.687528	-0.42438
C	3.891463	-1.40618	-0.43459	C	-0.59985	2.416691	-0.45533
C	-1.98885	-2.38622	-0.35271	C	-2.79664	3.605653	-0.38255
C	1.494627	-2.90514	-1.12149	C	0.255949	3.409581	-1.08075
H	2.261438	-3.33337	-1.48349	H	-0.0131	4.261666	-1.40275
C	-3.77486	-0.67684	0.433405	C	6.272803	2.881704	-0.43935
H	-4.43441	-1.23389	0.830562	C	-2.35216	4.785477	0.200683
C	2.590512	-0.69686	-0.42435	H	-1.48723	4.82343	0.591917
C	-0.60738	-2.41606	-0.45521	C	-4.07713	3.579947	-0.92692
C	-2.80787	-3.59816	-0.38237	H	-4.39829	2.778502	-1.32374
C	0.245317	-3.41164	-1.08058	C	4.469978	1.809757	0.742318
H	-0.02638	-4.2629	-1.40254	H	4.050815	1.605392	1.569789
C	6.263788	-2.90249	-0.43921	C	-4.89525	4.703833	-0.90298
C	-2.36707	-4.77934	0.200919	H	-5.765	4.663598	-1.28387

H	-1.50226	-4.81997	0.592155	C	-4.45046	5.883657	-0.32663
C	-4.08828	-3.56849	-0.92674	C	5.650703	2.527796	0.731156
H	-4.40693	-2.76607	-1.3236	H	6.043266	2.782435	1.558326
C	4.464313	-1.82487	0.742407	C	5.705264	2.467244	-1.61535
H	4.045789	-1.61916	1.569868	H	6.119301	2.697444	-2.43937
C	-4.90989	-4.68982	-0.90275	C	-3.16678	5.90684	0.212836
H	-5.77951	-4.6469	-1.28364	H	-2.84144	6.71135	0.599509
C	-4.46878	-5.871	-0.32633	C	7.560434	3.677607	-0.40952
C	5.642794	-2.54659	0.731281	H	8.311183	3.076097	-0.21895
H	6.034562	-2.80241	1.558464	H	7.6996	4.106729	-1.27952
C	5.697543	-2.48632	-1.61523	H	7.505597	4.362477	0.288297
H	6.110861	-2.71785	-2.43924	C	4.554909	1.731537	-1.62715
C	-3.18518	-5.89816	0.213128	H	4.193872	1.442794	-2.45696
H	-2.86235	-6.70366	0.59984	Cl	-0.35593	-1.68667	2.922781
C	7.548932	-3.7024	-0.40934	O	-5.3078	-7.02831	-0.28685
H	8.301552	-3.10323	-0.2188	O	-5.28587	7.043584	-0.2872
H	7.686759	-4.132	-1.27931	C	-5.45799	-7.55432	-1.60808
H	7.49196	-4.38707	0.288513	H	-5.93868	-8.50903	-1.55938
C	4.549488	-1.74704	-1.62707	H	-6.05326	-6.88471	-2.19303
H	4.189352	-1.45721	-2.45689	H	-4.4944	-7.66283	-2.06045
N	0.213867	1.37966	-0.06892	C	-5.3978	7.596124	-1.60138
C	1.461739	1.592913	-0.51803	H	-5.96545	6.932824	-2.22001
C	-2.6363	1.118548	-0.2515	H	-5.89077	8.544342	-1.54882
H	-4.42093	7.724646	-2.01864				

Table S7. Selected TD-DFT calculated oscillator strengths and compositions of the major electronic transitions of **1a.Pd(II)**.

Wavelength (nm)	Oscillator Strength	Major contribution
592.120889308	0.0365	HOMO->LUMO (91%)
585.493922423	0.0002	H-1->LUMO (98%)
570.409426814	0.0005	H-2->LUMO (96%)
545.48899209	0.0255	HOMO->L+1 (84%)
538.616764465	0.0002	H-1->L+1 (89%)
532.898620357	0.0027	H-2->L+1 (89%)
524.600968995	0.0021	H-4->LUMO (88%)
505.088984447	0.0163	H-4->L+1 (12%), H-3->LUMO (68%)
488.030675112	0.0067	H-4->L+1 (83%)
485.43202307	0.0045	H-6->LUMO (49%), H-3->L+1 (46%)
483.991853114	0.001	H-5->LUMO (87%)
451.015616632	0.0244	H-7->LUMO (46%), H-6->L+1 (42%)
449.674281925	0.0541	H-7->L+1 (11%), H-6->LUMO (15%), H-5->L+1 (66%)
435.536561676	0.2253	H-7->L+1 (15%), H-6->LUMO (15%), H-5->L+1 (29%), H-3->L+1 (35%)
430.38111987	0.0147	H-2->L+2 (14%), HOMO->L+2 (60%)
416.529574052	0.1327	H-7->LUMO (17%), H-6->L+1 (20%), H-2->L+2 (34%), HOMO->L+2 (12%)
408.51463925	0.0587	H-8->LUMO (42%), H-7->LUMO (13%), H-2->L+2 (32%)
406.46557064	0.0001	H-1->L+2 (88%)
402.337074936	0.0015	H-9->LUMO (88%)
396.724027301	0.1379	H-13->LUMO (16%), H-11->LUMO (51%), H-8->LUMO (17%)
394.414483894	0.0962	H-12->LUMO (36%), H-10->LUMO (22%), H-7->L+1 (25%)
389.495454298	0.3757	H-11->LUMO (25%), H-8->LUMO (31%), H-6->L+1 (15%)
385.64290206	0.4281	H-10->LUMO (26%), H-8->L+1 (20%), H-7->L+1 (35%)
382.939101869	0.0013	H-4->L+2 (86%)
374.088625086	0.0002	H-9->L+1 (97%)

371.655254833	0.0124	H-12->LUMO (30%), H-10->LUMO (42%), H-8->L+1 (26%)
367.502128263	0.366	H-12->LUMO (22%), H-8->L+1 (49%)
361.902545352	0.2305	H-13->LUMO (71%), H-11->LUMO (19%)
359.73942554	0.0496	H-12->L+1 (36%), H-10->L+1 (51%)
357.725823054	0.001	H-14->LUMO (76%), H-11->L+1 (14%)
355.591800305	0.0032	H-15->LUMO (86%), H-14->L+1 (11%)
354.068575298	0.0039	H-14->LUMO (14%), H-13->L+1 (10%), H-11->L+1 (67%)
347.479591413	0.0452	H-12->L+1 (56%), H-10->L+1 (42%)
337.951298859	0.0958	H-13->L+1 (81%), H-11->L+1 (13%)
331.712531804	0.0011	H-16->LUMO (72%), H-15->L+1 (13%)
331.650419998	0.0026	H-15->LUMO (10%), H-14->L+1 (86%)
330.562809641	0.0376	H-5->L+2 (42%), H-3->L+2 (38%)
329.272303108	0.0207	H-16->LUMO (19%), H-15->L+1 (69%)
319.703445017	0.0128	H-16->L+1 (94%)
309.241496052	0.0607	H-6->L+2 (78%), HOMO->L+2 (15%)
308.641042076	0.0021	H-7->L+2 (26%), H-5->L+2 (27%), H-3->L+2 (42%)
306.277495645	0.005	H-18->LUMO (94%)
301.672043145	0.1017	H-19->LUMO (22%), H-17->LUMO (71%)
300.232935423	0.0382	H-19->LUMO (76%), H-17->LUMO (19%)
295.397391147	0.0012	H-20->LUMO (97%)
292.222572387	0.0018	H-18->L+1 (92%)
288.926624283	0.0029	H-19->L+1 (24%), H-17->L+1 (63%)
285.994171001	0.0149	H-19->L+1 (70%), H-17->L+1 (16%)
281.942451421	0.0024	H-7->L+2 (65%), H-5->L+2 (23%)
281.41130558	0.0067	H-20->L+1 (95%)

Table S8. Selected TD-DFT calculated oscillator strengths and compositions of the major electronic transitions of **1b.Pd(II)**.

Wavelength (nm)	Oscillator Strength	Major contribution
583.537407692	0.0482	HOMO->LUMO (88%)
573.576022447	0.0001	H-1->LUMO (97%)
560.735348977	0.0004	H-2->LUMO (96%)
538.780605824	0.0382	HOMO->L+1 (82%)
528.086689719	0.0003	H-1->L+1 (88%)
524.467821541	0.0025	H-2->L+1 (88%)
514.970065676	0.0027	H-4->LUMO (86%)
496.771347913	0.0149	H-4->L+1 (13%), H-3->LUMO (67%)
483.425714556	0.0189	H-5->LUMO (58%), H-3->L+1 (36%)
479.6479284	0.0068	H-4->L+1 (81%)
475.05342355	0.0	H-6->LUMO (86%)
449.788474559	0.0666	H-7->LUMO (34%), H-5->L+1 (45%)
443.783352467	0.1192	H-7->L+1 (13%), H-6->L+1 (52%), H-5->LUMO (15%), H-3->L+1 (17%)
429.382486622	0.2405	H-6->L+1 (44%), H-3->L+1 (33%)
429.011048485	0.0118	H-5->L+2 (11%), H-2->L+2 (17%), HOMO->L+2 (53%)
415.496625376	0.1377	H-7->LUMO (19%), H-5->L+1 (16%), H-2->L+2 (38%), HOMO->L+2 (13%)
405.30955545	0.2129	H-8->LUMO (21%), H-7->LUMO (27%), H-2->L+2 (30%)
405.203585242	0.0001	H-1->L+2 (89%)
395.660559779	0.0002	H-11->LUMO (13%), H-9->LUMO (75%)
393.650600115	0.2005	H-13->LUMO (42%), H-8->LUMO (45%)
389.58112494	0.1061	H-12->LUMO (22%), H-11->LUMO (26%), H-9->LUMO (21%), H-7->L+1 (23%)
389.434284048	0.3354	H-13->LUMO (33%), H-10->LUMO (24%), H-8->LUMO (26%)
383.780700217	0.5419	H-11->LUMO (22%), H-7->L+1 (45%)
382.007003365	0.0006	H-4->L+2 (86%)
375.334341453	0.0747	H-13->LUMO (17%), H-10->LUMO (71%)
367.87286892	0.0	H-9->L+1 (96%)
365.551767586	0.0911	H-12->LUMO (41%), H-11->LUMO (16%), H-8->L+1 (33%)

365.32557314	0.0511	H-12->LUMO (20%), H-11->LUMO (22%), H-8->L+1 (52%)
357.385544253	0.0778	H-12->L+1 (34%), H-11->L+1 (59%)
356.030878165	0.0044	H-14->LUMO (67%), H-13->L+1 (13%), H-10->L+1 (12%)
353.836167272	0.0	H-15->LUMO (85%), H-14->L+1 (12%)
353.010059257	0.0335	H-14->LUMO (22%), H-13->L+1 (18%), H-10->L+1 (51%)
347.742730163	0.0673	H-13->L+1 (63%), H-10->L+1 (33%)
342.478849269	0.0219	H-12->L+1 (63%), H-11->L+1 (36%)
329.903126529	0.0151	H-16->LUMO (21%), H-6->L+2 (29%), H-3->L+2 (33%)
329.429782687	0.0143	H-16->LUMO (42%), H-15->L+1 (20%), H-6->L+2 (14%), H-3->L+2 (14%)
329.281048023	0.0012	H-15->LUMO (11%), H-14->L+1 (86%)
326.867715094	0.0076	H-16->LUMO (24%), H-15->L+1 (62%)
317.05457873	0.0073	H-17->L+1 (13%), H-16->L+1 (82%)
313.995322424	0.0485	H-5->L+2 (71%), HOMO->L+2 (22%)
309.210646712	0.0136	H-17->LUMO (14%), H-7->L+2 (22%), H-6->L+2 (26%), H-3->L+2 (32%)
305.89211737	0.1976	H-17->LUMO (65%)
304.891658705	0.0034	H-18->LUMO (96%)
297.46687383	0.0015	H-19->LUMO (96%)
293.335682713	0.0219	H-20->LUMO (31%), H-17->L+1 (53%)
292.133062398	0.0037	H-20->LUMO (67%), H-17->L+1 (23%)
291.06320401	0.0043	H-18->L+1 (91%)
283.690721701	0.0108	H-19->L+1 (91%)
280.716808957	0.0023	H-7->L+2 (67%), H-6->L+2 (23%)
278.7602424	0.0073	H-20->L+1 (96%)

Table S9. Selected TD-DFT calculated oscillator strengths and compositions of the major electronic transitions of **1c.Pd(II).**

Wavelength (nm)	Oscillator Strength	Major contribution
594.648407732	0.0426	HOMO->LUMO (89%)
587.937182342	0.0002	H-1->LUMO (98%)
572.199524701	0.0006	H-2->LUMO (96%)
547.294928102	0.0349	HOMO->L+1 (84%)
539.953806342	0.0002	H-1->L+1 (88%)
533.678516754	0.0025	H-2->L+1 (88%)
526.449802608	0.0021	H-4->LUMO (86%), H-1->L+1 (10%)
505.851460678	0.0142	H-4->L+1 (12%), H-3->LUMO (67%)
489.031645218	0.0061	H-4->L+1 (83%)
488.607657191	0.0159	H-5->LUMO (54%), H-3->L+1 (39%)
484.976307499	0.0004	H-6->LUMO (84%)
454.204465737	0.0575	H-7->LUMO (37%), H-5->L+1 (47%)
451.90331321	0.0941	H-7->L+1 (11%), H-6->L+1 (57%), H-5->LUMO (16%), H-3->L+1 (13%)
437.04111182	0.2384	H-7->L+1 (10%), H-6->L+1 (38%), H-5->LUMO (10%), H-3->L+1 (36%)
430.545518673	0.0198	H-2->L+2 (16%), HOMO->L+2 (56%)
418.187375244	0.1989	H-7->LUMO (27%), H-5->L+1 (20%), H-2->L+2 (22%), HOMO->L+2 (12%)
409.418462544	0.062	H-8->LUMO (29%), H-7->LUMO (13%), H-2->L+2 (42%)
406.839025471	0.0002	H-1->L+2 (88%)
402.441550936	0.0017	H-9->LUMO (88%)
397.46166895	0.3583	H-13->LUMO (35%), H-8->LUMO (43%)
394.289053943	0.0942	H-12->LUMO (34%), H-11->LUMO (24%), H-7->L+1 (25%)
394.163703743	0.293	H-13->LUMO (42%), H-10->LUMO (30%), H-8->LUMO (14%)
388.689551107	0.4915	H-11->LUMO (20%), H-8->L+1 (11%), H-7->L+1 (44%)
383.306105893	0.0007	H-4->L+2 (84%)
380.133042103	0.0432	H-13->LUMO (18%), H-10->LUMO (65%)
373.930672293	0.0002	H-9->L+1 (97%)
372.000939159	0.0044	H-12->LUMO (47%), H-11->LUMO (50%)

370.378470537	0.1981	H-8->L+1 (80%)
360.796743721	0.0726	H-12->L+1 (44%), H-11->L+1 (49%)
358.056409773	0.0291	H-13->L+1 (21%), H-10->L+1 (71%)
351.369361821	0.0373	H-13->L+1 (74%), H-10->L+1 (22%)
347.967199944	0.0251	H-12->L+1 (52%), H-11->L+1 (47%)
345.042698946	0.0108	H-14->LUMO (87%)
343.379934673	0.0008	H-15->LUMO (86%), H-14->L+1 (12%)
332.192463125	0.002	H-17->LUMO (68%), H-16->LUMO (28%)
330.977557427	0.0149	H-6->L+2 (46%), H-3->L+2 (45%)
323.01850562	0.0048	H-17->L+1 (34%), H-16->L+1 (13%), H-14->L+1 (44%)
319.489249394	0.2355	H-17->LUMO (28%), H-16->LUMO (54%)
318.43074022	0.0125	H-15->L+1 (81%), H-14->LUMO (10%)
317.883734616	0.0	H-17->L+1 (33%), H-16->L+1 (13%), H-14->L+1 (42%)
312.72812645	0.0082	H-20->LUMO (10%), H-18->LUMO (24%), H-17->L+1 (10%), H-5->L+2 (40%)
310.60498788	0.024	H-20->LUMO (22%), H-18->LUMO (32%), H-5->L+2 (31%)
307.851698397	0.0146	H-7->L+2 (24%), H-6->L+2 (27%), H-3->L+2 (43%)
305.011668214	0.088	H-20->LUMO (13%), H-17->L+1 (18%), H-16->L+1 (59%)
301.181054784	0.0012	H-21->LUMO (93%)
298.18945384	0.0013	H-20->L+1 (19%), H-19->LUMO (18%), H-18->L+1 (44%)
296.996581738	0.0081	H-22->LUMO (17%), H-20->LUMO (33%), H-18->LUMO (24%)
295.319993836	0.0014	H-22->LUMO (80%)
291.576579211	0.024	H-20->L+1 (25%), H-19->LUMO (62%)
286.814548469	0.0085	H-21->L+1 (93%)

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