Electronic Supplementary Information

Electronic Infrared Light Absorption of Tri-palladium Complex Containing Two π-Expanded Tetracene Ligands

Tsuyoshi Suzuki,[a] Takafumi Nakagawa,[a] Kei Ohkubo,[b] Shunichi Fukuzumi,[b] and Yutaka Matsuo*[a]

[a] *Department of Chemistry, School of Science, The University of Tokyo 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

[b] *Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA (JST), Suita, Osaka 565-0871, Japan*

E-mail: matsuo@chem.s.u-tokyo.ac.jp

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1. X-ray crystallographic studies

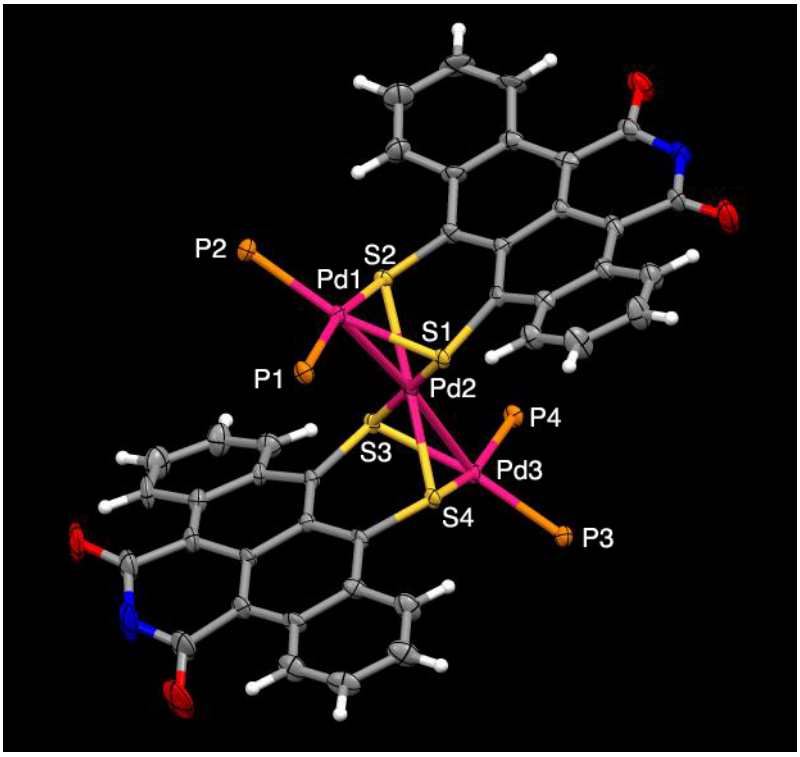


Figure S1. Closed view of complex **1** drawn with thermal ellipsoids with the 50% probability level. Hexyl chains at TIDS ligands, hydrogen atoms, and the phenyl groups at the phosphine ligands are omitted for clarity. Selected bond lengths [Å], angles [º], and torsion angles [º]: Pd1–P1 2.335(2), Pd1–P2 2.365(1), Pd1–S1 2.355(1), Pd1–S2 2.377(1), Pd1–Pd2 2.8818(5), Pd2–S1 2.315(1), Pd2–S2 2.336(1), Pd2–S3 2.353(1), Pd2–S4 2.351(1), Pd2–Pd3 2.9241(5), Pd3–P3 2.342(1), Pd3–P4 2.320(2), Pd3–S3 2.350(1), Pd3–S4 2.344(1), S1–S2 3.030(1), S3–S4 3.058(1), P1–Pd1–P2 100.59(5), P2–Pd1–S2 89.85(5), S2–Pd1–S1 79.64(4), S1–P1–P1 91.12 (5), Pd1–S1–Pd2 76.21(4), Pd1–S2–Pd2 75.38(4), S2–Pd2–S1 81.31(4), S1–Pd2–S4 96.95(4), S4–Pd2–S3 81.07(4), S3–Pd2–S2 100.53(4), Pd2–S3–Pd3 76.88(4), Pd2–S4–Pd3 77.03(4), P3–Pd3–P4 98.60(5), P4–Pd3–S3 92.27(5), S3–Pd3–S4 81.28(4), S4–Pd3–P3 88.96(5), Pd1–Pd2–Pd3 174.08(2), P2–P1–Pd1–S1 172.49(5), S1–S2–Pd2–S3 176.83(5), P4–Pd3–P3–S4 163.31(5). Space group $P\bar{1}$ for $C_{127}H_{108}Cl_6N_2O_4P_4Pd_3S_4$, F_W 2510.17, a = 17.4188(6), b = 17.5604(6), c = 22.7255(4) Å, α = 87.6505(10)º, β = 71.9113(12)º, γ = 60.5328(7)º, V = 5700.3(3) Å^3, Z = 2, R_1 (all data) = 0.0705, wR_2 (I > 2.0σ(I)) = 0.2286, unique reflections = 19978, parameters = 1327.

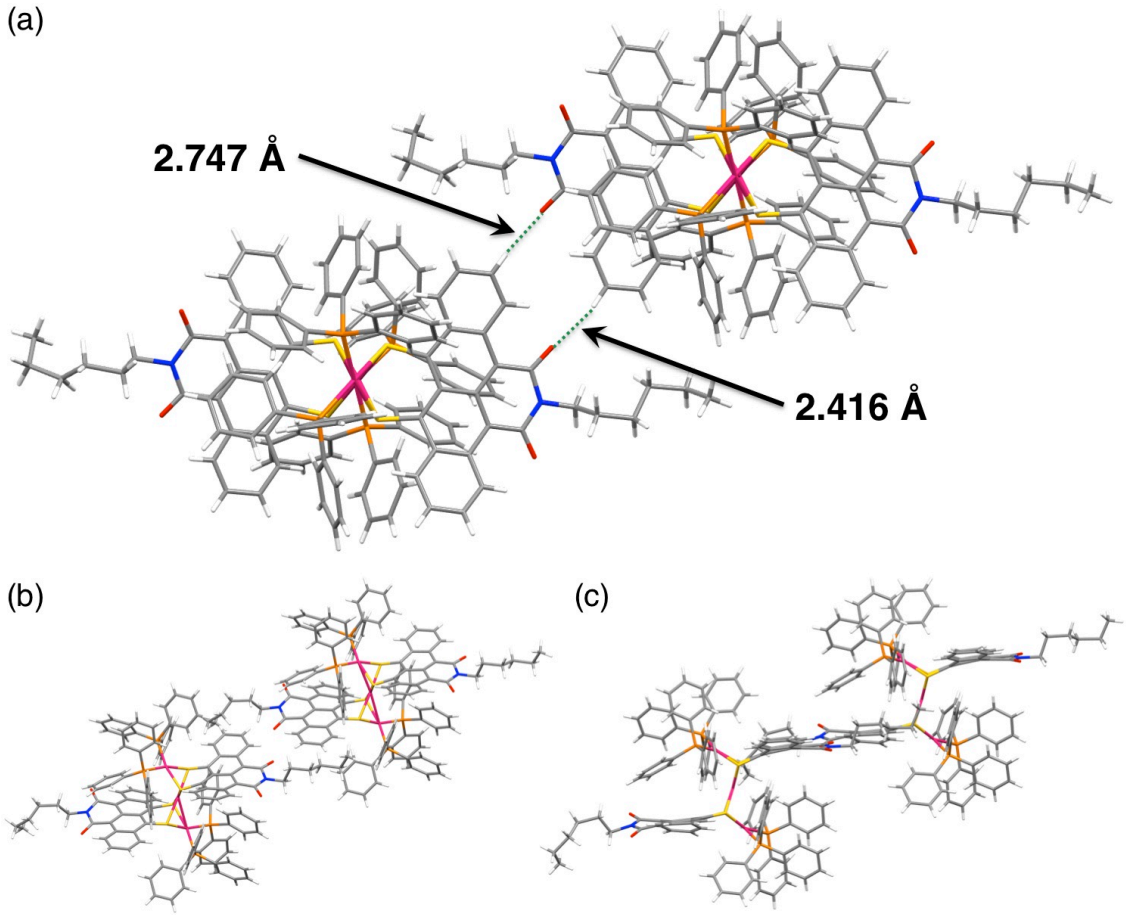
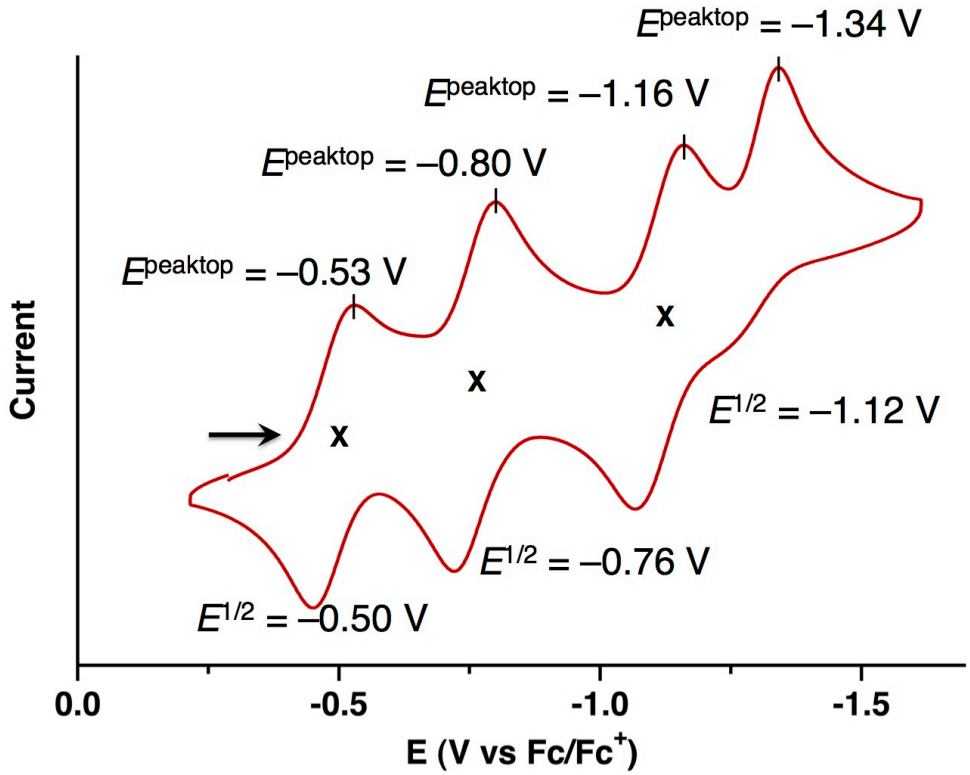


Figure S2. Aggregation manner in the crystal state of **1**. (a) Short C–H···O=C distance is observed (2.416 Å), which is much less than the sum of van der Waals radii (2.72 Å). (b, c) Two figures in other view are also shown. Two HexylTIDS ligands are aligning in parallel with the H···O interaction.

2. Electrochemical and ESR data

(a)



(b)

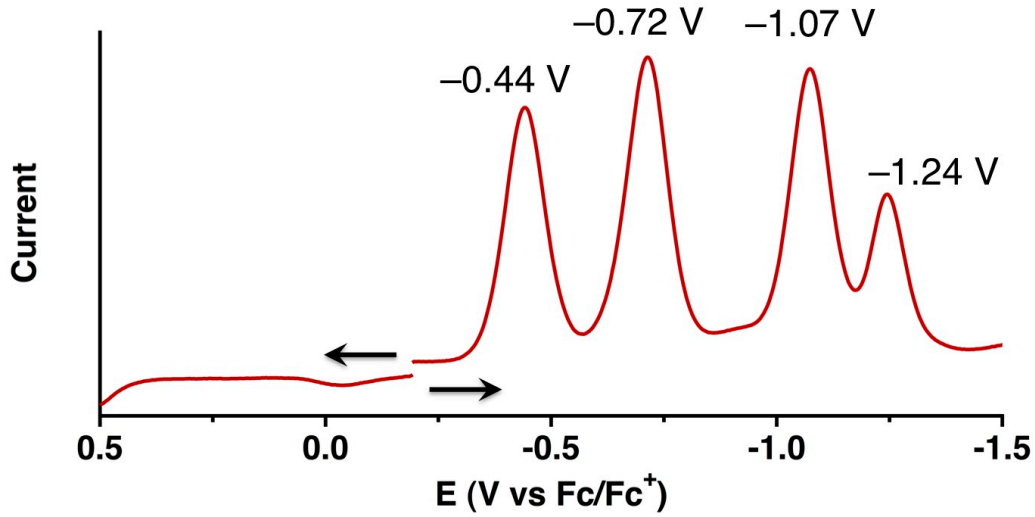


Figure S3. Electrochemical properties of the complex **1**. Conditions of cyclic voltammetry (upper part): solvent, CH_2Cl_2; concentration, 5.0 x 10^{-4} M; scan rate, 100 mV/s. Those of deferential potential voltammetry (lower part): solvent, CH_2Cl_2; concentration, 5.0 x 10^{-4} M; pulse amplitude, 50 mV; pulse width, 150 mV; pulse period, 300 ms; differential voltage of pulse amplitude, 4 mV.

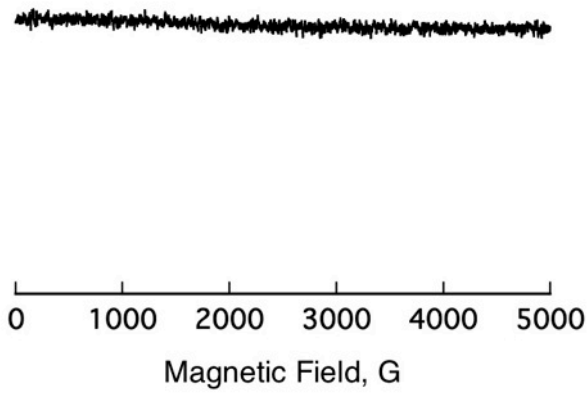


Figure S4. ESR spectra of the complex **1** measured in THF at 77 K. No peak was observed to represent that the complex **1** dose not have Pd(I) species.

3. DFT calculations

All calculations were carried out by Gaussian09 package[1] at the B3LYP level. Palladium atoms were represented by the LANL2DZ or SDD basis set and a 6-31G(d) basis set was used for other atoms (C, H, N, O, S, and P). The calculation levels are described as "B3LYP/LANL2DZ/6-31G(d)" and "B3LYP/SDD/6-31G(d)". Frequency calculations showed no imaginary frequency for the all model compounds.

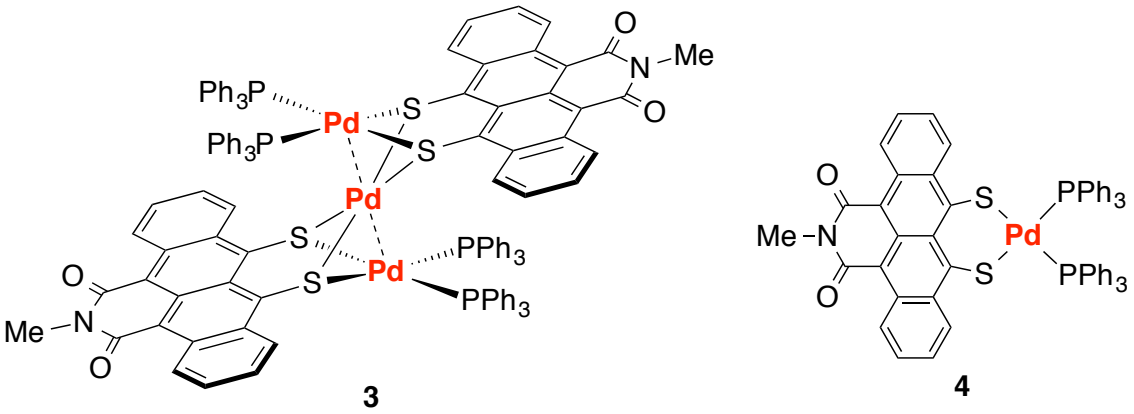


Chart S1. Structures of $Pd_3(MeTIDS)_2(PPh_3)_4$ (**3**) and $Pd(HexylTIDS)(PPh_3)_2$ (**4**), the methyl substituted analogue of the trinuclear complex **1** and the mononuclear complex **2** used for DFT calculations

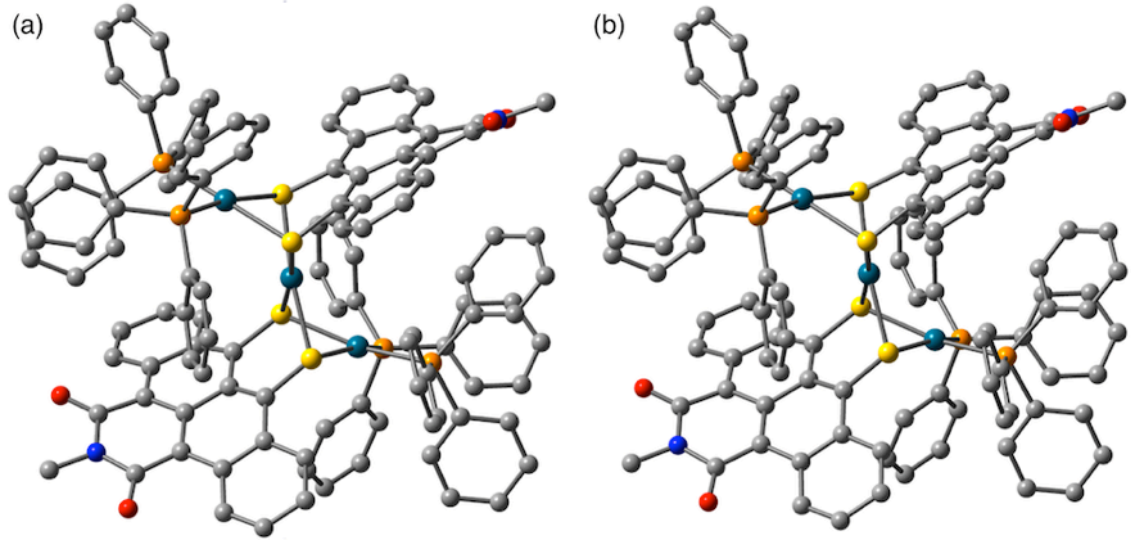


Figure S5. Optimized structures of **3** calculated at (a) B3LYP/LANL2DZ/6-31G(d) and at (b) B3LYP/SDD/6-31G(d). The structures are almost identical to each other.

Optimized structures of **3** and **4** are shown below.

3 calculated at B3LYP/LANL2DZ/6-31G(d)

213

Pd	-2.985985	-0.829221	-0.040173
Pd	0.000935	0.001384	-0.060455
Pd	3.006306	0.917540	0.250253
S	-1.277371	-1.174067	-1.743471
S	-1.117206	-1.662225	1.301905
S	1.343195	1.494528	-1.429859
S	1.070153	1.396716	1.610958
P	-4.535798	-1.234824	1.838694
P	-4.391441	0.469053	-1.552008
P	4.651155	0.553010	-1.542500
P	4.347945	0.202342	2.152036
O	3.094612	-6.821868	0.423455
O	1.130778	-7.174636	-3.635966
O	-0.905941	7.964982	-2.012950
O	-2.999183	6.743369	1.800820
C	-0.162516	-3.742062	3.178266
C	0.387106	-4.505100	4.183738
C	1.260406	-5.564625	3.858321
C	1.544884	-5.851887	2.542931
C	0.970401	-5.101808	1.470886
C	1.150364	-5.453600	0.093935
C	0.355471	-4.850471	-0.918258
C	0.296352	-5.413393	-2.224765
C	-0.589865	-4.854331	-3.208992
C	-0.900158	-5.496104	-4.445961
C	-1.740939	-4.917775	-5.371380
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H	7.082822	-1.055174	2.545756
C	-2.687585	8.568793	-0.192736
H	-2.018750	9.427898	-0.279681
H	-3.318450	8.542046	-1.086028
H	-3.300187	8.638141	0.702996
C	3.007453	-8.039681	-1.905472
H	4.020517	-7.626752	-1.924787
H	2.978290	-8.823403	-1.145240

H	2.737382	-8.432283	-2.882401
N	-1.897710	7.339539	-0.095807
N	2.042113	-6.991351	-1.566971

3 calculated at B3LYP/SDD/6-31G(d)

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Pd	-2.992791	-0.797457	-0.040775
Pd	-0.000184	0.006844	-0.064979
Pd	3.010271	0.879699	0.248801
S	-1.289891	-1.134059	-1.731524
S	-1.134476	-1.619857	1.289841
S	1.357324	1.468206	-1.416238
S	1.086759	1.357325	1.602493
P	-4.527856	-1.205195	1.817729
P	-4.378520	0.503917	-1.534595
P	4.626277	0.519854	-1.538961
P	4.338571	0.150242	2.125712
O	2.990314	-6.856427	0.444266
O	1.036724	-7.182170	-3.622593
O	-0.776229	7.982754	-1.971571
O	-2.898554	6.773514	1.831212
C	-0.222928	-3.712856	3.179746
C	0.308851	-4.483619	4.189440
C	1.164663	-5.558852	3.869931
C	1.450168	-5.853429	2.555885
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C	1.073196	-5.453072	0.103803
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C	1.490068	4.234817	-4.719024
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C	0.831143	3.133176	-1.171465
C	0.355021	3.660804	0.068425
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C	-0.021363	3.617374	2.535141
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C	-0.910201	7.098074	-1.120083
C	-5.065110	-2.970702	1.734719
C	-4.322440	-3.871395	0.954176
C	-4.679765	-5.219935	0.889935
C	-5.786401	-5.685674	1.601037
C	-6.535322	-4.798284	2.377825
C	-6.179394	-3.450805	2.445444
C	-6.116059	-0.284356	2.063487
C	-6.210196	0.768232	2.988659

C	-7.400565	1.481303	3.136363
C	-8.517943	1.152605	2.367993
C	-8.435315	0.108335	1.445438
C	-7.244163	-0.600894	1.287598
C	-3.710879	-1.026585	3.465709
C	-2.877698	0.083200	3.682279
C	-2.282563	0.295500	4.926341
C	-2.496649	-0.612938	5.965160
C	-3.306218	-1.730378	5.754427
C	-3.913105	-1.936108	4.513744
C	-4.724988	2.211975	-0.943703
C	-4.295954	2.598467	0.334579
C	-4.454387	3.915269	0.772268
C	-5.056138	4.858552	-0.061117
C	-5.489487	4.485537	-1.336680
C	-5.313226	3.176239	-1.782758
C	-3.681132	0.835975	-3.212904
C	-2.548129	1.662285	-3.308804
C	-1.976679	1.939991	-4.549587
C	-2.524339	1.389973	-5.711511
C	-3.645242	0.564410	-5.626101
C	-4.222528	0.286249	-4.384037
C	-5.986440	-0.317464	-1.911146
C	-5.965444	-1.711326	-2.094533
C	-7.133006	-2.403416	-2.420304
C	-8.339557	-1.712275	-2.557396
C	-8.370802	-0.329096	-2.367940
C	-7.202830	0.365853	-2.045975
C	6.236116	-0.369310	-1.312836
C	6.405254	-1.704612	-1.707477
C	7.632869	-2.345758	-1.529981
C	8.707864	-1.665482	-0.957863
C	8.547855	-0.337976	-0.554785
C	7.322428	0.304685	-0.727211
C	5.184754	2.120178	-2.269556
C	4.564914	3.319035	-1.886171

C	4.980073	4.539519	-2.425052
C	6.019159	4.576171	-3.354331
C	6.646314	3.388803	-3.742715
C	6.236768	2.170129	-3.202950
C	3.797882	-0.415523	-2.892364
C	3.850296	-0.029445	-4.239282
C	3.204342	-0.793036	-5.214517
C	2.507738	-1.949304	-4.859535
C	2.446149	-2.338753	-3.519673
C	3.077679	-1.570488	-2.541231
C	3.484100	0.031825	3.765959
C	2.875700	-1.155906	4.199188
C	2.224342	-1.208670	5.433155
C	2.171240	-0.080238	6.251845
C	2.762487	1.110354	5.823455
C	3.404923	1.170168	4.586560
C	5.726603	1.295638	2.525371
C	6.570727	1.091557	3.632291
C	7.584131	2.002982	3.926997
C	7.758067	3.142510	3.136003
C	6.908429	3.371023	2.053814
C	5.898994	2.452678	1.752074
C	5.035469	-1.538854	1.881614
C	4.159234	-2.541253	1.423572
C	4.591554	-3.862963	1.295696
C	5.915899	-4.190502	1.594444
C	6.802045	-3.197581	2.012499
C	6.367090	-1.879216	2.159957
H	-0.885476	-2.895007	3.434117
H	0.050021	-4.272867	5.224095
H	1.587426	-6.173424	4.660871
H	2.098868	-6.681248	2.312634
H	-0.515377	-6.424942	-4.647578
H	-1.975346	-5.377691	-6.319159
H	-2.966485	-3.114958	-5.879147
H	-2.488553	-1.975067	-3.770394

H	0.929173	2.237462	3.912247
H	0.049681	3.253326	5.946912
H	-1.467280	5.248147	5.792626
H	-2.005253	6.204906	3.599047
H	0.074974	7.075467	-3.508239
H	1.049417	6.180589	-5.575481
H	1.933505	3.831550	-5.625742
H	1.817993	2.451887	-3.619530
H	-3.461086	-3.518976	0.394501
H	-4.090729	-5.901099	0.282375
H	-6.066025	-6.734446	1.549562
H	-7.399852	-5.153679	2.932270
H	-6.776472	-2.771253	3.045597
H	-5.359341	1.027676	3.609070
H	-7.452480	2.290391	3.859780
H	-9.446262	1.704402	2.488586
H	-9.297275	-0.158017	0.840266
H	-7.201670	-1.409618	0.565798
H	-2.675948	0.780877	2.873669
H	-1.644688	1.162281	5.069223
H	-2.028327	-0.453643	6.932855
H	-3.470161	-2.446175	6.555702
H	-4.538004	-2.810101	4.365444
H	-3.804071	1.871938	0.973659
H	-4.080774	4.221167	1.744173
H	-5.151669	5.885013	0.279466
H	-5.941669	5.221017	-1.996755
H	-5.605799	2.912361	-2.794999
H	-2.111093	2.097801	-2.414161
H	-1.101594	2.580617	-4.603212
H	-2.078016	1.605806	-6.678485
H	-4.080724	0.137811	-6.526054
H	-5.099603	-0.350456	-4.336089
H	-5.032523	-2.257431	-1.977800
H	-7.098418	-3.480395	-2.559271
H	-9.250270	-2.249669	-2.807748

H	-9.306874	0.213980	-2.468587
H	-7.246329	1.437588	-1.886167
H	5.586517	-2.246530	-2.167185
H	7.745227	-3.378785	-1.846995
H	9.664493	-2.164648	-0.828782
H	9.378494	0.203489	-0.109754
H	7.221356	1.339956	-0.419088
H	3.748472	3.300776	-1.171537
H	4.480423	5.455409	-2.123359
H	6.340380	5.524791	-3.775785
H	7.458580	3.410934	-4.464314
H	6.743216	1.257197	-3.501227
H	4.385846	0.867449	-4.531799
H	3.248241	-0.480360	-6.254470
H	2.005672	-2.542471	-5.618353
H	1.896388	-3.230111	-3.234383
H	3.001211	-1.867288	-1.498650
H	2.913716	-2.052413	3.591054
H	1.762668	-2.140517	5.745583
H	1.674091	-0.127063	7.217110
H	2.725385	1.997888	6.449605
H	3.856081	2.104960	4.269131
H	6.424556	0.230500	4.277159
H	8.231203	1.829252	4.782494
H	8.543681	3.854759	3.373106
H	7.022348	4.263568	1.444858
H	5.229869	2.641621	0.918000
H	3.129218	-2.293838	1.176446
H	3.905511	-4.642149	0.977021
H	6.249930	-5.219390	1.493920
H	7.838317	-3.444267	2.228278
H	7.074054	-1.120876	2.475056
C	-2.548291	8.607532	-0.148238
H	-1.863466	9.454788	-0.226885
H	-3.177212	8.599386	-1.043262
H	-3.161824	8.681221	0.746513

C	2.887754	-8.079056	-1.881714
H	3.908328	-7.685085	-1.905600
H	2.845173	-8.855999	-1.115282
H	2.609431	-8.473947	-2.855399
N	-1.781535	7.363204	-0.058887
N	1.942210	-7.010732	-1.550018

4 calculated at B3LYP/LANL2DZ/6-31G(d)

106

Pd	-0.642978	0.134417	-0.242662
S	0.930370	-1.369894	-1.174396
P	-2.112391	1.864816	0.627368
S	1.079128	1.726981	-0.275120
P	-2.280915	-1.668787	-0.475749
O	7.250472	-2.321847	1.384893
O	7.704625	1.940169	-0.019558
N	7.405540	-0.207206	0.648685
C	-2.091564	-2.973420	0.816244
C	5.522957	0.990923	-0.335848
C	3.270524	-0.066036	-0.350429
C	4.417920	-2.496123	0.634252
C	3.053103	-2.470043	0.158559
C	4.103795	-4.847600	1.256518
H	4.506290	-5.758858	1.692681
C	-2.545349	0.330920	2.940043
H	-1.899440	-0.396367	2.457959
C	2.494890	-1.256551	-0.339007
C	5.236537	-1.337988	0.483327
C	6.931030	0.983806	0.082390
C	-5.760840	2.668751	-1.208816
H	-6.802679	2.790838	-0.925696
C	4.696712	-0.136205	-0.062227
C	-0.937681	-2.984062	1.614935

H	-0.170770	-2.232712	1.457724
C	-1.366753	3.527970	0.923482
C	-1.682826	4.655720	0.153434
H	-2.397533	4.582686	-0.658888
C	-4.807722	-1.250103	0.746111
H	-4.282278	-1.353109	1.688925
C	2.707097	1.208596	-0.673797
C	-3.466132	2.201236	-0.574261
C	-5.376548	2.808969	-2.542478
H	-6.116404	3.048007	-3.301563
C	3.557050	2.238542	-1.176158
C	3.016942	3.388508	-1.831852
H	1.943207	3.450272	-1.959894
C	-2.857284	1.526434	2.277948
C	4.985008	2.121825	-1.022090
C	-3.042721	0.075963	4.220941
H	-2.785409	-0.853329	4.721491
C	-3.856197	1.016022	4.853692
H	-4.242126	0.820558	5.850457
C	-3.089960	2.320929	-1.924529
H	-2.050198	2.176477	-2.208747
C	-4.111010	-1.363010	-0.469414
C	-0.431658	3.653460	1.965644
H	-0.163668	2.787895	2.563996
C	-4.037551	2.632173	-2.899515
H	-3.729548	2.732313	-3.936744
C	-4.812783	2.369165	-0.227675
H	-5.132045	2.253655	0.801899
C	-2.021505	-2.503199	-2.101695
C	-6.205457	-1.002892	-1.651498
H	-6.742682	-0.910108	-2.591372
C	-2.130916	-3.890366	-2.272703
H	-2.334860	-4.532480	-1.422685
C	-6.890019	-0.908838	-0.439523
H	-7.964305	-0.745214	-0.428702
C	4.891574	-3.725595	1.201336

H	5.902115	-3.750604	1.575734
C	2.280240	-3.673784	0.217881
H	1.268113	-3.649050	-0.162398
C	-4.157581	2.220362	4.210705
H	-4.774108	2.964306	4.707801
C	-2.887998	-4.943166	1.999796
H	-3.650944	-5.702944	2.146725
C	6.661540	-1.367106	0.868549
C	-1.959448	-4.460193	-3.535152
H	-2.036970	-5.537751	-3.651743
C	-1.725120	-1.700732	-3.215653
H	-1.598466	-0.628856	-3.090481
C	-3.652742	2.480680	2.937407
H	-3.860876	3.436109	2.464846
C	-6.185156	-1.029737	0.759625
H	-6.706244	-0.959803	1.710774
C	2.781416	-4.831291	0.751776
H	2.163860	-5.724729	0.795143
C	-3.069228	-3.963592	1.023380
H	-3.978764	-3.963647	0.431086
C	-0.759985	-3.965262	2.593348
H	0.145949	-3.963340	3.192252
C	0.161314	4.884576	2.238240
H	0.884934	4.964615	3.044396
C	-1.084251	5.887358	0.429426
H	-1.342157	6.754333	-0.172847
C	-1.564570	-2.272658	-4.478204
H	-1.330182	-1.639380	-5.329222
C	-4.827932	-1.228447	-1.668355
H	-4.317085	-1.315174	-2.621020
C	-1.681479	-3.654016	-4.640350
H	-1.544692	-4.101365	-5.620994
C	5.230397	4.252372	-2.205081
H	5.879596	5.018382	-2.622302
C	-0.163671	6.005205	1.470569
H	0.302754	6.963675	1.680983

C	3.826636	4.369843	-2.341629
H	3.394851	5.217617	-2.866807
C	5.790163	3.171895	-1.568142
H	6.861205	3.095537	-1.468099
C	-1.733155	-4.946030	2.786581
H	-1.594596	-5.709997	3.546857
C	8.807510	-0.263537	1.072212
H	9.264186	0.690770	0.823528
H	8.865100	-0.450957	2.147825
H	9.314553	-1.085134	0.560432

4 calculated at B3LYP/SDD/6-31G(d)

106

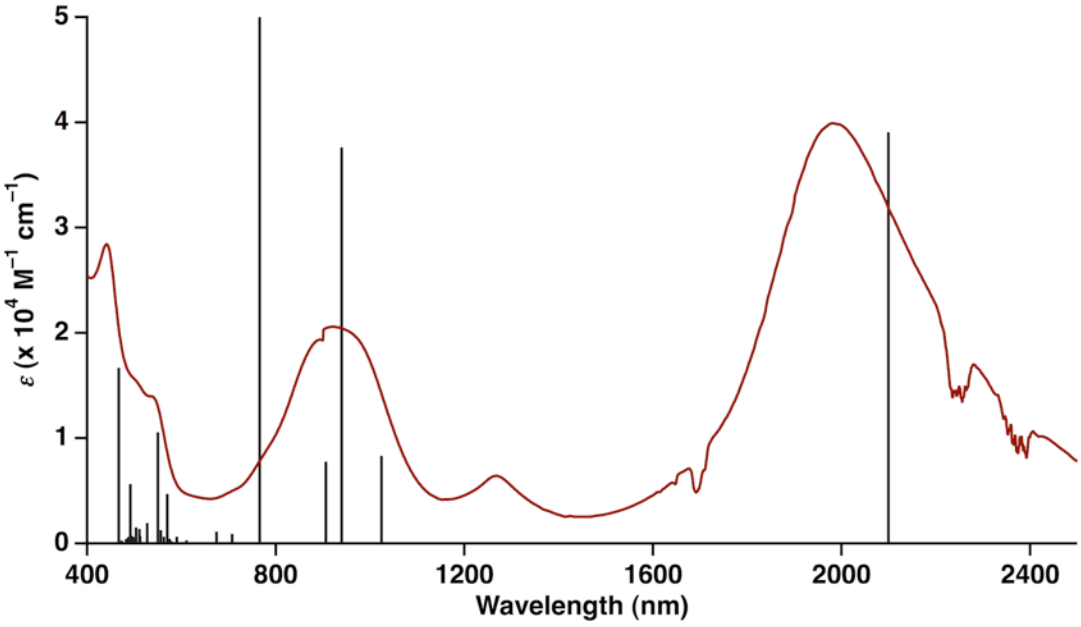
Pd	-0.643138	0.128775	-0.225792
S	0.921971	-1.381962	-1.119226
P	-2.114303	1.843387	0.618664
S	1.060267	1.712824	-0.222478
P	-2.263088	-1.663500	-0.478463
O	7.294193	-2.313961	1.300575
O	7.685342	1.977783	-0.030587
N	7.417048	-0.183484	0.605071
C	-2.098625	-2.970748	0.816461
C	5.509782	1.010942	-0.335618
C	3.264991	-0.062043	-0.327202
C	4.440294	-2.486675	0.638334
C	3.066565	-2.466072	0.189358
C	4.143865	-4.835709	1.278411
H	4.556659	-5.743473	1.712200
C	-2.578889	0.313551	2.932089
H	-1.925537	-0.415504	2.463265
C	2.496012	-1.256440	-0.303645
C	5.252048	-1.325863	0.469793
C	6.923141	1.011800	0.065736

C	-5.739059	2.673578	-1.254543
H	-6.784147	2.792677	-0.982322
C	4.695702	-0.124321	-0.058810
C	-0.960701	-2.987140	1.637744
H	-0.188382	-2.237896	1.499379
C	-1.370835	3.504978	0.937849
C	-1.661171	4.634098	0.159915
H	-2.355777	4.564815	-0.669972
C	-4.811076	-1.247192	0.704137
H	-4.300896	-1.351580	1.655074
C	2.688790	1.208517	-0.641540
C	-3.452361	2.195863	-0.597902
C	-5.338636	2.831492	-2.581423
H	-6.068934	3.081431	-3.346216
C	3.524945	2.248481	-1.145737
C	2.969060	3.398632	-1.788046
H	1.893620	3.452783	-1.904276
C	-2.884089	1.504909	2.259520
C	4.955422	2.142655	-1.006925
C	-3.093807	0.063516	4.207136
H	-2.841496	-0.862981	4.715465
C	-3.918763	1.004129	4.823815
H	-4.318576	0.812206	5.815779
C	-3.059930	2.333559	-1.941948
H	-2.016992	2.192390	-2.216005
C	-4.094463	-1.356607	-0.500108
C	-0.463905	3.626892	2.005067
H	-0.217278	2.760719	2.611784
C	-3.995491	2.658505	-2.924242
H	-3.674442	2.772754	-3.956092
C	-4.803145	2.360276	-0.266045
H	-5.135384	2.230823	0.757612
C	-1.984542	-2.503758	-2.099940
C	-6.171135	-1.000817	-1.714890
H	-6.693506	-0.908848	-2.663195
C	-2.083540	-3.892279	-2.264982

H	-2.290925	-4.531413	-1.413671
C	-6.875105	-0.908994	-0.513937
H	-7.949780	-0.747684	-0.520103
C	4.927900	-3.712278	1.201630
H	5.945782	-3.733593	1.555736
C	2.297915	-3.671248	0.269668
H	1.278521	-3.651001	-0.090813
C	-4.213694	2.204564	4.170701
H	-4.839037	2.949501	4.655136
C	-2.922568	-4.942465	1.978713
H	-3.690255	-5.700650	2.108088
C	6.686287	-1.353099	0.818839
C	-1.897659	-4.467806	-3.522914
H	-1.967599	-5.546451	-3.634128
C	-1.684282	-1.705521	-3.216166
H	-1.564416	-0.632219	-3.096624
C	-3.691002	2.460064	2.903674
H	-3.893995	3.413337	2.424659
C	-6.189085	-1.029685	0.696041
H	-6.725278	-0.962175	1.638953
C	2.811988	-4.824987	0.799504
H	2.197302	-5.719434	0.859843
C	-3.082257	-3.959311	1.002076
H	-3.980113	-3.955874	0.392215
C	-0.804562	-3.971736	2.616471
H	0.089653	-3.973784	3.232888
C	0.129033	4.854813	2.291885
H	0.831796	4.931438	3.116624
C	-1.063742	5.862868	0.450856
H	-1.302151	6.730968	-0.157800
C	-1.509152	-2.283059	-4.474194
H	-1.271089	-1.652608	-5.326328
C	-4.793051	-1.223636	-1.710031
H	-4.267732	-1.310298	-2.654733
C	-1.615657	-3.665997	-4.630128
H	-1.467551	-4.117624	-5.607153

C	5.171574	4.283557	-2.176826
H	5.810216	5.057976	-2.594802
C	-0.169449	5.976517	1.515110
H	0.296536	6.932618	1.736928
C	3.765549	4.390131	-2.298813
H	3.321613	5.237922	-2.813755
C	5.746489	3.203392	-1.553189
H	6.819061	3.135628	-1.463903
C	-1.783438	-4.950860	2.787906
H	-1.661403	-5.717683	3.548123
C	8.827464	-0.235868	1.000123
H	9.270842	0.727667	0.763198
H	8.907535	-0.445557	2.070154
H	9.331662	-1.041669	0.461150

(a)



(b)

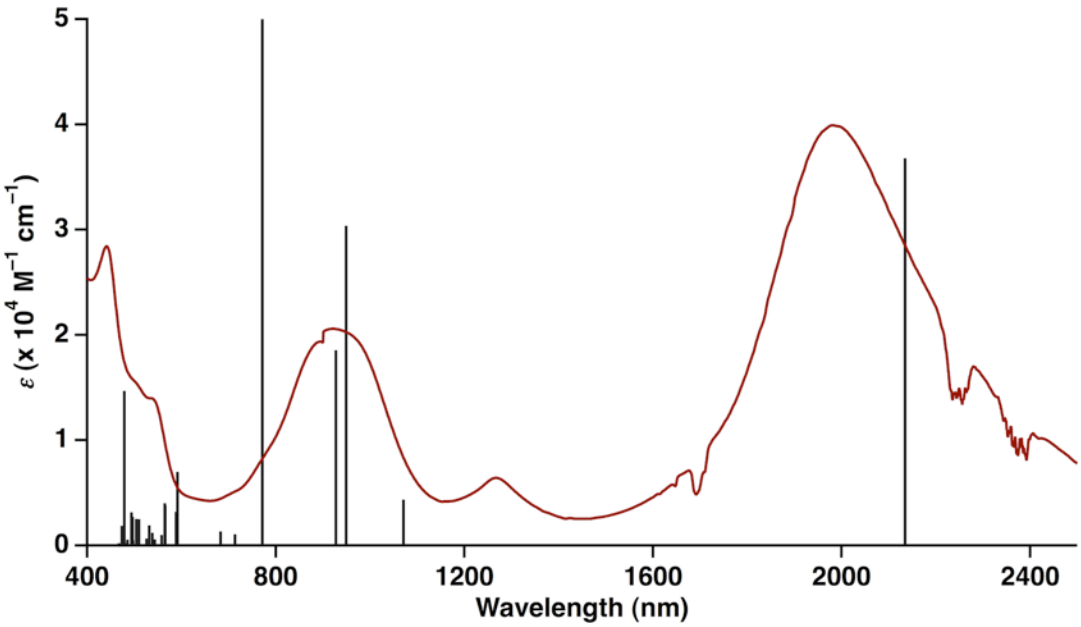


Figure S6. Simulated absorption bands of **3** calculated at (a) B3LYP/LANL2DZ/6-31G(d), and at (b) B3LYP/SDD/6-31G(d) (black) with experimental data of the complex **1** (red). Both calculation conditions gave similar results.

Table S1. Selected distances between palladium atoms and the peripheral atoms in trimetallic palladium complex **1** and **3**.

	Crystal (**1**) (Å)	Calculation (**3**) (Å) [a]	Calculation (**3**) (Å) [b]	Difference (%) [a]	Difference (%) [b]
Pd···Pd	2.8828(5)	3.099	3.100	6.976	7.006
	2.9241(5)	3.150	3.157	7.171	7.377
Pd–P	2.335(2)	2.418	2.439	3.433	4.264
	2.365(1)	2.445	2.469	3.272	4.212
	2.342(1)	2.437	2.460	3.898	4.797
	2.320(2)	2.412	2.435	3.814	4.723
Pd–S	2.355(1)	2.429	2.437	3.047	3.365
	2.377(1)	2.423	2.447	1.898	2.861
	2.315(1)	2.396	2.418	3.381	4.260
	2.336(1)	2.402	2.424	2.748	3.630
	2.353(1)	2.396	2.426	1.795	3.009
	2.351(1)	2.402	2.430	2.123	3.251
	2.350(1)	2.400	2.415	2.083	2.692
	2.344(1)	2.419	2.433	3.100	3.658

[a] Calculated at B3LYP/SDD/6-32G(d) level.

[b] Calculated at B3LYP/LANL2DZ/6-31G(d) level.

Table S2. Optical transitions of **3** calculated at B3LYP/SDD/6-31G(d). Transitions with the coefficients less than 0.3 are omitted.

Entry	Wavelength [nm]	Oscillator strength	Transition	The largest coefficient in the CI expansion
1	2099.43	0.1302	HOMO –> LUMO	0.74847
2	1024.05	0.0277	HOMO –> LUMO+1	0.53154
			HOMO –> LUMO+2	0.43898
3	939.57	0.1254	HOMO –> LUMO+1	–0.40969
			HOMO –> LUMO+2	0.45228
4	906.11	0.0259	HOMO–1 –> LUMO	0.60777
5	765.60	0.2014	HOMO–2 –> LUMO	0.67489
6	707.47	0.0030	HOMO –> LUMO+3	0.67517
7	674.27	0.0037	HOMO–3 –> LUMO	0.68077
8	610.78	0.0010	HOMO –> LUMO+4	0.62580
9	590.19	0.0021	HOMO –> LUMO+4	–0.31909
			HOMO –> LUMO+5	0.33865
			HOMO –> LUMO+6	0.39961
			HOMO –> LUMO+8	–0.31359
10	577.96	0.0007	HOMO–4 -> LUMO	0.67921

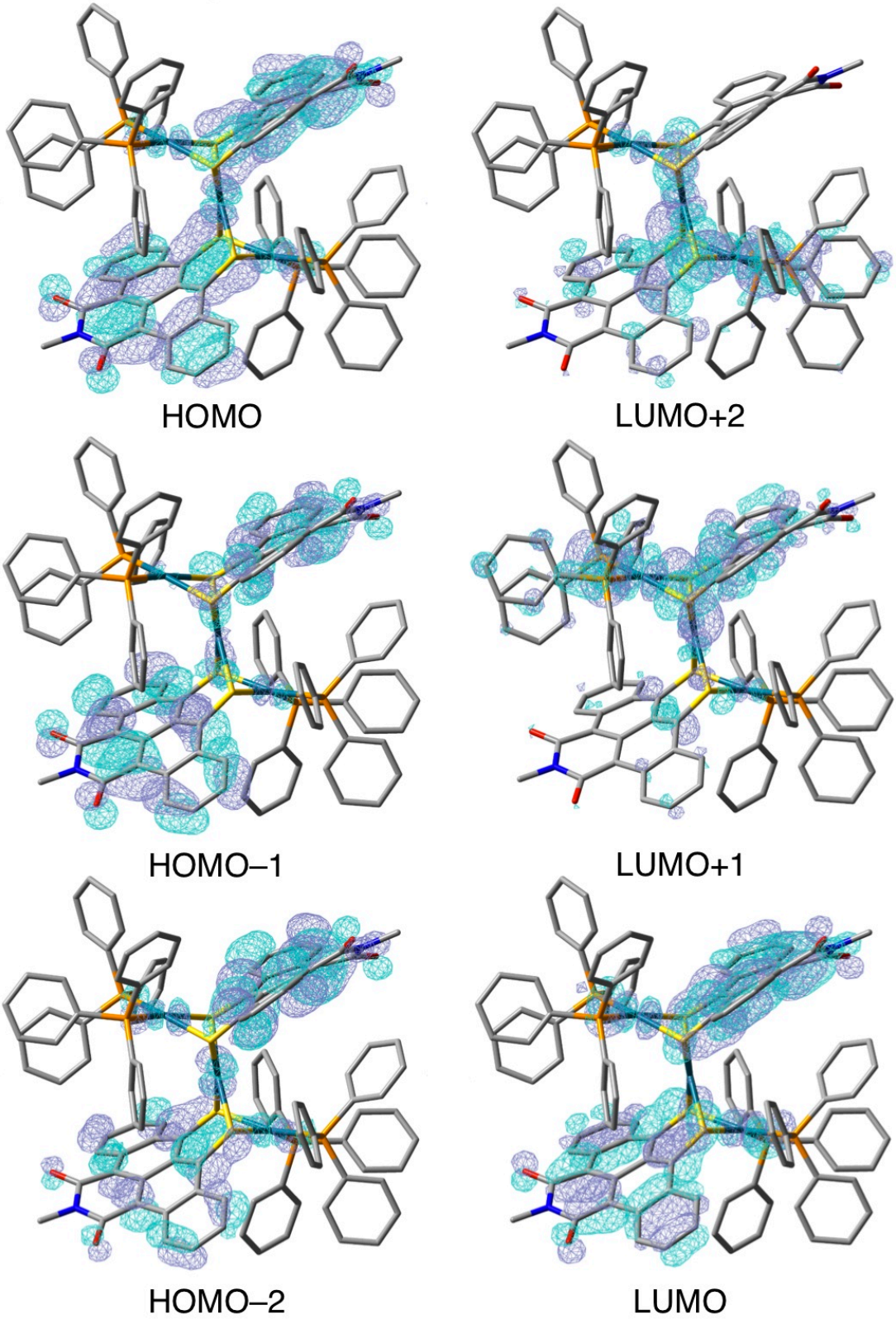


Figure S7. Molecular orbitals of **3** calculated at B3LYP/SDD/6-31G(d) level.

The structures of HOMO and LUMO in **1** were successfully explained by molecular orbital interaction analysis (Figure S7). For the analysis, **$Pd_3(MeTIDS)_2(PPh_3)_4$** molecule was divided into three subunits: two mononuclear Pd complex subunits (**[$Pd(MeTIDS)(PPh_3)_2$]** and **[$Pd(MeTIDS)(PPh_3)_2$]'**) and one **[Pd]** atom. The molecular orbitals of each unit were obtained by single-point DFT calculation at the B3LYP/SDD/6-31G(d) level. When the LUMOs of **[$Pd(MeTIDS)(PPh_3)_2$]** interact with each other, a bonding state and an antibonding orbitals should be considered (**[bonding]** and **[antibonding]**, respectively). Because of the symmetry matching of the molecular orbitals, **[antibonding]** can interact with the d_{xy} orbital of **[Pd]** to generate HOMO of $Pd_3(MeTIDS)_2(PPh_3)_4$. On the other hand, **[bonding]** does not have interaction with **[Pd]**, and generates LUMO of **$Pd_3(MeTIDS)_2(PPh_3)_4$**. Consequently, a narrow HOMO–LUMO gap is formed in **$Pd_3(MeTIDS)_2(PPh_3)_4$**.

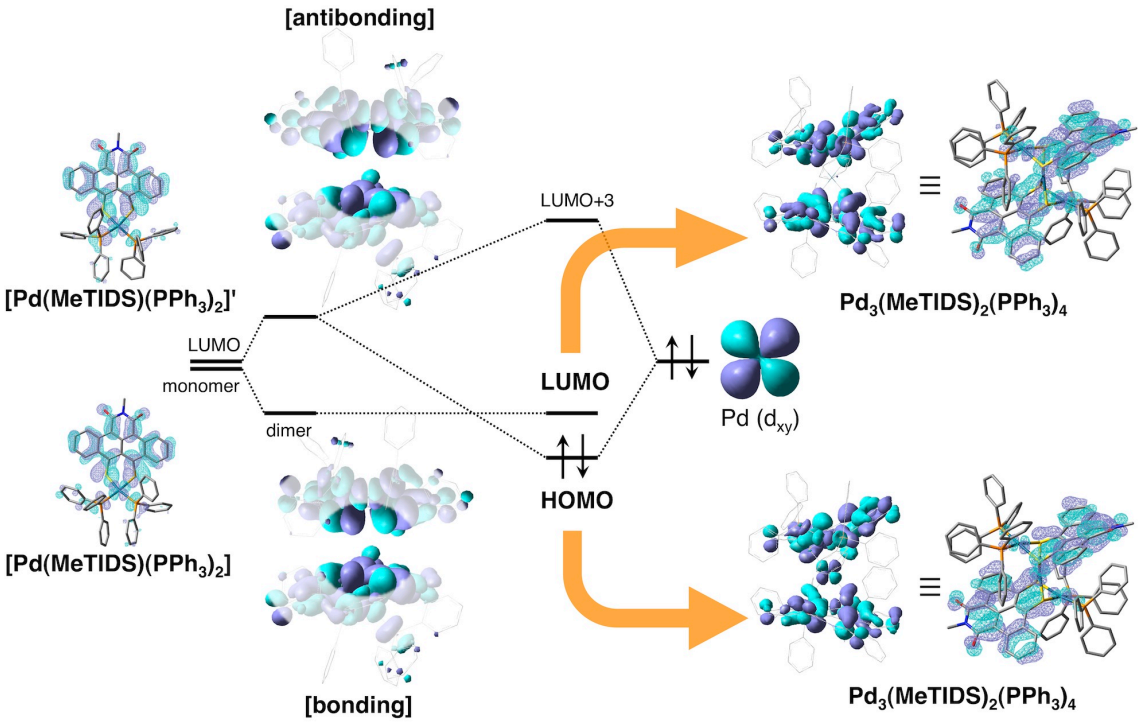


Figure S8. Molecular orbital interaction analysis of **3**. The optimized structure of **3** was divided into three units: two partial mononuclear complexes (**[$Pd(MeTIDS)(PPh_3)_2$]** and **[$Pd(MeTIDS)(PPh_3)_2$]'**) and the central palladium (**[Pd]**). Each molecular orbital was obtained by single point calculation at B3LYP/SDD/6-31G(d) level.

Table S3. Wiberg bond indexes between three palladium atoms and peripheral sulfur and carbon atoms in **3**. [a]

	Pd1	Pd2	Pd3	S4	S5	S6	S7	C30	C32	C50	C52
Pd1	–	**0.1443**	0.0119	**0.4958**	**0.4832**	0.0102	0.0141	0.0423	0.0325	0.0051	0.0070
Pd2	–	–	**0.1325**	**0.3597**	**0.3506**	**0.3406**	**0.3438**	0.0347	0.0359	0.0336	0.0347
Pd3	–	–	–	0.0097	0.0121	**0.4957**	**0.5078**	0.0038	0.0051	0.0286	0.0287
S4	–	–	–	–	0.1004	0.0304	0.1043	**1.1419**	0.0237	0.0064	0.0029
S5	–	–	–	–	–	0.1014	0.0299	0.0244	**1.1335**	0.0044	0.0079
S6	–	–	–	–	–	–	0.1017	0.0074	0.0029	**1.1192**	0.0229
S7	–	–	–	–	–	–	–	0.0039	0.0068	0.0207	**1.1169**
C30	–	–	–	–	–	–	–	–	0.0136	0.0042	0.0044
C32	–	–	–	–	–	–	–	–	–	0.0041	0.0042
C50	–	–	–	–	–	–	–	–	–	–	0.0129
C52	–	–	–	–	–	–	–	–	–	–	–

[a] Calculations were performed at the B3LYP/SDD/6-31G(d) level.

Table S4. Second order perturbation theory analysis of Fock matrix in NBO basis for **3**. Stabilization energies derived from the interactions between electron-filled donor atoms and electron-empty acceptor atoms are shown in kcal/mol. [a]

		Acceptor										
		Pd1	**Pd2**	**Pd3**	**S4**	**S5**	**S6**	**S7**	**C30**	**C32**	**C50**	**C52**
Donor	**Pd1**	–	**110.50**	30.19	23.19	14.05	5.71	6.06	7.38	7.45	0.82	0.71
	Pd2	**155.59**	–	**598.48**	**118.04**	97.92	**308.54**	**176.54**	**611.93**	78.47	**167.96**	**129.37**
	Pd3	28.29	**130.89**	–	4.67	5.20	16.50	16.46	1.52	0.56	7.27	7.15
	S4	16.59	**225.94**	4.79	–	0.96	0.62	1.34	1.29	<0.05	0.22	0.26
	S5	17.30	28.37	5.18	1.39	–	1.15	1.10	<0.05	1.50	0.29	0.18
	S6	5.71	**143.97**	17.93	1.49	1.25	–	1.29	0.30	0.19	1.49	<0.05
	S7	5.17	31.59	16.53	1.58	0.80	0.84	–	0.36	0.10	<0.05	1.43
	C30	<0.05	0.65	<0.05	<0.05	<0.05	<0.05	<0.05	–	<0.05	<0.05	<0.05
	C32	<0.05	0.95	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	–	<0.05	<0.05
	C50	<0.05	0.69	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	–	<0.05
	C52	<0.05	0.97	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	–

[a] Calculations were performed at the B3LYP/SDD/6-31G(d) level. Donations to the own empty levels from themselves are omitted. The highest values among several interactions for each donor-acceptor combination are listed.

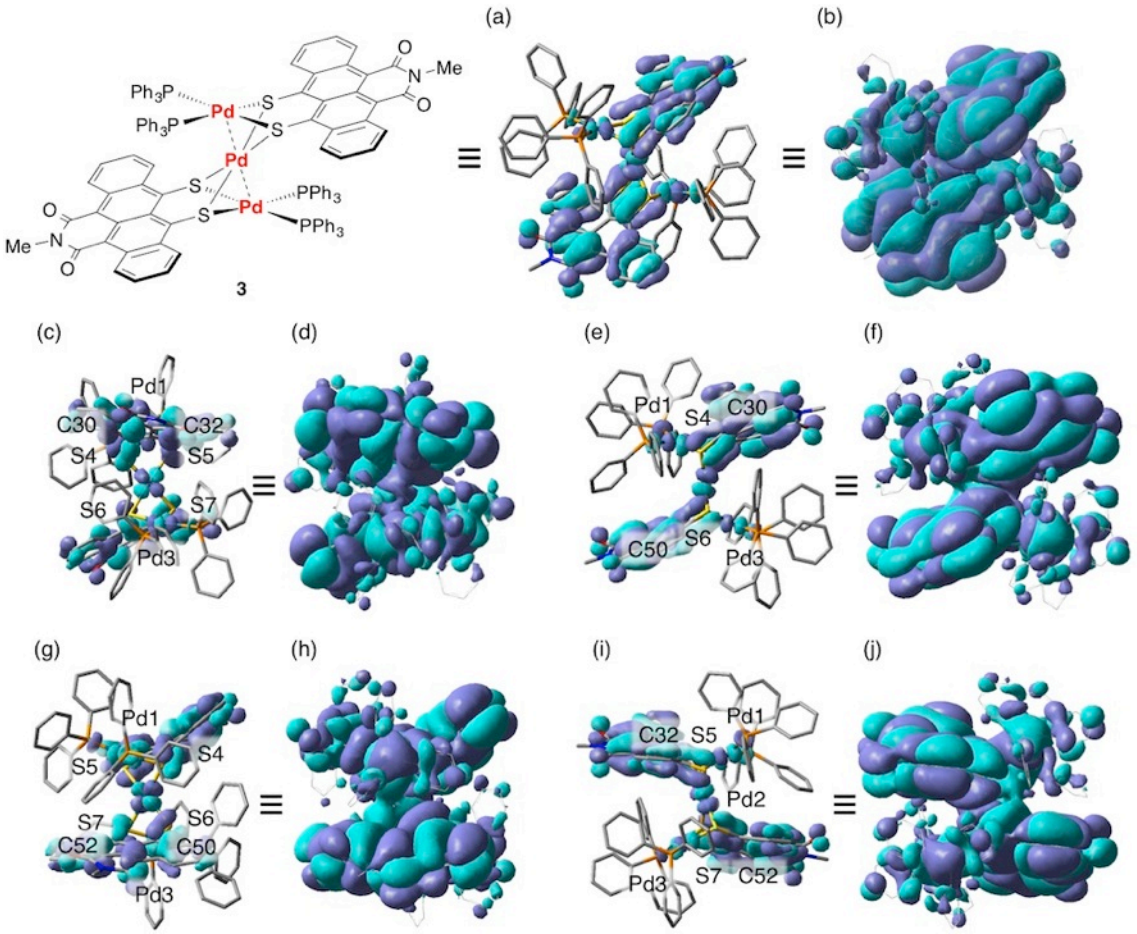


Figure S9. HOMO orbitals of **3** drawn at several angles. The isovalues for orbital surfaces are 0.02 (a, c, e, g, i) and 0.003 (b, d, f, h, j). Pd2···C32 and Pd2···C52 are bonding interaction; Pd2···C30 and Pd2···C50 are antibonding interaction.

Herein, donation from the central palladium to the carbon atoms appears asymmetrically (Table S2). The asymmetricity would be induced from the asymmetiric structure of $Pd_3(MeTIDS)_2(PPh_3)_4$. The same asymmetricity is also observed in the partial interactions between the central palladium and the carbon atoms vicinal to sulfur atoms, which are bonding mode for the two C···Pd interactions (*e.g.* Figure S8j), but antibonding for the other C···Pd interactions (*e.g.* Figure S8f). A single point calculation for NBO analysis using the crystal structure of the complex **1** provided similar asymmetric trends. In the end, the multi-center interaction of the central palladium with peripheral palladium, sulfur and carbon atoms and donative nature of the central palladium stabilize the trinuclear structure and fix the both TIDS ligands in parallel to have extended π-conjugation system.

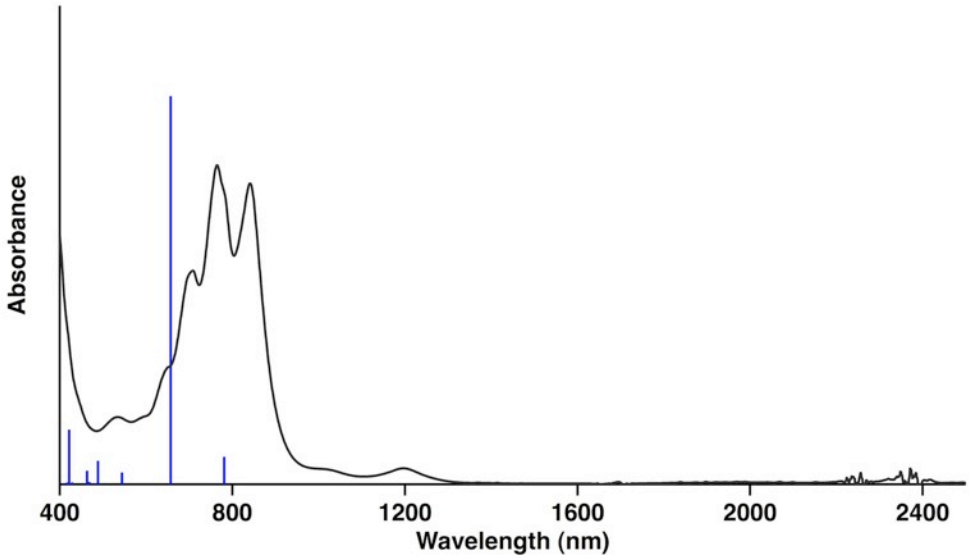


Figure S10. Simulated absorption bands of **4** calculated at B3LYP/LANL2DZ/6-31G(d) (blue line). Black line is an experimental spectrum of the complex **2** in CH_2Cl_2 containing PPh_3.

5. Time-resolved Transient Absorption Measurements.

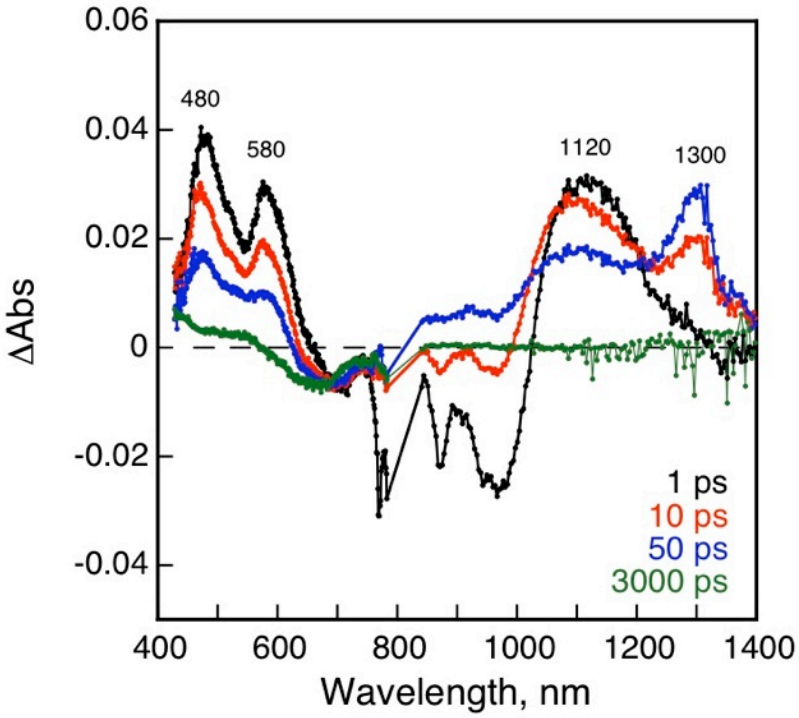


Figure S11. Transient absorption measured at 1, 10, 50, and 3000 ps after excitation at 800 nm in toluene

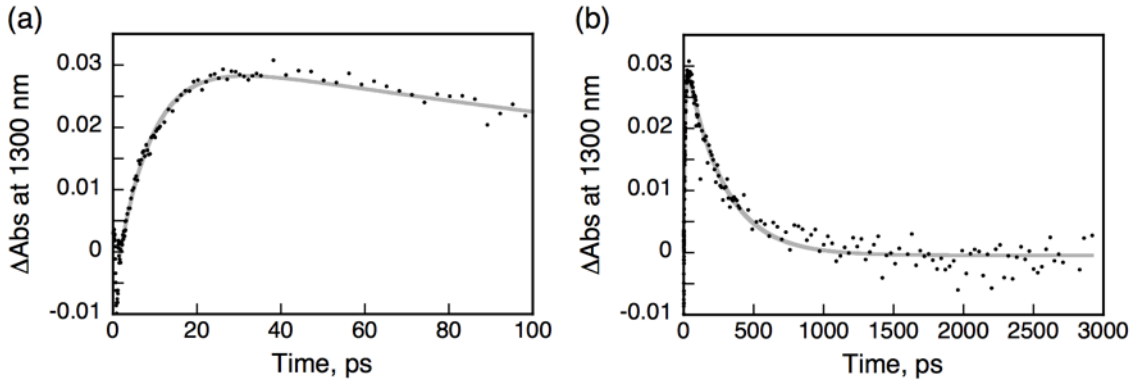


Figure S12. Time-depending profile of an absorption peak at 1300 nm in the transient absorption spectra shown in Figure S13

1 a) *Gaussian 09*, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X.

Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009; b) *Gaussian 09*, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010; the Gaussian09 package of b) was used for the calculations performed at Research Center for Computational Science, Okazaki, Japan.