Electronic Supplementary Material for PCCP

Supporting Information

Decomposition pathways for the photoactivated anticancer complex *cis*,*trans*,*cis*-$[Pt(N_3)_2(OH)_2(NH_3)_2]$: Insights from DFT calculations

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UV-Vis Properties of *cis,trans,cis*-[$Pt(N_3)(OH)_2(NH_3)_2$]

Table S1. Absorption properties for aqueous solutions of *cis,trans,cis*-[$Pt(N_3)(OH)_2(NH_3)_2$]

	Experimental	B3LYP/ LANL2DZ/ 6-31G**+	B3LYP/ LANL2DZ/ 6-311G**+	PBE1PBE/ LANL2DZ/ 6-31G**+	PBE1PBE/ LANL2DZ/ 6-311G**+
λ_{max} (nm)	256	274	266	258	254
$\varepsilon(M^{-1}\ cm^{-1})$	13305	9269	10799	9977	11240

Table S2. Selected singlet transitions for *cis,trans,cis*-[Pt(N$_3$)(OH)$_2$(NH$_3$)$_2$] in water at the B3LYP/LANL2DZ/6-31G+**

B3LYP/LANL2DZ/6-31G**+			
Transition	**Energy, eV (nm)**	***f***	**Major Composition**
S10	4.34 (285)	0.1198	HOMO−4→LUMO (79%)
S11	4.44 (279)	0.1011	HOMO−5→LUMO (72%) HOMO−4→LUMO+1 (10%)
S12	4.89 (253)	0.0569	HOMO−6→LUMO+1 (12%) HOMO−5→LUMO+1 (68%)
S13	4.96 (250)	0.0724	HOMO−7→LUMO (10%) HOMO−4→LUMO+1 (75%)
S14	5.38 (231)	0.0504	HOMO−7→LUMO (62%) HOMO→LUMO+5 (11%)
S15	5.40 (230)	0.0442	HOMO−9→LUMO (11%) HOMO−7→LUMO+1 (18%) HOMO−6→LUMO+1 (22%) HOMO−5→LUMO+1 (11%)
S16	5.510 (225)	0.0394	HOMO−9→LUMO (48%) HOMO−8→LUMO (8%)

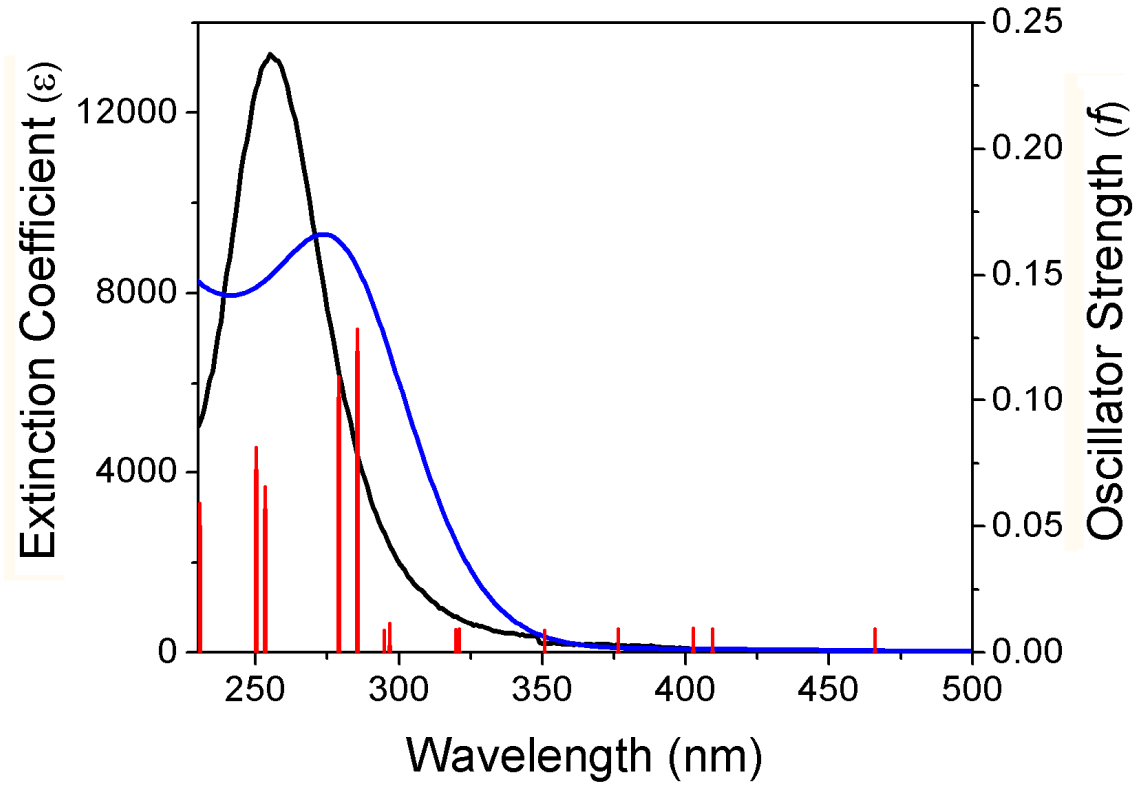


Table S3. Selected singlet transitions for *cis,trans,cis*-[Pt(N$_3$)(OH)$_2$(NH$_3$)$_2$] in water at the B3LYP/LANL2DZ/6-311G+**

B3LYP/LANL2DZ/6-311G**+			
Transition	**Energy, eV (nm)**	***f***	**Major Composition**
S10	4.30 (288)	0.1126	HOMO−4→LUMO (79%)
S11	4.41 (280)	0.0923	HOMO−5→LUMO (65%) HOMO−4→LUMO+1 (16%)
S12	4.78 (259)	0.0749	HOMO−6→LUMO+1 (11%) HOMO−5→LUMO+1 (68%)
S13	4.86 (255)	0.1106	HOMO−7→LUMO (9%) HOMO−4→LUMO+1 (72%)
S14	5.36 (231)	0.0819	HOMO−7→LUMO (25%) HOMO−6→LUMO+1 (28%) HOMO−5→LUMO+1 (12%)
S15	5.39 (230)	0.0512	HOMO−7→LUMO+1 (64%) HOMO→LUMO+4 (12%)
S16	5.49 (226)	0.0474	HOMO−9→LUMO (54%)

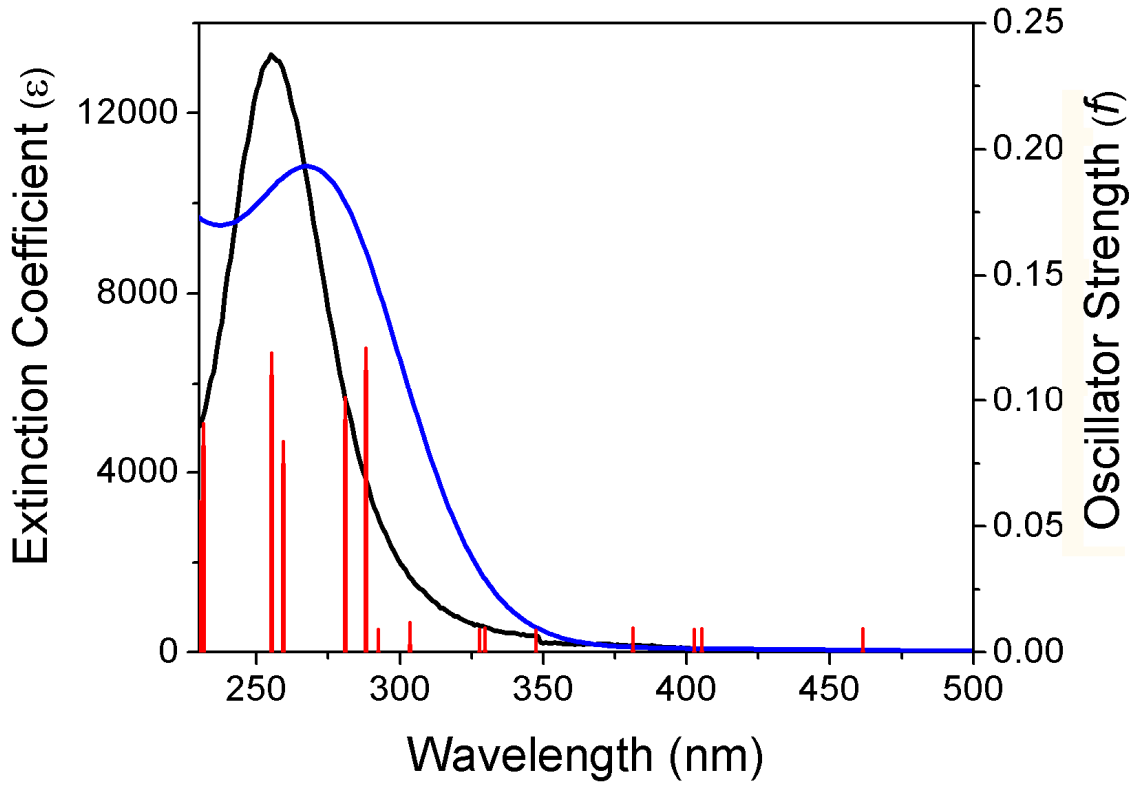


Table S4. Selected singlet transitions for *cis,trans,cis*-[Pt(N$_3$)(OH)$_2$(NH$_3$)$_2$] in water at the PBE1PBE/LANL2DZ/6-31G+**

PBE1PBE/LANL2DZ/6-31G**+			
Transition	**Energy, eV (nm)**	***f***	**Major Composition**
S10	4.67 (265)	0.1277	HOMO−4→LUMO (79%)
S11	4.78 (259)	0.1252	HOMO−5→LUMO (72%)
S12	5.23 (237)	0.0447	HOMO−5→LUMO+1 (72%)
S13	5.31 (233)	0.0629	HOMO−4→LUMO+1 (82%)
S14	5.70 (217)	0.0171	HOMO−7→LUMO (52%) HOMO→LUMO+5 (22%)
S15	5.72 (216)	0.0168	HOMO−9→LUMO (17%) HOMO−7→LUMO+1 (12%) HOMO−6→LUMO+1 (14%) HOMO−2→LUMO+5 (14%)
S16	5.83 (212)	0.0475	HOMO−9→LUMO (33%) HOMO−6→LUMO+1 (17%)

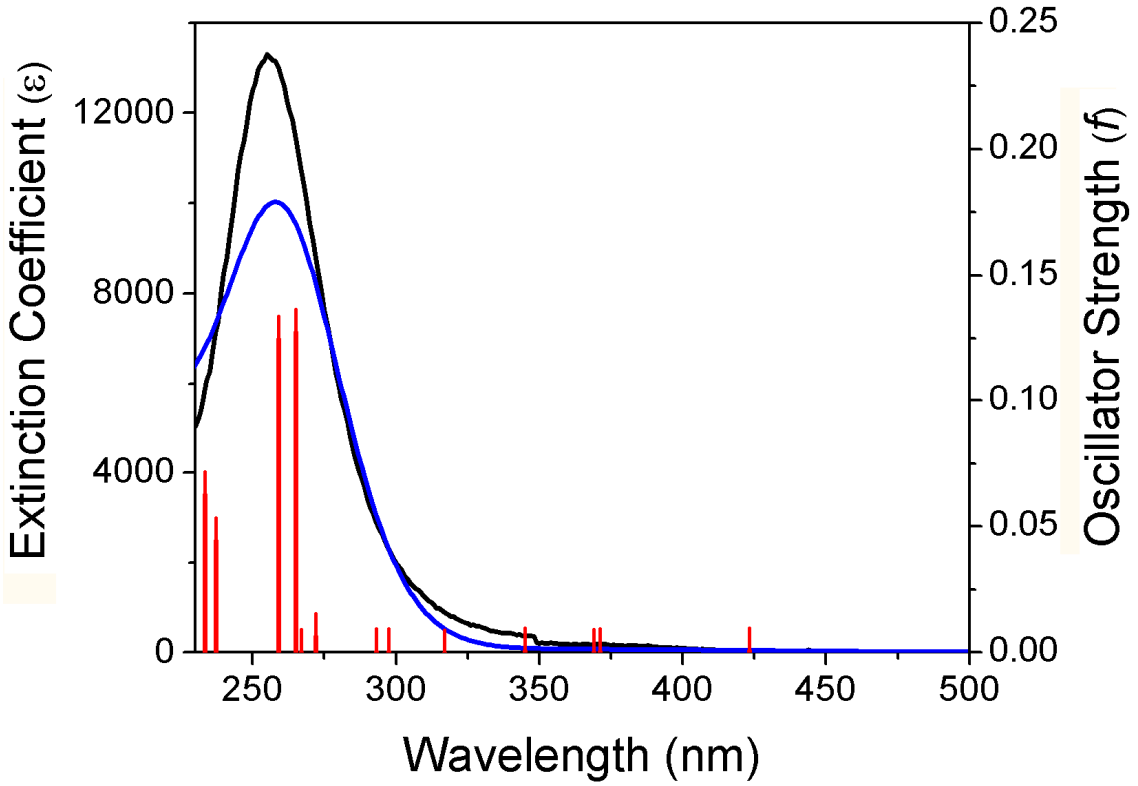


Figure S1. Calculated Orbital Energies for *cis,trans,cis*-[Pt(N_3)(OH)$_2$(NH_3)$_2$].

B3LYP/ LANL2DZ/ 6-31G**+	B3LYP/ LANL2DZ/ 6-311G**+	PBE1PBE/ LANL2DZ/ 6-31G**+	PBE1PBE/ LANL2DZ/ 6-311G**+
1	2	3	4

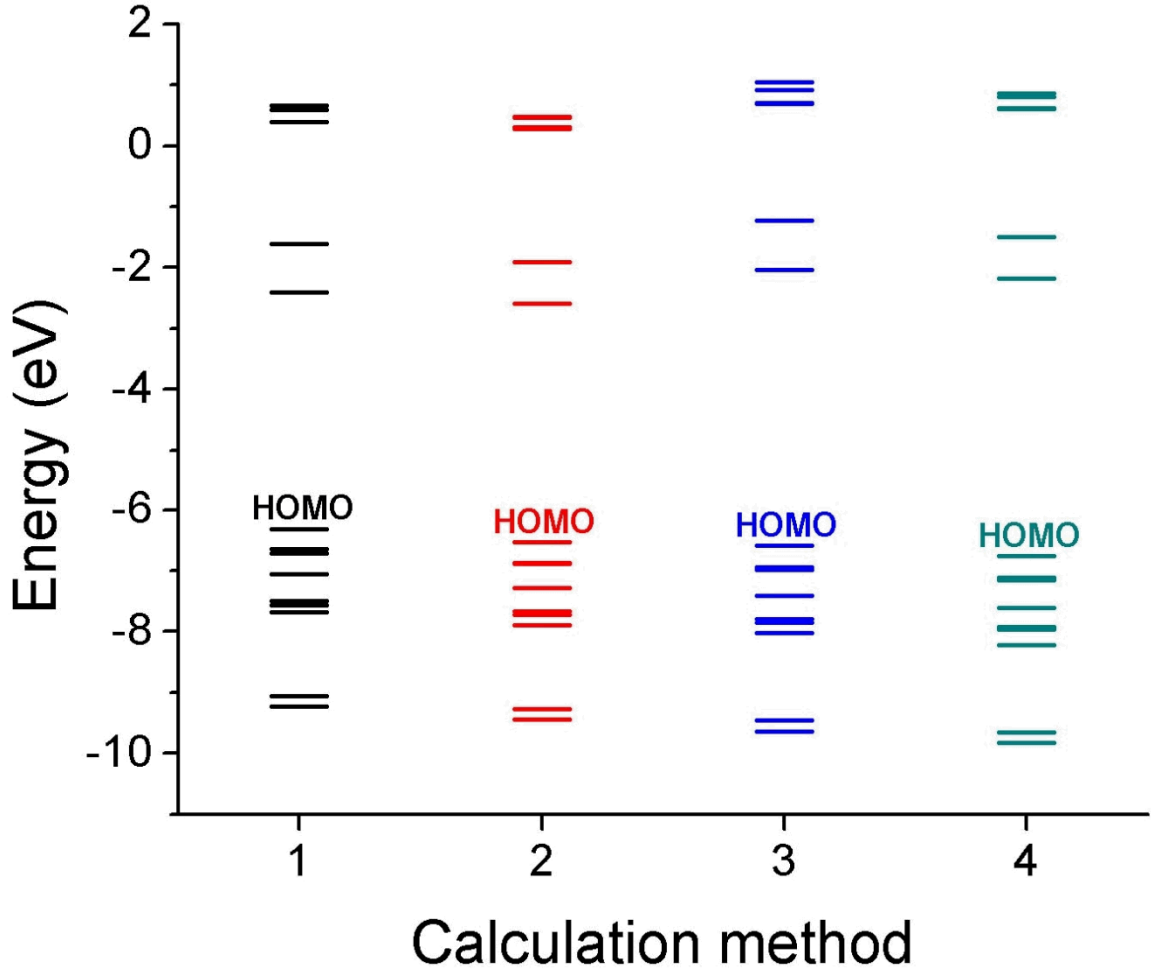


Figure S2. Calculated Orbital shapes for *cis,trans,cis*-[Pt(N$_3$)(OH)$_2$(NH$_3$)$_2$] at the PBE1PBE/LANL2DZ/6-311G+ level.**

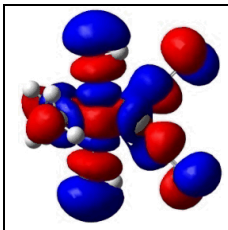
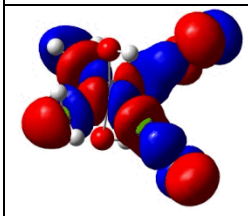
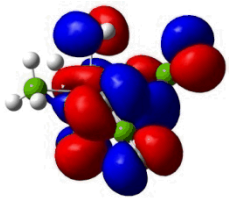
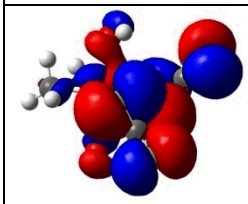
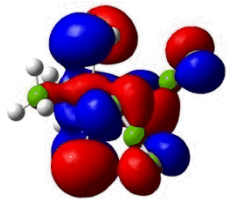
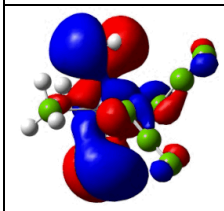
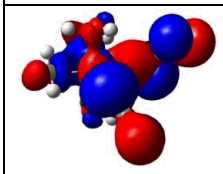
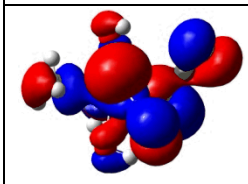
	LUMO+1
	LUMO
	HOMO
	HOMO−1
	HOMO−2
	HOMO−3
	HOMO−4
	HOMO−5

Figure S3. EDDMs of selected singlet transitions for *cis,trans,cis*-[Pt(N_3)(OH)$_2$(NH_3)$_2$] at the PBE1PBE/LANL2DZ/6-311G+ level** (electron density migrates from light blue areas to dark blue areas).

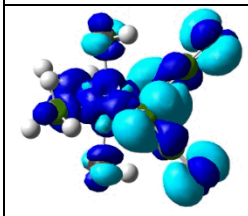
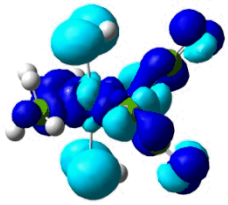
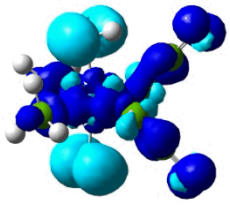
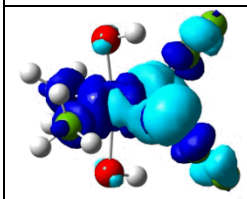
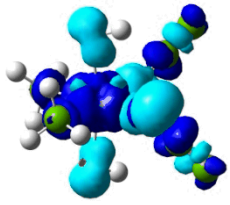
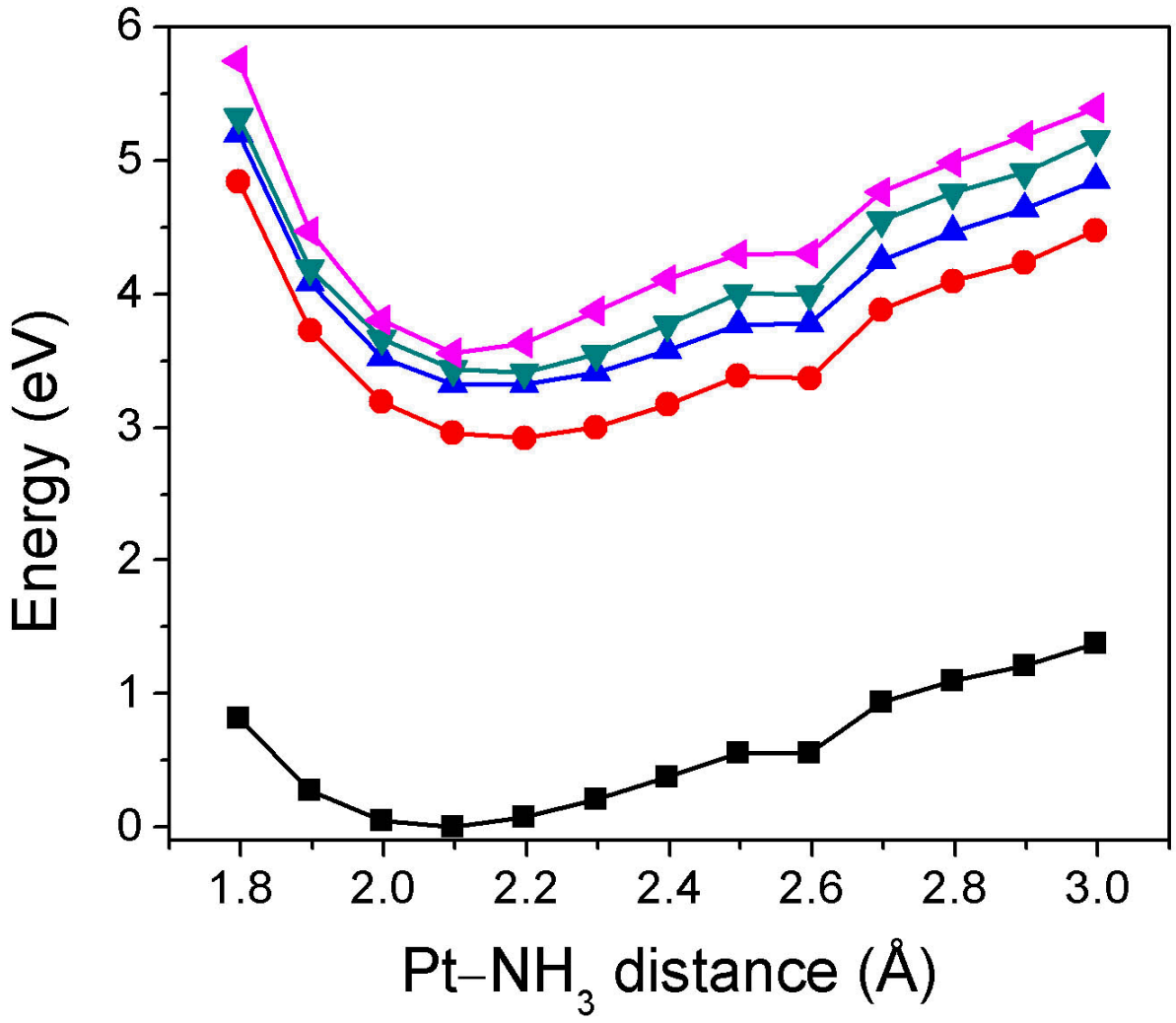
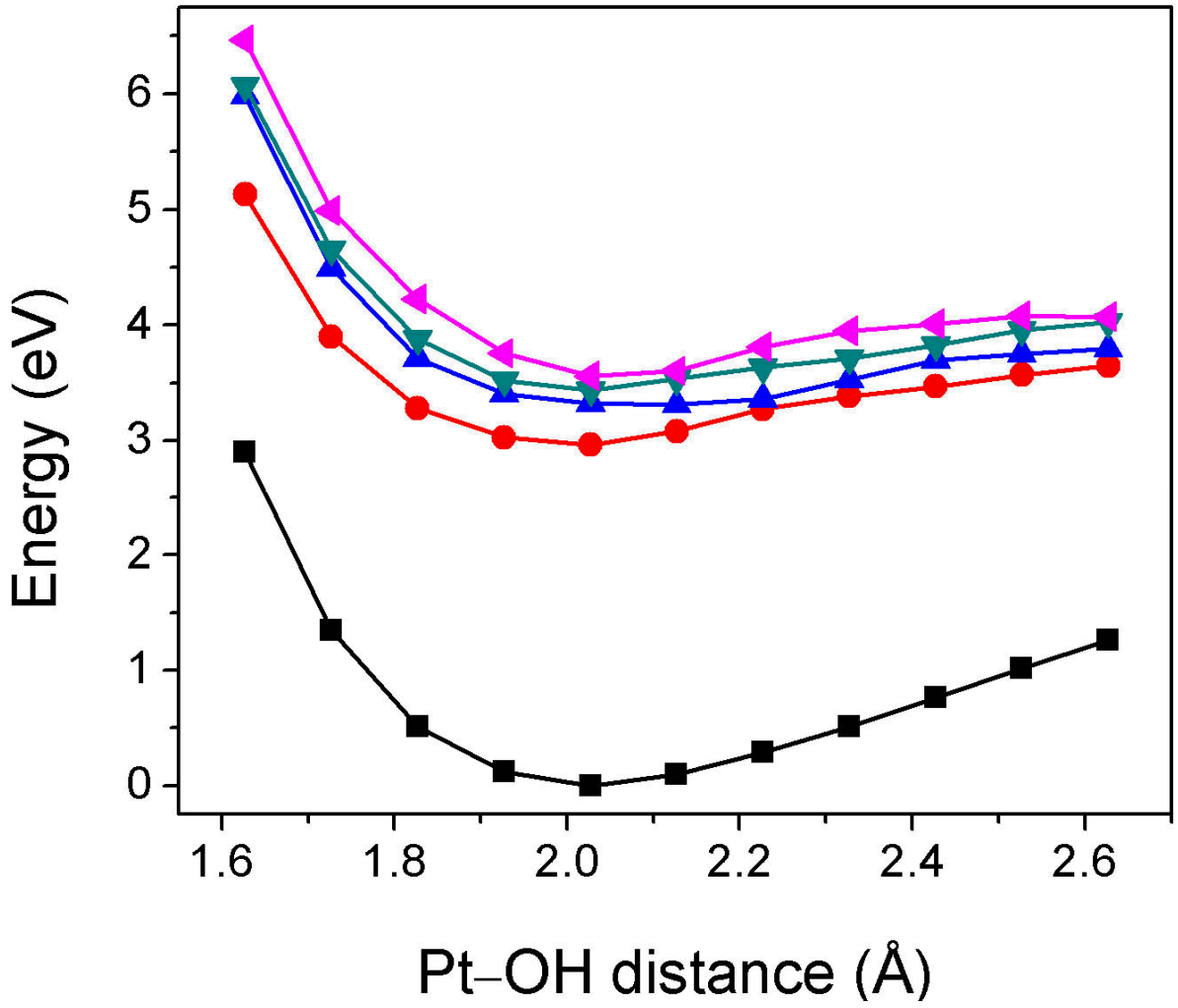
	S1
	S2
	S3
	S4
	S5
	S9
	S11

Figure S4. Potential Energy Curves along the Pt–NH_3 coordinate.



Potential energy curve for *cis,trans,cis*-[$Pt(N_3)(OH)_2(NH_3)_2$] along the Pt–NH_3 coordinate: –■– = GS, –●– = S1, –▲– = S2, –▼– = S3 and –◀– = S4.

Figure S5. Potential Energy Curves along the Pt–OH coordinate.



Potential energy curve for *cis,trans,cis*-[Pt(N_3)(OH)$_2$(NH_3)$_2$] along the Pt–OH coordinate: –■– = GS, –●– = S1, –▲– = S2, –▼– = S3 and –◀– = S4.