Electronic Supplementary Information

A tricarboxylated PtCl(terpyridine) derivative exhibiting pH-dependent photocatalytic activity for H_2 evolution from water.

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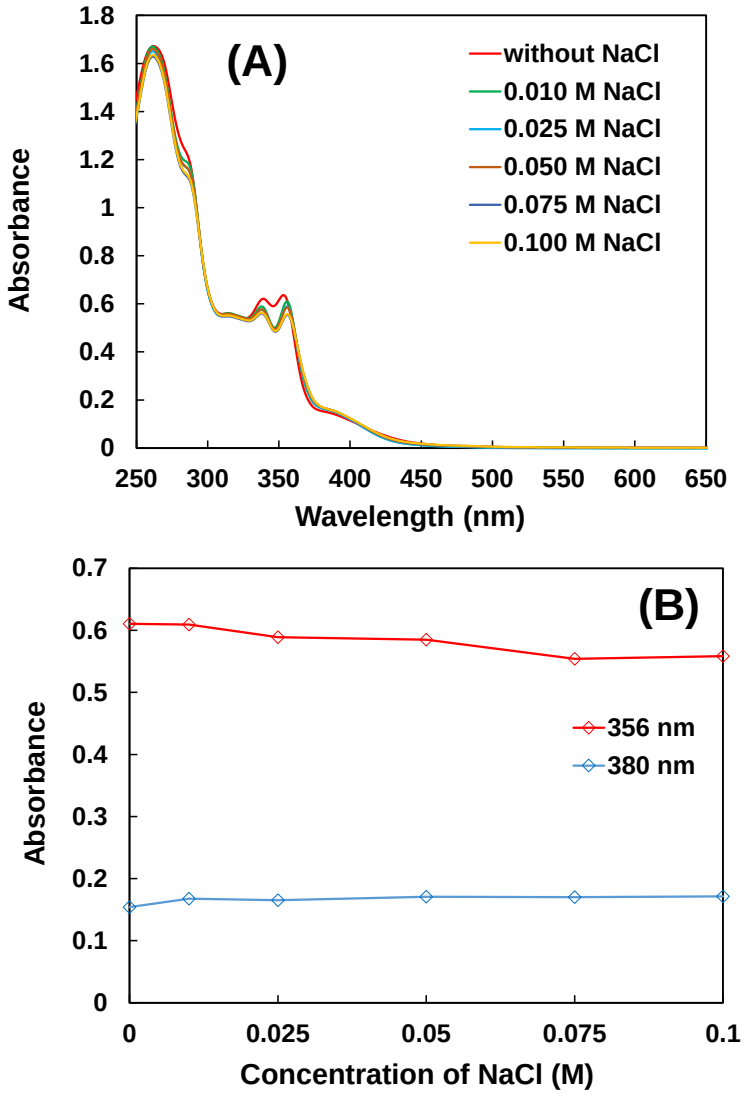

Fig. S1 (A) Absorption spectra of aqueous 0.1 mM $Na_2[PtCl(tctpy)]\bullet 5H_2O$ solutions in the presence of NaCl at various concentrations (0 - 0.1 M) at 20 °C in air, using a quartz cell having an optical path length of 5 mm. (B) Plots of absorbance at 356 and 380 nm as a function of the NaCl concentration, given from the raw data in Fig. S1A.

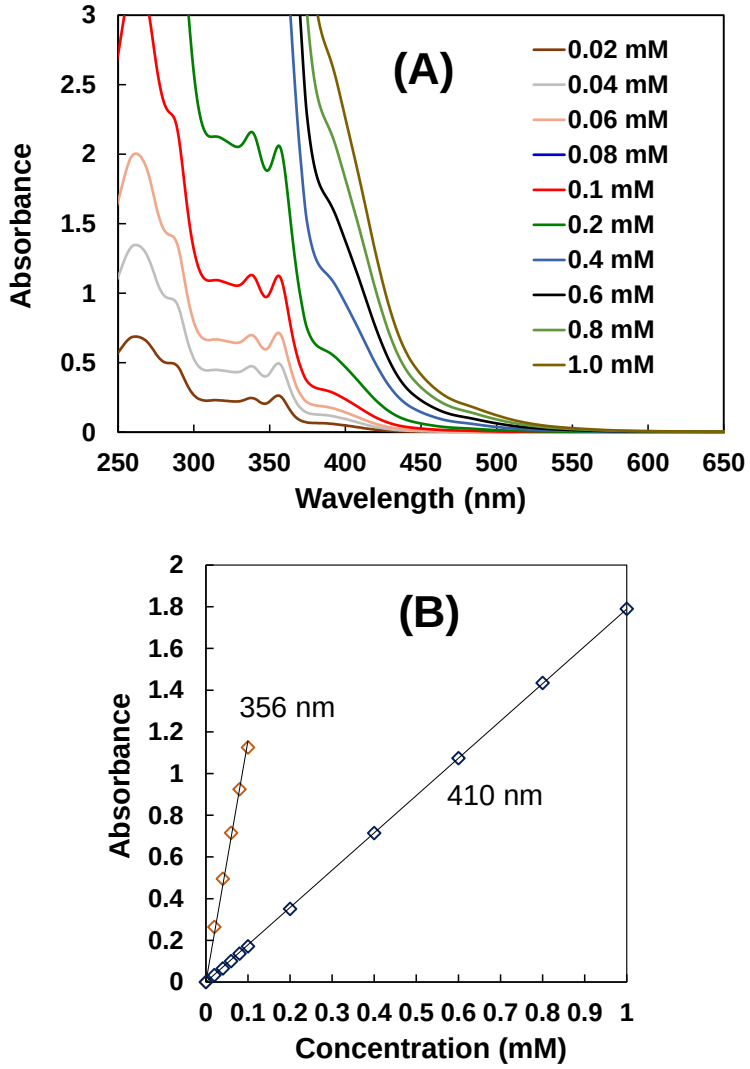

Fig. S2 (A) Concentration dependence (0.02-1.0 mM) of absorption spectra of aqueous solutions of $Na_2[PtCl(tctpy)]\bullet 5H_2O$ containing 0.1 M NaCl at 20 °C in air. (B) Plots of absorbance at 356 and 410 nm vs. the $Na_2[PtCl(tctpy)]\bullet 5H_2O$ concentration, given from the raw data in Fig. S2A.

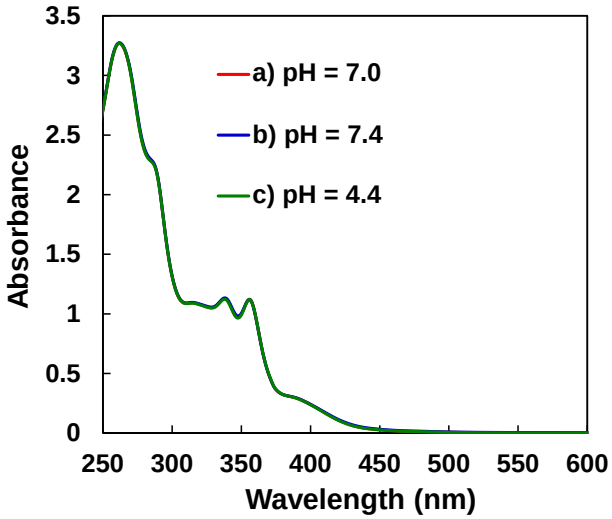

Fig. S3 UV-vis absorption spectra (at 20 °C in air) of aqeuous 0.1 mM $Na_2[PtCl(tctpy)]\bullet 5H_2O$ solutions containing 0.1 M NaCl a) in the absence of any buffer reagent (pH = 7.0), and in the presence of b) 0.1 M CH_3COONa (pH = 7.4), and c) 0.06 M CH_3COOH and 0.04 M CH_3COONa (pH = 4.4).

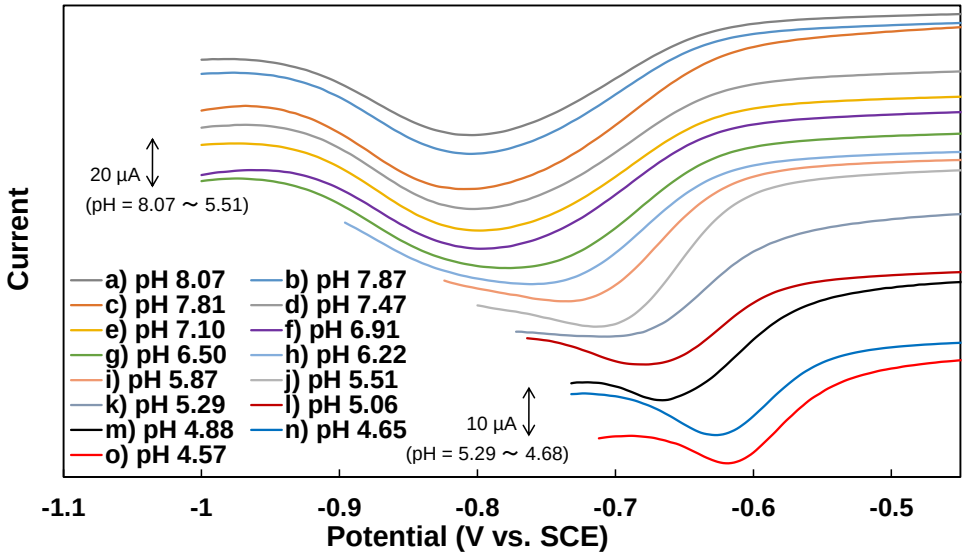

Fig. S4 a)-f) Square wave voltammograms recorded for solutions of $Na_2[PtCl(tctpy)]•5H_2O$ (0.1 mM) in aqueous HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer (10 mM) containing 0.1 M KCl at several pH conditions in the dark at room temperature. g)-j) Square wave voltammograms recorded for solutions of $Na_2[PtCl(tctpy)]•5H_2O$ (0.1 mM) in aqueous MES (2-(N-morpholino)ethanesulfonic acid) buffer (10 mM) containing 0.1 M KCl at several pH conditions in the dark at room temperature. k)-o) Square wave voltammograms recored for $Na_2[PtCl(tctpy)]•5H_2O$ (0.1 mM) in aqueous acetate buffer solutions (10 mM) containing 0.1 M KCl at several pH conditions in the dark at room temperature. All data were recorded at a scan rate of 100 mV/s under Ar.

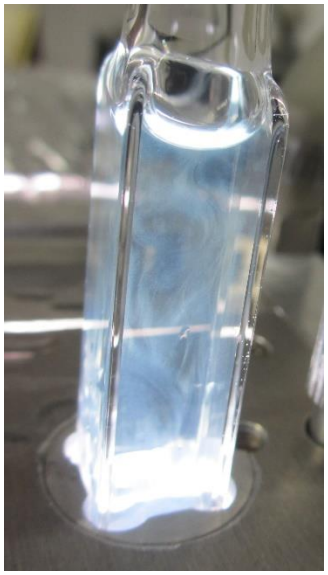

Fig. S5 A photograph showing how the deposition of $PtCl(tpy^{-}•)$ occurs during the experiment in Fig. S6A.

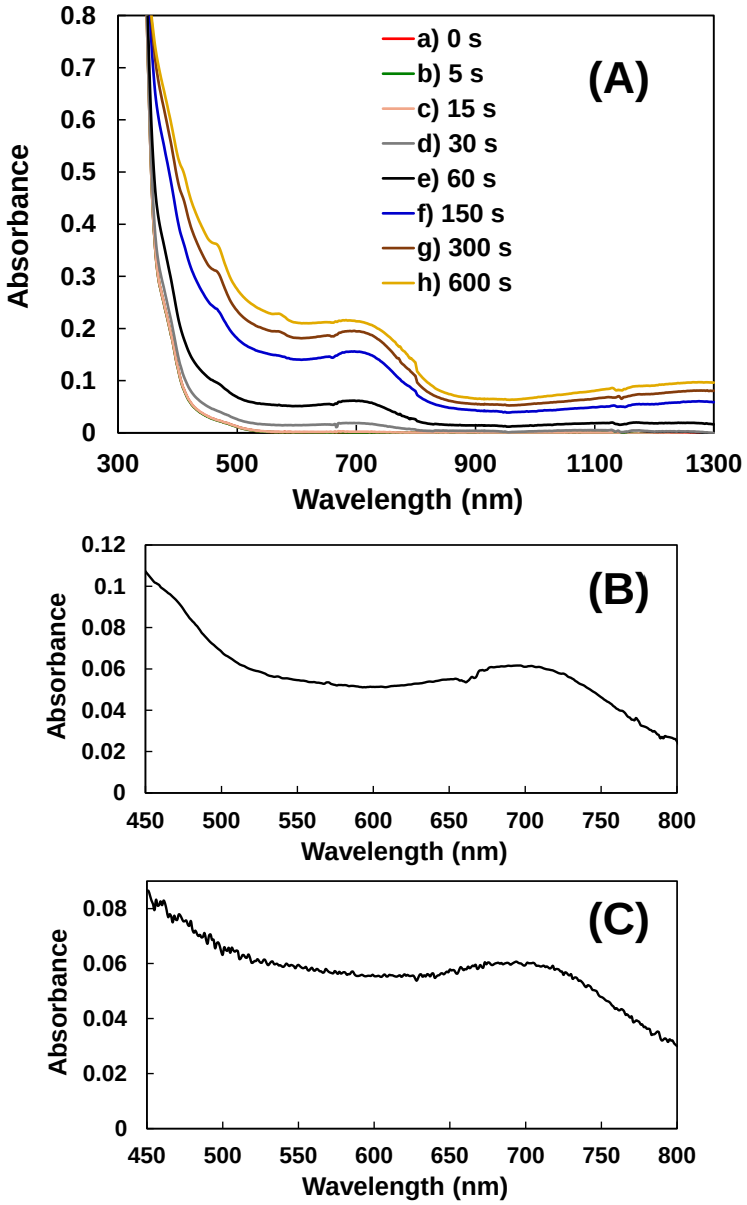

Fig. S6 (A) Spectral changes during the photolysis (300 W Xe lamp, 400-800 nm) of an aqueous acetate buffer solution (0.1 M, pH = 5.0) containing 0.1 mM [PtCl(tpy)]Cl•2H_2O, 30 mM $Na_2[YH_2]$, and 0.1 M NaCl at 20 °C under Ar atmosphere. (B) Magnification for the spectrum recorded at 60 s in Fig. S6A. (C) A UV-vis absorption spectrum observed at 60 min after mixing an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa, 0.1 M NaCl, pH 5.0; 0.25 mL) containing MV^{+}• (0.1 mM) and MV^{2+} (0.4 mM) with a solution of 0.2 mM [PtCl(tpy)]Cl•2H_2O in the same buffer solution (0.25 mL) at 20 °C under Ar atmosphere. The mixture of MV^{+}• and MV^{2+} was prepared as previously described (K. Yamauchi, S. Masaoka and K. Sakai, *J. Am. Chem. Soc.*, 2009, **131**, 8404.).

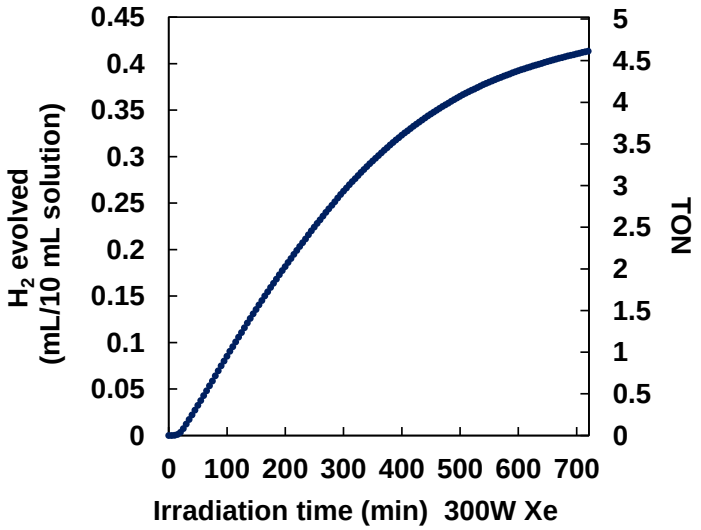

Fig. S7 Photochemical H_2 production from an aqueous 0.4 mM $Na_2[PtCl(tctpy)]\bullet 5H_2O$ solution containing 0.1 M NaCl, 15 mM $Na_2[YH_2]$, and 15 mM $Na_3[YH]$ (pH = 6.2) at 20 °C under Ar atmosphere.

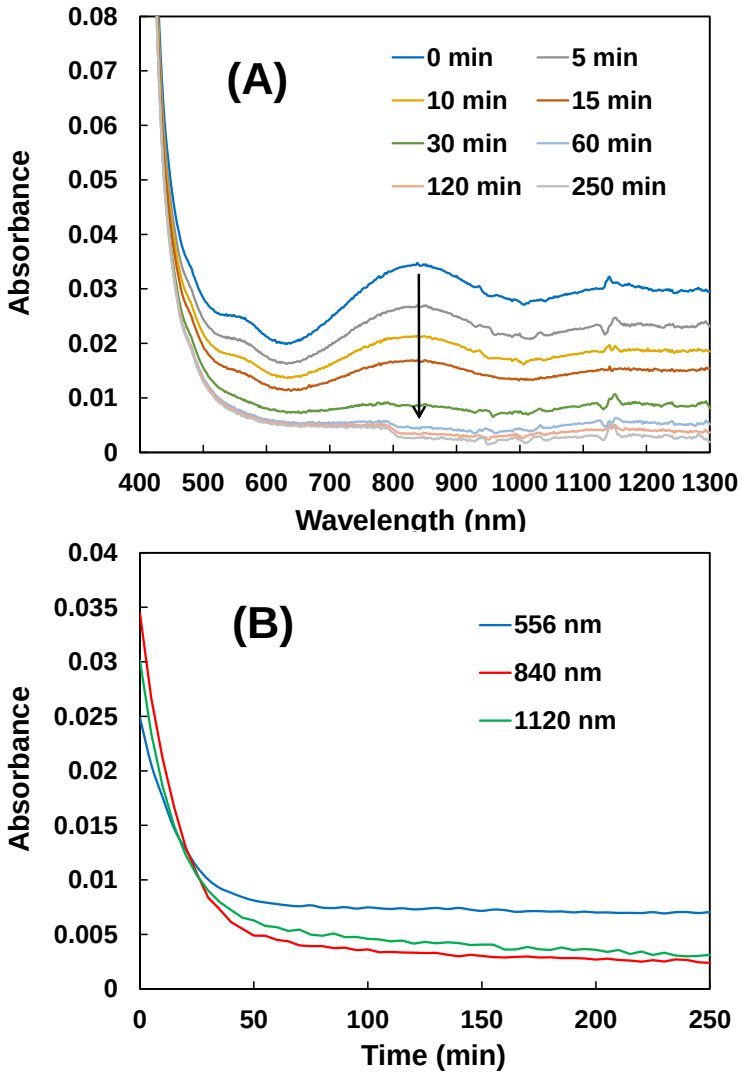

Fig. S8 (A) Spectral changes showing the dark reaction (eq. 10) of the one-electron-reduced species generated by photoirradiation of an aqueous 0.1 mM $Na_2[PtCl(tctpy)]\bullet 5H_2O$ solution containing 0.1 M NaCl, 15 mM $Na_2[YH_2]$, and 15 mM $Na_3[YH]$ (pH = 6.2) at 20 °C under Ar atmosphere. (B) Time-course of absorbance changes at 556, 840, and 1120 nm, given from the raw data in Fig. S8A.

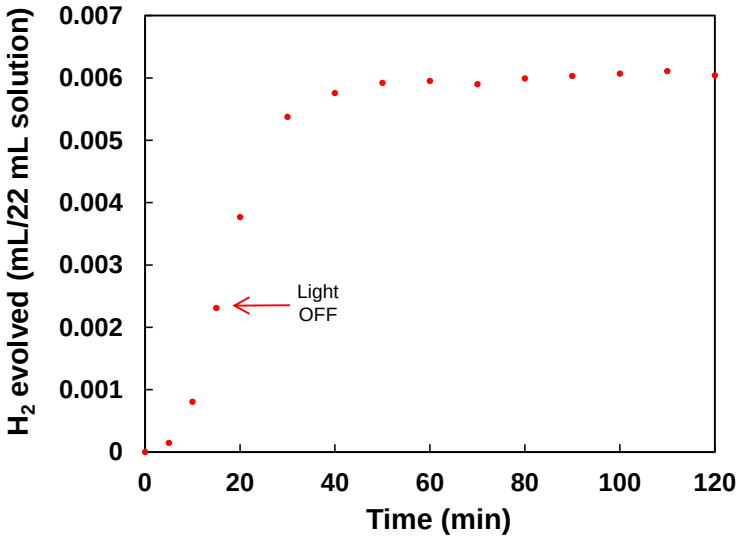

Fig. S9 Photoresponse property in H_2 production from an aqueous 0.1 mM $Na_2[PtCl(tctpy)]\bullet 5H_2O$ solution in the presence of 0.1 M NaCl, 15 mM $Na_2[YH_2]$, and 15 mM $Na_3[YH]$ (pH = 6.2) at 20 °C under Ar atmosphere. The light-off action was made at 15 min after starting photoirradiation (300 W Xe lamp, 400-800 nm). In this experiment, the photolysis was carried out for ca. 22 mL solution sealed in a vial having a total volume of ca. 30 mL under Ar at ambient pressure. Part of the gas above the solution (0.1 mL for each measurement) was manually collected by a gas-tight syringe and was injected onto a Shimadzu GC-8A gas chromatograph. The solution was bubbled with Ar for at least 30 min prior to the photolysis. The gas above the solution was ca. 8 mL, the exact volume for which was determined prior to the measurement.

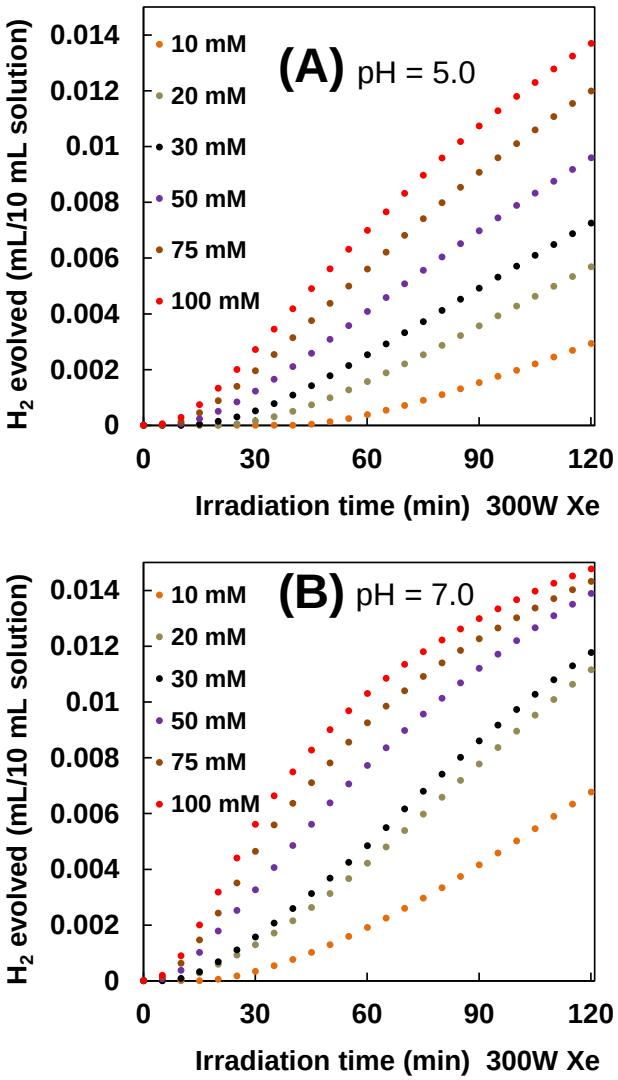

Fig. S10 (A) Photochemical H_2 production from an aqueous 0.1 mM $Na_2[PtCl(tctpy)]\bullet 5H_2O$ solution (at 20 °C under Ar atmosphere) in the presence of 0.1 M NaCl, $Na_2[YH_2]$, and $Na_3[YH]$ at pH = 5.0, with the total EDTA concentration of 10, 20, 30, 50, 75, or 100 mM. (B) Photochemical H_2 production from an aqueous 0.1 mM $Na_2[PtCl(tctpy)]\bullet 5H_2O$ solution (at 20 °C under Ar atmosphere) in the presence of 0.1 M NaCl, $Na_2[YH_2]$, and $Na_3[YH]$ at pH = 7.0 with the total EDTA concentration of 10, 20, 30, 50, 75, or 100 mM.

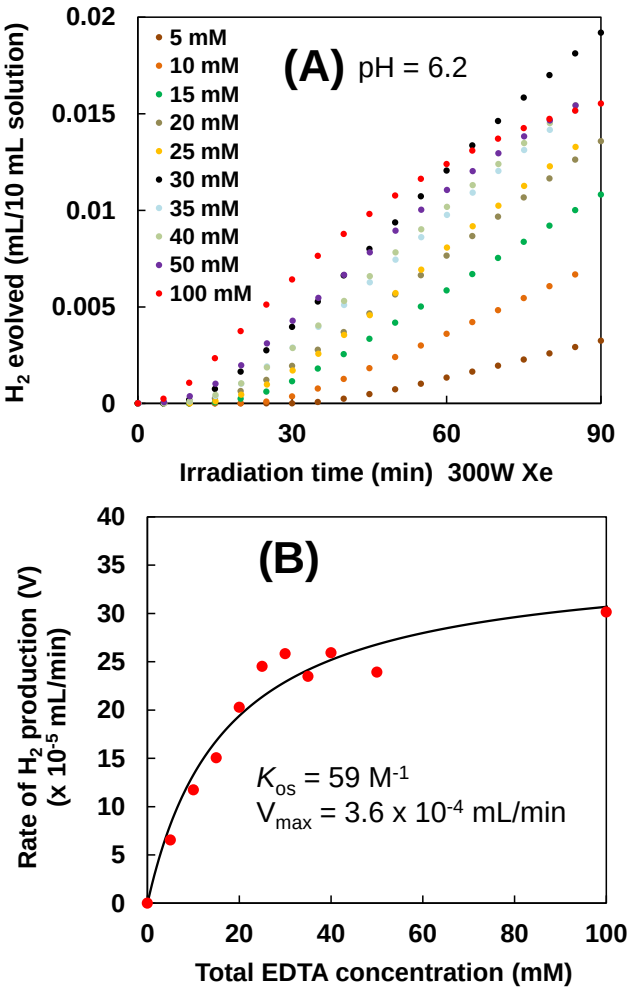

Fig. S11 (A) Photochemical H_2 production from an aqueous 0.1 mM $Na_2[PtCl(tctpy)]\bullet 5H_2O$ solution (at 20 °C under Ar atmosphere) in the presence of 0.1 M NaCl, $Na_2[YH_2]$, and $Na_3[YH]$ at pH = 6.2 with the total EDTA concentration of 5, 10, 15, 20, 25, 30, 35, 40, 50, or 100 mM. (B) The dependence of the maximum H_2 evolution rate on the EDTA concentration (0–100 mM), estimated from the data given in Fig. S11A. A Solid line is calculated one based on $V = V_{max}[EDTA]_{total} / (K_{os}^{-1} + [EDTA]_{total})$.

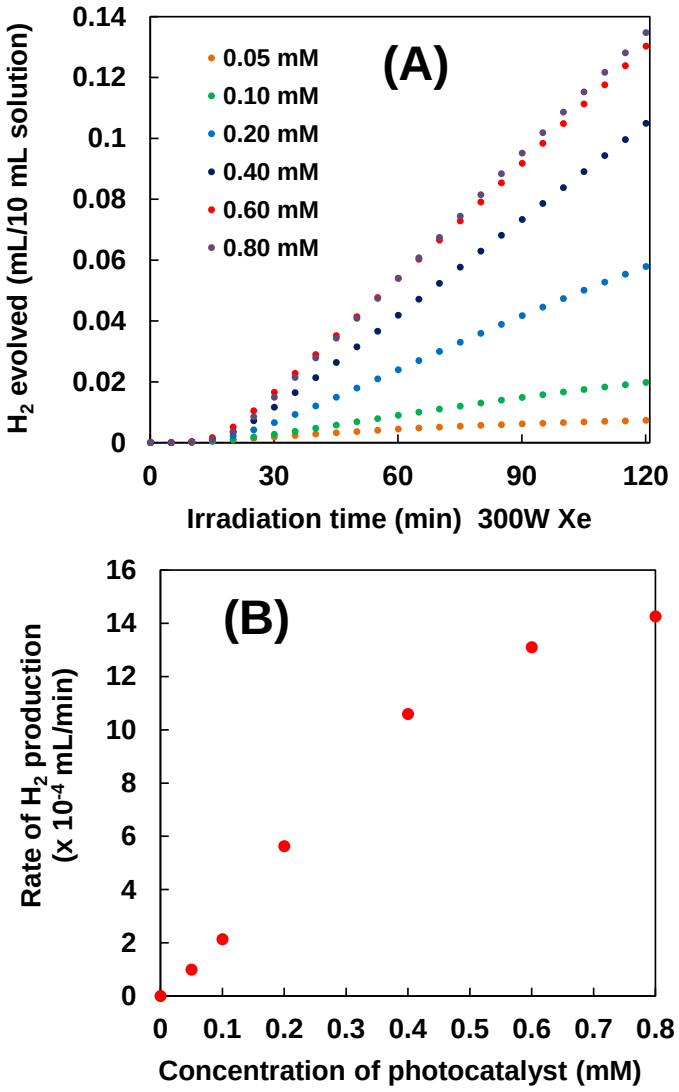

Fig. S12 (A) Photochemical H_2 production from an aqueous solution containing 0.1 M NaCl, 15 mM $Na_2[YH_2]$, and 15 mM $Na_3[YH]$ (pH = 6.2) at 20 °C under Ar atmosphere, in the presence of 0.05, 0.10, 0.20, 0.40, 0.60, or 0.80 mM $Na_2[PtCl(tctpy)]•5H_2O$. (B) The maximum rate of H_2 production, estimated from the H_2 evolution curves in Fig. S12A, is plotted vs. the concentration of $Na_2[PtCl(tctpy)]•5H_2O$.

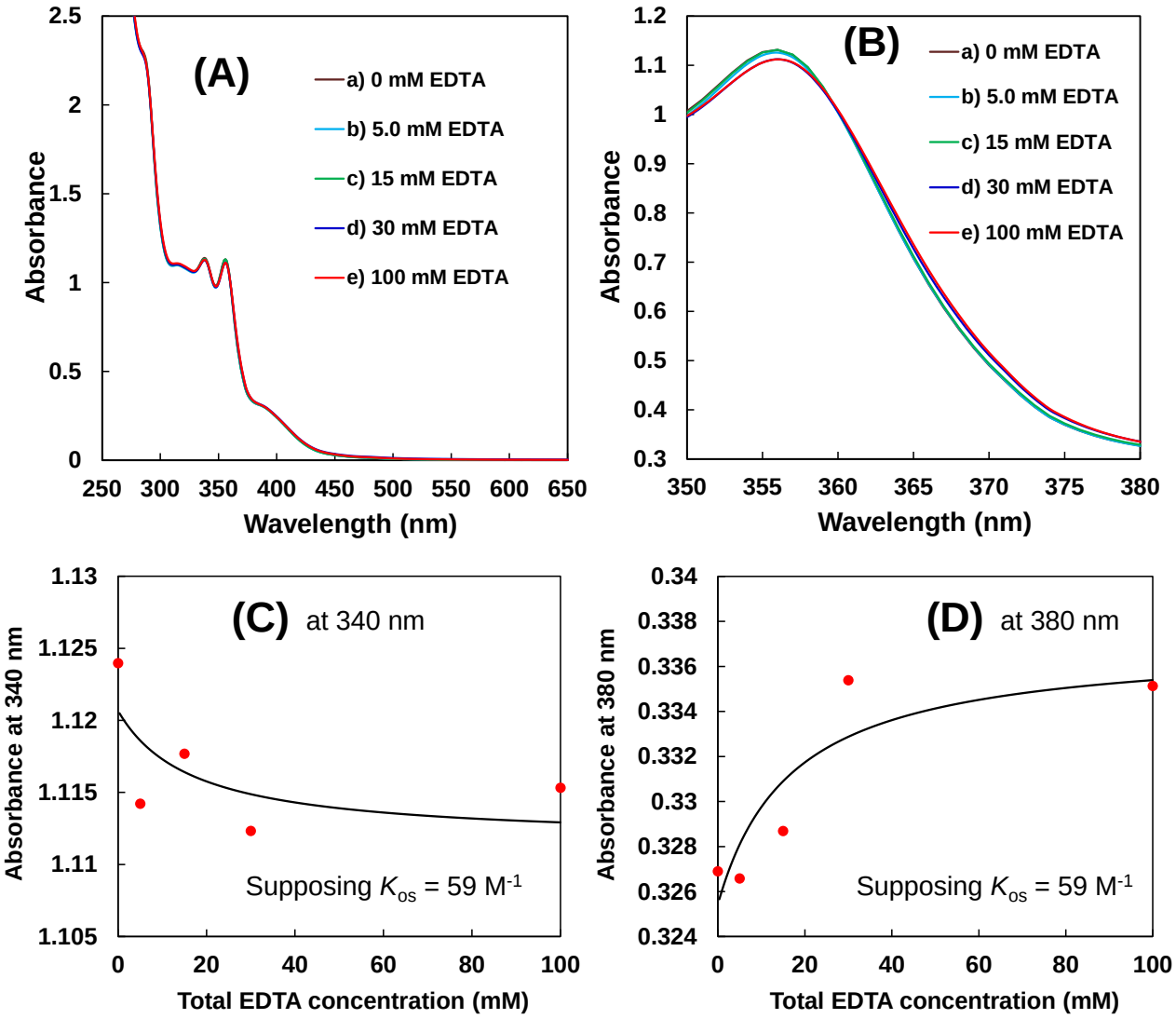

Fig. S13 (A) a) UV-vis absorption spectra of aqueous 0.1 mM $Na_2[PtCl(tctpy)]\bullet 5H_2O$ solutions (at 20 °C in air) containing 0.1 M NaCl, a) in the absence of either $Na_2[YH_2]$ or $Na_3[YH]$ (pH = 7.0), and in the presence of b) 2.5 mM $Na_2[YH_2]$ and 2.5 mM $Na_3[YH]$ (pH = 6.2), c) 7.5 mM $Na_2[YH_2]$ and 7.5 mM $Na_3[YH]$ (pH = 6.2), d) 15 mM $Na_2[YH_2]$ and 15 mM $Na_3[YH]$ (pH = 6.2), and e) 50 mM $Na_2[YH_2]$ and 50 mM $Na_3[YH]$ (pH = 6.2). (B) Magnification of Fig. S13A. (C,D) Plots of absorbance at 340 and 380 nm as a function of the EDTA concentration, given from the raw data in Fig. S13A. Solid lines are calculated ones based on $A = C_t \times (\varepsilon_{non} + \varepsilon_{add}K_{os}[EDTA]_{total})/(1 + K_{os}[EDTA]_{total})$, where C_t is the total concentration of $[PtCl(tctpy)]^{2-}$ ($C_t = 10^{-4}$ M), ε_{non} and ε_{add} are the molar absorptivities of $[PtCl(tctpy)]^{2-}$ and $\{[PtCl(tctpy)][EDTA]\}^{2-}$, respectively, and K_{os} = 59 M^{-1} determined by the fitting in Fig. S11B was adopted.

Table S1 Geometry optimized for $[PtCl(tctpy)]^{2-}$ in its singlet state. Optimized at the M06 level of DFT using the LanL2DZ basis set for Pt and the 6-31+G(d,p) basis set for H, C, N, O, and Cl.[a]

Atom	X	Y	Z
Pt1	0.000011	-1.307071	-0.000204
N2	-0.000005	0.647861	0.000062
C3	-0.000022	3.371233	-0.000274
C4	-1.188989	1.282906	-0.000027
C5	1.188971	1.28292	-0.000018
C6	1.207601	2.671262	-0.000218
C7	-1.207638	2.671249	-0.000235
H8	2.136253	3.234936	-0.000186
H9	-2.136286	3.234927	-0.000223
N10	2.03245	-0.9653	-0.000034
C11	4.691145	-0.153917	0.000313
C12	2.341015	0.367855	0.000114
C13	3.014114	-1.874323	-0.000128
C14	4.351926	-1.503155	0.00003
C15	3.660645	0.786364	0.000346
H16	2.695467	-2.913972	-0.000374
H17	5.13245	-2.257684	0.000032
H18	3.917436	1.842191	0.000566
C19	-2.341017	0.367833	0.0001
C20	-4.351914	-1.503193	-0.000002
C21	-3.660655	0.78633	0.000324
N22	-2.032437	-0.965319	-0.000051
C23	-3.014096	-1.874341	-0.00015
C24	-4.691155	-0.153958	0.000281
H25	-3.917462	1.84215	0.000546
H26	-2.695438	-2.913988	-0.000398
H27	-5.132426	-2.257732	-0.000005
Cl28	0.000082	-3.699439	-0.000229
C29	-6.157079	0.297346	0.000485
C30	-0.000036	4.906722	-0.000264
C31	6.15705	0.297407	0.000529
O32	6.344771	1.536449	0.000399
O33	7.00855	-0.620871	0.000671
O34	1.128343	5.450201	-0.000247
O35	-1.128427	5.450174	-0.00043
O36	-6.344847	1.536378	0.000471
O37	-7.00858	-0.620928	0.00073

[a]Part of the Gaussian output file:

SCF Done: E(RM06) = -1885.37462786 A.U. after 10 cycles

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	A	A	A
Frequencies --	24.5484	32.7281	44.2665
Red. masses --	15.2120	15.7365	14.3315

Zero-point correction= 0.237633 (Hartree/Particle)
Thermal correction to Energy= 0.261667
Thermal correction to Enthalpy= 0.262611
Thermal correction to Gibbs Free Energy= 0.180824
Sum of electronic and zero-point Energies= -1885.136995
Sum of electronic and thermal Energies= -1885.112961
Sum of electronic and thermal Enthalpies= -1885.112017
Sum of electronic and thermal Free Energies= -1885.193804

Item	Value	Threshold	Converged?
Maximum Force	0.000055	0.000450	YES
RMS Force	0.000012	0.000300	YES

Table S2 Comparison of the geometrical parameters (bond lengths in Å and angles in degree) of $[PtCl(tctpy)]^{2-}$ and $[PtCl(tpy)]^{+}$.

	$[PtCl(tctpy)]^{2-}$	$[PtCl(tpy)]^{+}$
Pt1-N10	2.053	2.061
Pt1-N2	1.943	1.957
Pt1-N22	2.053	2.061
Pt1-Cl28	2.420	2.388
N10-Pt1-N2	80.45	80.49
N2-Pt1-N22	80.45	80.49
N22-Pt1-Cl28	99.54	99.50
N10-Pt1-Cl28	99.54	99.50

Table S3 Geometry optimized for $[PtCl(tpy)]^+$ (2,2';6',2"-terpyridine) in its singlet state. Optimized at the M06 level of DFT using the LanL2DZ basis set for Pt and the 6-31+G(d,p) basis set for H, C, N, O, and Cl.[a]

Atom	X	Y	Z
Pt1	0.000001	-0.704617	0.000031
N2	-0.000002	1.25208	0.000025
C3	0.000004	3.960149	0.000111
C4	-1.189979	1.88399	0.000016
C5	1.189977	1.883987	0.000017
C6	1.211803	3.273923	0.000069
C7	-1.211799	3.273927	0.000068
H8	2.150389	3.818571	0.000067
H9	-2.150382	3.818579	0.000065
N10	2.033	-0.364259	0.000013
C11	4.678923	0.434471	-0.000156
C12	2.341335	0.967813	-0.000019
C13	3.008244	-1.278552	-0.000025
C14	4.349419	-0.91394	-0.000109
C15	3.662697	1.38609	-0.000106
H16	2.685135	-2.316623	-0.000008
H17	5.112735	-1.684659	-0.000114
H18	3.900983	2.444945	-0.00013
C19	-2.341338	0.967818	-0.000019
C20	-4.349419	-0.913941	-0.000109
C21	-3.662701	1.386092	-0.000105
N22	-2.033003	-0.364254	0.000012
C23	-3.008243	-1.278549	-0.000027
C24	-4.678925	0.43447	-0.000155
H25	-3.900991	2.444945	-0.000127
H26	-2.685131	-2.31662	-0.000011
H27	-5.112734	-1.684662	-0.000114
Cl28	-0.000003	-3.092968	0.000072
H29	0.000007	5.04554	0.000177
H30	-5.717913	0.749571	-0.000245
H31	5.717909	0.749576	-0.000247

[a]Part of the Gaussian output file:

SCF Done: E(RM06) = -1321.21763728 A.U. after 9 cycles

	1	2	3
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Red. masses --	6.0014	13.2495	4.0667

Zero-point correction= 0.231812 (Hartree/Particle)
Thermal correction to Energy= 0.247544
Thermal correction to Enthalpy= 0.248488
Thermal correction to Gibbs Free Energy= 0.187957
Sum of electronic and zero-point Energies= -1320.985825
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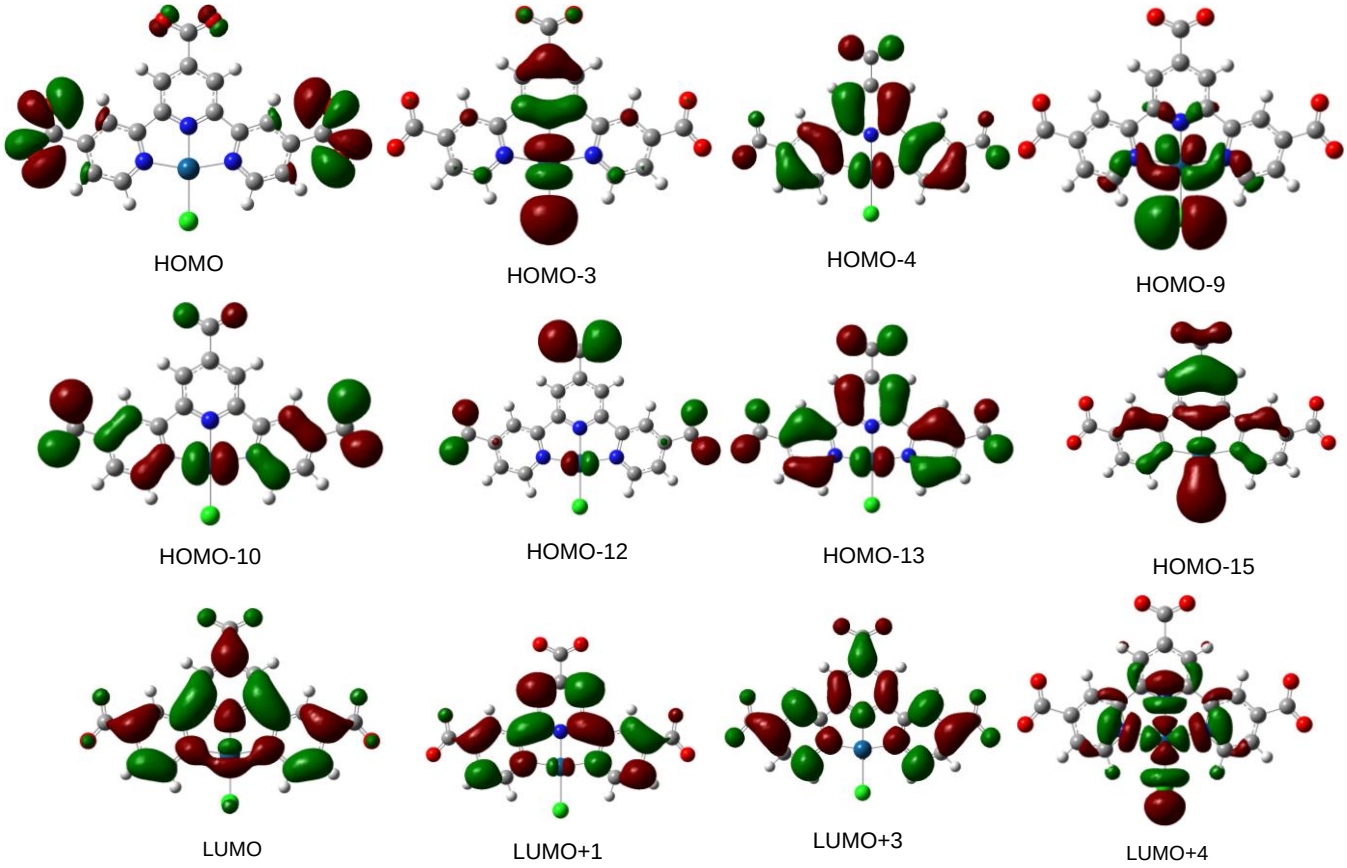
Sum of electronic and thermal Enthalpies= -1320.969149
Sum of electronic and thermal Free Energies= -1321.029680

Item	Value	Threshold	Converged?
Maximum Force	0.000016	0.000450	YES
RMS Force	0.000004	0.000300	YES

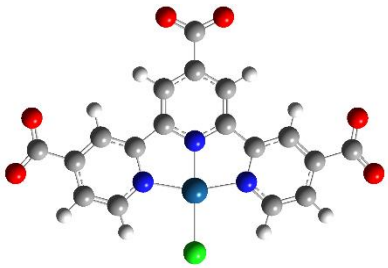
Table S4 Electronic transitions for water-solvated $[PtCl(tctpy)]^{2-}$ (singlet) calculated by the TD-DFT method, using the optimized geometry in Table S1. To minimize publication materials, only the selected transitions (f > 0.01 and |CI coef| > 0.3) above λ = 250 nm are summarized in this Table.

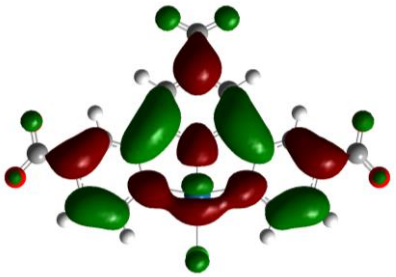


Excited State	E (cm^{-1})	λ (nm)	f[a] (> 0.01)	Major contributions	|CI coef| (> 0.3)
2	25908	385.98	0.0404	HOMO-3 -> LUMO	0.67069
13	29365	340.54	0.0191	HOMO-3 -> LUMO+1	0.59011
14	30081	332.44	0.2076	HOMO-10 -> LUMO	0.3837
				HOMO-9 -> LUMO+4	0.39648
17	30739	325.32	0.1958	HOMO-9 -> LUMO+4	0.5309
19	31698	315.48	0.022	HOMO-12 -> LUMO	0.65572
24	32332	309.29	0.1216	HOMO-13 -> LUMO	0.59181
				HOMO-10 -> LUMO	0.30487
25	32659	306.19	0.0979	HOMO-4 -> LUMO+1	0.5937
31	34393	290.76	0.0762	HOMO-12 -> LUMO+1	0.4665
				HOMO-10 -> LUMO+1	0.41379
34	35548	281.31	0.0263	HOMO-13 -> LUMO+1	0.38778
				HOMO-12 -> LUMO+1	0.45028
39	37139	269.26	0.2096	HOMO-13 -> LUMO+1	0.34269
				HOMO-3 -> LUMO+3	0.47873
42	37796	264.58	0.0247	HOMO-14 -> LUMO	0.5056
				HOMO-13 -> LUMO+1	0.36623
43	38241	261.5	0.4631	HOMO-4 -> LUMO+3	0.63104
53	39730	251.7	0.1329	HOMO-15 -> LUMO	0.624

[a]Oscillator strength.

Table S5 Geometry optimized for $[PtCl(tctpy^{-}\bullet)]^{3-}$ (Fig. 10A) in its doublet state. Optimized at the UM06 level of DFT using the LanL2DZ basis set for Pt and the 6-31+G(d,p) basis set for H, C, N, O, and Cl.[a]





SOMO

Atom	X	Y	Z	Mulliken spin density
Pt1	0.000001	1.303603	0.000062	0.026959
N2	0.000002	-0.639860	0.000008	0.174009
C3	0.000001	-3.382430	-0.000187	0.159684
C4	1.208026	-1.287717	-0.000053	0.109161
C5	-1.208025	-1.287716	-0.000033	0.109162
C6	-1.212219	-2.672549	-0.000128	-0.055487
C7	1.212224	-2.672548	-0.000146	-0.055484
H8	-2.142316	-3.235037	-0.000170	0.002783
H9	2.142321	-3.235036	-0.000202	0.002783
N10	-2.024092	0.960905	0.000076	0.067422
C11	-4.699694	0.147836	0.000082	0.068804
C12	-2.340352	-0.384514	0.000021	0.065263
C13	-3.019606	1.872165	0.000139	0.014713
C14	-4.349465	1.511254	0.000140	0.057878
C15	-3.677861	-0.786930	0.000027	-0.017064
H16	-2.698223	2.911545	0.000182	-0.001252
H17	-5.126299	2.269547	0.000184	-0.002293
H18	-3.934873	-1.843433	-0.000010	0.000736
C19	2.340355	-0.384513	-0.000021	0.06526
C20	4.349467	1.511254	0.000055	0.057877
C21	3.677862	-0.786931	-0.000041	-0.017063
N22	2.024094	0.960904	0.000035	0.06742
C23	3.019607	1.872165	0.000073	0.014713
C24	4.699693	0.147839	-0.000004	0.068803
H25	3.934875	-1.843433	-0.000085	0.000736
H26	2.698224	2.911544	0.000118	-0.001252
H27	5.126302	2.269547	0.000088	-0.002293
Cl28	-0.000005	3.723952	0.000106	0.001066
C29	6.160758	-0.289998	-0.000031	-0.004834
C30	0.000002	-4.901252	-0.000316	-0.01344
C31	-6.160761	-0.290001	0.000069	-0.004835
O32	-6.374992	-1.528419	-0.000100	0.007791
O33	-7.013922	0.632291	0.000236	0.001937
O34	-1.125721	-5.465102	-0.000364	0.010306
O35	1.125727	-5.465100	-0.000366	0.010306
O36	6.374983	-1.528417	-0.000104	0.007791

O37	7.013914	0.632296	0.000018	0.001937

[a]Part of the Gaussian output file:

SCF Done: E(UM06) = -1885.49784299 A.U. after 11 cycles

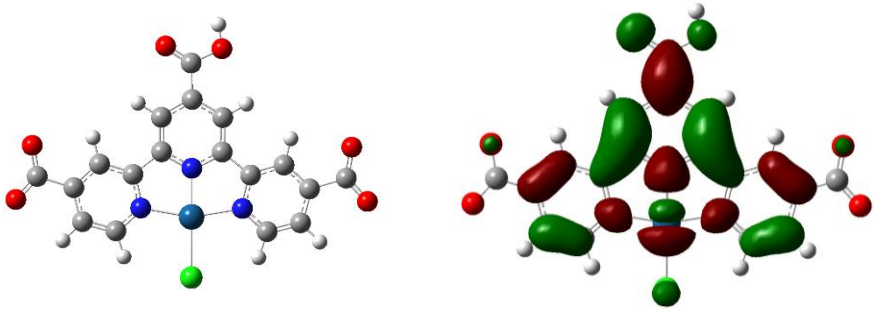
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7613, after 0.7501

	1	2	3
	A	A	A
Frequencies --	25.1947	32.0362	45.1544
Red. masses --	15.3238	15.6397	13.3465

Zero-point correction= 0.234034 (Hartree/Particle)
Thermal correction to Energy= 0.258401
Thermal correction to Enthalpy= 0.259345
Thermal correction to Gibbs Free Energy= 0.176380
Sum of electronic and zero-point Energies= -1885.263809
Sum of electronic and thermal Energies= -1885.239442
Sum of electronic and thermal Enthalpies= -1885.238498
Sum of electronic and thermal Free Energies= -1885.321463

Item	Value	Threshold	Converged?
Maximum Force	0.000017	0.000450	YES
RMS Force	0.000003	0.000300	YES

Table S6 Geometry optimized for $[PtCl(tctpyH^{-}\bullet)]^{2-}$ (Fig. 10B) in its doublet state. Optimized at the UM06 level of DFT using the LanL2DZ basis set for Pt and the 6-31+G(d,p) basis set for H, C, N, O, and Cl.[a]



SOMO

Atom	X	Y	Z	Mulliken spin density
Pt1	-0.012871	-1.320893	-0.000351	0.020451
N2	-0.002341	0.621451	-0.001396	0.185986
C3	0.012507	3.360414	0.000071	0.15816
C4	-1.207456	1.278955	-0.000409	0.060541
C5	1.209298	1.266089	-0.000418	0.104069
C6	1.232934	2.642679	0.000148	0.020172
C7	-1.214648	2.654207	0.000133	0.056638
H8	2.176446	3.179599	0.000887	0.000309
H9	-2.145359	3.214823	0.000820	-0.00072
N10	2.017494	-0.986056	-0.000054	0.035002
C11	4.692214	-0.202319	0.000247	0.021093
C12	2.341291	0.350303	-0.000201	0.026401
C13	2.998311	-1.907278	0.000344	-0.003186
C14	4.334216	-1.556823	0.000528	0.056053
C15	3.678165	0.744332	-0.000143	0.006998
H16	2.665938	-2.942969	0.000514	-0.000282
H17	5.105472	-2.320731	0.000933	-0.002219
H18	3.946998	1.797492	-0.000357	-0.000026
C19	-2.349261	0.374773	-0.000198	0.029291
C20	-4.363274	-1.509172	0.000525	0.042171
C21	-3.681147	0.784354	-0.000184	-0.002773
N22	-2.040102	-0.964754	-0.000036	0.028863
C23	-3.031318	-1.874832	0.000358	0.003027
C24	-4.705976	-0.150895	0.000215	0.024377
H25	-3.937694	1.840625	-0.000448	0.00045
H26	-2.710972	-2.914275	0.000546	-0.000495
H27	-5.142771	-2.264652	0.000954	-0.001688
Cl28	-0.023804	-3.735882	0.000452	0.002452
C29	-6.169391	0.294455	0.000282	-0.001618
C30	-0.026936	4.815476	0.000095	0.051731
C31	6.160863	0.225617	0.000332	-0.002091
O32	6.378118	1.461846	-0.000412	0.004367
O33	7.002962	-0.704314	0.000947	0.000407

O34	-1.047401	5.493522	0.000536	0.063187
O35	1.197452	5.386387	0.000278	0.007534
H36	1.067542	6.347513	0.000521	-0.00083
O37	-6.371338	1.533301	-0.000413	0.004867
O38	-7.022884	-0.625026	0.000985	0.00133

[a]Part of the Gaussian output file:

SCF Done: E(UM06) = -1885.96246847 A.U. after 11 cycles

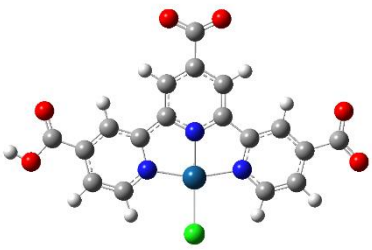
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7577, after 0.7500

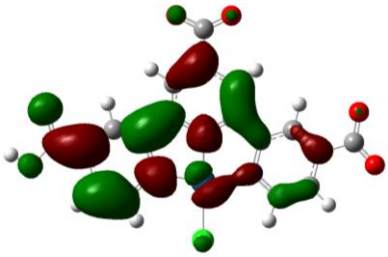
	1	2	3
	A	A	A
Frequencies --	24.9169	43.2143	46.1730
Red. masses --	14.8061	13.7905	13.3106

Zero-point correction= 0.247671 (Hartree/Particle)
Thermal correction to Energy= 0.272133
Thermal correction to Enthalpy= 0.273077
Thermal correction to Gibbs Free Energy= 0.190537
Sum of electronic and zero-point Energies= -1885.714798
Sum of electronic and thermal Energies= -1885.690335
Sum of electronic and thermal Enthalpies= -1885.689391
Sum of electronic and thermal Free Energies= -1885.771932

Item	Value	Threshold	Converged?
Maximum Force	0.000138	0.000450	YES
RMS Force	0.000028	0.000300	YES

Table S7 Geometry optimized for $[PtCl(tctpyH^{-}\bullet)]^{2-}$ (Fig. 10C) in its doublet state. Optimized at the UM06 level of DFT using the LanL2DZ basis set for Pt and the 6-31+G(d,p) basis set for H, C, N, O, and Cl.[a]





SOMO

Atom	X	Y	Z	Mulliken spin density
Pt1	0.017106	-1.304397	0.000010	0.014664
N2	0.027667	0.646488	-0.000014	0.088853
C3	0.034526	3.377841	0.000031	0.063982
C4	-1.173810	1.286524	0.000031	0.055442
C5	1.225862	1.285986	-0.000013	0.027173
C6	1.250798	2.666118	0.000007	0.022174
C7	-1.168913	2.685217	0.000061	-0.032393
H8	2.182121	3.224791	0.000015	-0.000349
H9	-2.094747	3.254608	0.000113	0.00207
N10	2.054091	-0.965089	0.000013	0.012944
C11	4.722111	-0.161742	-0.000049	0.033211
C12	2.369873	0.368704	-0.000023	0.030969
C13	3.039249	-1.877403	-0.000009	0.014397
C14	4.375090	-1.514047	-0.000026	0.015353
C15	3.696776	0.778793	-0.000069	-0.010343
H16	2.716499	-2.916106	0.000002	-0.000892
H17	5.152436	-2.271963	-0.000008	-0.000644
H18	3.955083	1.834421	-0.000107	0.000621
C19	-2.304851	0.391498	0.000077	0.141998
C20	-4.327238	-1.511419	0.000123	0.1898
C21	-3.629123	0.804676	-0.000019	-0.056526
N22	-1.992889	-0.973126	0.000175	0.141809
C23	-3.004864	-1.874858	0.000192	0.004743
C24	-4.664797	-0.125252	0.000007	0.130061
H25	-3.870864	1.865075	-0.000103	0.00316
H26	-2.696323	-2.917908	0.000295	-0.00174
H27	-5.098025	-2.274729	0.000169	-0.006855
Cl28	0.016147	-3.712299	-0.000074	0.002164
C29	-6.039796	0.359334	-0.000119	0.044599
C30	0.043531	4.906328	0.000040	-0.007331
C31	6.187802	0.279965	-0.000044	-0.001798
O32	6.389568	1.518141	-0.000163	0.003959
O33	7.037381	-0.642236	0.000076	0.001623

O34	1.174778	5.451516	0.000147	0.004421
O35	-1.078318	5.470157	-0.000031	0.007834
O36	-6.379024	1.535911	-0.000282	0.057956
O37	-6.949534	-0.637638	-0.000016	0.003502
H38	-7.829197	-0.228404	-0.000122	-0.000612

[a]Part of the Gaussian output file:

SCF Done: E(UM06) = -1885.96056781 A.U. after 11 cycles

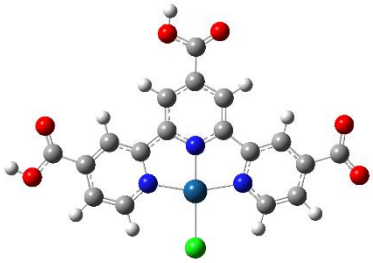
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7592, after 0.7501

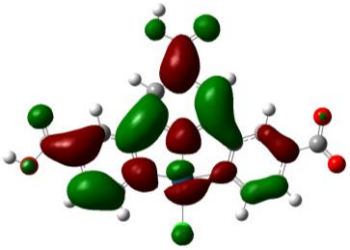
	1	2	3
	A	A	A
Frequencies --	23.1118	31.5739	41.1872
Red. masses --	12.6447	15.6594	10.0645

Zero-point correction= 0.247333 (Hartree/Particle)
Thermal correction to Energy= 0.271904
Thermal correction to Enthalpy= 0.272848
Thermal correction to Gibbs Free Energy= 0.189461
Sum of electronic and zero-point Energies= -1885.713235
Sum of electronic and thermal Energies= -1885.688664
Sum of electronic and thermal Enthalpies= -1885.687720
Sum of electronic and thermal Free Energies= -1885.771107

Item	Value	Threshold	Converged?
Maximum Force	0.000057	0.000450	YES
RMS Force	0.000006	0.000300	YES

Table S8 Geometry optimized for [PtCl(tctpyH$_2^{-}$•)]$^{-}$ (Fig. 10D) in its doublet state. Optimized at the UM06 level of DFT using the LanL2DZ basis set for Pt and the 6-31+G(d,p) basis set for H, C, N, O, and Cl.[a]





SOMO

Atom	X	Y	Z	Mulliken spin density
Pt1	0.032484	-1.317612	-0.000040	0.021114
N2	0.033848	0.627572	0.000055	0.156977
C3	0.018651	3.354300	-0.000054	0.117646
C4	-1.179036	1.265866	0.000035	0.109467
C5	1.232804	1.277678	-0.000023	0.023643
C6	1.250744	2.652312	-0.000092	0.092352
C7	-1.191745	2.655217	0.000009	-0.03345
H8	2.180860	3.212441	-0.000183	-0.002575
H9	-2.130903	3.200170	0.000023	0.002468
N10	2.063815	-0.969518	-0.000047	0.012301
C11	4.730319	-0.163761	0.000085	0.023602
C12	2.377917	0.365570	-0.000023	0.021146
C13	3.049873	-1.881798	-0.000015	0.011781
C14	4.384643	-1.517168	0.000051	0.016336
C15	3.705428	0.775804	0.000050	-0.004115
H16	2.727675	-2.920542	-0.000050	-0.000727
H17	5.162736	-2.274232	0.000073	-0.000713
H18	3.964417	1.831325	0.000082	0.000486
C19	-2.303444	0.362757	0.000027	0.0762
C20	-4.308702	-1.555676	0.000082	0.134851
C21	-3.639124	0.762866	0.000073	-0.031629
N22	-1.987236	-0.987510	-0.000008	0.088298
C23	-2.977360	-1.904193	0.000047	-0.007105
C24	-4.649385	-0.183964	0.000089	0.054901
H25	-3.900844	1.817898	0.000107	0.001806
H26	-2.651882	-2.941783	0.000045	-0.000619
H27	-5.072880	-2.325116	0.000128	-0.005166
Cl28	0.034842	-3.726174	-0.000181	0.002863
C29	-6.048198	0.287066	0.000121	0.009844
C30	0.060387	4.822136	-0.000130	0.031143
C31	6.195864	0.279505	0.000172	-0.001866
O32	6.395903	1.517878	0.000123	0.003137
O33	7.045873	-0.642013	0.000256	0.001025
O34	-6.932130	-0.720378	0.000015	0.000597
H35	-7.824811	-0.338018	0.000040	-0.000242

O36	-6.384025	1.457321	0.000236	0.025226
O37	1.085680	5.483160	-0.000321	0.043364
O38	-1.158179	5.389458	0.000063	0.006265
H39	-1.036206	6.352239	-0.000042	-0.000633

[a]Part of the Gaussian output file:

SCF Done: E(UM06) = -1886.41872664 A.U. after 12 cycles

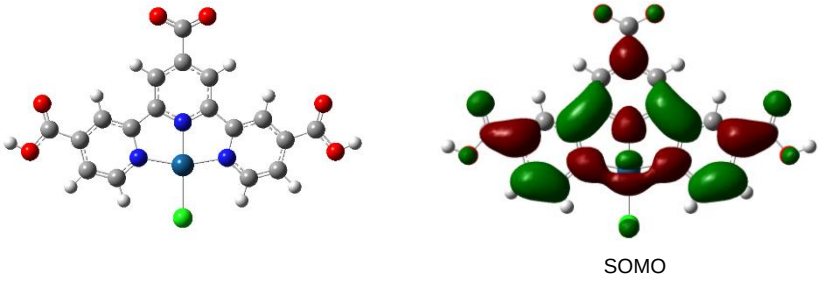
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7592, after 0.7501

	1	2	3
	A	A	A
Frequencies --	23.2149	34.5850	45.3653
Red. masses --	12.2532	10.6040	13.5703

Zero-point correction= 0.260294 (Hartree/Particle)
Thermal correction to Energy= 0.284995
Thermal correction to Enthalpy= 0.285939
Thermal correction to Gibbs Free Energy= 0.202818
Sum of electronic and zero-point Energies= -1886.158433
Sum of electronic and thermal Energies= -1886.133732
Sum of electronic and thermal Enthalpies= -1886.132788
Sum of electronic and thermal Free Energies= -1886.215909

Item	Value	Threshold	Converged?
Maximum Force	0.000035	0.000450	YES
RMS Force	0.000006	0.000300	YES

Table S9 Geometry optimized for [PtCl(tctpyH$_2^{-}$•)]$^{-}$ (Fig. 10E) in its doublet state. Optimized at the UM06 level of DFT using the LanL2DZ basis set for Pt and the 6-31+G(d,p) basis set for H, C, N, O, and Cl.[a]



SOMO

Atom	X	Y	Z	Mulliken spin density
Pt1	0.000000	-1.294200	-0.000009	0.006502
N2	-0.000004	0.654368	-0.000075	0.099162
C3	0.000008	3.386236	0.000022	0.075537
C4	-1.200765	1.295224	-0.000039	0.05108
C5	1.200766	1.295209	-0.000036	0.050359
C6	1.210056	2.682928	0.000014	-0.024519
C7	-1.210058	2.682931	0.000009	-0.024959
H8	2.137665	3.249206	0.000005	0.001857
H9	-2.137659	3.249220	-0.000007	0.001869
N10	2.015889	-0.960548	0.000034	0.076554
C11	4.679601	-0.150278	-0.000010	0.085576
C12	2.333197	0.387685	-0.000020	0.089644
C13	3.010009	-1.874554	0.000076	0.018198
C14	4.340148	-1.519572	0.000062	0.099292
C15	3.661416	0.794508	-0.000053	-0.042137
H16	2.689132	-2.913432	0.000148	-0.001695
H17	5.106035	-2.287631	0.000112	-0.003671
H18	3.915253	1.851401	-0.000104	0.002284
C19	-2.333207	0.387694	-0.000025	0.08975
C20	-4.340150	-1.519560	0.000061	0.099503
C21	-3.661426	0.794517	-0.000061	-0.042103
N22	-2.015902	-0.960521	0.000033	0.076718
C23	-3.010000	-1.874534	0.000073	0.01764
C24	-4.679600	-0.150282	-0.000013	0.085272
H25	-3.915274	1.851407	-0.000119	0.002279
H26	-2.689117	-2.913411	0.000141	-0.001677
H27	-5.106032	-2.287624	0.000108	-0.003678
Cl28	0.000011	-3.702738	-0.000006	0.003041
C29	-6.075605	0.323265	-0.000024	0.017172
C30	0.000007	4.913545	0.000045	-0.007012
C31	6.075589	0.323272	-0.000022	0.017522
O32	-6.963162	-0.681859	0.000049	0.001746
H33	-7.854354	-0.296242	0.000054	-0.000348
O34	-6.408218	1.494873	-0.000094	0.03254
O35	1.126945	5.467287	0.000097	0.008195

O36	-1.126933	5.467282	0.000032	0.008217
O37	6.408213	1.494883	-0.000076	0.032862
O38	6.963161	-0.681849	0.000015	0.001777
H39	7.854344	-0.296213	0.000015	-0.000351

[a]Part of the Gaussian output file:

SCF Done: E(UM06) = -1886.41552042 A.U. after 12 cycles

Annihilation of the first spin contaminant:
S**2 before annihilation 0.7611, after 0.7501

	1	2	3
	A	A	A
Frequencies --	21.1989	35.3085	35.6430
Red. masses --	10.7963	11.9106	10.8126

Zero-point correction= 0.259334 (Hartree/Particle)
Thermal correction to Energy= 0.284183
Thermal correction to Enthalpy= 0.285128
Thermal correction to Gibbs Free Energy= 0.201163
Sum of electronic and zero-point Energies= -1886.156186
Sum of electronic and thermal Energies= -1886.131337
Sum of electronic and thermal Enthalpies= -1886.130393
Sum of electronic and thermal Free Energies= -1886.214358

Item	Value	Threshold	Converged?
Maximum Force	0.000018	0.000450	YES
RMS Force	0.000004	0.000300	YES

Table S10 Electronic transitions for water-solvated $[PtCl(tctpy^{-\bullet})]^{3-}$ (Fig. 10A) in its doublet state calculated by the TD-DFT method, using the optimized geometry in Table S5. To minimize publication materials, only the selected transitions (f > 0.01 and |CI coef| > 0.3) above λ = 350 nm are summarized in this Table.

Excited State	E (cm^{-1})	l (nm)	f[a] (> 0.01)	Major contributions	|CI coef| (> 0.3)
1	5742	1741.63	0.0794	HOMO_α -> LUMO_α	0.97849
3	12185	820.68	0.0349	HOMO_α -> LUMO+1_α	0.9817
4	12501	799.95	0.0819	HOMO_α -> LUMO+2_α	0.97519
5	17536	570.26	0.0433	HOMO_α -> LUMO+4_α	0.97066
12	24617	406.23	0.0142	HOMO-3_α -> LUMO_α	0.44031
				HOMO-1_β -> HOMO_β	0.83835
14	25995	384.69	0.115	HOMO_α -> LUMO+14_α	0.75078
				HOMO_α -> LUMO+17_α	0.58009
20	27494	363.71	0.0183	HOMO-2_α -> LUMO_α	0.77637
				HOMO-8_β -> HOMO_β	0.33928
				HOMO-1_β -> LUMO_β	0.4785

[a]Oscillator strength.

Table S11 Electronic transitions for water-solvated $[PtCl(tctpyH^{-\bullet})]^{2-}$ (Fig. 10B) in its doublet state calculated by the TD-DFT method, using the optimized geometry in Table S6. To minimize publication materials, only the selected transitions (f > 0.01 and |CI coef| > 0.3) above λ = 350 nm are summarized in this Table.

Excited State	E (cm^{-1})	l (nm)	f[a] (> 0.01)	Major contributions	|CI coef| (> 0.3)
1	6895	1450.33	0.0457	HOMO_α -> LUMO_α	0.97711
2	12458	802.69	0.0982	HOMO_α -> LUMO+1_α	0.98949
4	15033	665.21	0.0525	HOMO_α -> LUMO+2_α	0.97555
5	17418	574.11	0.0266	HOMO_α -> LUMO+4_α	0.97191
6	22488	444.68	0.0202	HOMO-2_β -> LUMO_β	0.41097
				HOMO-1_β -> HOMO_β	0.75174
9	24437	409.22	0.0255	HOMO-4_α -> LUMO_α	0.54614
				HOMO-2_α -> LUMO_α	0.38088
				HOMO-1_β -> HOMO_β	0.59098
19	27583	362.54	0.0588	HOMO-1_α -> LUMO_α	0.44706
				HOMO-9_β -> HOMO_β	0.61995
				HOMO-1_β -> LUMO_β	0.50697
21	27875	358.75	0.1068	HOMO_α -> LUMO+13_α	0.76143
				HOMO_α -> LUMO+17_α	0.36163

[a]Oscillator strength.

Table S12 Electronic transitions for water-solvated $[PtCl(tctpyH^{-}\bullet)]^{2-}$ (Fig. 10C) in its doublet state calculated by the TD-DFT method, using the optimized geometry in Table S7. To minimize publication materials, only the selected transitions (f > 0.01 and |CI coef| > 0.3) above λ = 350 nm are summarized in this Table.

Excited State	E (cm^{-1})	l (nm)	fa (> 0.01)	Major contributions	|CI coef| (> 0.3)
1	7632	1310.34	0.0901	HOMO_α -> LUMO_α	0.97529
2	9878	1012.38	0.0754	HOMO_α -> LUMO+1_α	0.9581
4	15707	636.67	0.0257	HOMO_α -> LUMO+2_α	0.97663
5	19401	515.43	0.0492	HOMO_α -> LUMO+4_α	0.9264
9	24425	409.42	0.0115	HOMO-4_α -> LUMO_α	0.38416
				HOMO-1_α -> LUMO_α	0.3469
				HOMO-2_β -> HOMO_β	0.57593
				HOMO-1_β -> HOMO_β	0.44378
11	24889	401.78	0.0272	HOMO_α -> LUMO+8_α	0.89066
				HOMO_α -> LUMO+11_α	0.34812
14	25847	386.89	0.0355	HOMO-5_α -> LUMO+3_α	0.47278
				HOMO_α -> LUMO+8_α	0.31566
				HOMO_α -> LUMO+11_α	0.58259
				HOMO-5_β -> LUMO+3_β	0.46392
15	25963	385.17	0.0339	HOMO-5_α -> LUMO+3_α	0.52364
				HOMO_α -> LUMO+11_α	0.54761
				HOMO-5_β -> LUMO+3_β	0.49662
18	26906	371.67	0.0141	HOMO-1_α -> LUMO_α	0.73986
				HOMO-9_β -> HOMO_β	0.37358
24	28291	353.47	0.2194	HOMO-1_α -> LUMO_α	0.40665
				HOMO-9_β -> HOMO_β	0.72074

[a]Oscillator strength.

Table S13 Electronic transitions for water-solvated $[PtCl(tctpyH_2^{-}\bullet)]^{-}$ (Fig. 10D) in its doublet state calculated by the TD-DFT method, using the optimized geometry in Table S8. To minimize publication materials, only the selected transitions (f > 0.01 and |CI coef| > 0.3) above **λ** = 350 nm are summarized in this Table.

Excited State	E (cm^{-1})	l (nm)	f[a] (> 0.01)	Major contributions	|CI coef| (> 0.3)
1	6898	1449.75	0.0839	HOMO_α -> LUMO_α	0.93309
				HOMO_α -> LUMO+1_α	0.31116
2	9817	1018.64	0.0625	HOMO_α -> LUMO_α	0.32872
				HOMO_α -> LUMO+1_α	0.90271
4	14952	668.8	0.0617	HOMO_α -> LUMO+2_α	0.93379
5	17917	558.12	0.0349	HOMO_α -> LUMO+4_α	0.94616
6	21761	459.54	0.0106	HOMO-3_β -> LUMO_β	0.32894
				HOMO-1_β -> HOMO_β	0.79343
9	23798	420.21	0.0161	HOMO-3_α -> LUMO_α	0.51147
				HOMO-3_β -> LUMO_β	0.37472
				HOMO-1_β -> HOMO_β	0.50509
13	26023	384.28	0.0434	HOMO_α -> LUMO+8_α	0.6056
				HOMO_α -> LUMO+12_α	0.7017
16	26503	377.32	0.0378	HOMO-2_α -> LUMO_α	0.72822
				HOMO-1_β -> LUMO_β	0.40523
18	26679	374.82	0.0113	HOMO_α -> LUMO+8_α	0.78121
				HOMO_α -> LUMO+12_α	0.56802
21	27660	361.53	0.0923	HOMO-8_β -> HOMO_β	0.41421
				HOMO-7_β -> HOMO_β	0.62136
				HOMO-1_β -> LUMO_β	0.38916
23	28000	357.14	0.0975	HOMO-2_α -> LUMO_α	0.43479
				HOMO-1_β -> LUMO_β	0.77229

[a]Oscillator strength.

Table S14 Electronic transitions for water-solvated [PtCl(tctpyH_2^{-}•)]$^{-}$ (Fig. 10E) in its doublet state calculated by the TD-DFT method, using the optimized geometry in Table S9. To minimize publication materials, only the selected transitions (f > 0.01 and |CI coef| > 0.3) above λ = 350 nm are summarized in this Table.

Excited State	E (cm^{-1})	l (nm)	f[a] (> 0.01)	Major contributions	|CI coef| (> 0.3)
1	5711	1750.94	0.1713	HOMO_α -> LUMO_α	0.97796
2	10666	937.52	0.0755	HOMO_α -> LUMO+2_α	0.97615
3	10727	932.25	0.0153	HOMO_α -> LUMO+1_α	0.98429
5	18839	530.81	0.024	HOMO_α -> LUMO+4_α	0.97655
13	25219	396.53	0.1136	HOMO_α -> LUMO+12_α	0.94759
23	27403	364.92	0.1135	HOMO-1_β -> LUMO_β	0.92608
27	27941	357.9	0.0172	HOMO_α -> LUMO+10_α	0.78057
28	27941	357.9	0.1731	HOMO-8_β -> HOMO_β	0.63548
				HOMO-7_β -> HOMO_β	0.55126
31	28492	350.98	0.014	HOMO-8_α -> LUMO_α	0.41345
				HOMO-3_α -> LUMO_α	0.31012
				HOMO-1_β -> LUMO+2_β	0.31328

[a]Oscillator strength.