Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Synthesis, crystal structure, spectroscopic and electrochemical properties, and H_2-evolving activity of a new $[PtCl(terpyridine)]^+$ derivative with viologen-like redox properties

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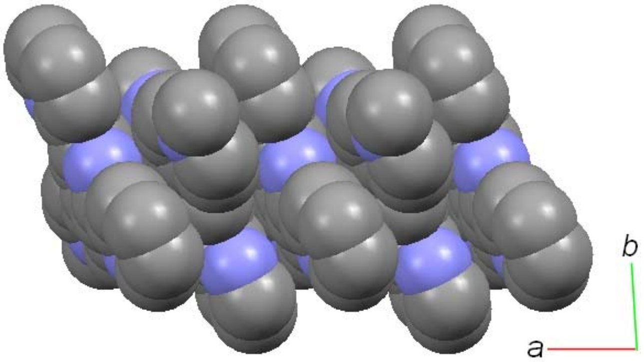


Fig. S1. A space-filling representation showing the π-stacking interactions of Mepytpy$^+$cations in the crystal.

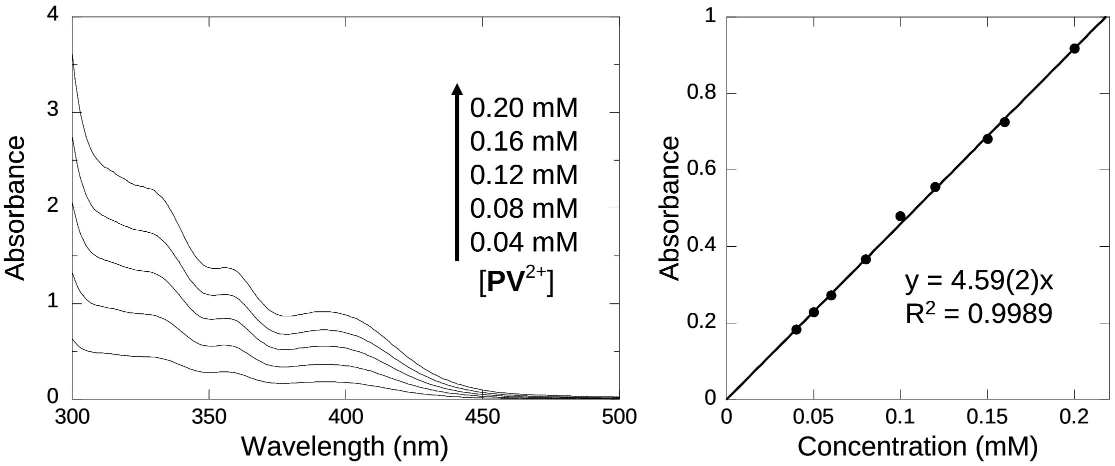


Fig. S2. (left) UV-vis absorption spectra of [**PV**]$(ClO_4)_2 \cdot H_2O$ in aqueous 0.1 M NaCl solutions at various **PV**$^{2+}$ concentrations, under air, at 20 °C. (right) The concentration dependence of absorbance at 397 nm in the concentration range of 0.04–0.20 mM, revealing that **PV**$^{2+}$ does not form a dimer under these conditions.

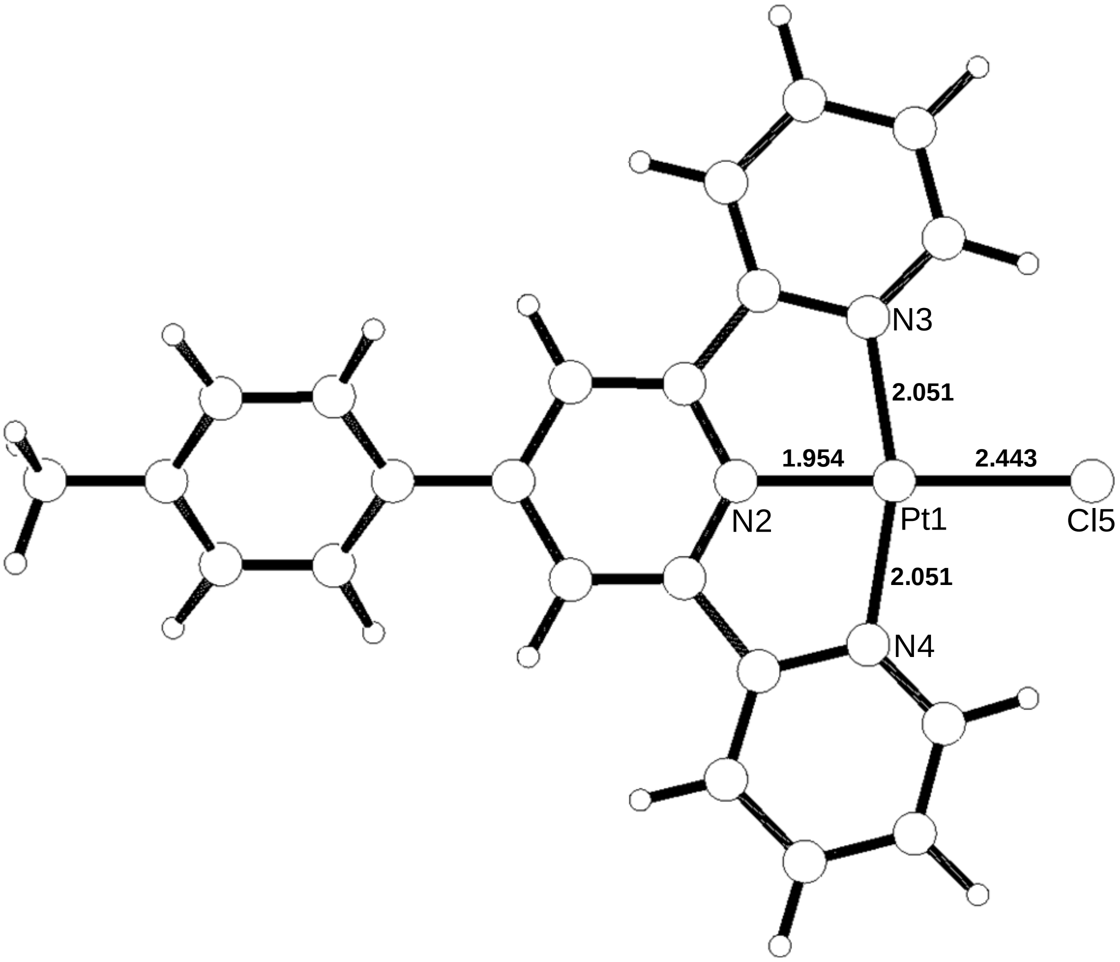


Fig. S3. One of the energy-minimized conformers afforded by the B3LYP level of DFT calculations using the LanL2DZ basis set and the PCM method (water) in Gaussian 03. The optimized geometry is given in Table S1. Comparison of the optimized geometry and the crystal structure of **PV**$^{2+}$ is made in Table S5.

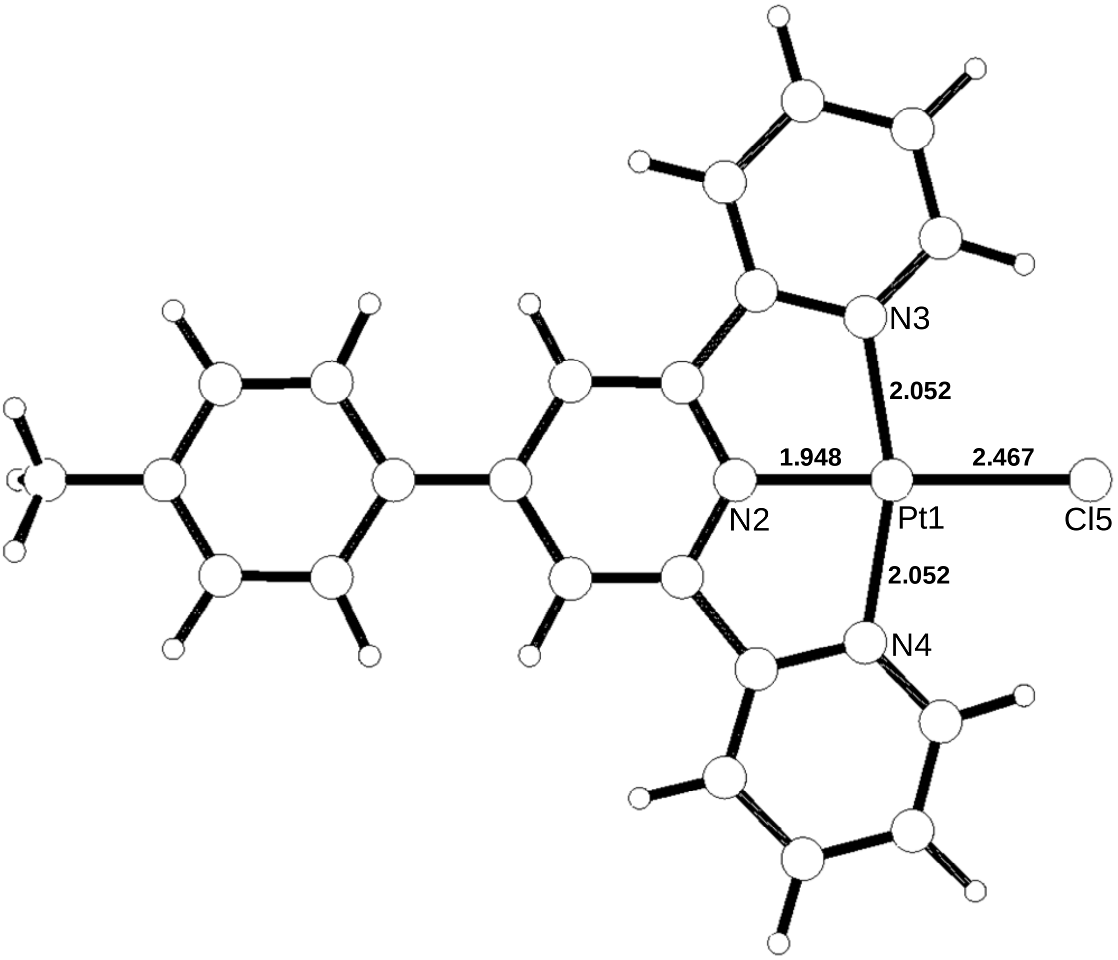


Fig. S4. One-electron-reduced species of $\mathbf{PV}^{2+}$ (*i.e.*, $\mathbf{PV}^{+\bullet}$) in water, which was optimized at the UB3LYP level of DFT using the LanL2DZ basis set and the PCM method (water) in Gaussian 03. The final coordinates are given in Table S2.

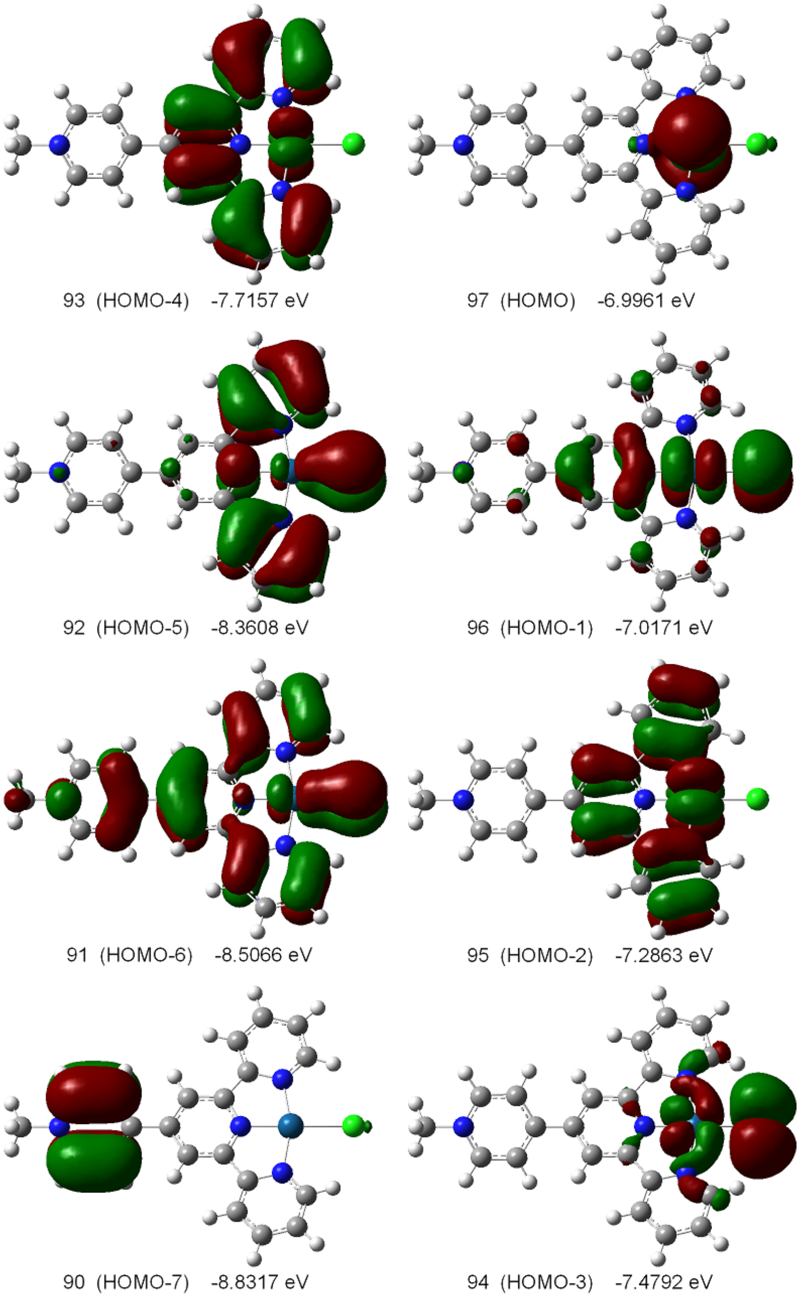
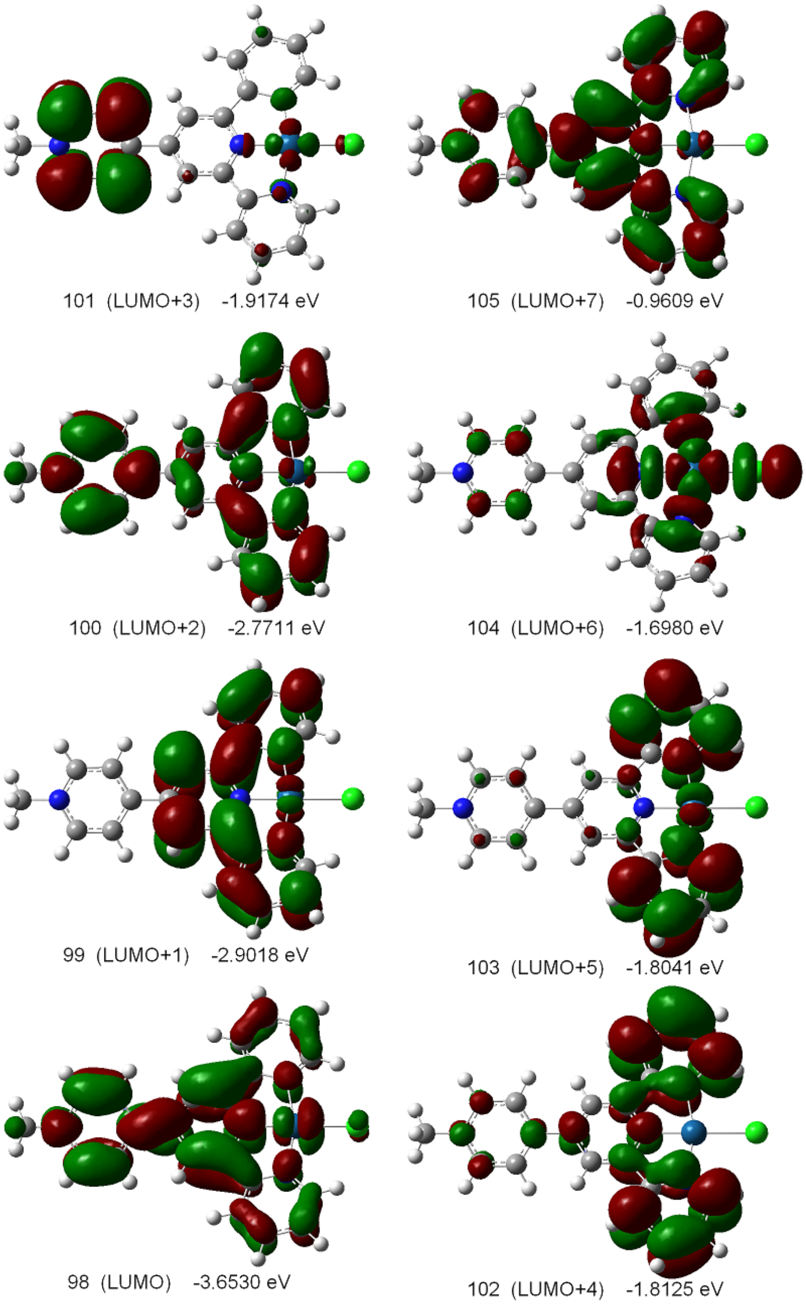


Fig. S5. Frontier molecular orbitals (occupied MOs) of a fully optimized structure of **PV**$^{2+}$ in water (PCM), obtained by using the B3LYP level of DFT and the LanL2DZ basis set implemented in the Gaussian 03 suite programs.



101 (LUMO+3) -1.9174 eV

105 (LUMO+7) -0.9609 eV

100 (LUMO+2) -2.7711 eV

104 (LUMO+6) -1.6980 eV

99 (LUMO+1) -2.9018 eV

103 (LUMO+5) -1.8041 eV

98 (LUMO) -3.6530 eV

102 (LUMO+4) -1.8125 eV

Fig. S6. Frontier molecular orbitals (unoccupied MOs) of a fully optimized structure of **PV**$^{2+}$ in water (PCM), obtained by using the B3LYP level of DFT and the LanL2DZ basis set implemented in the Gaussian 03 suite programs.

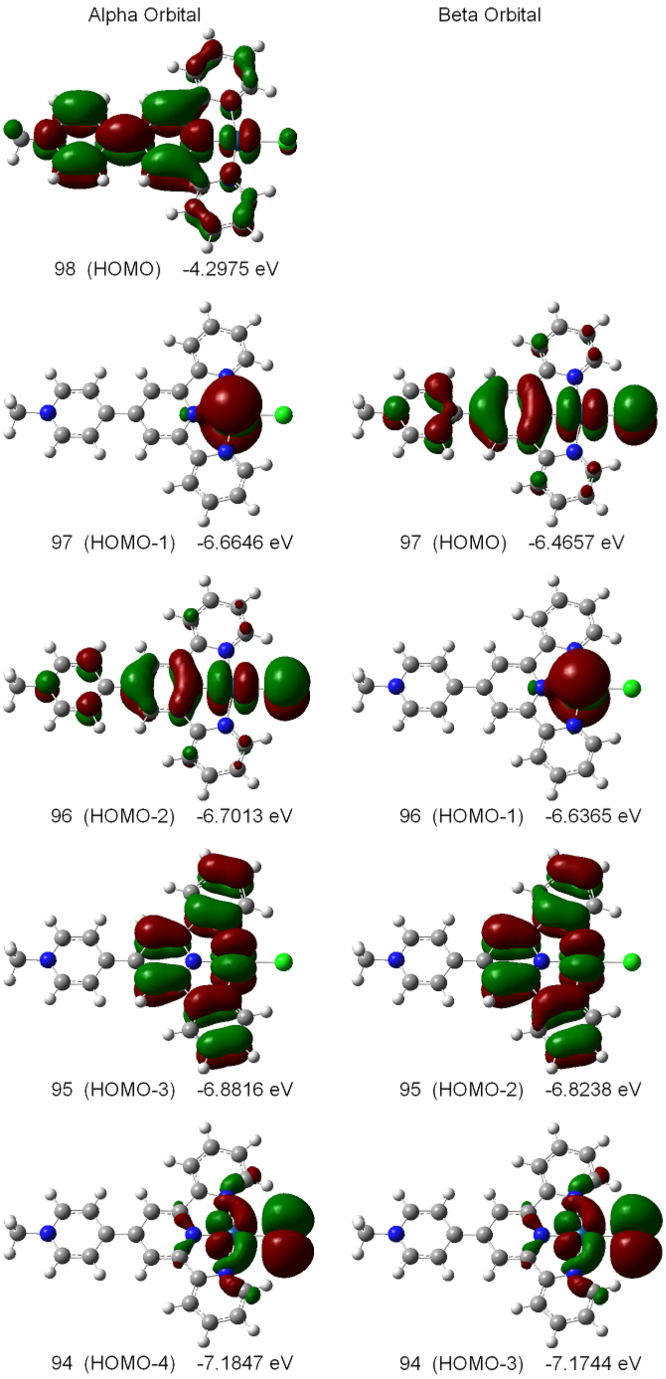


Fig. S7. Frontier molecular orbitals (occupied MOs) of a fully optimized structure of **PV**$^{+\bullet}$ in water (PCM), obtained by using the UB3LYP level of DFT and the LanL2DZ basis set implemented in the Gaussian 03 suite programs.

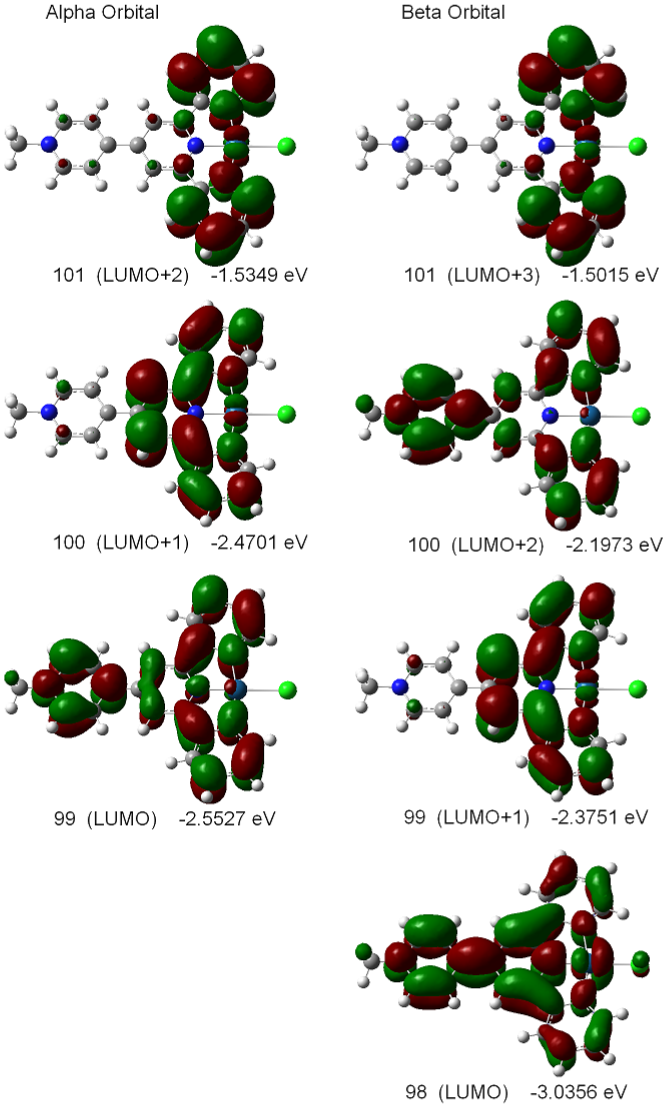


Fig. S8. Frontier molecular orbitals (unoccupied MOs) of a fully optimized structure of **PV**$^{+\bullet}$ in water (PCM), obtained by using the UB3LYP level of DFT and the LanL2DZ basis set implemented in the Gaussian 03 suite programs.

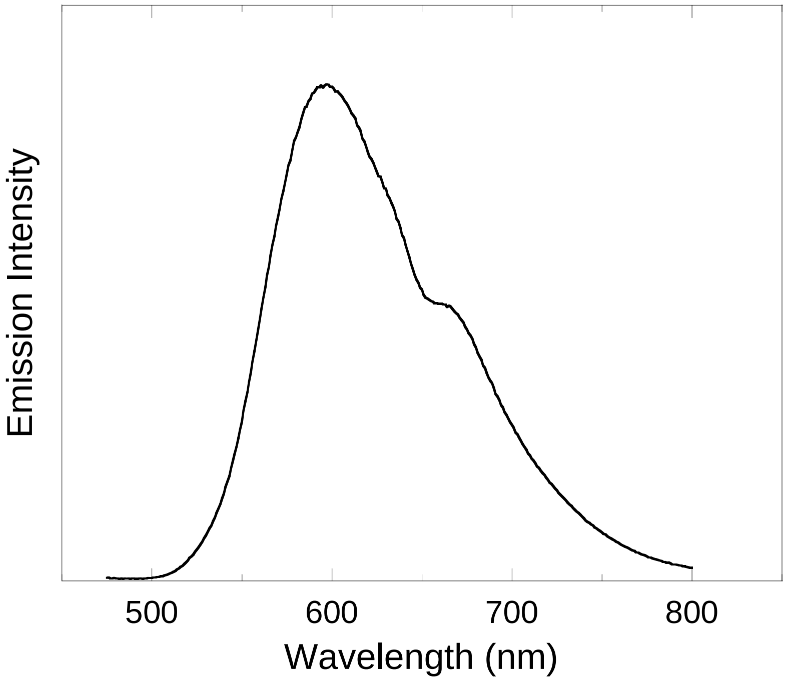


Fig. S9. Solid-state emission spectrum of [**PV**]$(ClO_4)_2 \cdot H_2O$ (λ_{ex} = 400 nm) at room temperature.

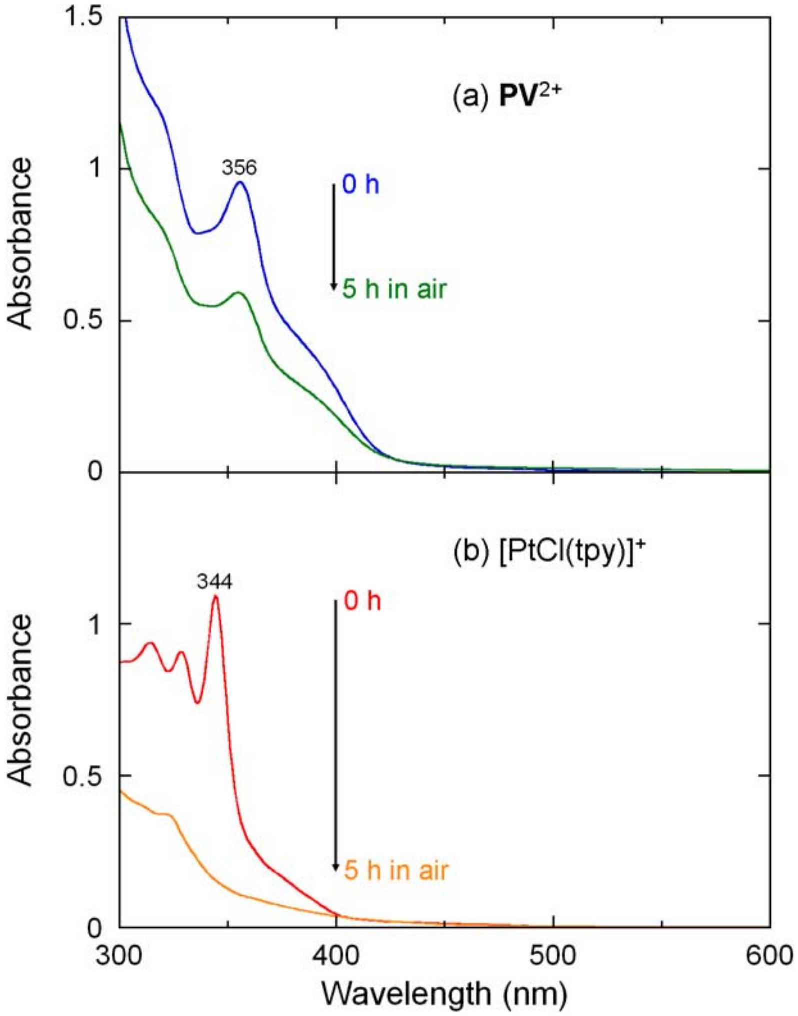


Fig. S10. Spectral changes given during the 5 h photolysis for (a) **PV**$^{2+}$ and (b) [PtCl(tpy)]$^{+}$. The experimental conditions are same to those in Figs. 9a,b. In both cases, spectra were measured before and after the photolysis, where the visible chromophores of radical species were bleached by exposing the solution to air (O_2) before the measurement. The loss in the initial forms of **PV**$^{2+}$ and [PtCl(tpy)]$^{+}$ are estimated from the decrease in their characteristic absorption at 356 and 344 nm, respectively.

Table S1. Cartesian coordinates of a fully optimized structure of $[PtCl(Mepytpy)]^{2+}$ (**PV**$^{2+}$) in water. The structure was optimized at B3LYP level of DFT using the LANL2DZ basis set and the PCM method (water) in Gaussian 03.

Atom	X	Y	Z	Atom	X	Y	Z
Pt1	2.083536	-0.000132	0.000946	C23	0.975492	-4.712732	0.098056
N2	0.128961	-0.000180	-0.001794	H24	-1.055244	-3.949133	0.074779
N3	1.759692	-2.025610	0.043936	H25	3.117432	-5.120496	0.115003
N4	1.759842	2.025358	-0.043938	C26	0.975549	4.712435	-0.100416
Cl5	4.526598	-0.000095	0.004641	H27	-1.055162	3.948668	-0.082236
C6	-0.513807	-1.202144	0.019248	H28	3.117480	5.120373	-0.111870
C7	-0.513653	1.201786	-0.024503	H29	0.670486	-5.758045	0.118744
C8	2.696023	-3.005483	0.068712	H30	0.670500	5.757717	-0.122050
C9	0.410078	-2.355573	0.046562	C31	-4.112972	0.000232	-0.004280
C10	2.696148	3.005317	-0.066465	C32	-4.846296	-1.035500	-0.629217
C11	0.410226	2.355233	-0.049935	C33	-4.844963	1.038450	0.619370
C12	-1.913801	1.223018	-0.024637	C34	-6.236778	1.020246	0.606007
C13	-1.913979	-1.223254	0.016786	C35	-6.238965	-1.013618	-0.618830
C14	0.003227	-3.694357	0.073338	H36	-4.355406	-1.855348	-1.150092
C15	2.336234	-4.363279	0.095976	H37	-4.352683	1.859034	1.137760
H16	3.734224	-2.689803	0.066454	N38	-6.915993	0.004083	-0.007124
C17	0.003322	3.693979	-0.078018	H39	-6.828152	1.800680	1.082095
C18	2.336307	4.363084	-0.094784	H40	-6.830657	-1.792420	-1.096932
H19	3.734373	2.689750	-0.061479	C41	-8.409958	-0.007079	0.026049
C20	-2.626309	-0.000066	-0.004276	H42	-8.745772	-0.454861	0.966840
H21	-2.440815	2.174514	-0.063972	H43	-8.783338	-0.592528	-0.816774
H22	-2.441296	-2.174670	0.054657	H44	-8.778190	1.018749	-0.049603

E(RB + HF − LYP) = −1163.28306599 hartree

Sum of electronic and zero-point Energies = −1162.940238 hartree

Table S2. Cartesian coordinates of a fully optimized structure of $[\mathrm{PtCl(Mepytpy)}]^{+\bullet}$ (**PV**$^{+\bullet}$) in water. The structure was optimized at UB3LYP level of DFT using the LANL2DZ basis set and the PCM method (water) in Gaussian 03.

Atom	X	Y	Z	Atom	X	Y	Z
Pt1	2.091057	0.000010	0.000740	C23	0.982873	-4.717572	0.000447
N2	0.142798	-0.000017	-0.001986	H24	-1.047446	-3.961962	-0.003148
N3	1.758997	-2.025019	0.000992	H25	3.130345	-5.119265	0.004108
N4	1.758944	2.025042	0.000472	C26	0.982736	4.717569	-0.000114
Cl5	4.558211	0.000055	0.003987	H27	-1.047559	3.961897	-0.003303
C6	-0.518976	-1.209830	-0.002808	H28	3.130196	5.119331	0.003218
C7	-0.519007	1.209779	-0.002916	H29	0.682277	-5.764369	0.000243
C8	2.699236	-3.008162	0.002790	H30	0.682107	5.764356	-0.000337
C9	0.405512	-2.357132	-0.001174	C31	-4.107093	-0.000045	-0.006855
C10	2.699153	3.008213	0.002090	C32	-4.880187	-1.212889	-0.009655
C11	0.405449	2.357110	-0.001466	C33	-4.880155	1.212820	-0.007829
C12	-1.906580	1.229132	-0.004744	C34	-6.260531	1.190290	-0.009369
C13	-1.906549	-1.229203	-0.004719	C35	-6.260565	-1.190311	-0.011223
C14	0.010186	-3.705277	-0.001460	H36	-4.409572	-2.191823	-0.012792
C15	2.347594	-4.363754	0.002607	H37	-4.409507	2.191743	-0.009351
H16	3.735127	-2.685419	0.004348	N38	-6.961686	0.000002	-0.013274
C17	0.010081	3.705243	-0.001790	H39	-6.849617	2.104806	-0.009333
C18	2.347470	4.363794	0.001864	H40	-6.849681	-2.104806	-0.012651
H19	3.735054	2.685507	0.003576	C41	-8.443600	-0.000004	0.040031
C20	-2.656662	-0.000044	-0.005564	H42	-8.786221	-0.000595	1.081426
H21	-2.415134	2.188827	-0.005448	H43	-8.826479	-0.889815	-0.467003
H22	-2.415082	-2.188910	-0.005283	H44	-8.826492	0.890352	-0.466049

E(UB + HF − LYP) = −1163.42986083 hartree

Sum of electronic and zero-point Energies = −1163.089124 hartree

Table S3. The absorption transitions for **PV**$^{2+}$ in aqueous media calculated by the TD-DFT method, based on the optimized geometry in Table S1. The corresponding MOs are shown in Figs. S5 and S6.

Excited State	E (cm^{-1})	λ (nm)	f^a (> 0.05)	Transition	|CI coef| (> 0.3)
3	23269	429.76	0.1543	96 → 98 (HOMO-1 → LUMO)	0.64699
8	28899	346.03	0.2636	93 → 98 (HOMO-4 → LUMO)	0.57701
				96 → 99 (HOMO-1 → LUMO+1)	0.33235
10	29734	336.31	0.0569	96 → 100 (HOMO-1 → LUMO+2)	0.68173
11	30534	327.50	0.0762	95 → 99 (HOMO-2 → LUMO+1)	0.63029
19	34947	286.15	0.0937	91 → 98 (HOMO-6 → LUMO)	0.58371
				93 → 99 (HOMO-4 → LUMO+1)	0.30235
21	35494	281.74	0.3447	93 → 99 (HOMO-4 → LUMO+1)	0.33033
				93 → 100 (HOMO-4 → LUMO+2)	0.49598
22	35503	281.67	0.3669	93 → 99 (HOMO-4 → LUMO+1)	0.36074
				93 → 100 (HOMO-4 → LUMO+2)	0.34203
				97 → 102 (HOMO → LUMO+4)	0.33947
23	35505	281.65	0.0739	97 → 102 (HOMO → LUMO+4)	0.60486
25	36662	272.76	0.1091	96 → 102 (HOMO-1 → LUMO+4)	0.66303
29	38305	261.06	0.0593	92 → 99 (HOMO-5 → LUMO+1)	0.42381
				95 → 102 (HOMO-2 → LUMO+4)	0.51157
34	39795	251.29	0.4435	92 → 99 (HOMO-5 → LUMO+1)	0.49587
				95 → 102 (HOMO-2 → LUMO+4)	0.35379
37	40368	247.72	0.1047	88 → 98 (HOMO-9 → LUMO)	0.45249
				95 → 103 (HOMO-2 → LUMO+5)	0.37126
38	40579	246.43	0.2090	91 → 99 (HOMO-6 → LUMO+1)	0.60828
39	40833	244.90	0.0552	86 → 98 (HOMO-11 → LUMO)	0.56744
52	44468	224.88	0.0549	96 → 105 (HOMO-1 → LUMO+7)	0.64540

[a] Oscillator strength.

Table S4. The absorption transitions for **PV**$^{+\bullet}$ in aqueous media calculated by the TD-DFT method, based on the optimized geometry in Table S2. The corresponding MOs are shown in Figs. S7 and S8.

Excited State	E (cm^{-1})	λ (nm)	f^a (> 0.05)	Transition	|CI coef| (> 0.3)
2	10519	950.67	0.2953	98α → 99α (HOMO → LUMO)	0.9315
7	21136	473.13	0.1607	97β → 98β (HOMO → LUMO)	0.8898
10	23917	418.11	0.0673	95α →100α (HOMO-3 → LUMO+1)	0.5786
				98α →105α (HOMO → LUMO+6)	0.3045
				95β → 99β (HOMO-2 → LUMO+1)	0.5270
				97β → 98β (HOMO → LUMO)	0.3216
12	24663	405.47	0.0809	98α →105α (HOMO → LUMO+6)	0.8775
23	28689	348.56	0.1000	96α → 100α (HOMO-2 → LUMO+1)	0.6949
				93β → 98β (HOMO-4 → LUMO)	-0.5743
24	28998	344.85	0.3261	96α → 99α (HOMO-2 → LUMO)	0.4408
				97β → 100β (HOMO → LUMO+2)	0.7083
29	30905	323.57	0.1875	95α → 100α (HOMO-3 → LUMO+1)	-0.3753
				92β → 98β (HOMO-5 → LUMO)	0.6333
				95β → 99β (HOMO-3 → LUMO+1)	0.4143
				97β → 100β (HOMO → LUMO+2)	-0.3190
31	31449	317.98	0.0853	95α → 99α (HOMO-3 → LUMO)	0.5104
				95β → 100β (HOMO-2 → LUMO+2)	0.6025
33	31790	314.56	0.0648	93α → 99α (HOMO-5 → LUMO)	0.6230
				93β → 100β (HOMO-4 → LUMO+2)	-0.3601

[a] Oscillator strength.

Table S5. Comparison of the geometrical parameters (bond lengths in Å and angles in degree) of **PV**$^{2+}$ between the crystallographically observed and DFT-based structures.

X-ray data		DFT results	
Pt1—N1	2.020(4)	Pt1—N4	2.051
Pt1—N2	1.964(3)	Pt1—N2	1.954
Pt1—N3	2.023(4)	Pt1—N3	2.051
Pt1—Cl1	2.3167(10)	Pt1—Cl5	2.443
N1—Pt1—N2	79.70(13)	N4—Pt1—N2	80.92
N2—Pt1—N3	82.54(13)	N2—Pt1—N3	80.91
N1—Pt1—Cl1	99.03(10)	N4—Pt1—Cl5	99.07
N3—Pt1—Cl1	98.73(10)	N3—Pt1—Cl5	99.08