Electronic Supplementary Information

Redox tuning in Pt(bpy)-viologen catalyst-acceptor dyads enabling photocatalytic hydrogen evolution from water

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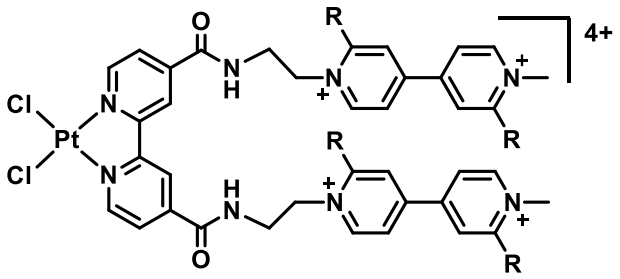
Materials

All solvents and reagents were of the highest quality available and were used as received. [**Pt(bpy)(MV^{2+})$_2$**](PF$_6$)$_4$•H$_2$O (see below) was prepared according to the literature method.[1]



R = H: **Pt(bpy)(MV^{2+})$_2$**
R = Me: **Pt(bpy)(dmMV^{2+})$_2$**

General methods

^{1}H NMR spectra were acquired on a JEOL JNM-ECA 600 spectrometer. UV-Vis-NIR spectra were recorded on a Shimadzu UV-3600 spectrophotometer, where sample solutions were thermostated at 20 °C during the measurements. Square wave voltammograms (SWVs) were recorded on BAS ALS Model 602DKM and 750C electrochemical analyzers in a three-electrode system consisting of a platinum working electrode, a platinum wire counter electrode, and an Ag/Ag$^+$ as a reference, where tetrabutylammonium perchlorate (TBAP; 0.1 M) was added as a supporting electrolyte. Potentials were all corrected using the ferrocene/ferrocenium couple as an internal standard (Fc/Fc$^+$). Dynamic light scattering (DLS) measurements were carried out by using an Otsuka Electronics ELSZ-2 particle analyzer equipped with a diode laser (660 nm). Sample solutions used for the DLS measurements were filtered with a Whatman syringe filter (0.2 μm) twice to remove possible insoluble impurities and particles in solution before initiating each photolysis experiment. Photochemical hydrogen evolution measurements were performed by using the automated H_2/O_2 monitoring system developed in our group as previously reported.[2]

Syntheses

Synthesis of *N*,2,2'-trimethyl-4,4'-bipyridinium iodide.

To a solution of 2,2'-dimethyl-4,4'-bipyridine[3–5] (0.57 g, 3.0 mmol) in $CHCl_3$ (3.0 mL) was added iodomethane (0.3 mL, 5.5 mmol). The solution was stirred at room temperature for 2 days. The light yellow powder deposited was collected by filtration, washed with $CHCl_3$, and dried in vacuo. Yield:

0.70 g (2.1 mmol, 70%). Anal. Calcd. for $C_{13}H_{15}IN_2$: H, 4.64; C, 47.87; N, 8.59. Found: H, 4.57; C 47.81; N 8.53. ^{1}H NMR (DMSO-d_6/TMS, ppm; DMSO = dimethylsulfoxide, TMS = tetramethylsilane): δ = 9.09 (d, *J* = 6.2 Hz, 1H), 8.73 (d, *J* = 4.8 Hz, 1H), 8.58 (d, *J* = 1.4 Hz, 1H), 8.42 (dd, *J* = 6.2, 2.0 Hz, 1H), 7.92 (s, 1H), 7.82 (dd, *J* = 5.52, 2.1 Hz, 1H), 4.25 (s, 3H), 2.84 (s, 3H), 2.61 (s, 3H).

Synthesis of *N*-(2-ammonioethyl)-*N'*,2,2'-trimethyl-4,4'-bipyridinium bis(hexafluorophosphate) iodide.

A suspension of *N*,2,2'-trimethyl-4,4'-bipyridinium iodide (0.33 g, 1.0 mmol) and 2-bromoethylammonium bromide (2.1 g, 10 mmol) in acetonitrile (2 mL) was sealed in a pressure-resistant vessel and was reacted at 100 °C for 16 h. After the vial was cooled down to room temperature, ethanol (10 mL) was added to the mixture. The resulting brown powder was collected by filtration and washed with ethanol (10 mL). The solid was dissolved in water (10 mL), and the solution was filtered to remove insoluble materials. To the filtrate was added a saturated aqueous NH_4PF_6 solution (ca. 1 mL), followed by the addition of a saturated aqueous Na_2CO_3 solution for neutralization. The resulting suspension was cooled down to 4 °C. The brown solid was collected by filtration, washed with minimum amount of water, and dried in vacuo. Yield: 0.11 g (0.21 mmol, 21%). Anal. Calcd. for $C_{15}H_{22}F_{12}N_3P_2I$: H, 3.35; C, 27.25; N, 6.36. Found: H, 3.65; C 27.67; N 6.36. ^{1}H NMR (DMSO-d_6/TMS, ppm): δ = 9.27 (d, *J* = 6.2 Hz, 1H), 9.22 (d, *J* = 6.2 Hz, 1H), 8.82 (s, 1H), 8.77 (s, 1H), 8.66 (d, *J* = 6.8, 1H), 8.59 (d, *J* = 6.2 Hz, 1H), 8.09 (s, br, 2H), 4.85 (t, *J* = 6.5 Hz, 2H), 4,32 (s, 3H), 3.50 (s, br, 2H).

Synthesis of bpy(dmMV^{2+})$_2$(PF$_6$)$_4$•2H$_2$O.

A dark brown solution of *N*-(2-ammonioethyl)-*N'*,2,2'-trimethyl-4,4'-bipyridinium bis(hexafluorophosphate) iodide (0.11 g, 0.21 mmol), 4,4'-dicarboxysuccinimidyl-2,2'-bipyridine[1] (42 mg, 0.096 mmol) and (*N*,*N*-dimethylamino)pyridine (2.1 mg, 0.018 mmol) in dry-*N*,*N*-dimethylformamide (DMF; 1 mL) was stirred at 30 °C for 12 h under Ar atmosphere. The solution was evaporated to ca. 0.1 mL, followed by the addition of water (1.5 mL). The brown precipitate deposited was collected by filtration, and recrystallized by the gradual evaporation from 1:1 acetone-water mixture (4 mL). Resulting brown solid was purified on a Sephadex LH-20 column using a 1:1 methanol-acetonitrile mixture as eluent. The 3rd band was collected and evaporated to give the off white solid. Yield: 22 mg (0.018 mmol, 17%). Anal. Calcd. for $C_{42}H_{46}F_{24}N_8O_2P_4$•2$H_2O$: H, 3.85; C, 38.49; N, 8.55. Found: H, 3.62; C 37.97; N 8.55. ^{1}H NMR (CD_3CN/TMS, ppm): δ = 8.81 (d, *J* = 4.8 Hz, 2H), 8.78 (d, *J* = 6.2 Hz, 2H), 8.76 (d, *J* = 6.9 Hz, 2H), 8.71 (s, 2H), 8.32 (d, *J* = 2.04, 2H), 8.27 (d, *J* = 1.4 Hz, 2H), 8.13-8.16 (m, 4H), 7.71 (t, *J* = 5.9 Hz, 2H), 7.65 (dd, *J* = 4.8, 2.0 Hz, 2H), 4.79 (t, *J* = 6.2 Hz, 4H), 4.22 (s, 6H), 3.95 (q, *J* = 6.2 Hz, 4H), 3.02 (s, 6H), 2.83 (s, 6H).

Synthesis of [Pt(bpy)(dmMV^{2+})$_2$](PF$_6$)$_4$•H$_2$O.

A suspension of bpy(dmMV^{2+})$_2$(PF$_6$)$_4$•2H$_2$O (22 mg, 0.018 mmol) and *cis*-PtCl$_2$(DMSO)$_2$ (8.3 mg, 0.20 mmol) in methanol (6 mL) was refluxed for 6 h. The resulting yellow suspension was filtered and recrystallized by gradual evaporation from 1:1 acetone-water mixture (2 mL). The yellow solid was dissolved in acetonitrile, and the solution was filtered with a syringe filter with a diameter of 0.45 μm. The filtrate was evaporated to dryness to afford the yellow powder. Yield: 17 mg (0.011 mmol, 60%). Anal. Calcd. for C$_{42}$H$_{46}$Cl$_2$F$_{24}$N$_8$O$_2$P$_4$Pt•H$_2$O: C 31.99, H 3.20, N 7.11; Found: C 32.20, H 3.04, N 7.09. ^{1}H NMR (CD$_3$CN/TMS, ppm): δ = 9.81 (d, *J* = 6.2 Hz, 2H), 8.77 (d, *J* = 2.8 Hz, 2H), 8.76 (d, *J* = 2.8 Hz, 2H), 8.60 (s, 2H), 8.33 (d, *J* = 2.1 Hz, 2H), 8.27 (d, *J* = 2.0 Hz, 2H), 8.15 (m, 4H), 7.96 (s, br, 2H), 7.86 (dd, *J* = 1.4 Hz, 6.2 Hz, 2H), 4.81 (t, *J* = 6.2 Hz, 4H), 4.23 (s, 6H), 3.97 (dt, *J* = 6.2 Hz, 5.5 Hz, 4H), 3.01 (s, 6H), 2.84 (s, 6H).

Analysis for the thermal hydrogen production by Pt(bpy)(dmMV$^+$•)$_2$.

Since the delayed vent of H$_2$ is detected for 10 min in our analysis as discussed in MS, the H$_2$ evolution curve shown in Fig. 3a was deconvoluted into those of actual and delayed H$_2$ production. It was found that the apparent H$_2$ evolution profile in the range 35-220 min (i.e., 10-195 min after the light-off event) is well fitted to the equation described in Table S1. The apparent H$_2$ evolution profile (Fig. 3a) was thus subtracted with its function curve which is extended to 25 min, leading to the expression for delayed H$_2$ vent component (Fig. 3b) and thermal H$_2$ evolution profile of **Pt(bpy)(dmMV$^+$•)$_2$** (Fig. 3c). The rate of thermal H$_2$ evolution at the sampling point of 25 min (i.e., soon after the light-off event) was estimated to be 0.32 μL/min by the differentiation of the equation.

Table S1. The equation for the H$_2$ evolution profile of **Pt(bpy)(dmMV$^+$•)$_2$**, determined by the least-squares fitting of the apparent H$_2$ evolution profile (Fig. 3a) in the range 35-220 min.

Formula	$f(t) = A_1 e^{-k_1 \mathrm{t}} + A_2 \ln \mathrm{t} + y_0$ [mL]
A_1	-0.01439
k_1	0.06638
A_2	-0.003419
y_0	-0.003427

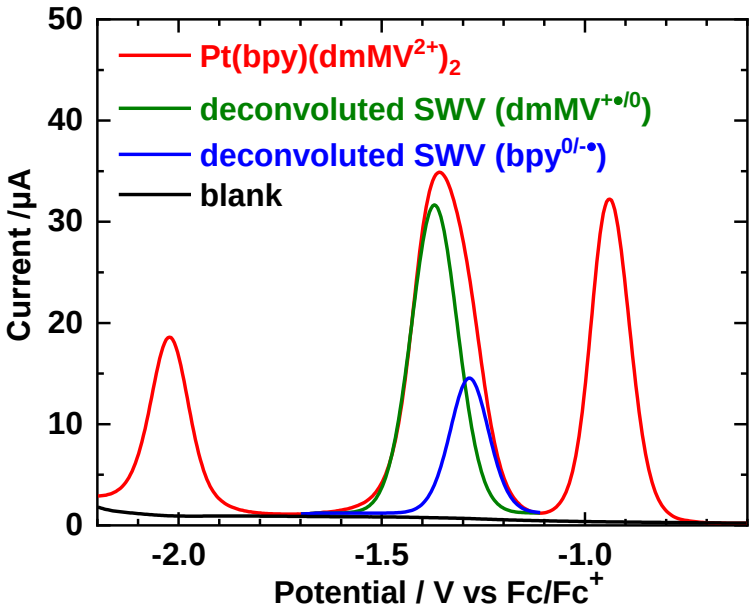


Fig. S1 A SWV of a DMF solution containing TBAP (0.1 M) in the presence of [**Pt(bpy)(dmMV^{2+})$_2$**](PF$_6$)$_4$•H$_2$O (1 mM) under Ar atmosphere at 20 °C. Deconvolution was carried out for the potential range where the successive reductions of viologen and bpy appear (-1.1 V ~ -1.7 V vs Fc/Fc$^+$).

Table S2. Redox potentials of **Pt(bpy)(MV^{2+})$_2$** and **Pt(bpy)(dmMV^{2+})$_2$** determined by SWV.[a]

Compound	$V^{2+/+\bullet}$	$V^{+\bullet/0}$	$bpy^{0/-\bullet}$	$Pt^{II/I}$	Ref.
Pt(bpy)(MV^{2+})$_2$	-0.80	-1.20	-1.30	-1.90	1
Pt(bpy)(dmMV^{2+})$_2$	-0.94	-1.37	-1.28	-2.02	This work

[a]The potentials are given in V vs Fc/Fc$^+$, and determined by the SWVs recorded in DMF containing TBAP (0.1 M) (see Fig. S1). V^{2+} denotes either MV^{2+} or $dmMV^{2+}$.

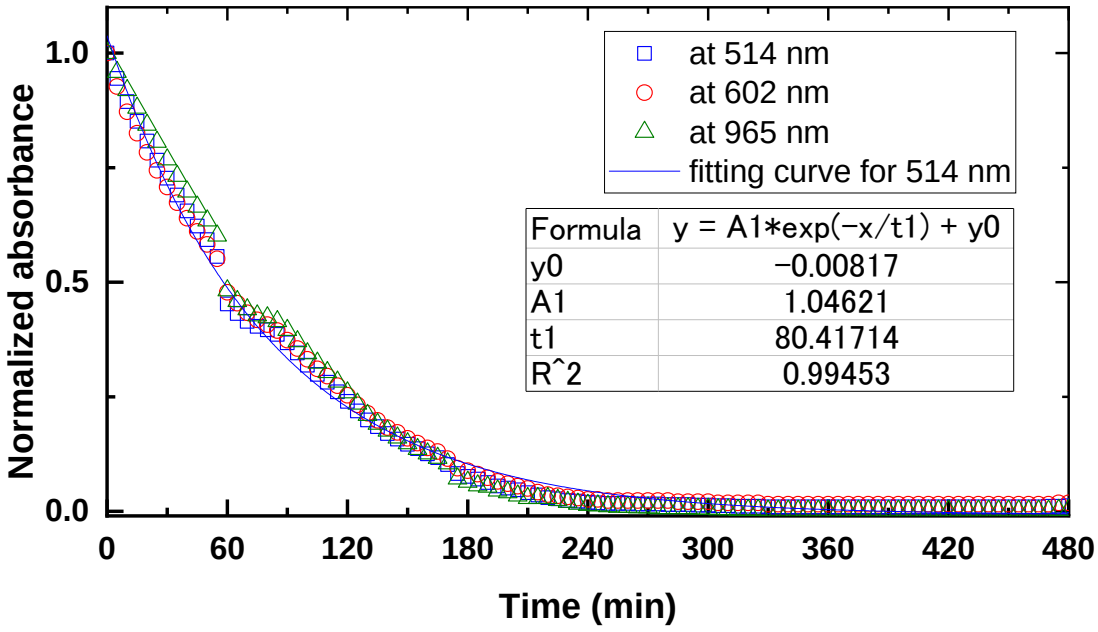


Fig. S2 The time-course of normalized absorbance changes at 514, 602 and 965 nm in the dark after 40-min photolysis of an aqueous acetate buffer solution (pH 5.0; 0.1 M) containing EDTA (disodium salt; 30 mM) and NaCl (0.1 M) in the presence of [**Pt(bpy)(dmMV^{2+})$_2$**](PF$_6$)$_4$•H$_2$O (0.1 mM) under Ar atmosphere at 20 °C. The fitting curve was simulated for the decay at 514 nm.

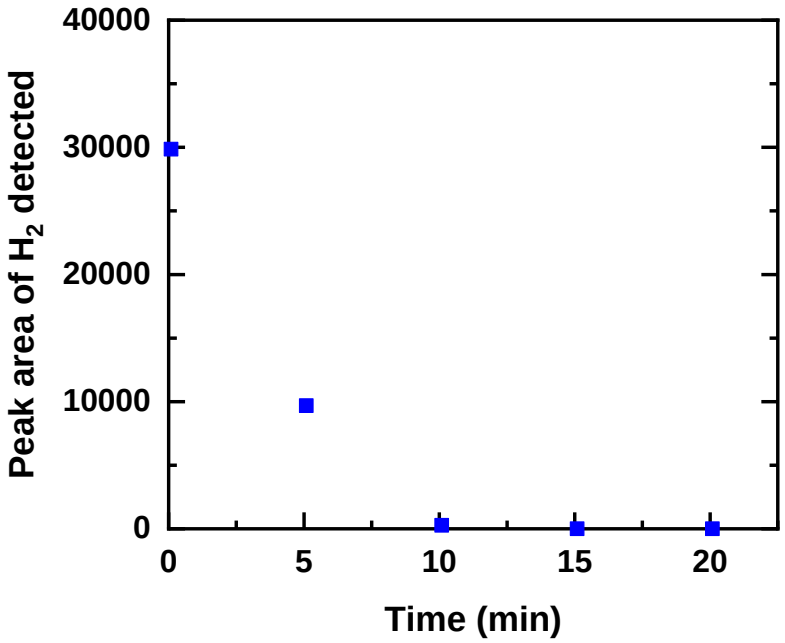


Fig. S3 The time-course for the peak area of H_2 detected by gas chromatography in our automated H_2 monitoring system, where pure water (10 mL) was bubbled with 500 ppm of H_2 gas prior to this experiment.

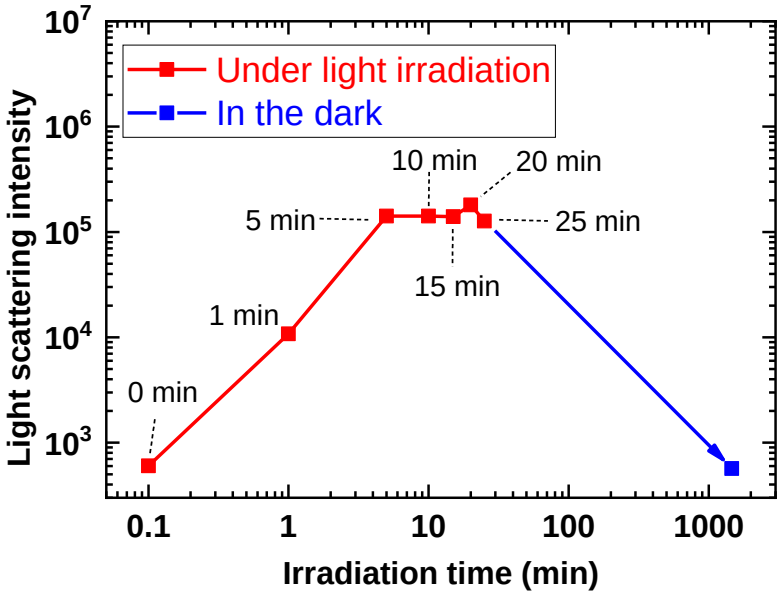


Fig. S4 Changes in light scattering intensity of an aqueous acetate buffer solution (pH 5.0; 0.1 M) containing [**Pt(bpy)(dmMV^{2+})$_2$**](PF$_6$)$_4$•H$_2$O (0.1 mM), EDTA (30 mM; disodium salt), and NaCl (0.1 M) under Ar atmosphere at 20 °C. The light irradiation by 300 W Xe lamp ($400 < \lambda < 800$ nm) was carried out only for the first 25 min, followed by leaving the solution in the dark for 24 h.

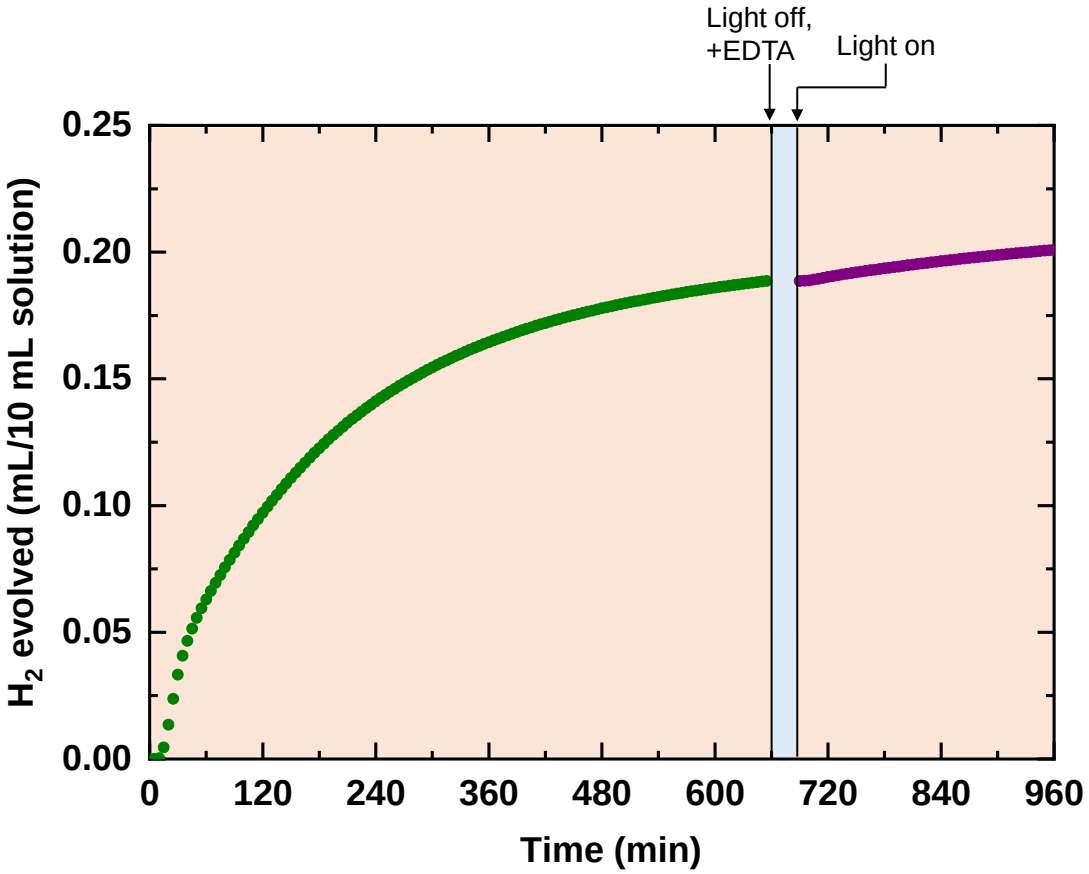
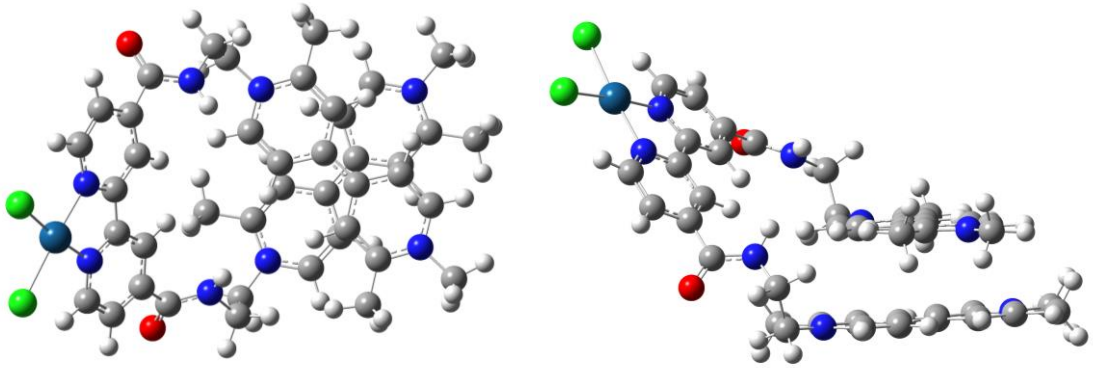


Fig. S5 Photochemical H_2 evolution from an aqueous acetate buffer solution (pH 5.0; 0.1 M) containing [**Pt(bpy)(dmMV^{2+})$_2$**]$(PF_6)_4$•H_2O (0.1 mM), EDTA (30 mM; disodium salt) and NaCl (0.1 M), followed by adding EDTA (30 mM; disodium salt) at 11 h under Ar atmosphere at 20 °C. After the addition of EDTA, the solution was bubbled with Ar for 30 min prior to the photolysis.

Table S3. Gibbs free energies computed for **Pt(bpy)(dmMV^{+}•)$_2$** in its closed-shell singlet, open-shell singlet and triplet states. All the structures were fully optimized at M06/LanL2DZ(Pt)/6-31G**(HCNOCl) level of DFT with solvation in water taken into consideration using polarizable continuum model (PCM) method implemented in Gaussian 16 package.[6]

Spin state	Gibbs energy (kcal/mol)	Relative energy (kcal/mol)	Coordinate
closed-shell singlet	-2041726.54	0.6	Table S4
open-shell singlet	-2041727.13	0.0	Table S5
triplet	-2041724.83	2.3	Table S6

Table S4. Geometry optimized for **Pt(bpy)(dmMV^{+}•)$_2$** in its closed-shell singlet state. Optimized at the M06 level of DFT using LanL2DZ(Pt) and 6-31G**(HCNOCl) basis sets with solvation in water taken into consideration (PCM).[a]



Top view Side view

atom	x	y	z	Mulliken charge
Pt	-6.26249	-0.07077	0.44014	0.37855
Cl	-7.79531	-1.88162	0.55784	-0.36132
Cl	-7.94308	1.37911	1.28592	-0.36096
C	4.26561	-2.57796	2.39327	0.31340
C	3.67472	-1.54974	1.70459	-0.16629

C	4.25079	-0.25301	1.60689	0.08331
C	5.47530	-0.08642	2.31947	-0.15832
C	6.03902	-1.12634	2.99163	0.07076
N	5.46626	-2.36584	3.03069	-0.43709
C	3.64412	0.80465	0.86941	0.07691
C	4.20161	2.11394	0.82357	-0.17471
C	2.43276	0.64353	0.13146	-0.12984
C	3.63128	3.15080	0.13502	0.30821
C	1.89770	1.68480	-0.56045	0.06048
N	2.46104	2.93512	-0.56387	-0.43865
C	6.12018	-3.43870	3.77737	-0.26951
H	2.72031	-1.76754	1.23361	0.11884
H	5.99248	0.86614	2.36054	0.14708
H	6.97072	-1.01925	3.53784	0.19329
H	5.12307	2.34153	1.35078	0.12948
H	1.91169	-0.30769	0.07860	0.12819
H	0.99802	1.57665	-1.15936	0.17300
H	7.08449	-3.07944	4.13702	0.18176
H	5.51364	-3.73792	4.63709	0.18804
H	6.28836	-4.30661	3.13460	0.18426
C	8.04350	0.55801	0.07780	0.30915
C	7.07673	-0.35067	-0.26605	-0.17392
C	5.95470	-0.01741	-1.07469	0.08714
C	5.93491	1.32498	-1.54921	-0.15856
C	6.91780	2.20158	-1.20320	0.06954
N	7.95843	1.84838	-0.39301	-0.43492
C	4.93464	-0.96323	-1.39435	0.07974
C	3.80679	-0.63530	-2.19872	-0.18115
C	4.97992	-2.31539	-0.94816	-0.15181
C	2.80435	-1.52743	-2.48546	0.31892
C	3.98421	-3.18389	-1.26456	0.06189
N	2.89571	-2.81598	-2.01155	-0.43919
C	8.96241	2.84731	-0.03267	-0.26941
H	7.20435	-1.35618	0.12173	0.13142
H	5.15135	1.69331	-2.20369	0.15065
H	6.92610	3.22594	-1.56156	0.19269

H	3.69508	0.36020	-2.61600	0.13156
H	5.80637	-2.70146	-0.36028	0.15119
H	4.00889	-4.22434	-0.95314	0.19054
H	8.97814	3.00425	1.04961	0.18587
H	9.95563	2.53543	-0.36657	0.18654
H	8.70982	3.78959	-0.51899	0.18158
C	1.88432	-3.85221	-2.25798	-0.13323
H	2.41894	-4.76972	-2.52611	0.19223
H	1.27294	-3.57627	-3.11858	0.17278
C	1.72749	4.03240	-1.20378	-0.14261
H	1.21145	3.62641	-2.07961	0.18426
H	2.44033	4.77635	-1.56493	0.18200
C	1.00240	-4.12858	-1.04927	-0.08336
H	1.60711	-4.17345	-0.13812	0.14501
H	0.54233	-5.11336	-1.19092	0.18068
N	-0.05972	-3.15395	-0.84913	-0.53002
C	-1.23972	-3.36435	-1.49172	0.53923
O	-1.37562	-4.20390	-2.37096	-0.52034
C	-2.41365	-2.54617	-1.04337	0.02688
C	-2.34969	-1.19269	-0.72699	-0.08427
C	-3.64420	-3.19386	-0.98496	-0.12874
C	-3.51226	-0.52660	-0.35236	0.32181
H	-1.40892	-0.65245	-0.79795	0.16451
C	-4.75653	-2.49469	-0.55636	0.12250
H	-3.72600	-4.24078	-1.25768	0.19387
H	-5.73372	-2.95738	-0.44985	0.19287
C	-3.59184	0.91261	-0.08547	0.32468
C	-2.52802	1.79124	-0.24084	-0.08440
C	-5.01747	2.68223	0.46372	0.12003
C	-2.73319	3.15533	-0.06460	0.01757
H	-1.55771	1.41658	-0.55036	0.15962
C	-4.00399	3.60493	0.27818	-0.12728
H	-6.02417	2.96957	0.75455	0.19288
H	-4.19986	4.66597	0.39362	0.19376
C	0.72279	4.68555	-0.26294	-0.09969
C	-1.66617	4.16842	-0.35509	0.55715

O	-1.95470	5.21036	-0.92549	-0.52040
N	-0.40767	3.82326	0.02230	-0.54412
H	0.32379	5.58771	-0.73607	0.19003
H	1.20859	4.98456	0.67390	0.17047
H	-0.05561	-2.60255	-0.00061	0.33063
N	-4.68929	-1.19306	-0.24315	-0.65953
N	-4.81726	1.36882	0.27821	-0.66184
H	-0.28867	3.06446	0.68187	0.32245
C	4.26129	4.50204	0.09564	-0.45460
H	4.55094	4.78139	-0.92515	0.17919
H	3.59912	5.28850	0.47522	0.17189
H	5.16377	4.50202	0.71135	0.16837
C	3.65571	-3.93367	2.47762	-0.44653
H	4.28390	-4.69084	1.99196	0.17759
H	3.50696	-4.25143	3.51580	0.17961
H	2.68009	-3.93300	1.98659	0.15680
C	9.18608	0.20089	0.96317	-0.44980
H	10.15236	0.37741	0.47687	0.17801
H	9.17418	0.78802	1.88987	0.17484
H	9.12948	-0.85599	1.23284	0.16752
C	1.61596	-1.13268	-3.29394	-0.44443
H	1.54608	-1.70206	-4.22836	0.18554
H	0.68352	-1.29076	-2.73708	0.15168
H	1.68322	-0.07339	-3.55166	0.16796

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[a]Part of the Gaussian output file:

Charge/Multiplicity: Charge = 2 Multiplicity = 1

SCF Done: E(RM06) = -3254.43321225 A.U. after 6 cycles

Item	Value	Threshold	Converged?
Maximum Force	0.000013	0.000450	YES
RMS Force	0.000002	0.000300	YES

1 2 3

	A	A	A
Frequencies --	11.7982	17.4964	27.4828
Red. masses --	7.4035	6.5832	5.3650

Zero-point correction=	0.824769 (Hartree/Particle)
Thermal correction to Energy=	0.876991
Thermal correction to Enthalpy=	0.877935
Thermal correction to Gibbs Free Energy=	0.737588
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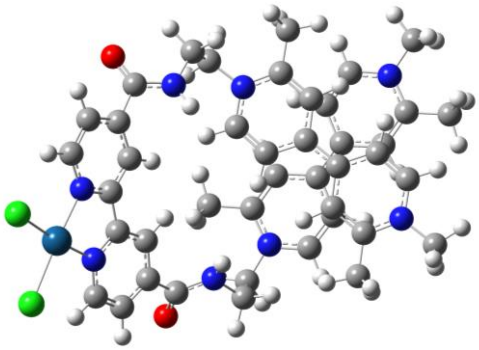
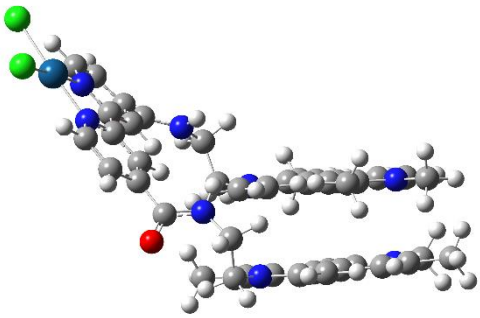
Sum of electronic and thermal Energies=	-3253.556222
Sum of electronic and thermal Enthalpies=	-3253.555278
Sum of electronic and thermal Free Energies=	-3253.695624

Table S5. Geometry optimized for **Pt(bpy)(dmMV$^{+\bullet}$)$_2$** in its open-shell singlet state. Optimized at the M06 level of DFT using LanL2DZ(Pt) and 6-31G**(HCNOCl) basis sets with solvation in water taken into consideration (PCM).[a]



Top view



Side view

atom	x	y	z	Mulliken charge	Mulliken spin density
Pt	-6.25982	-0.06988	0.43771	0.37858	0.00001
Cl	-7.79244	-1.88082	0.55734	-0.36136	0.00000
Cl	-7.94035	1.38040	1.28305	-0.36100	0.00000

C	4.25317	-2.57566	2.40667	0.31396	0.02097
C	3.66270	-1.54551	1.72069	-0.16656	0.03005
C	4.23737	-0.24793	1.62952	0.08438	0.07174
C	5.46218	-0.08389	2.34156	-0.15876	0.02179
C	6.02568	-1.12545	3.01107	0.07134	0.02047
N	5.45278	-2.36517	3.04670	-0.43675	0.06873
C	3.63347	0.81089	0.89088	0.07784	0.09820
C	4.19382	2.11889	0.84452	-0.17553	0.02157
C	2.42886	0.64861	0.14267	-0.13013	0.00771
C	3.62868	3.15505	0.15107	0.30868	0.03159
C	1.89874	1.68887	-0.55409	0.05988	0.03350
N	2.46210	2.93968	-0.55454	-0.43866	0.07168
C	6.10515	-3.43955	3.79245	-0.26966	-0.00518
H	2.71112	-1.76359	1.24405	0.11962	-0.00221
H	5.98147	0.86761	2.38167	0.14776	-0.00166
H	6.95813	-1.02028	3.55632	0.19331	-0.00142
H	5.11432	2.34534	1.37404	0.13006	-0.00182
H	1.91141	-0.30427	0.08295	0.12849	-0.00115
H	1.00455	1.57962	-1.16104	0.17308	-0.00197
H	7.06938	-3.08157	4.15359	0.18186	0.00008
H	5.49736	-3.73936	4.65110	0.18826	0.00381
H	6.27316	-4.30673	3.14870	0.18434	0.00288
C	8.04240	0.56035	0.06899	0.30958	-0.02086
C	7.07926	-0.35154	-0.27594	-0.17427	-0.02937
C	5.96186	-0.02473	-1.09332	0.08811	-0.07447
C	5.94030	1.31661	-1.57108	-0.15961	-0.02007
C	6.92031	2.19608	-1.22541	0.07001	-0.02287
N	7.95874	1.84814	-0.40947	-0.43487	-0.06893
C	4.94311	-0.97256	-1.41071	0.07957	-0.09573
C	3.81197	-0.64558	-2.21089	-0.18141	-0.02505
C	4.98661	-2.32265	-0.95765	-0.15222	-0.00588
C	2.80751	-1.53685	-2.49133	0.31886	-0.02808
C	3.98901	-3.19084	-1.26783	0.06167	-0.03621
N	2.89827	-2.82437	-2.01342	-0.43938	-0.07089
C	8.96230	2.84874	-0.05327	-0.26948	0.00520
H	7.20372	-1.35383	0.12131	0.13127	0.00210

H	5.15682	1.68159	-2.22758	0.15112	0.00152
H	6.92757	3.21933	-1.58692	0.19254	0.00165
H	3.69778	0.35023	-2.62694	0.13129	0.00200
H	5.81252	-2.70626	-0.36720	0.15122	0.00101
H	4.01213	-4.22972	-0.95112	0.18988	0.00227
H	8.98085	3.00753	1.02864	0.18556	-0.00340
H	9.95508	2.53741	-0.38933	0.18664	-0.00332
H	8.70733	3.78998	-0.54038	0.18150	-0.00004
C	1.88565	-3.86010	-2.25541	-0.13319	0.00477
H	2.41901	-4.77928	-2.52044	0.19184	-0.00265
H	1.27437	-3.58663	-3.11692	0.17258	-0.00030
C	1.73238	4.03659	-1.19886	-0.14259	-0.00481
H	1.22019	3.63006	-2.07672	0.18408	0.00137
H	2.44708	4.78011	-1.55728	0.18190	0.00081
C	1.00342	-4.13202	-1.04585	-0.08292	-0.00434
H	1.60818	-4.17471	-0.13466	0.14471	0.00045
H	0.54249	-5.11684	-1.18463	0.18041	-0.00035
N	-0.05784	-3.15581	-0.84789	-0.52991	0.00019
C	-1.23738	-3.36541	-1.49153	0.53901	-0.00010
O	-1.37311	-4.20486	-2.37090	-0.52033	-0.00015
C	-2.41117	-2.54642	-1.04409	0.02688	-0.00003
C	-2.34692	-1.19285	-0.72802	-0.08437	-0.00010
C	-3.64194	-3.19370	-0.98599	-0.12876	-0.00008
C	-3.50942	-0.52623	-0.35407	0.32177	0.00001
H	-1.40595	-0.65296	-0.79866	0.16454	0.00008
C	-4.75416	-2.49411	-0.55785	0.12253	0.00003
H	-3.72398	-4.24066	-1.25849	0.19386	0.00000
H	-5.73149	-2.95650	-0.45137	0.19286	0.00000
C	-3.58898	0.91325	-0.08817	0.32463	-0.00003
C	-2.52514	1.79196	-0.24351	-0.08445	0.00021
C	-5.01546	2.68318	0.45814	0.12009	-0.00005
C	-2.73092	3.15624	-0.06903	0.01752	-0.00007
H	-1.55434	1.41720	-0.55159	0.15973	-0.00008
C	-4.00212	3.60590	0.27215	-0.12727	0.00013
H	-6.02240	2.97059	0.74808	0.19286	0.00000
H	-4.19831	4.66703	0.38610	0.19374	-0.00001

C	0.72365	4.69055	-0.26301	-0.09969	0.00452
C	-1.66442	4.16997	-0.35933	0.55709	0.00033
O	-1.95333	5.21096	-0.93132	-0.52051	0.00034
N	-0.40619	3.82687	0.02055	-0.54395	-0.00006
H	0.32466	5.59097	-0.73941	0.18997	0.00057
H	1.20611	4.99248	0.67464	0.17043	-0.00031
H	-0.05490	-2.60506	0.00106	0.33059	-0.00002
N	-4.68664	-1.19242	-0.24496	-0.65953	-0.00007
N	-4.81474	1.36965	0.27428	-0.66183	0.00013
H	-0.28723	3.06847	0.68059	0.32234	-0.00009
C	4.26201	4.50466	0.11010	-0.45449	-0.00250
H	4.55685	4.77933	-0.91047	0.17906	0.00219
H	3.60015	5.29411	0.48394	0.17179	0.00168
H	5.16184	4.50467	0.72965	0.16835	-0.00013
C	3.64548	-3.93280	2.48267	-0.44650	-0.00160
H	4.27633	-4.68611	1.99441	0.17760	0.00144
H	3.49475	-4.25642	3.51873	0.17975	0.00104
H	2.67116	-3.93118	1.98915	0.15685	-0.00012
C	9.17784	0.21063	0.96643	-0.44973	0.00191
H	10.14830	0.38862	0.48919	0.17776	-0.00134
H	9.15451	0.80153	1.89056	0.17487	-0.00144
H	9.12217	-0.84528	1.24002	0.16747	0.00007
C	1.61581	-1.14216	-3.29499	-0.44443	0.00264
H	1.54145	-1.71213	-4.22873	0.18533	-0.00199
H	0.68575	-1.29929	-2.73399	0.15130	-0.00207
H	1.68247	-0.08313	-3.55403	0.16781	-0.00002

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[a]Part of the Gaussian output file:

Charge/Multiplicity: Charge = 2 Multiplicity = 1 (Unrestricted)

SCF Done: E(UM06) = -3254.43340742 A.U. after 12 cycles

Annihilation of the first spin contaminant:

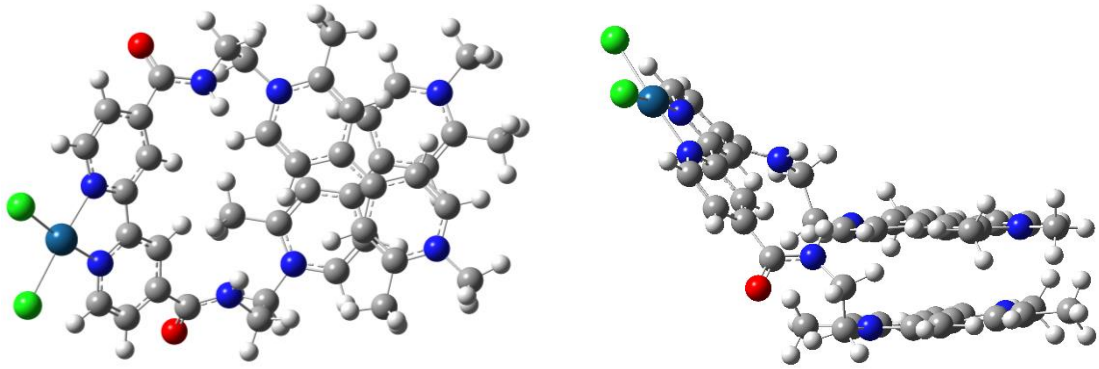
S**2 before annihilation 0.2476, after 0.0025

Item	Value	Threshold	Converged?
Maximum Force	0.000010	0.000450	YES
RMS Force	0.000001	0.000300	YES

	1	2	3
	A	A	A
Frequencies --	12.8664	16.0391	27.515
Red. masses --	7.4353	5.8780	5.398

Zero-point correction=	0.824630 (Hartree/Part
Thermal correction to Energy=	0.876982
Thermal correction to Enthalpy=	0.877926
Thermal correction to Gibbs Free Energy=	0.736845
Sum of electronic and zero-point Energies=	-3253.608777
Sum of electronic and thermal Energies=	-3253.556425
Sum of electronic and thermal Enthalpies=	-3253.555481
Sum of electronic and thermal Free Energies=	-3253.696563

Table S6. Geometry optimized for **Pt(bpy)(dmMV^{+}•)$_2$** in its triplet state. Optimized at the M06 level of DFT using LanL2DZ(Pt) and 6-31G**(HCNOCl) basis sets with solvation in water taken into consideration (PCM).[a]



Top view Side view

atom	x	y	z	Mulliken charge	Mulliken spin density
Pt	-6.08166	0.11681	0.32397	0.37680	0.00009
Cl	-7.74489	-1.57808	0.27571	-0.36021	0.00000
Cl	-7.70727	1.64284	1.14642	-0.36033	0.00000
C	4.05152	-3.25474	2.58412	0.32253	0.04402
C	3.55356	-2.09243	2.05686	-0.17638	0.05426
C	4.29297	-0.87870	2.02752	0.08359	0.15102
C	5.58832	-0.94703	2.61502	-0.17246	0.03685
C	6.06414	-2.11919	3.11488	0.07938	0.04885
N	5.32733	-3.27141	3.10236	-0.43995	0.14001
C	3.78276	0.31420	1.43574	0.08037	0.18750
C	4.40427	1.58138	1.61894	-0.18765	0.04225
C	2.65039	0.31567	0.57170	-0.13727	0.00417
C	3.95185	2.72812	1.02455	0.31190	0.06706
C	2.24148	1.46079	-0.03447	0.07033	0.08098
N	2.85685	2.66873	0.18437	-0.43492	0.14835
C	5.89354	-4.49427	3.66707	-0.27091	-0.01055
H	2.53485	-2.12294	1.68161	0.12938	-0.00366
H	6.24527	-0.08421	2.64929	0.15404	-0.00391
H	7.05698	-2.19945	3.54461	0.19754	-0.00302
H	5.26547	1.68293	2.27318	0.14286	-0.00358
H	2.12967	-0.60169	0.31133	0.12592	-0.00232
H	1.42686	1.47478	-0.75307	0.17409	-0.00467
H	6.93516	-4.30983	3.93010	0.18255	0.00023
H	5.35079	-4.79262	4.56890	0.18925	0.00790
H	5.85632	-5.30731	2.93780	0.18505	0.00571
C	7.25607	1.50747	-0.54315	0.31510	0.04560
C	6.46857	0.41429	-0.79177	-0.18066	0.05647
C	5.33861	0.45348	-1.65566	0.09273	0.15874
C	5.08566	1.72202	-2.25442	-0.17056	0.03397
C	5.89073	2.78801	-1.99919	0.05932	0.05134
N	6.96649	2.70705	-1.15587	-0.43353	0.14330
C	4.49978	-0.67957	-1.86966	0.07889	0.18350

C	3.32853	-0.62513	-2.67797	-0.19205	0.04621
C	4.75027	-1.94418	-1.26192	-0.15803	0.01215
C	2.47137	-1.68281	-2.83161	0.32503	0.05728
C	3.88782	-2.97875	-1.43400	0.07373	0.07649
N	2.74886	-2.87290	-2.19216	-0.44250	0.14233
C	7.81685	3.87803	-0.95546	-0.27106	-0.01050
H	6.74045	-0.50043	-0.27305	0.12993	-0.00439
H	4.24854	1.88298	-2.92586	0.15789	-0.00297
H	5.71787	3.75984	-2.45123	0.19509	-0.00347
H	3.06083	0.28767	-3.20109	0.14016	-0.00353
H	5.62419	-2.12505	-0.64412	0.14812	-0.00219
H	4.06252	-3.95156	-0.98197	0.18469	-0.00449
H	7.90821	4.11189	0.10882	0.18026	0.00559
H	8.81388	3.70753	-1.37249	0.19149	0.00827
H	7.36672	4.73170	-1.46358	0.18130	0.00019
C	1.86831	-4.04425	-2.23883	-0.13926	-0.00953
H	2.49740	-4.92780	-2.39152	0.19116	0.00516
H	1.20120	-3.97253	-3.09901	0.17449	0.00057
C	2.27952	3.86513	-0.43402	-0.13804	-0.00971
H	1.87130	3.57388	-1.40791	0.18093	0.00310
H	3.07212	4.59329	-0.62154	0.17674	0.00164
C	1.06207	-4.22519	-0.96163	-0.07302	0.01060
H	1.72077	-4.16968	-0.08874	0.13490	-0.00207
H	0.61738	-5.22732	-0.98279	0.18054	0.00071
N	0.00272	-3.24270	-0.79278	-0.53586	-0.00049
C	-1.18597	-3.45992	-1.41287	0.54559	0.00019
O	-1.34829	-4.34445	-2.24287	-0.52232	0.00043
C	-2.32870	-2.57139	-1.01895	0.03209	-0.00002
C	-2.19326	-1.23314	-0.66006	-0.09470	0.00015
C	-3.60132	-3.13267	-1.05520	-0.12916	0.00025
C	-3.32735	-0.49828	-0.33051	0.32083	0.00002
H	-1.21676	-0.75524	-0.66020	0.16978	-0.00008
C	-4.68878	-2.36750	-0.67832	0.12255	-0.00010
H	-3.73392	-4.16463	-1.36259	0.19334	-0.00001
H	-5.70053	-2.76231	-0.64869	0.19303	0.00000
C	-3.32416	0.93377	-0.01189	0.32528	-0.00008

C	-2.19520	1.74258	-0.05766	-0.08805	0.00046
C	-4.66663	2.77797	0.50551	0.12108	-0.00011
C	-2.32509	3.11180	0.15255	0.01716	-0.00013
H	-1.22716	1.31486	-0.30040	0.16538	-0.00012
C	-3.58592	3.63599	0.41760	-0.12725	0.00032
H	-5.66964	3.12202	0.74236	0.19288	0.00000
H	-3.72051	4.70378	0.55564	0.19401	-0.00001
C	1.18995	4.49251	0.42536	-0.10054	0.00916
C	-1.17883	4.06661	-0.00605	0.55216	0.00066
O	-1.34642	5.12666	-0.59117	-0.52044	0.00069
N	0.00628	3.65865	0.51730	-0.54071	-0.00015
H	0.88086	5.44031	-0.02531	0.18981	0.00125
H	1.56898	4.70542	1.43200	0.17131	-0.00055
H	0.02846	-2.64253	0.02099	0.32988	0.00014
N	-4.55229	-1.08349	-0.31886	-0.66085	0.00020
N	-4.53834	1.46054	0.29010	-0.66148	0.00031
H	0.00676	2.88250	1.16750	0.32390	-0.00020
C	4.63521	4.03687	1.23258	-0.43944	-0.00596
H	5.03956	4.43372	0.29192	0.15310	0.00365
H	3.96882	4.80141	1.64776	0.17615	0.00432
H	5.46956	3.90714	1.92597	0.17019	-0.00002
C	3.25842	-4.51464	2.61953	-0.45072	-0.00374
H	3.68990	-5.28147	1.96380	0.18180	0.00307
H	3.20729	-4.93808	3.62860	0.17807	0.00290
H	2.23608	-4.31883	2.28782	0.16262	-0.00004
C	8.41271	1.45587	0.39311	-0.44750	-0.00371
H	9.34611	1.76876	-0.08833	0.17746	0.00301
H	8.25430	2.11238	1.25840	0.17418	0.00333
H	8.54659	0.43679	0.76210	0.16795	-0.00014
C	1.25562	-1.58372	-3.68868	-0.44714	-0.00499
H	1.29128	-2.29053	-4.52628	0.18320	0.00420
H	0.33843	-1.78472	-3.12340	0.15067	0.00418
H	1.18154	-0.57670	-4.10386	0.17143	-0.00012

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[a]Part of the Gaussian output file:

Charge/Multiplicity: Charge = 2 Multiplicity = 3 (Unrestricted)

SCF Done: E(UM06) = -3254.42857867 A.U. after 6 cycles

Annihilation of the first spin contaminant:
S**2 before annihilation 2.0096, after 2.0001

Item	Value	Threshold	Converged?
Maximum Force	0.000022	0.000450	YES
RMS Force	0.000003	0.000300	YES

	1	2	3
	A	A	A
Frequencies --	11.7504	20.9159	23.6568
Red. masses --	6.3370	5.9568	6.8534

Zero-point correction= 0.824805 (Hartree/Particle)
Thermal correction to Energy= 0.877199
Thermal correction to Enthalpy= 0.878143
Thermal correction to Gibbs Free Energy= 0.735675
Sum of electronic and zero-point Energies= -3253.603774
Sum of electronic and thermal Energies= -3253.551380
Sum of electronic and thermal Enthalpies= -3253.550436
Sum of electronic and thermal Free Energies= -3253.692904

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