

Electronic Supplementary Information

Formation of supramolecular hetero-triads by controlling hydrogen bonding of conjugate bases with a diprotonated porphyrin based on electrostatic interaction

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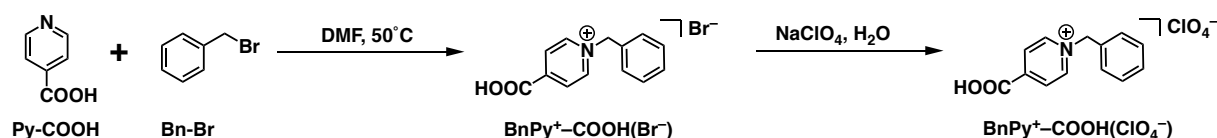
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Experimental Section

Materials.

General. Acetonitrile (MeCN) and *N,N*-dimethylformamide (DMF) were distilled over CaH₂ and NaOH, respectively, before use. Spectroscopic-grade acetone and methanol used for spectroscopic measurements were purchased from commercial sources and used without further purification. Chloroform (CHCl₃) was distilled over CaH₂ and CDCl₃ was purified by passing through alumina before ¹H NMR measurements. *p*-Toluene sulfonic acid (TsOH), trifluoroacetic acid (TFA), dichloroacetic acid (DCA), and *m*-nitrobenzoic acid (NBA, NO₂PhCOOH) were purchased from commercial sources and used without further purification. H₂DPP was synthesized according to the reported procedure.^{1,2}

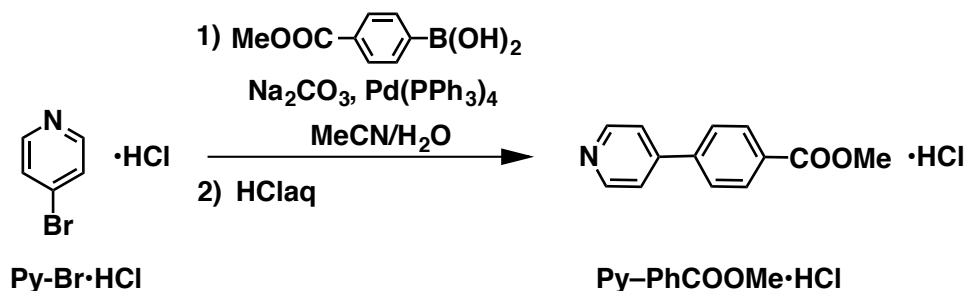
Synthesis.



***N*-Benzyl-4-carboxypyridinium bromide (BnPy⁺-COOH(Br⁻)).** BnPy⁺-COOH(Br⁻) was synthesized according to the modified procedure in the previous report.³ To a suspension of Py-COOH (615 mg, 5.00 mmol) in DMF (40 mL), benzylbromide (Bn-Br, 855 mg, 5.00 mmol) in DMF (5 mL) was added dropwise and stirred at 60 °C for 14 h under Ar. When the color of the suspension turned to yellow, the solvent was evaporated to dryness under vacuum at 50 °C. Obtained colorless solids were dissolved in MeOH, then ethyl acetate was added as a poor solvent to precipitate a colorless solid. The solid was filtered and dried to give the desired compound as a colorless solid (1.24 g, 4.23 mmol) in 85% yield. ¹H NMR (acetone-*d*₆ with one drop of methanol-*d*₄, 400 MHz): δ 6.18 (s, 2H, CH₂), 7.48-7.50 (m, 3H, H₂, H₄ of Ph), 7.65 (m, 2H, H₃ of Ph), 8.63 (d, *J* = 6.4 Hz, 2H, H₃ of Py-COOH), 9.47 (d, *J* = 6.4 Hz, 2H, H₂ of Py-COOH). ESI-MS (MeOH): *m/z* = 235.98 (M-Br⁻-H⁺+Na⁺).

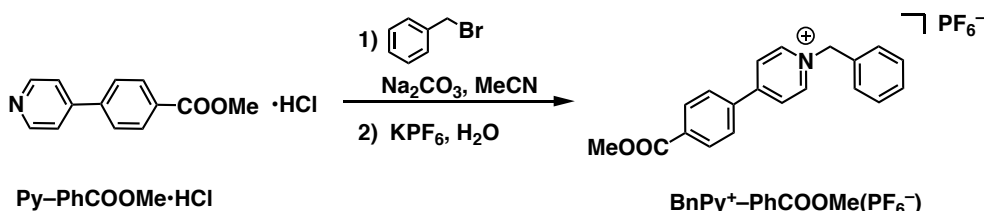
***N*-Benzyl-4-carboxypyridinium perchlorate (BnPy⁺-COOH(ClO₄⁻)).** BnPy⁺-COOH(Br⁻) (246 mg, 0.839 mmol) was dissolved in H₂O (5 mL), then an aqueous solution of NaClO₄ (2.2 g, 18 mmol in 2 mL) was added dropwise to form a colorless solid. Then, the colorless solid was filtered to afford the title compound as colorless needle-shaped crystals (55 mg, 0.18 mmol) in 21% yield. ¹H NMR (acetone-*d*₆, 400 MHz): δ 6.30 (s, 2H, CH₂), 7.50-7.52 (m, 3H,

H2, H4 of Ph), 7.67 (m, 2H, H3 of Ph), 8.68 (d, $J = 6.4$ Hz, 2H, H3 of Py-COOH), 9.47 (d, $J = 6.4$ Hz, 2H, H2 of Py-COOH). ^{13}C NMR (acetone- d_6 , 100 MHz): δ 65.0, 128.2, 129.5, 129.9, 133.2, 145.8, 146.4, 162.4. ESI-MS (MeOH): $m/z = 235.98$ ($\text{M}-\text{ClO}_4^- - \text{H}^+ + \text{Na}^+$). Elemental analysis (%): Calcd for $\text{C}_{13}\text{H}_{10}\text{NO}_2 \cdot \text{ClO}_4 \cdot 0.75\text{C}_4\text{H}_8\text{O}_2$: C 48.90, H 4.48, N: 4.15; Found: C 48.86, H 4.52, N 4.46. m.p. ($^\circ\text{C}$): 151-153 $^\circ\text{C}$.



4-Methoxycarbonylphenylpyridine hydrochloride (Py-PhCOOMe·HCl).

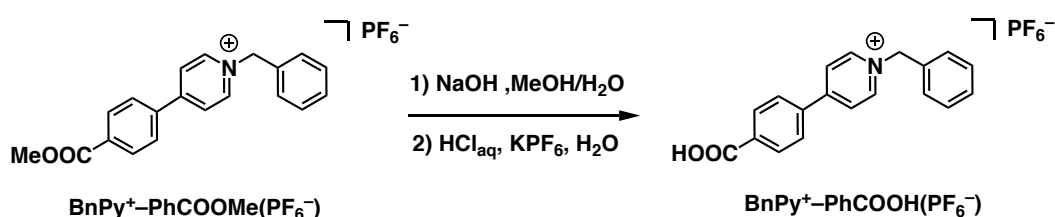
Py-PhCOOMe·HCl was synthesized according with the previous report.⁴ 4-Bromopyridine hydrochloride salt (Py-Br·HCl, 661 mg, 3.36 mmol), 4-methoxycarbonylphenylboronic acid (603 mg, 3.35 mmol), Na_2CO_3 (662 mg, 6.24 mmol), and $\text{Pd(PPh}_3)_4$ (260 mg, 0.225 mmol) was suspended in degassed MeCN (15 mL). Then, argon purged H_2O (15 mL) was added and heated at 90 $^\circ\text{C}$ for 20 h. The yellow hot suspension was filtered to obtain a yellow filtrate. When 1 M HCl_{aq} was added to the yellow solution until $\text{pH} = 1$ and the solution was concentrated, yellow solid appeared and the solid was removed by filtration. The colorless filtrate was evaporated to form colorless solids, which were recrystallized with MeOH/ether to obtain Py-PhCOOMe·HCl (518 mg, 2.08 mmol) in 62% yield. ^1H NMR (acetone- d_6 , 400 MHz): δ 3.96 (s, 3H, COOMe), 8.18 (d, $J = 8.8$ Hz, 2H, H2 of Ph), 8.25 (d, $J = 8.8$ Hz, 2H, H3 of Ph), 8.49 (d, $J = 6.8$ Hz, 2H, H3 of Py), 8.96 (d, $J = 6.8$ Hz, 2H, H2 of Py).



N-Benzyl-4-methoxycarboxyphenylpyridinium hexafluorophosphate (BnPy⁺-PhCOOMe(PF₆⁻)).

$\text{BnPy}^+ - \text{PhCOOMe}(\text{PF}_6^-)$ was synthesized according with the previous report.³ Py-PhCOOMe·HCl (170 mg, 0.682 mmol) and Na_2CO_3 (115 mg, 1.08 mmol) was suspended in MeCN (10 mL), Bn-Br (116 mg, 0.678 mmol) in MeCN (5 mL) was added

dropwise and stirred at 50 °C for 20 h under Ar. After removing MeCN, the obtained solid was dissolved in water with small portion of acetone. By adding sat. KPF₆aq to the solution, a colorless solid was formed and filtered to obtain BnPy⁺-PhCOOMe(PF₆⁻) (191 mg, 0.439 mmol) in 62% yield. ¹H NMR (acetone-*d*₆, 400 MHz): δ 3.95 (s, 3H, COOMe), 6.13 (s, 2H, CH₂), 7.44-7.54 (m, 3H, H₂, H₄ of Bn), 7.67 (m, 2H, H₃ of Bn), 8.19-8.27 (m, 4H, H₂, H₃ of Ph), 8.69 (d, *J* = 7.2 Hz, 2H, H₃ of Py), 9.36 (d, *J* = 7.2 Hz, 2H, H₂ of Py). ¹³C NMR (acetone-*d*₆, 100 MHz): δ 51.9, 64.0, 126.1, 128.2, 129.1, 129.5, 129.8, 130.4, 133.2, 133.7, 138.1, 145.1, 155.7, 165.5. m.p. (°C): 184-187 °C.



***N*-Benzyl-4-carboxyphenylpyridinium hexafluorophosphate (BnPy⁺-PhCOOH(PF₆⁻)):** BnPy⁺-PhCOOMe(PF₆⁻) (101 mg, 0.232 mmol) was dissolved in a MeOH/H₂O (1:2, v/v) mixed solvent (15 mL), then KOH (531 mg) in MeOH (5 mL) was added slowly and stirred at room temperature for 8 h. The pale yellow solution was neutralized with 2M HCl_{aq} and concentrated. Sat. KPF₆aq was added to form solids, which were filtered to give a pale yellow solid of BnPy⁺-PhCOOH(PF₆⁻) (73 mg, 0.17 mmol) in 75% yield. ¹H NMR (acetone-*d*₆, 400 MHz): δ 6.13 (s, 2H, CH₂), 7.52-7.54 (m, 3H, H₂, H₄ of Bn), 7.66 (m, 2H, H₃ of Bn), 8.20 (d, *J* = 8.6 Hz, 2H, H₂ of Ph), 8.27 (d, *J* = 8.6 Hz, 2H, H₃ of Ph), 8.69 (d, *J* = 7.2 Hz, 2H, H₃ of Py), 9.37 (d, *J* = 7.2 Hz, 2H, H₂ of Py). ¹³C NMR (acetone-*d*₆, 100 MHz): δ 64.8, 126.8, 129.3, 130.0, 130.4, 130.6, 131.5, 134.5, 138.9, 145.8, 156.5, 166.9. ESI-MS (MeOH): *m/z* = 290.06 (M-PF₆⁻). Elemental analysis (%): Calcd for C₁₉H₁₆NO₂•PF₆•0.5H₂O: C 51.36, H 3.86, N 3.15. Found: C 51.27, H 3.66, N 2.96. m.p. (°C): 208-210°C.

Measurements.

X-ray Crystallography on $[\text{H}_4\text{DPP}^{2+}(\text{Cl}^-)(\text{BnPy}^+-\text{PhCOO}^-)](\text{PF}_6^-)$. Single crystals of $[\text{H}_4\text{DPP}^{2+}(\text{Cl}^-)(\text{BnPy}^+-\text{PhCOO}^-)](\text{PF}_6^-)$ were grown by vapor diffusion of 2-propanol in acetone solution of H_2DPP in the presence of 2 eq of $\text{BnPy}^+-\text{PhCOOH}(\text{PF}_6^-)$ under diluted CHCl_3 and CH_2Cl_2 atmosphere. All measurements were performed at 120 K on a Bruker APEXII Ultra diffractometer. The structure was solved by a direct method (SIR-97) and expanded with differential Fourier techniques. All non-hydrogen atoms were refined anisotropically and the refinements were carried out with full matrix least squares on F. All calculations were performed using the Yadokari-XG crystallographic software package.⁵ In the structure refinements, contribution of the solvent molecules (5 molecules of 2-propanol and 3 molecules of acetone) of crystallization were subtracted from the diffraction pattern by the “Squeeze” program.⁶

Spectroscopic Measurements. ^1H NMR and ^{13}C NMR spectra were measured on Bruker AVANCE400, AVANCEHD400, and DPX400 spectrometers at 268-318 K. For the NMR measurements on protonated species of H_2DPP , a certain amount of HX was added to a solution of H_2DPP (0.15-0.40 mM) in acetone- d_6 or CDCl_3 with 1,4-dioxane as an internal standard. The formation yield of $\text{H}_4\text{DPP}^{2+}(\text{X}^-)_2$ (% H_4DPP) was calculated using eqn (S1) on the basis of initial concentration of H_2DPP ($[\text{H}_2\text{DPP}]_0$) and concentration of $\text{H}_4\text{DPP}^{2+}(\text{X}^-)_2$ ($[\text{H}_4\text{DPP}^{2+}]$) determined by the relative intensity of the ^1H NMR signal of *ortho*-protons of the *meso*-phenyl groups to that of 1,4-dioxane as an internal standard:

$$\% \text{H}_4\text{DPP} = \frac{[\text{H}_4\text{DPP}^{2+}]}{[\text{H}_2\text{DPP}]_0} \times 100\% \quad (\text{S1})$$

Electrochemical Measurements. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were carried out in acetone containing 0.1 M TBAPF₆ as an electrolyte at room temperature under Ar. All measurements were made using a BAS ALS-710D electrochemical analyzer with a glassy carbon as a working electrode, a platinum wire as a counter electrode, and Ag/AgNO₃ as a reference electrode. All redox potentials were determined relative to that of Fc/Fc⁺ as 0 V.

Cold Spray Ionization Mass Spectrometry (CSI-TOF-MS). CSI-TOF-MS spectra were measured on a JEOL JMS-T100CS spectrometer at 223 K. The sample was prepared by

mixing H₂DPP (0.01 mM) with 2 eq of BnPy⁺-COOH(ClO₄⁻) and H₄DPP²⁺(Cl⁻)₂ (0.01 mM) with 1:1 ratio in acetone.

Computational Methods. Geometry optimizations were performed using the hybrid (Hartree-Fock/DFT) B3LYP functional^{7,8} combined with the 6-31G** basis set.⁹ The RB3LYP functional was used for the closed-shell molecules. The Gaussian 09 program¹⁰ was used for all calculations.

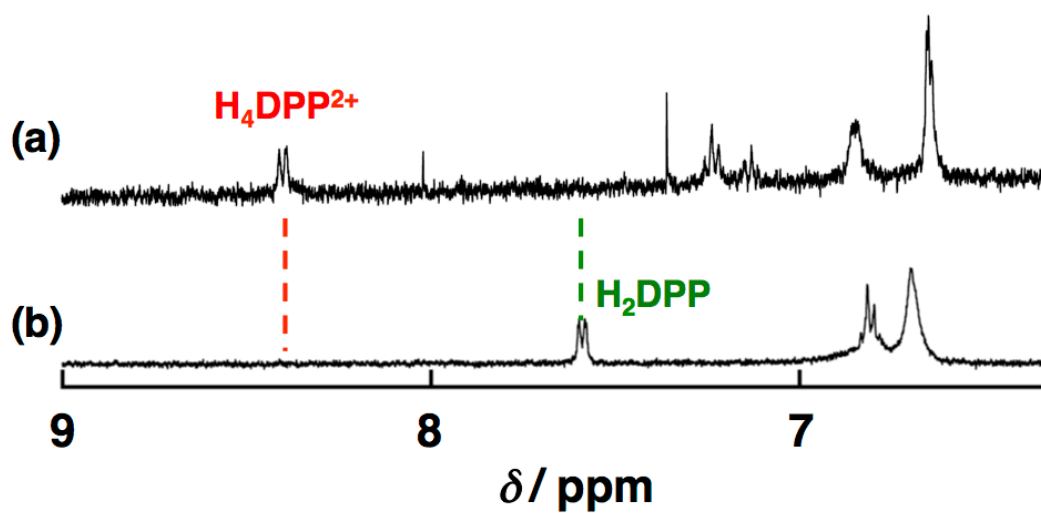


Fig. S1 ^1H NMR spectra of solutions of (a) H_2DPP (0.20 mM) containing 2 eq of NBA and (b) H_2DPP in acetone- d_6 at 298 K.

Table S1 Summary of reduction potential (E_{red}), and %H₄DPP

HX	p<i>K</i>_a in H₂O	<i>E</i>_{red} / V^a	%H₄DPP^b
TsOH	−1.3	−0.76	34
TFA	−0.25	−0.85	43
DCA	1.3	−0.89	46
NBA	3.4	−0.98	50
BnPy⁺-COOH	2.3	−0.86	36
BnPy⁺-PhCOOH	3.5	−0.98	45

^a Reduction potential of H₄DPP²⁺(X[−])₂, V vs. Fc/Fc⁺ in acetone containing 0.1 M TBAPF₆ as an electrolyte at 298 K, ^b Determined using eqn (S1).

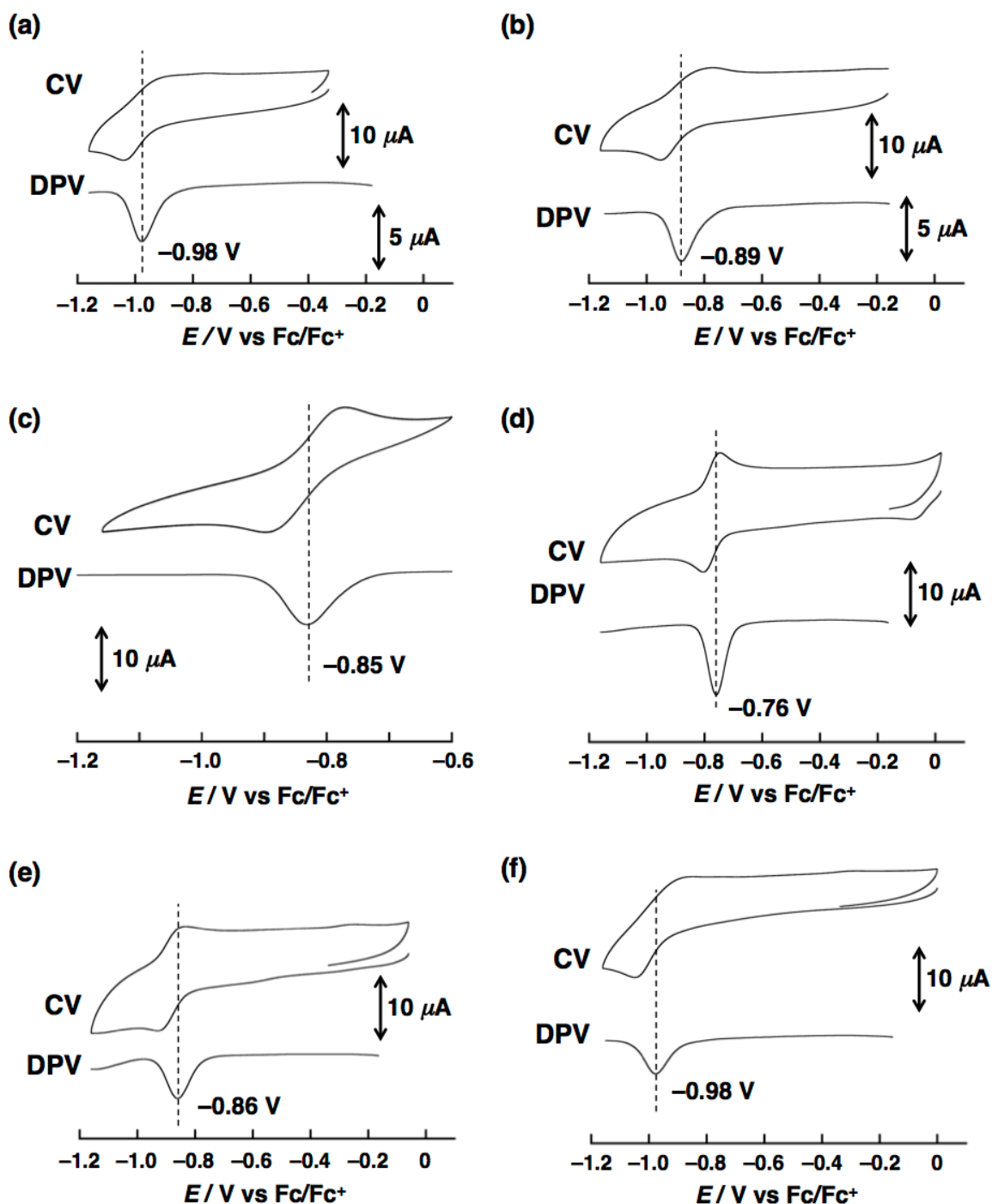


Fig. S2 Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of $\text{H}_4\text{DPP}^{2+}(\text{X}^-)_2$ (0.2 mM) in acetone containing 0.1 M TBAPF_6 as an electrolyte at 298 K; X^- = (a) $m\text{-NO}_2\text{PhCOO}^-$ (NBA), (b) $\text{Cl}_2\text{CHCOO}^-$ (DCA), (c) CF_3COO^- (TFA), (d) TsO^- , (e) $\text{BnPy}^+\text{-COO}^-$, and (f) $\text{BnPy}^+\text{-PhCOO}^-$.

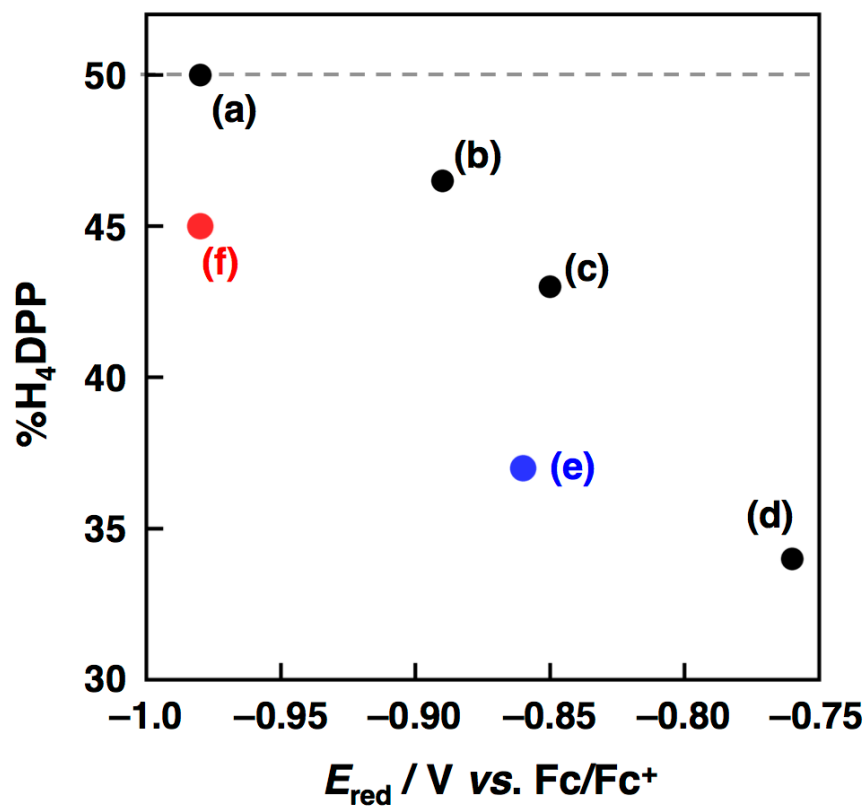


Fig. S3 A plot of %H₄DPP values relative to reduction potentials (E_{red}) of H₄DPP²⁺(X⁻)₂ (0.2 mM) determined in acetone containing 0.1 M TBAPF₆ as an electrolyte at room temperature.

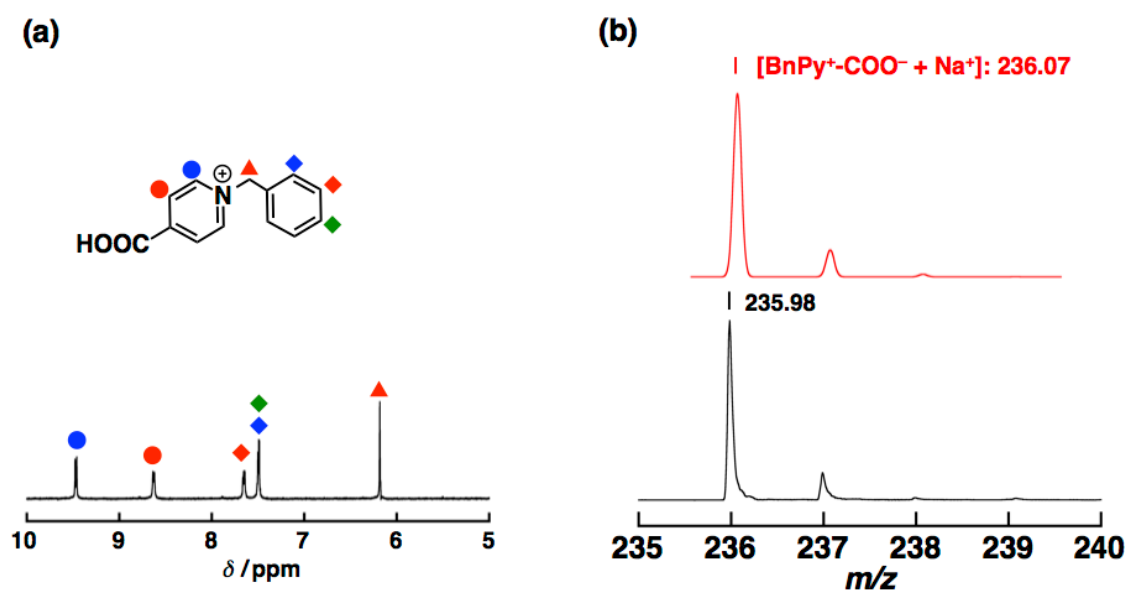


Fig. S4 (a) ^1H NMR spectrum of $\text{BnPy}^+-\text{COOH}(\text{ClO}_4^-)$ in acetone- d_6 at 298K. (b) ESI-TOF-MS spectrum (bottom) of $\text{BnPy}^+-\text{COOH}(\text{ClO}_4^-)$ in MeOH at room temperature and the computer-simulated isotropic pattern (upper).

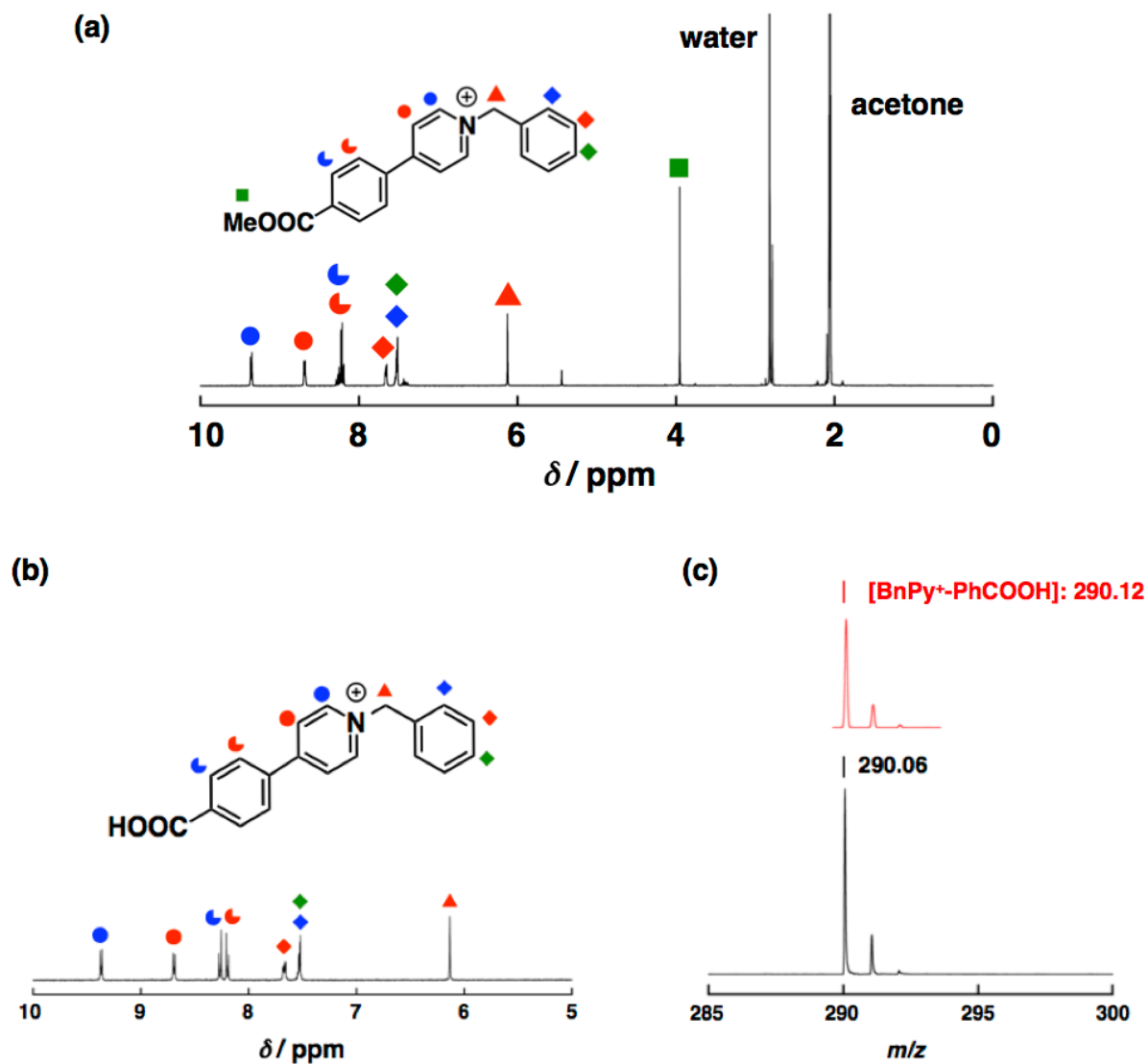


Fig. S5 (a) ^1H NMR spectrum of $\text{BnPy}^+-\text{PhCOOMe}(\text{PF}_6^-)$ in $\text{acetone-}d_6$ at 298K. (b) ^1H NMR spectrum of $\text{BnPy}^+-\text{PhCOOH}(\text{PF}_6^-)$ in $\text{acetone-}d_6$ at 298K. (c) ESI-TOF-MS spectrum (bottom) of $\text{BnPy}^+-\text{PhCOOH}(\text{PF}_6^-)$ in MeOH at room temperature and the computer-simulated isotropic pattern (upper).

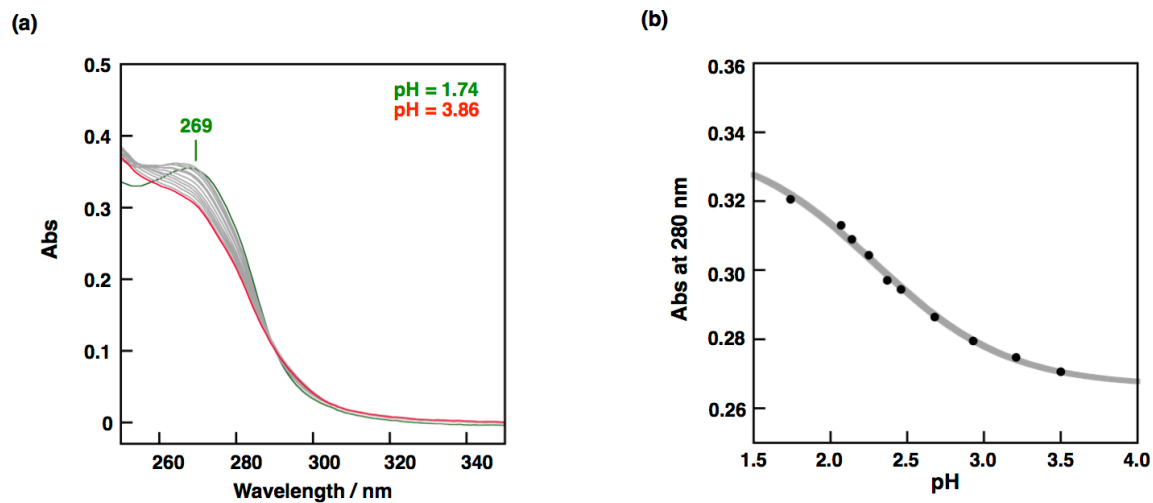


Fig. S6 (a) UV-Vis spectroscopic titration of BnPy⁺-COOH(ClO₄⁻) (0.3 mM) in Britton-Robinson buffer (0.1 M) with use of 8 M NaOH_{aq} at 298 K. (b) A plot of the absorbance at 280 nm vs. pH.

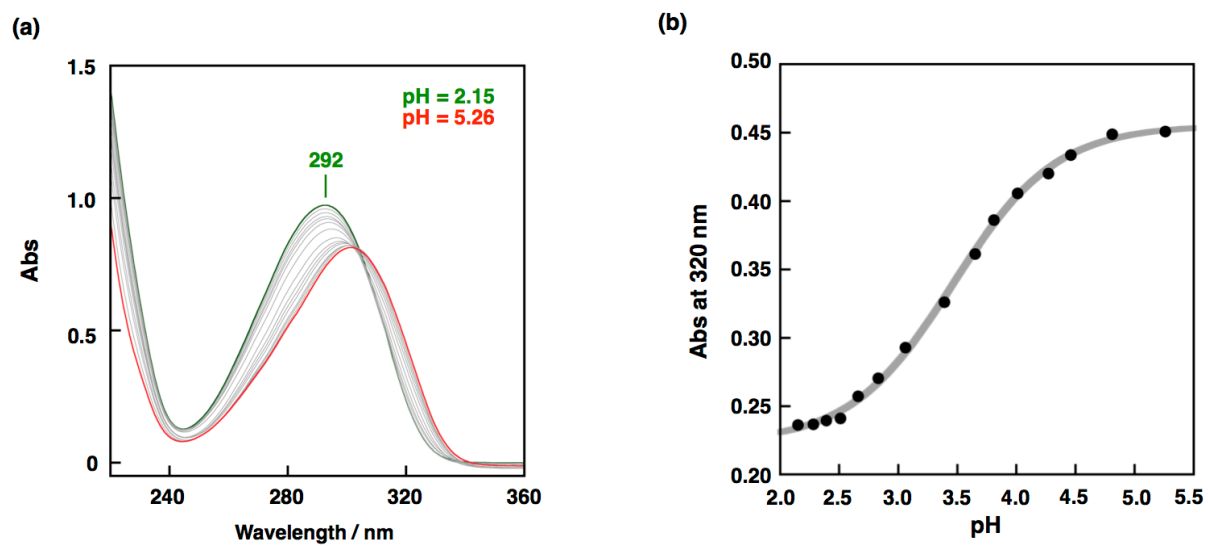


Fig. S7 (a) UV-Vis spectroscopic titration of BnPy⁺-PhCOOH(PF₆⁻) (0.2 mM) in Britton-Robinson buffer (0.1 M) with use of 8 M NaOH_{aq} at 298 K. (b) A plot of the absorbance at 320 nm vs. pH.

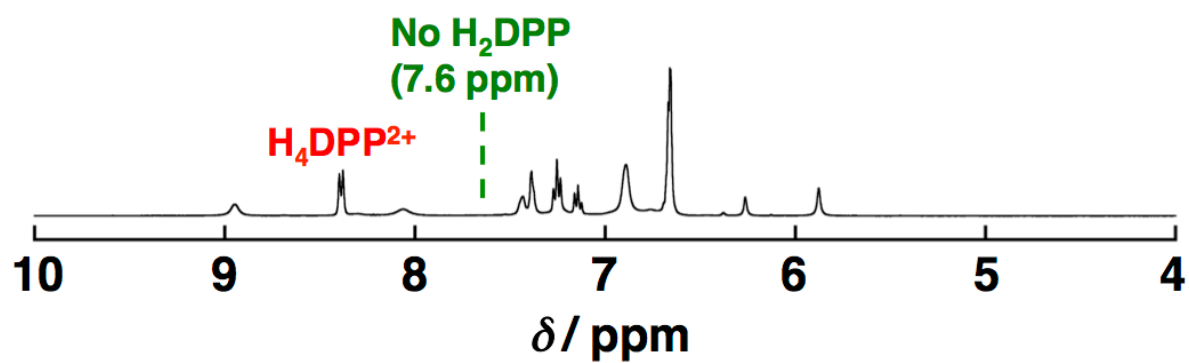


Fig. S8 ^1H NMR spectrum of H_2DPP (0.2 mM) containing 2 eq of $\text{BnPy}^+\text{-PhCOOH}$ in acetone- d_6 at 298 K.

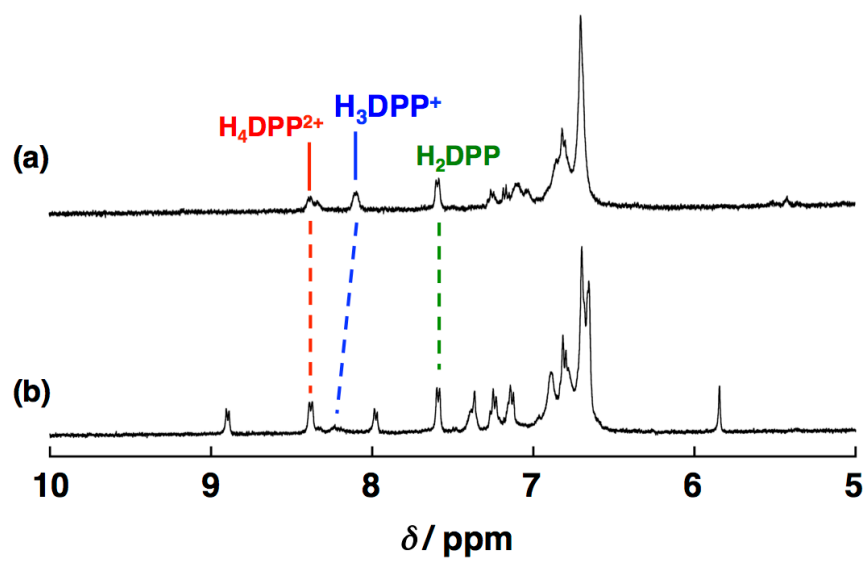


Fig. S9 ^1H NMR spectra of H_2DPP (0.15 mM) in acetone- d_6 at 298 K with 1 eq of (a) $\text{BnPy}^+-\text{COOH}$, and (b) $\text{BnPy}^+-\text{PhCOOH}$.

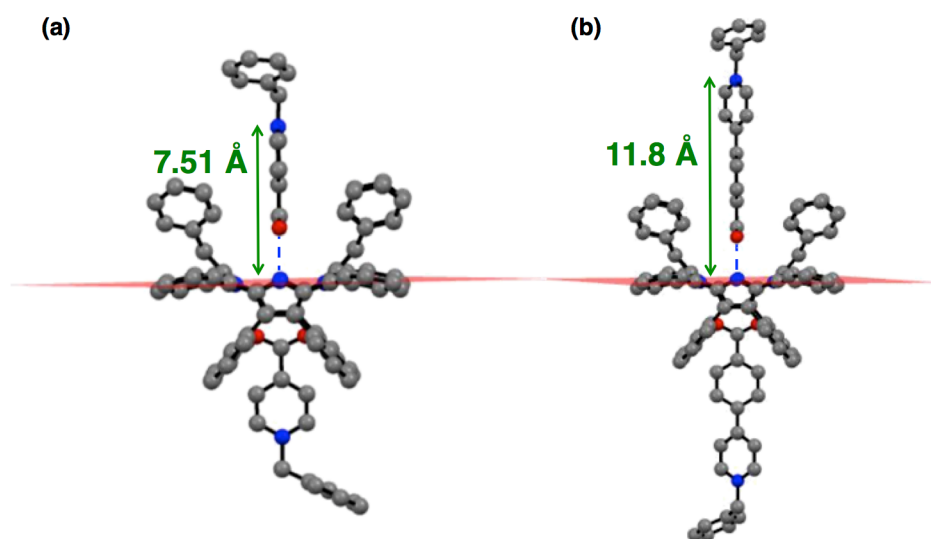


Fig. S10 DFT optimized structures of (a) $\text{H}_4\text{DPP}^{2+}(\text{BnPy}^+-\text{COO}^-)_2$ and (b) $\text{H}_4\text{DPP}^{2+}(\text{BnPy}^+-\text{PhCOO}^-)_2$ at the 6-31G** level of theory. Green arrows indicate the distances between positively charged nitrogen atoms in conjugate bases and the mean planes (red) of $\text{H}_4\text{DPP}^{2+}$.

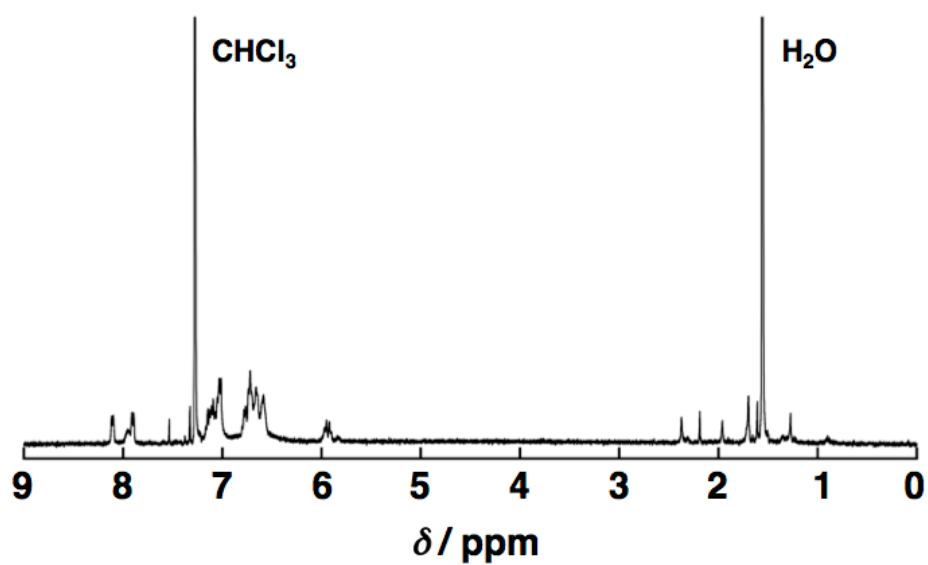


Fig. S11. ^1H NMR spectrum of a 1:1 mixture of $\text{H}_4\text{DPP}^{2+}(\text{TsO}^-)_2$ solution (0.4 mM) and the solution of $\text{H}_4\text{DPP}^{2+}(\text{Cl}^-)_2$ (0.4 mM) in CDCl_3 at 298 K.

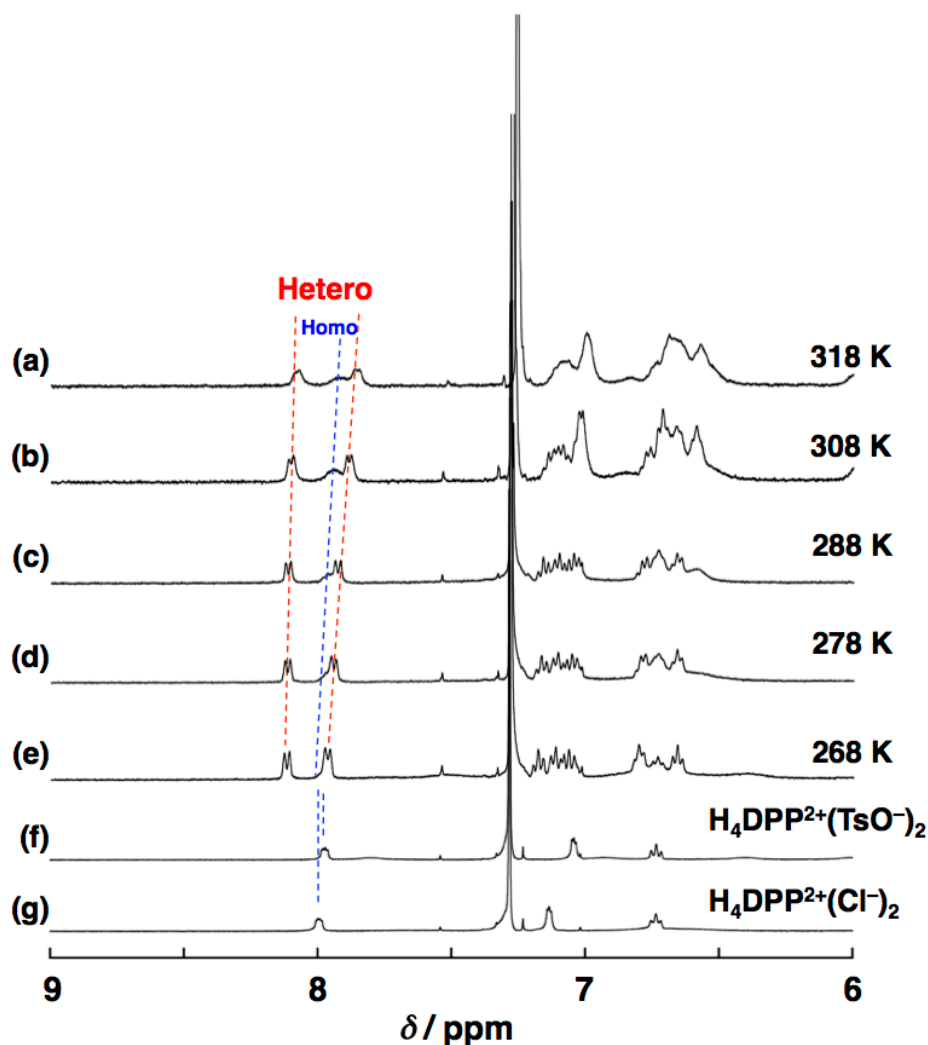


Fig. S12 Temperature dependence of ^1H NMR spectra of a 1:1 mixture of $\text{H}_4\text{DPP}^{2+}(\text{TsO}^-)_2$ solution (0.4 mM) and the solution of $\text{H}_4\text{DPP}^{2+}(\text{Cl}^-)_2$ (0.4 mM) in CDCl_3 at (a) 318 K, (b) 308 K, (c) 288 K, (d) 278 K, (e) 268 K. ^1H NMR spectrum of (f) $\text{H}_4\text{DPP}^{2+}(\text{TsO}^-)_2$ (0.4 mM), and (g) ^1H NMR spectrum of $\text{H}_4\text{DPP}^{2+}(\text{Cl}^-)_2$ (0.4 mM) in CDCl_3 at 268 K. Red dotted line: ^1H NMR signals derived from *ortho*-protons of the *meso*-phenyl groups of $\text{H}_4\text{DPP}^{2+}(\text{TsO}^-)(\text{Cl}^-)$; Blue dotted line: ^1H NMR signals derived from *ortho*-protons of the *meso*-phenyl groups of $\text{H}_4\text{DPP}^{2+}(\text{Cl}^-)_2$ and $\text{H}_4\text{DPP}^{2+}(\text{TsO}^-)_2$.

Table S2 Summary of equilibrium constants (K) in formation of $\text{H}_4\text{DPP}^{2+}(\text{TsO}^-)(\text{Cl}^-)$ and $\text{H}_4\text{DPP}^{2+}(\text{NO}_2\text{PhCOO}^-)(\text{Cl}^-)$ in chloroform at various temperatures.

Temp / K	$K \{ \text{H}_4\text{DPP}^{2+}(\text{TsO}^-)(\text{Cl}^-) \}$	$K \{ \text{H}_4\text{DPP}^{2+}(\text{NO}_2\text{PhCOO}^-)(\text{Cl}^-) \}$
268	1.6×10^2	1.0
273	–	1.2
278	1.2×10^2	1.6
288	54	1.8
298	39	3.5
308	28	–
318	16	–

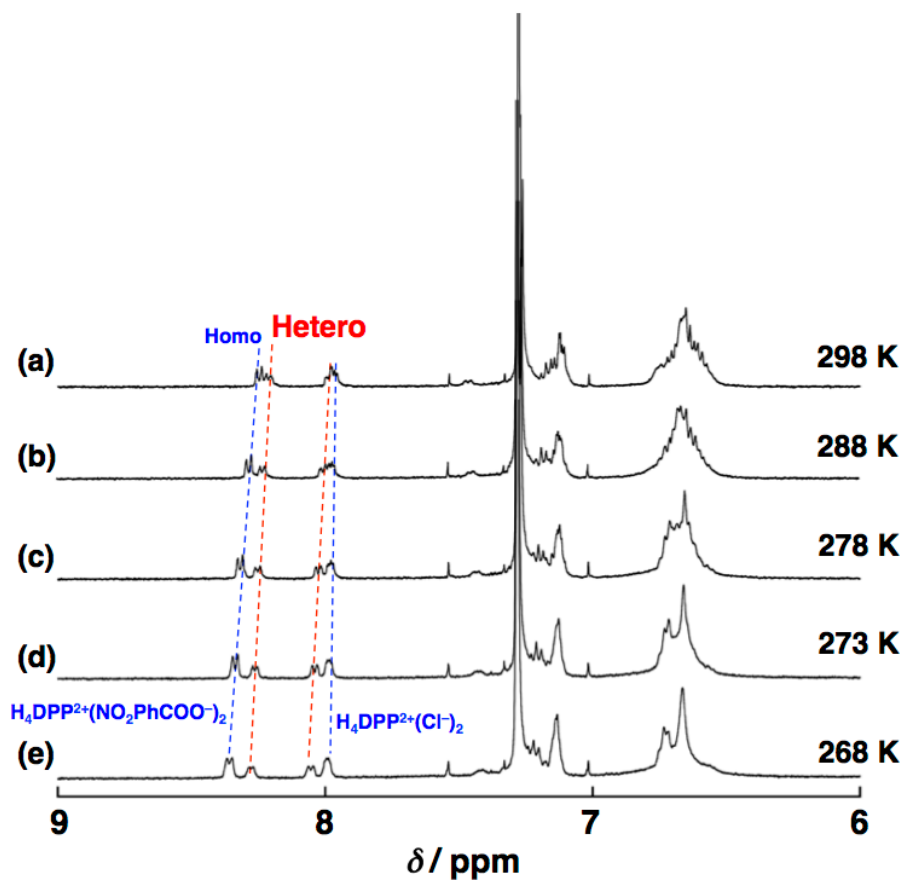


Fig. S13 Temperature dependence of ^1H NMR spectra of a 1:1 mixture of $\text{H}_4\text{DPP}^{2+}(\text{NO}_2\text{PhCOO}^-)_2$ solution (0.4 mM) and the solution of $\text{H}_4\text{DPP}^{2+}(\text{Cl}^-)_2$ (0.4 mM) in CDCl_3 at (a) 298 K, (b) 288 K, (c) 278 K, (d) 273 K, (e) 268 K. Red dotted line: ^1H NMR signals derived from *ortho*-protons of the *meso*-phenyl groups of $\text{H}_4\text{DPP}^{2+}(\text{NO}_2\text{PhCOO}^-)(\text{Cl}^-)$; Blue dotted line: ^1H NMR signals derived from *ortho*-protons of the *meso*-phenyl groups of $\text{H}_4\text{DPP}^{2+}(\text{Cl}^-)_2$ and $^1\text{H}_4\text{DPP}^{2+}(\text{NO}_2\text{PhCOO}^-)_2$.

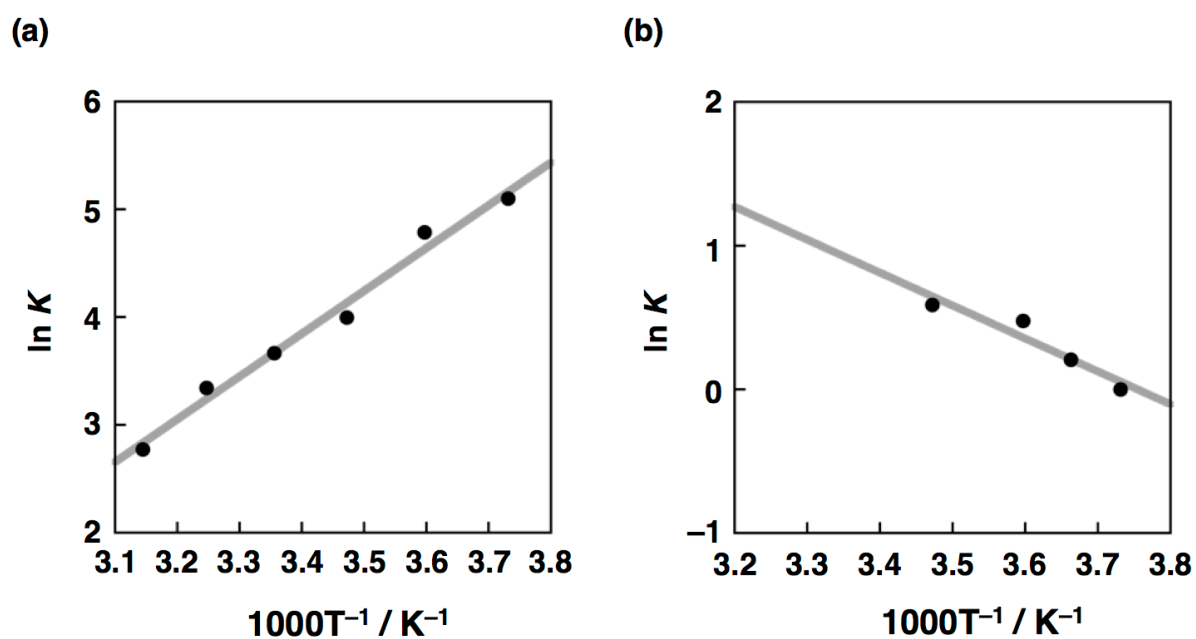


Fig. S14 van't Hoff plots for the formation of (a) $H_4DPP^{2+}(TsO^{-})(Cl^{-})$ and (b) $H_4DPP^{2+}(NO_2PhCOO^{-})(Cl^{-})$ in chloroform.

Table S3 Summary of thermodynamic parameters in formation of $\text{H}_4\text{DPP}^{2+}(\text{TsO}^-)(\text{Cl}^-)$ and $\text{H}_4\text{DPP}^{2+}(\text{NO}_2\text{PhCOO}^-)(\text{Cl}^-)$ in chloroform.

	$\text{H}_4\text{DPP}^{2+}(\text{TsO}^-)(\text{Cl}^-)$	$\text{H}_4\text{DPP}^{2+}(\text{NO}_2\text{PhCOO}^-)(\text{Cl}^-)$
$\Delta H / \text{kcal mol}^{-1}$	-7.8	+ 6.1
$\Delta S / \text{cal K}^{-1} \text{mol}^{-1}$	-19	+ 23
$\Delta G^a / \text{kcal mol}^{-1}$	-2.1	-0.67

a: at 298 K

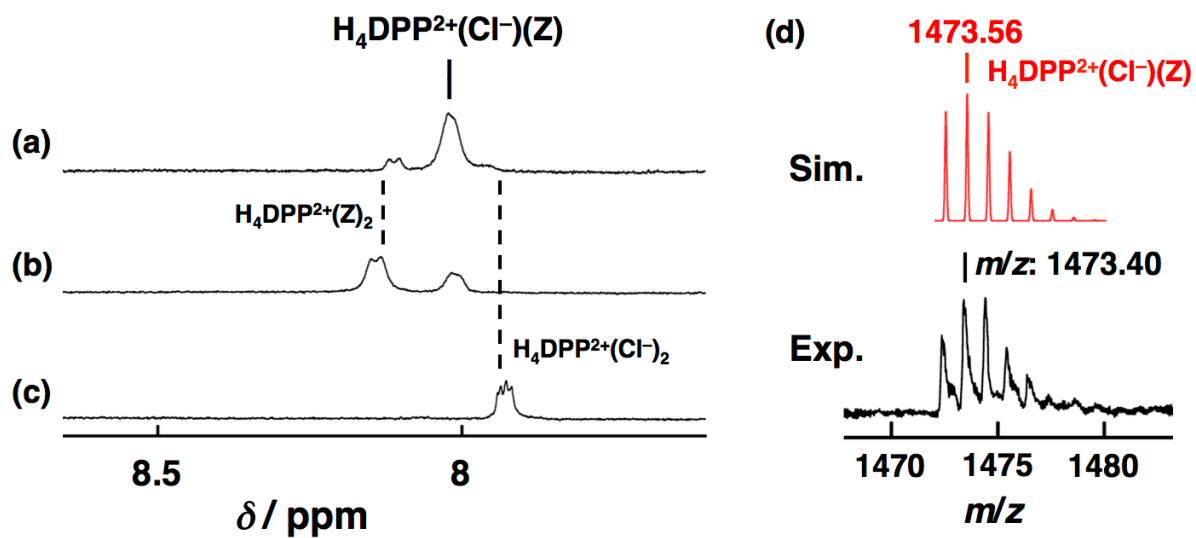


Fig. S15 ¹H NMR spectra of (a) mixture of H₂DPP solution with 2 eq of BnPy⁺-COOH (HZ⁺) and the solution of H₄DPP²⁺(Cl⁻)₂ with the ratio of 1:1, (b) H₄DPP²⁺(BnPy⁺-COO⁻)₂, (c) H₄DPP²⁺(Cl⁻)₂ in CDCl₃ at 298 K. (d) CSI-TOF-MS spectrum (bottom) of a mixture of H₂DPP (0.01 mM) with 2 eq of BnPy⁺-COOH and H₄DPP²⁺(Cl⁻)₂ (0.01 mM) with the 1:1 ratio in acetone at 223K and the computer-simulated isotropic pattern (upper).

Table S4 X-ray crystallographic data for [H₄DPP²⁺(Cl⁻)(BnPy⁺-PhCOO⁻)](PF₆⁻)

compound	[H ₄ DPP ²⁺ (Cl ⁻)(BnPy ⁺ -PhCOO ⁻)](PF ₆ ⁻)
crystal system	Monoclinic
space group	<i>P</i> 2 ₁
<i>T</i> / K	120
formula	[C ₉₂ H ₆₄ N ₄ •Cl•(C ₂₀ H ₃₀ NO ₂)]•PF ₆
FW	1722.34
<i>a</i> / Å	16.246(3)
<i>b</i> / Å	30.559(5)
<i>c</i> / Å	20.510(3)
<i>β</i> / deg	89.973(3)
<i>V</i> / Å ³	10182(3)
<i>Z</i>	4
<i>λ</i> / Å	0.71073 (Mo Kα)
<i>D_c</i> / g cm ⁻³	1.124
reflns measured	45645
reflns unique	21344
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0785
w <i>R</i> ₂ (all)	0.2182
GOF	1.035

Table S5 Cartesian coordinates of H₄DPP⁺(BnPy⁺-COO⁻)₂

Atom	Coordinates (Å)		
O	-2.577089	1.253477	0.746882
O	-2.674716	-0.947407	0.172125
C	-3.147077	0.149505	0.560543
O	2.825350	-0.129970	0.630993
O	2.438810	0.461564	-1.533632
C	3.154677	0.174105	-0.542392
N	0.045755	2.223108	0.587862
H	-0.863648	1.725338	0.595989
N	0.412842	-0.432273	2.026786
H	1.215352	-0.281387	1.387970
N	-0.146024	-1.913218	-0.572008
H	-1.007435	-1.422431	-0.270301
N	-0.307376	0.743611	-2.045832
H	0.663289	0.596953	-1.713608
C	0.414830	3.092235	-0.410775
C	1.516887	3.878736	0.084416
C	1.737778	3.495985	1.409026
C	0.770915	2.474899	1.726983
C	0.493518	1.826982	2.960700
C	0.023082	0.486764	2.971566
C	-0.832125	-0.194442	3.911492
C	-0.875802	-1.538453	3.534530
C	-0.051374	-1.681153	2.361068
C	0.322403	-2.846978	1.639578
C	0.551088	-2.775820	0.239985
C	1.426499	-3.551799	-0.603261
C	1.175445	-3.172325	-1.923316
C	0.149004	-2.161111	-1.890317
C	-0.537247	-1.516054	-2.954233
C	-0.990022	-0.178805	-2.802290
C	-2.118330	0.496463	-3.394438

C	-2.039030	1.840166	-3.024156
C	-0.865179	1.989282	-2.201197
C	-0.278024	3.158699	-1.648226
C	2.411526	4.699311	-0.767096
C	3.064366	4.089424	-1.852068
H	2.889591	3.035336	-2.048069
C	3.936057	4.822255	-2.655876
H	4.432657	4.339118	-3.492928
C	4.169377	6.173389	-2.393643
H	4.845865	6.744356	-3.022280
C	3.520338	6.789107	-1.323177
H	3.686391	7.842310	-1.118528
C	2.648111	6.058306	-0.517306
H	2.125441	6.554198	0.292934
C	2.913732	3.824795	2.249703
C	3.199212	5.132654	2.666069
H	2.518685	5.937538	2.412643
C	4.330302	5.403856	3.435176
H	4.531608	6.421714	3.754719
C	5.193547	4.371366	3.802543
H	6.071332	4.583369	4.405401
C	4.916377	3.064387	3.397916
H	5.581161	2.255028	3.687361
C	3.787330	2.790590	2.627948
H	3.576774	1.776813	2.299657
C	0.696708	2.549552	4.230344
C	0.321928	3.900621	4.355828
H	-0.142328	4.403074	3.513387
C	0.509882	4.581640	5.554203
H	0.202963	5.619499	5.639198
C	1.083527	3.930148	6.648485
H	1.232896	4.463242	7.582297
C	1.464299	2.590773	6.538032

H	1.919844	2.083720	7.382987
C	1.269507	1.905462	5.343209
H	1.584271	0.870805	5.253716
C	-1.713194	0.487142	4.889305
C	-2.612156	1.465252	4.429739
H	-2.634198	1.705371	3.370542
C	-3.475121	2.105992	5.317114
H	-4.162797	2.862536	4.949114
C	-3.455965	1.784206	6.675411
H	-4.126048	2.286298	7.366585
C	-2.563379	0.818739	7.141707
H	-2.533275	0.569880	8.198048
C	-1.698848	0.176343	6.256300
H	-0.988696	-0.550355	6.634015
C	-1.813462	-2.576115	4.028054
C	-1.777440	-3.058790	5.343677
H	-1.011570	-2.705091	6.024806
C	-2.692863	-4.018078	5.775222
H	-2.645743	-4.385425	6.795771
C	-3.658360	-4.511874	4.897612
H	-4.368055	-5.261614	5.233912
C	-3.700082	-4.042353	3.583647
H	-4.445003	-4.428978	2.893436
C	-2.786575	-3.083053	3.149803
H	-2.823592	-2.707037	2.131376
C	0.470014	-4.131607	2.348584
C	1.093791	-4.187579	3.609221
H	1.488288	-3.276213	4.046869
C	1.237976	-5.399144	4.277516
H	1.734014	-5.427622	5.242791
C	0.753711	-6.577539	3.705062
H	0.862877	-7.522122	4.228869
C	0.128602	-6.537342	2.456489

H	-0.258046	-7.449515	2.012622
C	-0.007941	-5.328203	1.782046
H	-0.511217	-5.296560	0.821117
C	2.565379	-4.361731	-0.108935
C	3.529046	-3.750693	0.711891
H	3.413784	-2.701998	0.970581
C	4.627152	-4.474575	1.173187
H	5.363829	-3.990120	1.808107
C	4.781766	-5.817925	0.826431
H	5.635218	-6.382360	1.189653
C	3.827902	-6.434418	0.016307
H	3.933986	-7.481630	-0.249842
C	2.728719	-5.712506	-0.447119
H	1.977974	-6.209541	-1.050940
C	1.995982	-3.490545	-3.116855
C	2.112254	-4.791276	-3.626220
H	1.549309	-5.598543	-3.171393
C	2.915171	-5.051629	-4.736222
H	2.988018	-6.064113	-5.121281
C	3.613099	-4.015164	-5.356619
H	4.234709	-4.218797	-6.223218
C	3.499897	-2.714895	-4.861420
H	4.035074	-1.902278	-5.345130
C	2.698391	-2.451959	-3.751788
H	2.617250	-1.443367	-3.356557
C	-0.777671	-2.238479	-4.217178
C	-1.169555	-3.590459	-4.206820
H	-1.315407	-4.092923	-3.256019
C	-1.402021	-4.271888	-5.397102
H	-1.717510	-5.310368	-5.372037
C	-1.239043	-3.619799	-6.621547
H	-1.417367	-4.153021	-7.550203
C	-0.845836	-2.279744	-6.647987

H	-0.707975	-1.772469	-7.597847
C	-0.620990	-1.593954	-5.458682
H	-0.296044	-0.558817	-5.482059
C	-3.277557	-0.190306	-4.012719
C	-3.967522	-1.163603	-3.269561
H	-3.631784	-1.395287	-2.262780
C	-5.079034	-1.808955	-3.808855
H	-5.602300	-2.560507	-3.224133
C	-5.519451	-1.496818	-5.096240
H	-6.382874	-2.003033	-5.517119
C	-4.837858	-0.535897	-5.843409
H	-5.166276	-0.294484	-6.849693
C	-3.725865	0.111520	-5.306310
H	-3.185643	0.834723	-5.906695
C	-3.096644	2.870183	-3.165231
C	-3.515462	3.353365	-4.412598
H	-3.025964	3.005092	-5.315215
C	-4.529636	4.306245	-4.502369
H	-4.836201	4.674955	-5.476423
C	-5.140516	4.792413	-3.346228
H	-5.927305	5.537234	-3.417572
C	-4.728045	4.321550	-2.098456
H	-5.195689	4.701609	-1.194246
C	-3.714887	3.368688	-2.005678
H	-3.400308	2.990263	-1.037131
C	-0.393363	4.444295	-2.361981
C	-0.229744	4.507380	-3.758547
H	0.004823	3.600539	-4.306683
C	-0.332634	5.720639	-4.431570
H	-0.189750	5.755162	-5.507208
C	-0.610770	6.893014	-3.725055
H	-0.694621	7.838743	-4.251430
C	-0.781154	6.845249	-2.339479

H	-1.008054	7.752528	-1.788173
C	-0.669027	5.634690	-1.663265
H	-0.820799	5.597021	-0.589350
C	4.669598	0.204380	-0.804895
C	5.172165	0.503360	-2.075733
C	5.582824	-0.062203	0.220039
C	6.537062	0.532324	-2.284980
H	4.483364	0.708856	-2.885604
C	6.940639	-0.022790	-0.035385
H	5.214349	-0.299594	1.210118
H	6.980254	0.761254	-3.246625
H	7.694782	-0.229090	0.713418
C	-4.656346	0.140512	0.855659
C	-5.414719	-1.024020	0.698455
C	-5.308319	1.299106	1.290915
C	-6.769621	-1.009350	0.971417
H	-4.930463	-1.931706	0.360611
C	-6.663818	1.266762	1.554426
H	-4.741710	2.213376	1.415845
H	-7.410641	-1.874270	0.857187
H	-7.217520	2.132557	1.897012
N	-7.376790	0.125229	1.394518
N	7.402041	0.272966	-1.274088
C	8.888339	0.382205	-1.527720
H	9.007627	0.285119	-2.608572
H	9.177084	1.397804	-1.243629
C	-8.844655	0.112981	1.754778
H	-8.908646	-0.251689	2.783573
H	-9.156241	1.159278	1.745825
C	9.708404	-0.642900	-0.789929
C	9.717061	-1.981366	-1.209865
C	10.488822	-0.260061	0.308617
C	10.491016	-2.921846	-0.534363

H	9.126325	-2.286248	-2.070128
C	11.266613	-1.203541	0.982278
H	10.503449	0.779112	0.627976
C	11.266242	-2.533619	0.562201
H	10.499361	-3.954330	-0.868479
H	11.876090	-0.897306	1.826275
H	11.875460	-3.266558	1.081430
C	-9.690507	-0.720725	0.828681
C	-10.206928	-1.948199	1.263306
C	-9.988019	-0.265577	-0.464456
C	-11.009529	-2.713917	0.415616
H	-9.997215	-2.298669	2.270909
C	-10.785970	-1.032558	-1.309913
H	-9.603547	0.691941	-0.806890
C	-11.297325	-2.257170	-0.870458
H	-11.414191	-3.658939	0.763100
H	-11.018860	-0.671779	-2.306572
H	-11.926362	-2.848635	-1.528060

Table S6 Cartesian coordinates of H₄DPP⁺(BnPy⁺-PhCOO⁻)₂

Atom	Coordinates (Å)		
O	2.719801	0.799748	-0.332361
O	2.480844	-1.293674	0.512261
C	3.147994	-0.303988	0.103677
O	-2.621189	-0.162185	-1.044481
O	-2.569689	0.702764	1.053122
C	-3.143440	0.328466	-0.006507
N	0.276291	1.983441	-0.753958
H	1.123714	1.409868	-0.541547
N	-0.098566	-0.790305	-1.951635
H	-0.983377	-0.503576	-1.477034
N	-0.157879	-1.985386	0.843344
H	0.790217	-1.586020	0.661913
N	-0.011982	0.809368	2.036052
H	-0.920145	0.704394	1.529360
C	-0.173898	2.989757	0.063039
C	-1.091933	3.797301	-0.702749
C	-1.120512	3.276738	-1.995798
C	-0.218078	2.151554	-2.022931
C	0.197357	1.340696	-3.111640
C	0.530992	-0.022416	-2.899012
C	1.469783	-0.868422	-3.594150
C	1.329930	-2.154704	-3.074771
C	0.303981	-2.097354	-2.062240
C	-0.293195	-3.140154	-1.306650
C	-0.767530	-2.886012	0.006710
C	-1.854368	-3.493444	0.735463
C	-1.823275	-2.976675	2.029725
C	-0.719652	-2.050036	2.093595
C	-0.192809	-1.333102	3.199384
C	0.412916	-0.064541	3.004478
C	1.473059	0.579771	3.741206

C	1.610781	1.867534	3.224970
C	0.636282	2.011146	2.170264
C	0.288894	3.148805	1.395574
C	-2.036239	4.778500	-0.116626
C	-2.928006	4.348326	0.880587
H	-2.902567	3.310026	1.198929
C	-3.847769	5.236830	1.435101
H	-4.532343	4.890523	2.204520
C	-3.892383	6.564760	1.007067
H	-4.606853	7.256933	1.442863
C	-3.008897	7.000787	0.019230
H	-3.030246	8.034167	-0.313646
C	-2.088060	6.114390	-0.538010
H	-1.386288	6.468565	-1.285061
C	-2.102714	3.588577	-3.061523
C	-2.171438	4.846642	-3.675988
H	-1.455973	5.615441	-3.406007
C	-3.127648	5.107875	-4.656647
H	-3.161355	6.085679	-5.127754
C	-4.031215	4.115550	-5.037596
H	-4.773863	4.319739	-5.803212
C	-3.970807	2.858934	-4.432689
H	-4.671342	2.081239	-4.723954
C	-3.014926	2.593917	-3.453431
H	-2.977302	1.622230	-2.969268
C	0.278994	1.916216	-4.467825
C	0.807070	3.204498	-4.672773
H	1.177803	3.766641	-3.821795
C	0.885040	3.745193	-5.952414
H	1.306720	4.735555	-6.094826
C	0.430703	3.013786	-7.052055
H	0.489100	3.437774	-8.049881
C	-0.099296	1.735396	-6.863915

H	-0.463066	1.166953	-7.714464
C	-0.170858	1.189873	-5.586097
H	-0.601377	0.204617	-5.439370
C	2.569497	-0.370500	-4.454927
C	3.491662	0.540879	-3.913096
H	3.373855	0.860520	-2.881498
C	4.555962	1.008122	-4.682467
H	5.263582	1.710383	-4.250571
C	4.715741	0.577923	-6.000792
H	5.543425	0.945728	-6.600027
C	3.802223	-0.323618	-6.547770
H	3.913300	-0.656451	-7.575396
C	2.737407	-0.794368	-5.780371
H	2.016221	-1.473783	-6.221483
C	2.248580	-3.300921	-3.272991
C	2.418558	-3.921066	-4.518545
H	1.829460	-3.591124	-5.367009
C	3.312311	-4.980672	-4.669339
H	3.425677	-5.454494	-5.639800
C	4.050786	-5.436525	-3.576977
H	4.743631	-6.264436	-3.695204
C	3.888387	-4.826523	-2.331910
H	4.458997	-5.177000	-1.476273
C	2.994979	-3.767912	-2.177552
H	2.878602	-3.280689	-1.213714
C	-0.420645	-4.490373	-1.888075
C	-0.807517	-4.663166	-3.230096
H	-1.037544	-3.789992	-3.832015
C	-0.929074	-5.936861	-3.776633
H	-1.241198	-6.052727	-4.810111
C	-0.659355	-7.063701	-2.996949
H	-0.751103	-8.057166	-3.425237
C	-0.271795	-6.908141	-1.664251

H	-0.051628	-7.780530	-1.056487
C	-0.157155	-5.635526	-1.113746
H	0.163966	-5.516605	-0.083995
C	-2.955164	-4.263526	0.108904
C	-3.694993	-3.664765	-0.925091
H	-3.442504	-2.655815	-1.238748
C	-4.753496	-4.347588	-1.521877
H	-5.317384	-3.872619	-2.320006
C	-5.090002	-5.634847	-1.099659
H	-5.912287	-6.167504	-1.568283
C	-4.359649	-6.237308	-0.074985
H	-4.608650	-7.241726	0.254086
C	-3.300549	-5.556806	0.524775
H	-2.721397	-6.042706	1.302194
C	-2.883322	-3.091490	3.059974
C	-3.202162	-4.309080	3.676902
H	-2.629304	-5.198145	3.436968
C	-4.224302	-4.380748	4.622630
H	-4.452864	-5.330597	5.096649
C	-4.944744	-3.236031	4.964659
H	-5.739502	-3.292720	5.702590
C	-4.634161	-2.018195	4.357225
H	-5.190835	-1.122681	4.619106
C	-3.611486	-1.942689	3.413092
H	-3.377672	-0.999416	2.927689
C	-0.274250	-1.908704	4.555900
C	-0.000634	-3.271241	4.776412
H	0.292961	-3.894914	3.938262
C	-0.069570	-3.812150	6.056513
H	0.158626	-4.862315	6.211436
C	-0.421974	-3.005498	7.140737
H	-0.478402	-3.428713	8.138993
C	-0.701357	-1.652361	6.936605

H	-0.986065	-1.023517	7.774723
C	-0.624850	-1.107808	5.658418
H	-0.861486	-0.060795	5.498632
C	2.417388	-0.127940	4.638839
C	3.151351	-1.211481	4.126945
H	3.006015	-1.504627	3.091109
C	4.069529	-1.884738	4.931020
H	4.632002	-2.719097	4.521320
C	4.268571	-1.491324	6.255478
H	4.981529	-2.018844	6.882221
C	3.541715	-0.418680	6.772650
H	3.683328	-0.111424	7.804493
C	2.623646	0.258050	5.970405
H	2.042732	1.072560	6.388830
C	2.725445	2.812991	3.470065
C	2.956967	3.390076	4.726439
H	2.276859	3.182830	5.545163
C	4.032003	4.255723	4.924409
H	4.192244	4.699369	5.902482
C	4.892006	4.558518	3.868443
H	5.726937	5.235651	4.022818
C	4.669269	3.990773	2.612780
H	5.334453	4.223041	1.785659
C	3.595386	3.125421	2.411508
H	3.429556	2.668971	1.439877
C	0.406459	4.499779	1.977326
C	0.001145	4.750850	3.301263
H	-0.421612	3.942056	3.888417
C	0.107313	6.026062	3.847545
H	-0.222417	6.205577	4.866357
C	0.628276	7.074513	3.085965
H	0.713649	8.068652	3.514013
C	1.039308	6.839553	1.772109

H	1.454304	7.648920	1.179131
C	0.926396	5.566757	1.221411
H	1.263693	5.382223	0.206603
C	-4.663189	0.491613	-0.035238
C	-5.340275	1.031788	1.065711
C	-5.398918	0.104478	-1.162630
C	-6.718405	1.195020	1.039156
H	-4.760697	1.313008	1.937187
C	-6.779475	0.247119	-1.191026
H	-4.861500	-0.302864	-2.010900
H	-7.222424	1.587758	1.916901
H	-7.322496	-0.030915	-2.089127
C	4.667924	-0.462948	0.140293
C	5.245657	-1.666138	0.565350
C	5.503051	0.591152	-0.251592
C	6.624901	-1.819788	0.589420
H	4.587903	-2.468314	0.878669
C	6.883854	0.453819	-0.210751
H	5.042475	1.511274	-0.591607
H	7.048283	-2.751850	0.951141
H	7.508577	1.275135	-0.548156
C	-7.465893	0.802212	-0.090769
C	7.471687	-0.758667	0.206329
C	-8.919726	0.969344	-0.121839
C	-9.756830	0.138339	-0.902396
C	-9.576302	1.972139	0.628886
C	-11.121876	0.313829	-0.914519
H	-9.341348	-0.676199	-1.481978
C	-10.944643	2.109903	0.580569
H	-9.012180	2.669904	1.234746
H	-11.790181	-0.321831	-1.481539
H	-11.468081	2.879787	1.134589
C	8.926690	-0.913636	0.243489

C	9.550735	-2.173850	0.090561
C	9.796785	0.184637	0.433369
C	10.920492	-2.294464	0.135249
H	8.963094	-3.063656	-0.096812
C	11.162380	0.013054	0.467074
H	9.403233	1.181729	0.585675
H	11.421771	-3.247316	0.014612
H	11.853412	0.833936	0.610809
N	11.720551	-1.214369	0.321162
N	-11.712038	1.290687	-0.181195
C	-13.201867	1.510761	-0.257527
H	-13.454287	2.117456	0.614570
H	-13.387832	2.110617	-1.152821
C	13.213316	-1.401612	0.436655
H	13.428419	-2.350746	-0.058821
H	13.434301	-1.517298	1.501506
C	14.013376	-0.275264	-0.163246
C	14.663597	0.645618	0.668326
C	14.129104	-0.149223	-1.555554
C	15.417685	1.682590	0.116010
H	14.595031	0.543494	1.748581
C	14.879570	0.887600	-2.104987
H	13.640326	-0.867302	-2.209366
C	15.523882	1.804536	-1.269442
H	15.925767	2.386661	0.766940
H	14.971466	0.975580	-3.182746
H	16.114468	2.607097	-1.699602
C	-13.997456	0.231438	-0.286823
C	-14.133334	-0.546306	0.872622
C	-14.621592	-0.181764	-1.470668
C	-14.877205	-1.723310	0.843049
H	-13.664739	-0.227293	1.800349
C	-15.369957	-1.360217	-1.497665

H	-14.537480	0.425382	-2.368664
C	-15.495676	-2.131395	-0.342379
H	-14.984207	-2.317466	1.744876
H	-15.857677	-1.668991	-2.416550
H	-16.081120	-3.045082	-0.360950

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