Electronic Supplementary Information

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

Wataru Suzuki,[a] Hiroaki Kotani,[a] Tomoya Ishizuka,[a] Yoshihito Shiota,[b]

Kazunari Yoshizawa,[b] and Takahiko Kojima*,[a]

[a] Department of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba and CREST (JST), 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, Japan

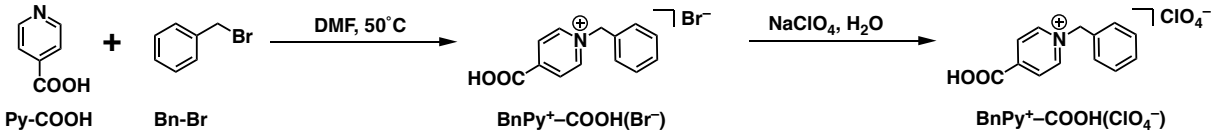
[b] Institute for Materials Chemistry and Engineering, Kyushu University and CREST (JST), Motooka, Nishi-Ku, Fukuoka 819-0395, Japan

Experimental Section

Materials.

General. Acetonitrile (MeCN) and *N*,*N*-dimethylformamide (DMF) were distilled over CaH_2 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 ($CHCl_3$) was distilled over CaH_2 and $CDCl_3$ was purified by passing through alumina before ^{1}H NMR measurements. *p*-Toluene sulfonic acid (TsOH), trifluoroacetic acid (TFA), dichloroacetic acid (DCA), and *m*-nitrobenzoic acid (NBA, $NO_2PhCOOH$) were purchased from commercial sources and used without further purification. H_2DPP was synthesized according to the reported procedure.[1,2]

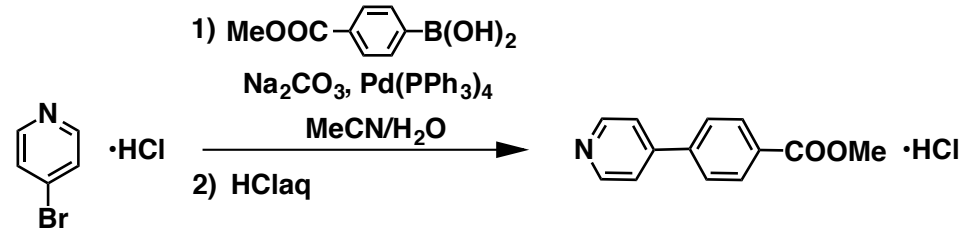
Synthesis.



***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. ^{1}H NMR (acetone-d_6 with one drop of methanol-d_4, 400 MHz): δ 6.18 (s, 2H, CH_2), 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 ($M–Br^––H^++Na^+$).

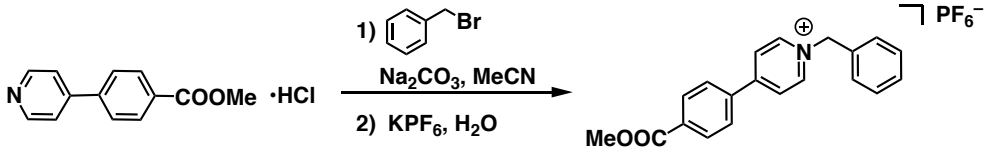
***N*-Benzyl-4-carboxypyridinium perchlorate ($BnPy^+$-COOH(ClO_4^-)).** $BnPy^+$-COOH(Br^-) (246 mg, 0.839 mmol) was dissolved in H_2O (5 mL), then an aqueous solution of $NaClO_4$ (2.2 g, 18 mmol in 2 mL) was added dropwise to form a colorless solid. Then, the colorless solid was filtered to afford the title compound as colorless needle-shaped crystals (55 mg, 0.18 mmol) in 21% yield. ^{1}H NMR (acetone-d_6, 400 MHz): δ 6.30 (s, 2H, CH_2), 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 ($M–ClO_4^-–H^++Na^+$). Elemental analysis (%): Calcd for $C_{13}H_{10}NO_2•ClO_4•0.75C_4H_8O_2$: C 48.90, H 4.48, N: 4.15; Found: C 48.86, H 4.52, N 4.46. m.p. (˚C): 151-153 ˚C.



Py-Br•HCl **Py–PhCOOMe•HCl**

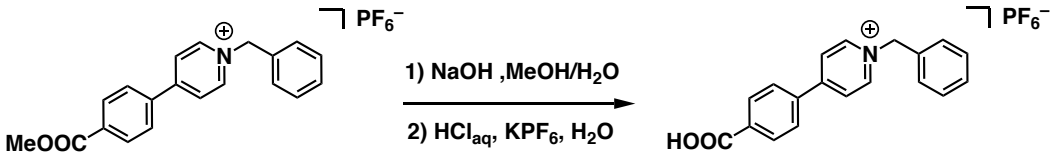
4-Methoxycarbonylphenylpyridine hydrochloride (Py-PhCOOMe•HCl). Py-PhCOOMe•HCl was synthesized according with the previous report.[4] 4-Bromopyridine hydrochloride salt (Py-Br•HCl, 661 mg, 3.36 mmol), 4-methoxycarbonylphenylboronic acid (603 mg, 3.35 mmol), Na_2CO_3 (662 mg, 6.24 mmol), and $Pd(PPh_3)_4$ (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 °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 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. ^{1}H 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).



Py–PhCOOMe•HCl **BnPy$^+$–PhCOOMe(PF_6^-)**

***N*-Benzyl-4-methoxycarboxyphenylpyridinium hexafluorophosphate (BnPy$^+$–PhCOOMe(PF_6^-))**. BnPy$^+$-PhCOOMe(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. KPF_6aq to the solution, a colorless solid was formed and filtered to obtain $BnPy^+$-PhCOOMe(PF_6^-) (191 mg, 0.439 mmol) in 62% yield. ^{1}H NMR (acetone-d_6, 400 MHz): δ 3.95 (s, 3H, COOMe), 6.13 (s, 2H, CH_2), 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).^{13}C 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.



$BnPy^+$–PhCOOMe(PF_6^-) $BnPy^+$–PhCOOH(PF_6^-)

***N*-Benzyl-4-carboxyphenylpyridinium hexafluorophosphate ($BnPy^+$–PhCOOH(PF_6^-))**: $BnPy^+$–PhCOOMe(PF_6^-) (101 mg, 0.232 mmol) was dissolved in a MeOH/H_2O (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. KPF_6aq was added to form solids, which were filtered to give a pale yellow solid of $BnPy^+$-PhCOOH(PF_6^-) (73 mg, 0.17 mmol) in 75% yield. ^{1}H NMR (acetone-d_6, 400 MHz): δ 6.13 (s, 2H, CH_2), 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). ^{13}C 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–PF_6^-). Elemental analysis (%): Calcd for $C_{19}H_{16}NO_2$•PF_6•0.5H_2O: 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 $[H_4DPP^{2+}(Cl^-)(BnPy^+\text{-}PhCOO^-)](PF_6^-)$. Single crystals of $[H_4DPP^{2+}(Cl^-)(BnPy^+\text{-}PhCOO^-)](PF_6^-)$ were grown by vapor diffusion of 2-propanol in acetone solution of H_2DPP in the presence of 2 eq of $BnPy^+\text{-}PhCOOH(PF_6^-)$ 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 $H_4DPP^{2+}(X^-)_2$ (%H_4DPP) was calculated using eqn (S1) on the basis of initial concentration of H_2DPP ($[H_2DPP]_0$) and concentration of $H_4DPP^{2+}(X^-)_2$ ($[H_4DPP^{2+}]$) 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:

$$\%H_4DPP = \frac{[H_4DPP^{2+}]}{[H_2DPP]_0} \times 100\% \qquad \text{(S1)}$$

Electrochemical Measurements. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were carried out in acetone containing 0.1 M $TBAPF_6$ 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 $Ag/AgNO_3$ 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 H_2DPP (0.01 mM) with 2 eq of $BnPy^+$-$COOH(ClO_4^-)$ and $H_4DPP^{2+}(Cl^-)_2$ (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 program[10] was used for all calculations.

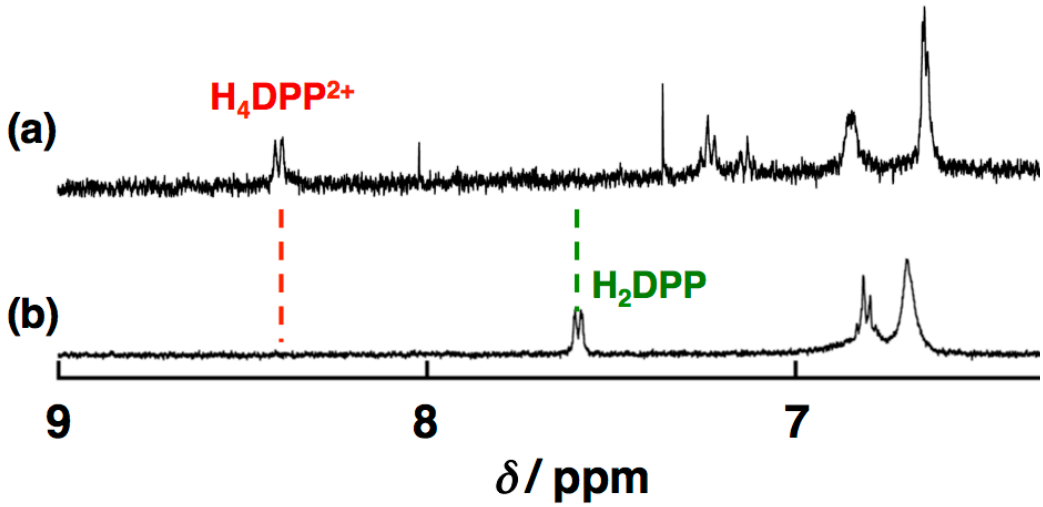


Fig. S1 ^{1}H NMR spectra of solutions of (a) H_2DPP (0.20 mM) containing 2 eq of NBA and (b) H_2DPP in acetone-d_6 at 298 K.

Table S1 Summary of reduction potential (E_{red}), and %H_4DPP

HX	pK_a in H_2O	E_{red} / V[a]	%H_4DPP[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 $H_4DPP^{2+}(X^-)_2$, V *vs*. Fc/Fc^+ in acetone containing 0.1 M $TBAPF_6$ as an electrolyte at 298 K, [b] Determined using eqn (S1).

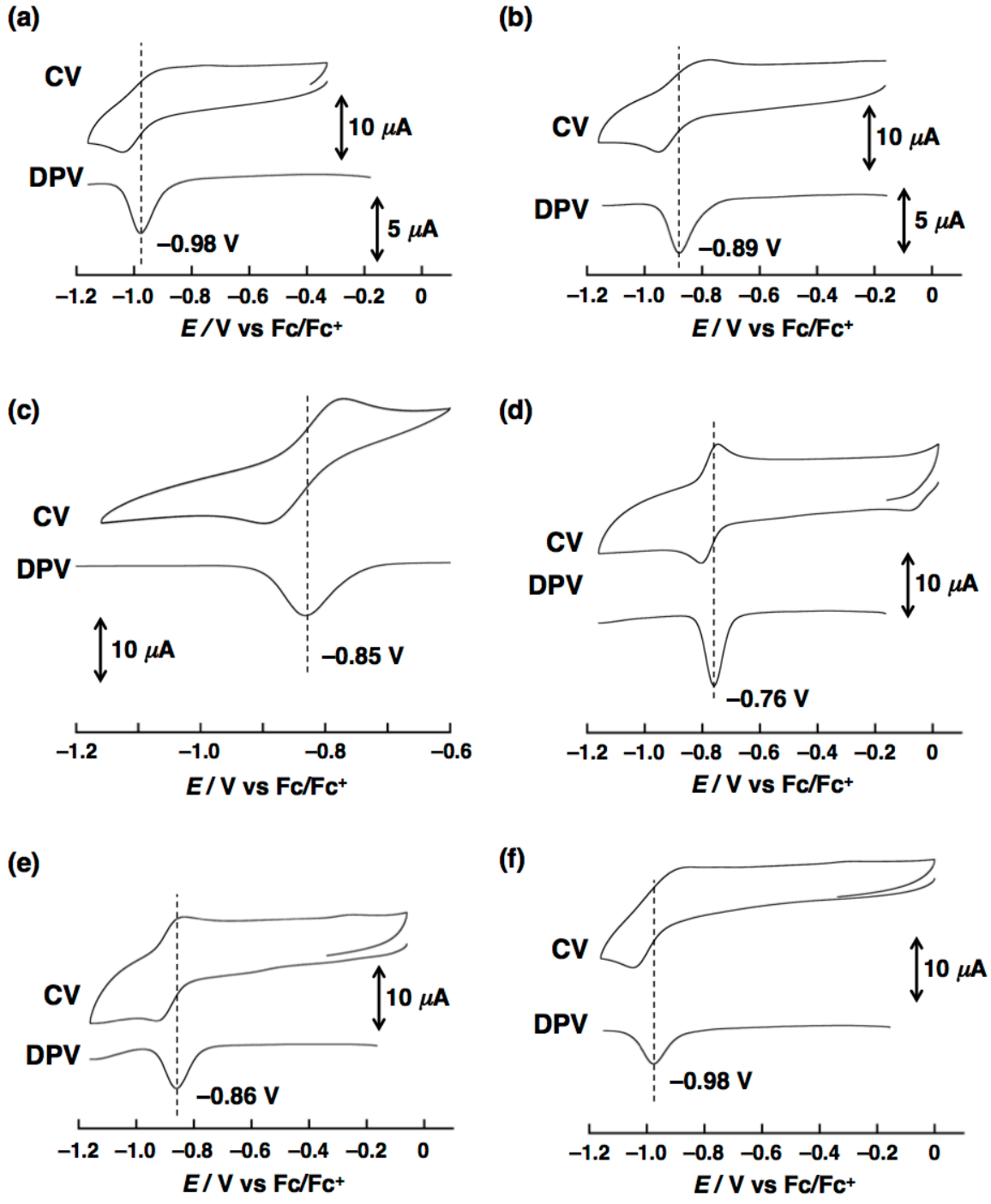


Fig. S2 Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of $H_4DPP^{2+}(X^-)_2$ (0.2 mM) in acetone containing 0.1 M $TBAPF_6$ as an electrolyte at 298 K; X^- = (a) *m*-NO_2PhCOO^- (NBA), (b) Cl_2CHCOO^- (DCA), (c) CF_3COO^- (TFA), (d) TsO^-, (e) $BnPy^+$-COO^-, and (f) $BnPy^+$-$PhCOO^-$.

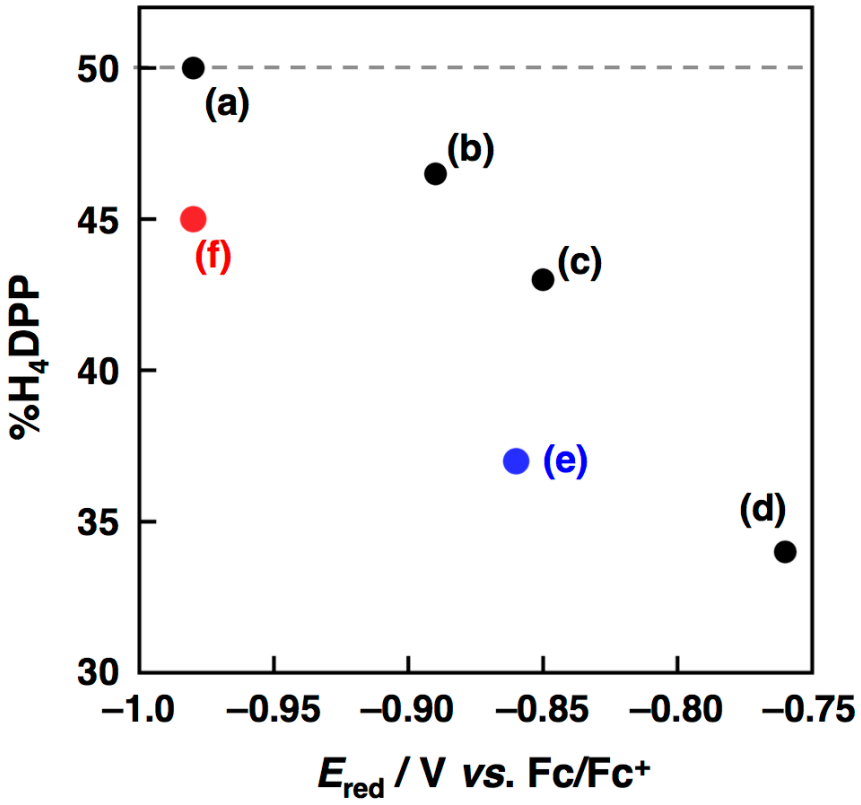


Fig. S3 A plot of %H_4DPP values relative to reduction potentials (E_{red}) of $H_4DPP^{2+}(X^-)_2$ (0.2 mM) determined in acetone containing 0.1 M $TBAPF_6$ as an electrolyte at room temperature.

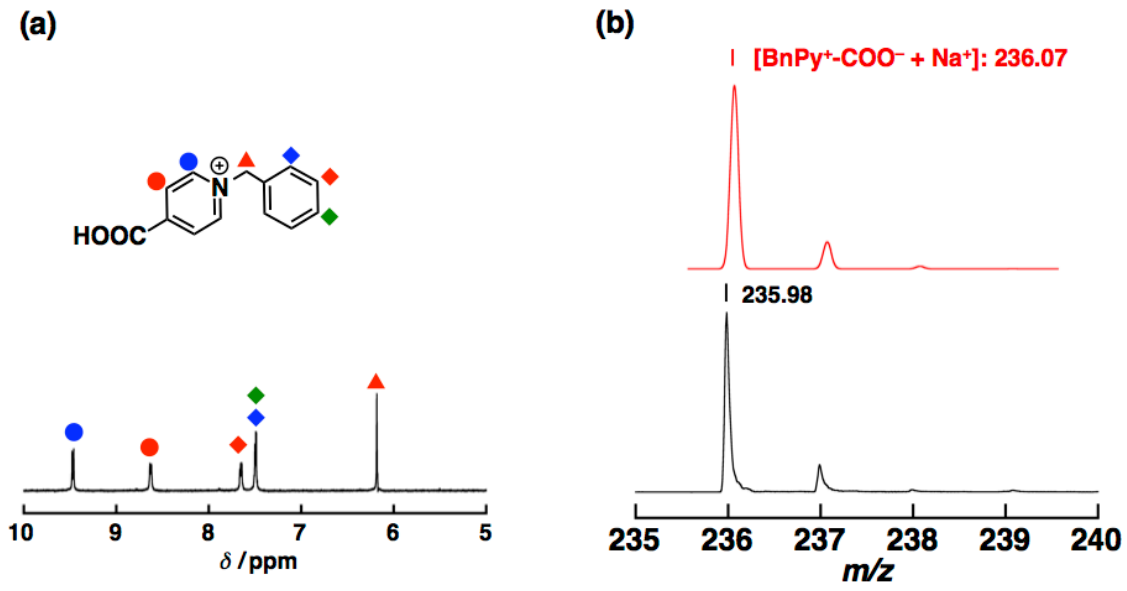


Fig. S4 (a) ^{1}H NMR spectrum of $BnPy^{+}$-$COOH(ClO_4^{-})$ in acetone-d_6 at 298K. (b) ESI-TOF-MS spectrum (bottom) of $BnPy^{+}$-$COOH(ClO_4^{-})$ in MeOH at room temperature and the computer-simulated isotropic pattern (upper).

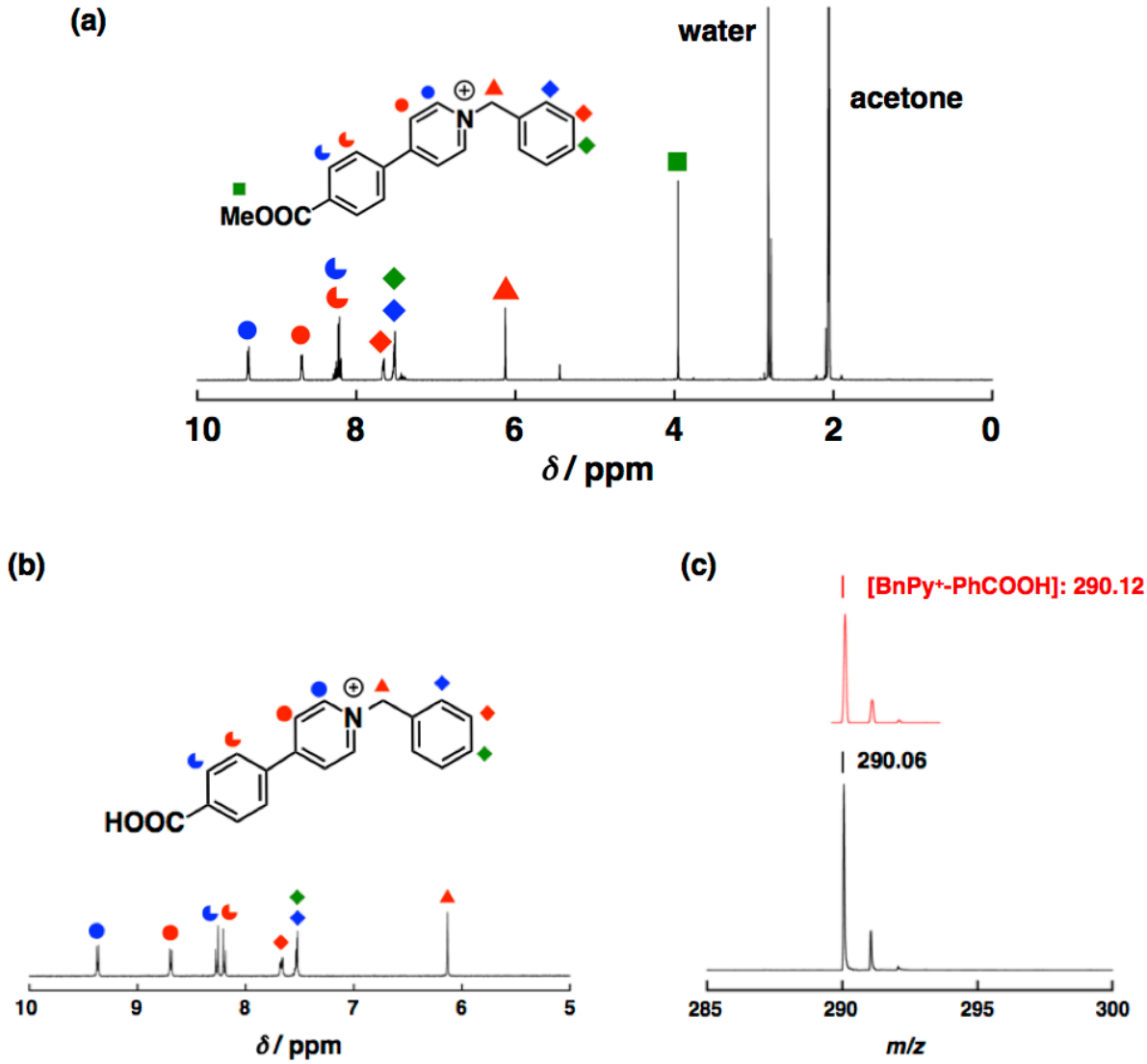


Fig. S5 (a) ^{1}H NMR spectrum of BnPy^{+}-PhCOOMe(PF_6^-) in acetone-d_6 at 298K. (b) ^{1}H NMR spectrum of BnPy^{+}-PhCOOH(PF_6^-) in acetone-d_6 at 298K. (c) ESI-TOF-MS spectrum (bottom) of BnPy^{+}-PhCOOH(PF_6^-) in MeOH at room temperature and the computer-simulated isotropic pattern (upper).

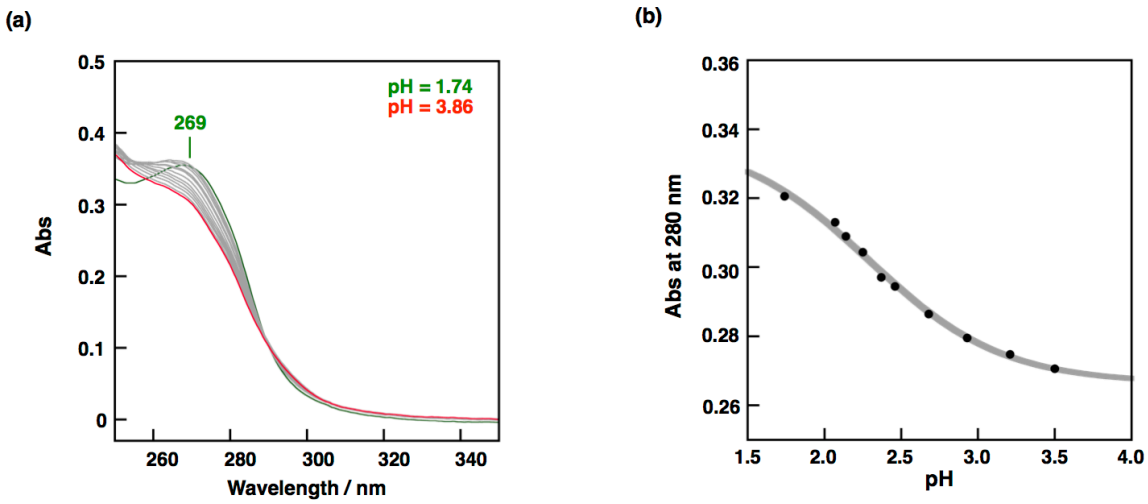


Fig. S6 (a) UV-Vis spectroscopic titration of $BnPy^{+}$-COOH(ClO_4^-) (0.3 mM) in Briton-Robinson buffer (0.1 M) with use of 8 M $NaOH_{aq}$ at 298 K. (b) A plot of the absorbance at 280 nm *vs*. pH.

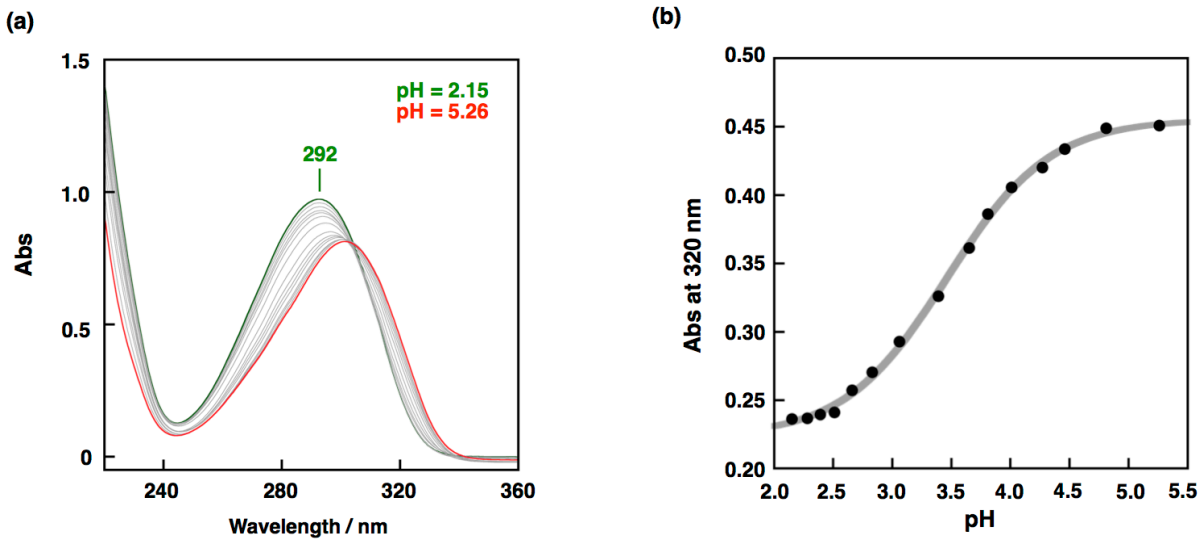


Fig. S7 (a) UV-Vis spectroscopic titration of $BnPy^{+}$-PhCOOH(PF_6^{-}) (0.2 mM) in Briton-Robinson buffer (0.1 M) with use of 8 M $NaOH_{aq}$ at 298 K. (b) A plot of the absorbance at 280 nm *vs*. pH.

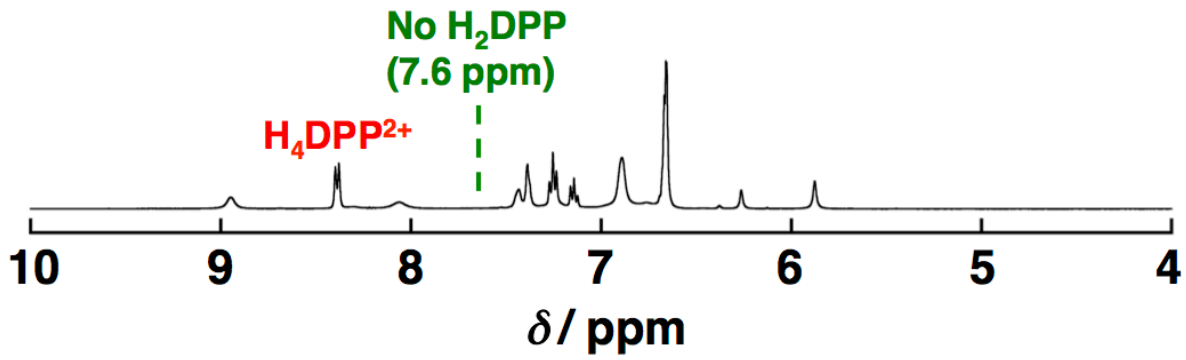


Fig. S8 ^{1}H NMR spectrum of H_2DPP (0.2 mM) containing 2 eq of $BnPy^{+}$-PhCOOH in acetone-d_6 at 298 K.

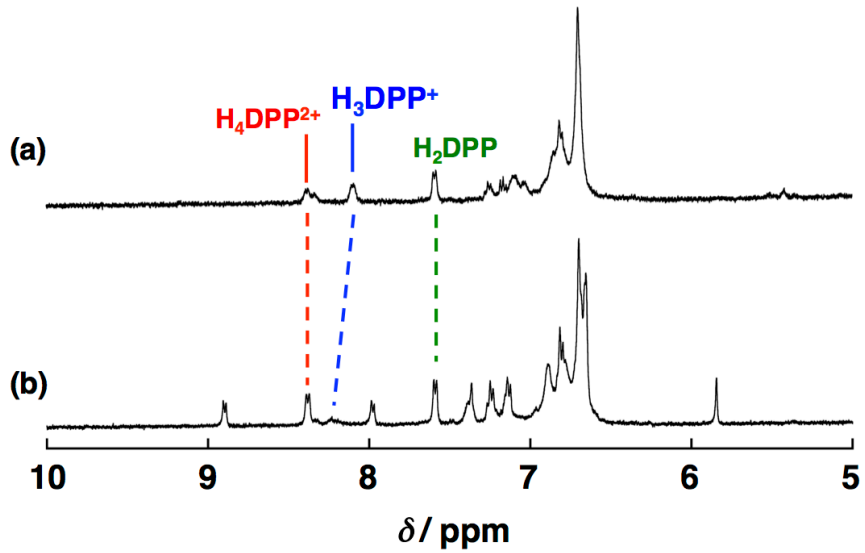


Fig. S9 ^{1}H NMR spectra of H_2DPP (0.15 mM) in acetone-d_6 at 298 K with 1 eq of (a) $BnPy^{+}$-COOH, and (b) $BnPy^{+}$-PhCOOH.

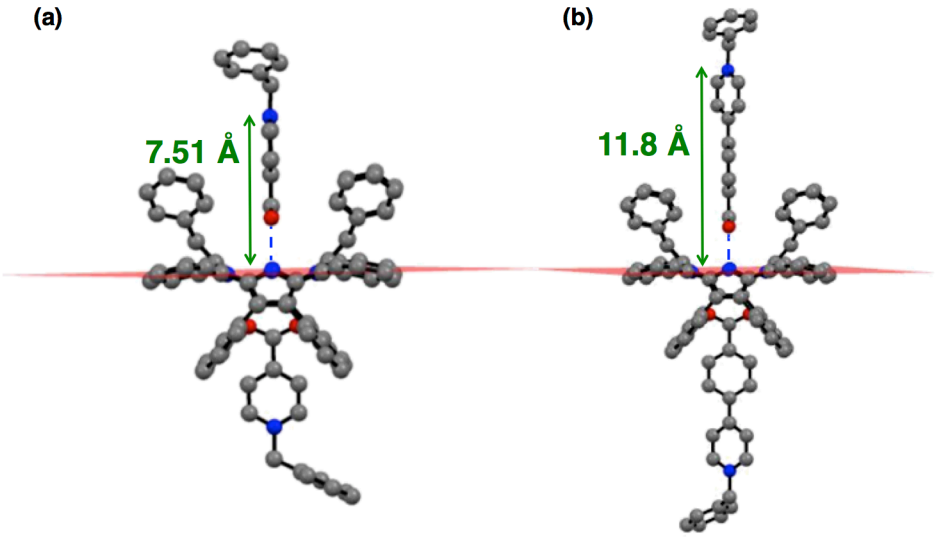


Fig. S10 DFT optimized structures of (a) $H_4DPP^{2+}(BnPy^{+}\text{-}COO^{-})_2$ and (b) $H_4DPP^{2+}(BnPy^{+}\text{-}PhCOO^{-})_2$ at the 6-31G** level of theory. Green arrows indicate the distances between positively charged nitrogen atoms in conjugate bases and the mean planes (red) of H_4DPP^{2+}.

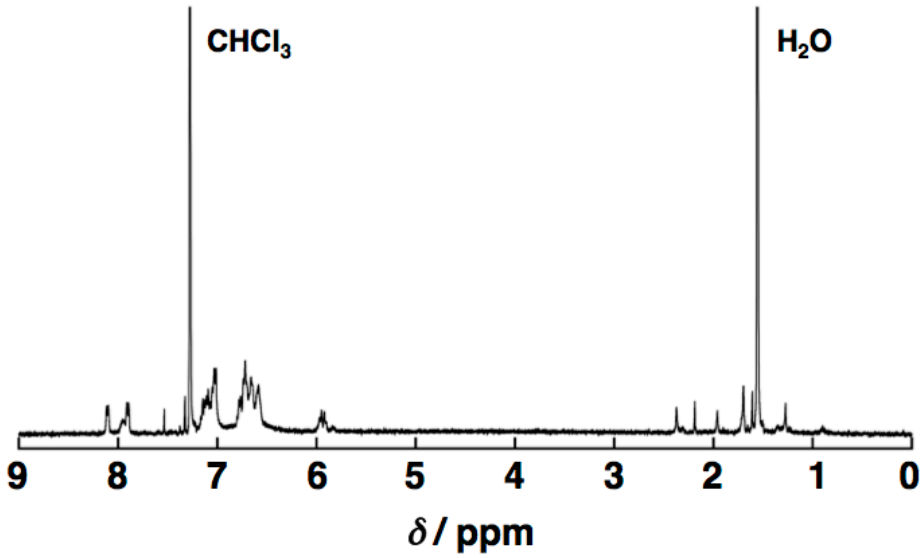


Fig. S11. ^{1}H NMR spectrum of a 1:1 mixture of $H_4DPP^{2+}(TsO^{-})_2$ solution (0.4 mM) and the solution of $H_4DPP^{2+}(Cl^{-})_2$ (0.4 mM) in $CDCl_3$ at 298 K.

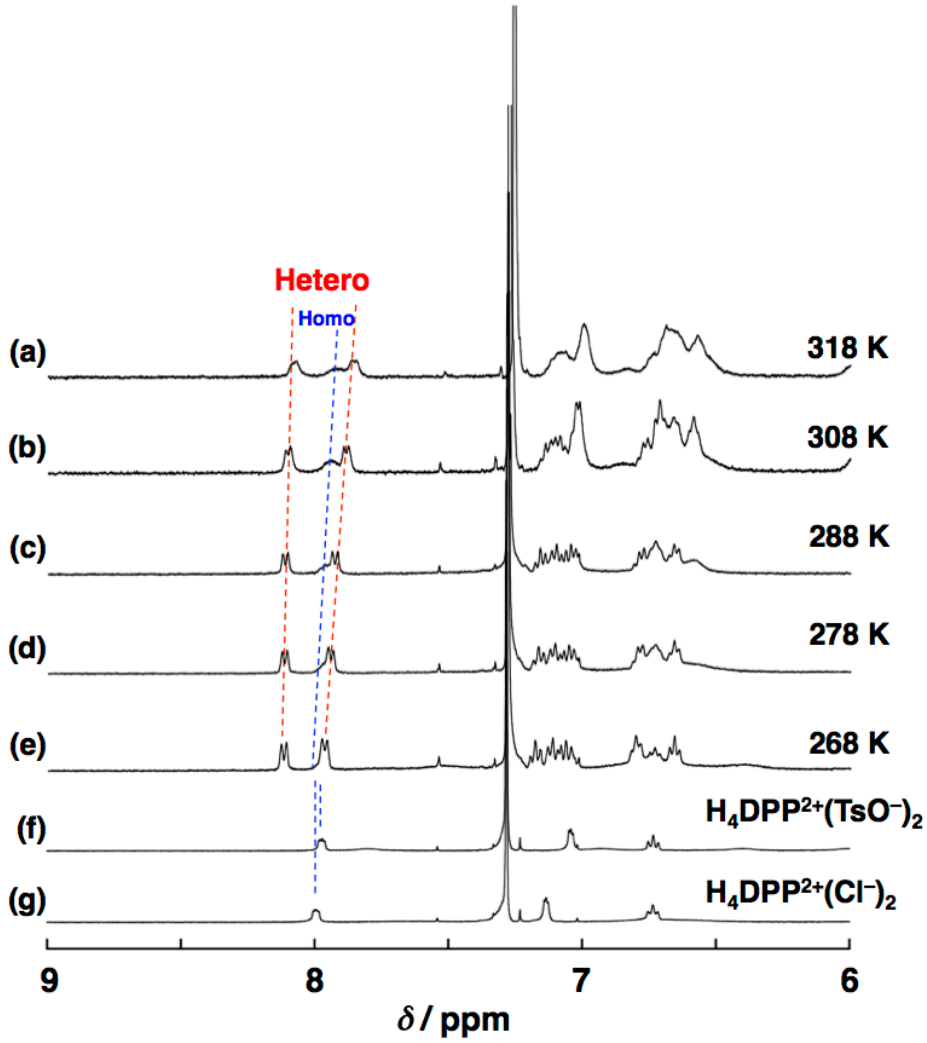


Fig. S12 Temperature dependence of ^{1}H NMR spectra of a 1:1 mixture of $H_4DPP^{2+}(TsO^-)_2$ solution (0.4 mM) and the solution of $H_4DPP^{2+}(Cl^-)_2$ (0.4 mM) in $CDCl_3$ at (a) 318 K, (b) 308 K, (c) 288 K, (d) 278 K, (e) 268 K. ^{1}H NMR spectrum of (f) $H_4DPP^{2+}(TsO^-)_2$ (0.4 mM), and (g) ^{1}H NMR spectrum of $H_4DPP^{2+}(Cl^-)_2$ (0.4 mM) in $CDCl_3$ at 268 K. Red dotted line: ^{1}H NMR signals derived from *ortho*-protons of the *meso*-phenyl groups of $H_4DPP^{2+}(TsO^-)(Cl^-)$; Blue dotted line: ^{1}H NMR signals derived from *ortho*-protons of the *meso*-phenyl groups of $H_4DPP^{2+}(Cl^-)_2$ and $H_4DPP^{2+}(TsO^-)_2$.

Table S2 Summary of equilibrium constants (*K*) in formation of $H_4DPP^{2+}(TsO^-)(Cl^-)$ and $H_4DPP^{2+}(NO_2PhCOO^-)(Cl^-)$ in chloroform at various temperatures.

Temp / K	*K* $\{H_4DPP^{2+}(TsO^-)(Cl^-)\}$	*K* $\{H_4DPP^{2+}(NO_2PhCOO^-)(Cl^-)\}$
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	–

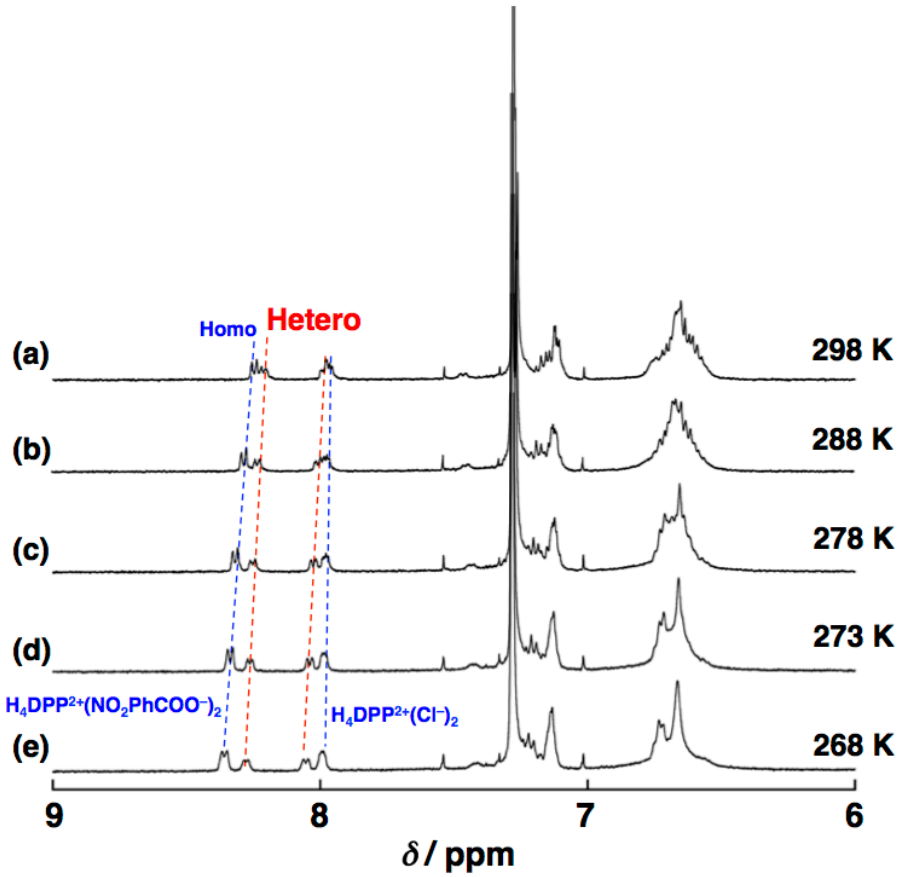


Fig. S13 Temperature dependence of ^{1}H NMR spectra of a 1:1 mixture of $H_4DPP^{2+}(NO_2PhCOO^-)_2$ solution (0.4 mM) and the solution of $H_4DPP^{2+}(Cl^-)_2$ (0.4 mM) in $CDCl_3$ at (a) 298 K, (b) 288 K, (c) 278 K, (d) 273 K, (e) 268 K. Red dotted line: ^{1}H NMR signals derived from *ortho*-protons of the *meso*-phenyl groups of $H_4DPP^{2+}(NO_2PhCOO^-)(Cl^-)$; Blue dotted line: ^{1}H NMR signals derived from *ortho*-protons of the *meso*-phenyl groups of $H_4DPP^{2+}(Cl^-)_2$ and $^1H_4DPP^{2+}(NO_2PhCOO^-)_2$.

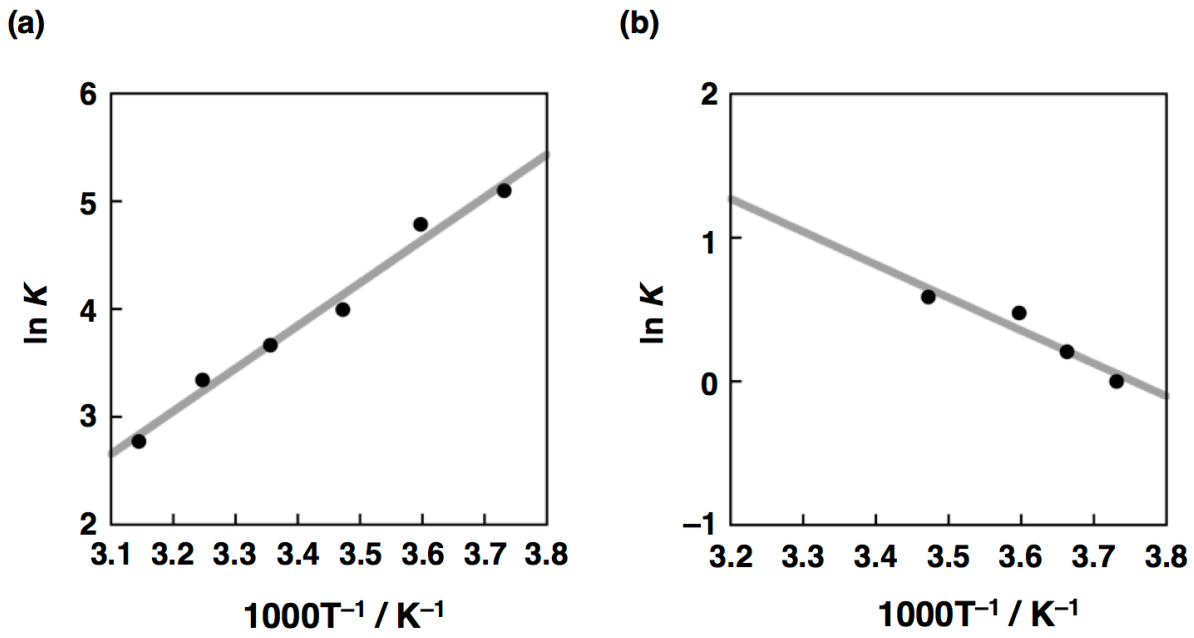


Fig. S14 van't Hoff plots for the formation of (a) $H_4DPP^{2+}(TsO^-)(Cl^-)$ and (b) $H_4DPP^{2+}(NO_2PhCOO^-)(Cl^-)$ in chloroform.

Table S3 Summary of thermodynamic parameters in formation of $H_4DPP^{2+}(TsO^-)(Cl^-)$ and $H_4DPP^{2+}(NO_2PhCOO^-)(Cl^-)$ in chloroform.

	$H_4DPP^{2+}(TsO^-)(Cl^-)$	$H_4DPP^{2+}(NO_2PhCOO^-)(Cl^-)$
ΔH / kcal mol^{-1}	–7.8	+ 6.1
ΔS / cal K^{-1} mol^{-1}	–19	+ 23
ΔG^a / kcal mol^{-1}	–2.1	–0.67

a: at 298 K

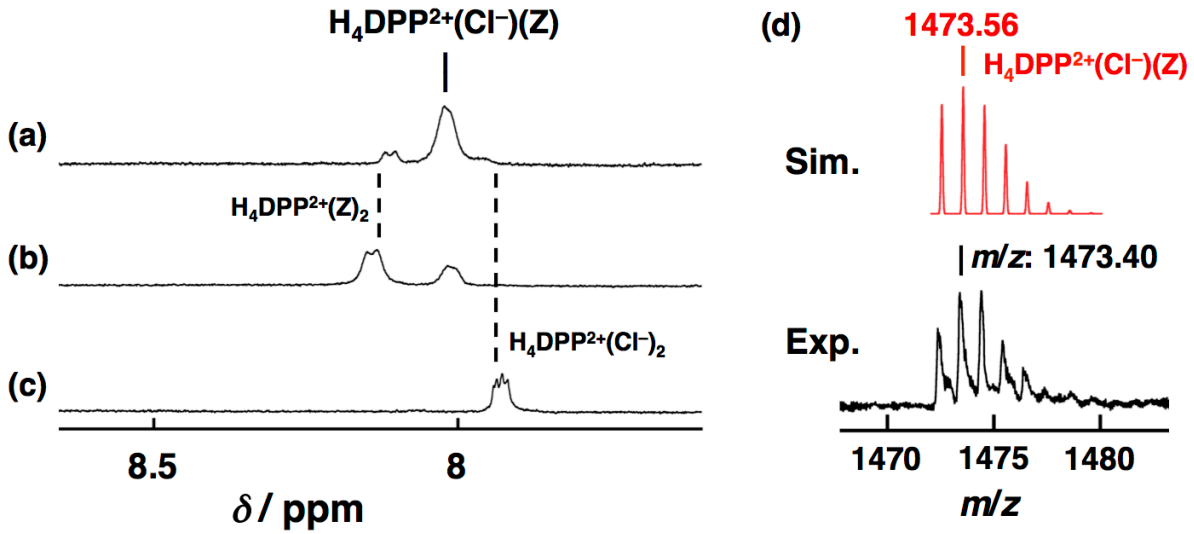


Fig. S15 ^{1}H NMR spectra of (a) mixture of H_2DPP solution with 2 eq of $BnPy^{+}$-COOH (HZ^{+}) and the solution of $H_4DPP^{2+}(Cl^{-})_2$ with the ratio of 1:1, (b) $H_4DPP^{2+}(BnPy^{+}\text{-}COO^{-})_2$, (c) $H_4DPP^{2+}(Cl^{-})_2$ in $CDCl_3$ at 298 K. (d) CSI-TOF-MS spectrum (bottom) of a mixture of H_2DPP (0.01 mM) with 2 eq of $BnPy^{+}$-COOH and $H_4DPP^{2+}(Cl^{-})_2$ (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 $[H_4DPP^{2+}(Cl^-)(BnPy^+\text{-}PhCOO^-)](PF_6^-)$

compound	$[H_4DPP^{2+}(Cl^-)(BnPy^+\text{-}PhCOO^-)](PF_6^-)$
crystal system	Monoclinic
space group	$P2_1$
T / K	120
formula	$[C_{92}H_{64}N_4\bullet Cl\bullet(C_{20}H_{30}NO_2)]\bullet PF_6$
FW	1722.34
a / Å	16.246(3)
b / Å	30.559(5)
c / Å	20.510(3)
β / deg	89.973(3)
V / Å^3	10182(3)
Z	4
λ / Å	0.71073 (Mo Ka)
D_c / g cm^{-3}	1.124
reflns measured	45645
reflns unique	21344
R_1 (I > 2s(I))	0.0785
wR_2 (all)	0.2182
GOF	1.035

Table S5 Cartesian coordinates of $H_4DPP^+(BnPy^+\text{-}COO^-)_2$

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 $H_4DPP^+(BnPy^+\text{-}PhCOO^-)_2$

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

References.

1 C. J. Medforth, M. O. Senge, K. M. Smith, L. D. Sparks and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1992, ***114***, 9859-9869.

2 C.-J. Liu, W.-Y. Yu, S.-M. Peng, C. W. Mak and C.-M. Che, *J. Chem. Soc. Dalton Trans.*, 1998, ***11***, 1805-1812.

3 M. Chen, M.-Z. Chen, C.-Q. Zhou, W.-E. Lin, J.-X. Chen, W.-H. Chen and Z.-H. Jiang, *Inorg. Chim. Acta*, 2013, ***405***, 461-469.

4 (*a*) T. K. Ronson, C. Carruthers, J. Fisher, T. Brotin, L. P. Harding, P. J. Rizkallah and M. J. Hardie, *Inorg. Chem.*, 2010, ***49***, 675-685. (*b*) J. Wu, D. Zhang, L. Chen, J. Li, J. Wang, C. Ning, N. Yu, F. Zhao, D. Chen, X. Chen, K. Chen, H. Jiang, H. Liu and D. Liu, *J. Med. Chem.*, 2013, **56**, 761-780.

5 (*a*) K. Wakita, Yadokari-XG, Software for Crystal Structure Analyses 2001; (*b*) C. Kabuto, S. Akine, T. Nemoto, E. Kwon, Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses. *J. Cryst. Soc. Jpn.*, 2009, ***51***, 218-224.

6 P. V. D. Sluis and A. L. Spek, *Acta Crystallogr.*, 1990, **A46**, 194-201.

7 D. Becke, *J. Chem. Phys.*, 1993, ***98***, 5648-5652.

8 W. Lee, and R. G. Yang, *Parr, Phys. Rev. B*, 1988, ***37***, 785-789.

9 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, ***56***, 2257-2261.

10 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.