Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Dipyridinoarsole: A new class of stable and modifiable heteroatom-bridged bipyridines

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1. Materials

Chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), methanol (MeOH), ethylacetate (EtOAc), iodomethane (CH_3I), ammonia solution (NH_3 , 28%), sodium sulfonate ($NaSO_4$), sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$), hydrogen peroxide (H_2O_2, 30%), and dichlorophenylphosphine ($PhPCl_2$) were purchased from Nacalai Tesque, Inc. Superdehydrated tetrahydrofuran (stabilizer free) (THF), distilled water, *n*-butyllithium solution (*n*-BuLi, 1.6 M in hexane), diethyl ether (Et_2O), and magnesium sulfate anhydrous ($MgSO_4$), ammonium chloride (NH_4Cl), iodine (I_2), *N*,*N*-dimethylformamide (DMF), acetonitrile (CH_3CN), and ferrocene were purchased from Wako Pure Chemical Industry, Ltd. Methyl Trifluoromethanesulfonate (MeOTf), 3-bromopyridine, copper(II) chloride ($CuCl_2$), lithium diisopropyl amide solution (2.0 M in THF/heptane/ethylbenzene), and benzyl bromide (BnBr) were purchased from Tokyo Chemical Industry Co., Ltd. Diidophenylarsine,[1] 3,3'-dibromo-4,4'-bipyridine,[2] and dipyridinophosphole-oxide (**6**)[2] were prepared according to literature procedures.

2. Measurement

^1H- (400 MHz) and ^{13}C- (100 MHz) NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer. The samples were analyzed in $CDCl_3$ using Me_4Si as an internal standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, m: multiplet. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. The UV−vis spectra were recorded on a Jasco spectrophotometer (V-670 KKN). Emission spectra were obtained on an FP-8500 instrument (JASCO), and absolute PL quantum yields (Φ) were determined using a JASCO ILFC-847S instrument. Emission lifetimes were measured using Quantaurus-Tau (Hamamatsu Photonics). Spectroelectrochemistry measurements were performed by an Ocean Optics USB4000-XR1 fibre spectrometer with DH2000-BAL tungsten halogen light source and a potentiostat HOKUTO DENKO HABF501. A three-electrode system equipped with the Pt mesh working electrode, Pt counter electrode and Ag/AgCl as a reference electrode was used in an electrolytic solution of DMF containing 0.1 M NBu_4PF_6. In the spectroelectrochemistry, the time for applying potentials was altered from 30 sec to 3 min, and it was confirmed that the UV-vis absorption spectra were not changed.

3. X-ray crystallographic data for single crystalline products

The single crystal was mounted on a nylon loop. Intensity data were collected at room temperature on a Rigaku XtaLAB mini with graphite monochromated Mo Kα radiation. Readout was performed in the 0.073 mm pixel mode. The data were collected at room temperature to a maximum 2θ value of 55.0°. Data were processed using the Crystal Clear program.[3] An empirical absorption correction[4] was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by the direct method[5] and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on observed reflections and variable parameters. All calculations were performed using the CrystalStructure[6] crystallographic software package except for refinement, which was performed using SHELXL2013.[6] Crystal data and more information on X-ray data collection are summarized in Tables S1-7.

4. Synthesis

Note
Low molecular weight organoarsenic compounds have volatility, and it is necessary to avoid the procedures generating volatile organoarsenic compounds. For safety, experiments should be performed in a fume hood. Besides, in a few cases, spontaneously flammable compounds are obtained as described in the literature,[7] and thus fire prevention measures should be taken.

*9-Phenyl-9H-arsolo[2,3-c:5,4-c']dipyridine (**1**)*
1.6 M *n*-hexane solution of *n*-BuLi (3.0 mL, 4.80 mmol, 2.0 eq) was added dropwise to a THF mixed solution (THF: 96 mL) of 3,3'-dibromo-4,4'-bipyridine (0.753 g, 2.40 mmol, 1.0 eq) at -100 °C under N_2 atmosphere and the mixture was stirred at that temperature for 1 hour. Then, separately prepared diiodophenylarsine (1.1 eq) was added dropwise into the mixture. The mixture was heated to 40 °C and stirring for 1 h. Distilled water was poured into the reaction mixture at 0 °C, and the organic layer was concentrated in vacuo. The aqueous layer was extracted with $CHCl_3$, and the combined organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified through the silica column chromatography (eluent: *n*-hexane/ EtOAc = 1/4). The title compound was obtained as white solids (56%, 413 mg, 1.35 mmol). The single crystal of **1** was obtained by slow evaporation of saturated solution in CH_2Cl_2.
^1H-NMR (acetone-d_6, 400 MHz): δ 9.12 (s, 2H), 8.78 (d, J = 5.2 Hz, 2H), 8.16 (dd, J = 5.2, 0.8 Hz, 2H), 7.32-7.26 (m, 5H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 152.72, 151.06, 150.00, 141.88, 132.21, 129.40, 129.16, 117.85 ppm. HR-FAB-MS (*m*/*z*): calculated for $C_{16}H_{12}N_2As$ $[M+H]^+$: 307.0216; found: 307.0223.

*9-Phenyl-9H-arsolo[2,3-c:5,4-c']dipyridine-9-oxide (**2**)*

A THF (2.7 mL) solution of **1** (39.9 mg, 0.130 mmol) and H_2O_2 (30%, 89.8 mg) was stirred for 3 h under ambient conditions. Then saturated $Na_2S_2O_3$ aq was added into the mixture at 0 °C. The products were extracted with $CHCl_3$, and the organic layer was dried over $MgSO_4$. After filtration, the volatiles were removed in vacuo. The crudes product was washed with the mixture of 2-propanol and hexane to obtain the title compound as white solids (83%, 34.8 mg, 0.108 mmol)

^{1}H-NMR (acetone-d_6, 400 MHz): δ 9.07 (s, 2H), 8.99 (d, J = 5.2 Hz, 2H), 7.91 (d, J = 5.2 Hz, 2H), 7.68-7.61 (m, 3H), 7.53 (dd, J = 7.4 Hz, 2H), 7.48-7.32 (m, 4H), 7.29-7.26 (m, 3H) ppm; ^{13}C-NMR (acetone-d_6, 100 MHz): δ 154.45, 151.65, 146.55, 133.36, 130.39, 130.36, 129.98, 128.30, 117.67 ppm; HR-FAB-MASS:(*m*/*z*): calculated for $C_{16}H_{11}N_2AsO_2Na$ $[M+Na]^+$: 344.9980 found: 344.9979.

*Gold(9-phenyl-9H-arsolo[2,3-c:5,4-c']dipyridine) chloride (**3**)*

A CH_2Cl_2 solution (10 mL) of **1** (29.8 mg, 0.0973 mmol) and AuCl (27.5 mg, 0.118 mmol, 1.2 eq) was stirred at room temperature under nitrogen atmosphere. After stirring for 2 h. After stirring for 3 h, the precipitate was filtered off and then the mixture was concentrated in vacuo to obtain the titled compound as yellow powders (62%, 32.5 mg, 0.0603 mmol). The single crystal of **2** was obtained by slow evaporation of saturated solution in CH_2Cl_2.

^{1}H-NMR (acetone-d_6, 400 MHz): δ 9.03 (s, 2H), 8.95 (d, J = 5.1 Hz, 2H), 7.97 (d, J = 5.3 Hz, 2H),7.52-7.49 (m, 1H), 7.41-7.40 (m, 4H) ppm; ^{13}C-NMR (acetone-d_6, 100 MHz) cannot be measured due to the low solubility. HR-FAB-MS (*m*/*z*): calculated for $C_{16}H_{12}N_2AsAuCl$ $[M+H]^+$: 538.9570; found: 538.9565.

*2,7-Dimethyl-9-Phenyl-9H-arsolo[2,3-c:5,4-c']dipyridium iodide (**4-I**)*

To a MeOH solution (MeOH:9.0 mL) of **1** (34.8 mg, 0.114 mmol) was added methyliodide (0.50 mL, 70 eq) and the mixture was headed to 60 °C for 3 d. After the mixture was cooled to room temperature, EtOAc was added to the mixuture and the precipitate was collected via vacuum filtration to obtain the title compound as black red powders (66%, 44.5 mg, 0.0754 mmol).

^{1}H-NMR (CD_3CN, 400 MHz): δ 9.27 (s, 2H), 8.91 (d, J = 6.4 Hz, 2H), 8.83 (d, J = 6.8 Hz, 2H), 7.41-7.39 (m, 1H), 7.33-7.32 (m, 4H), 4.38 (s, 6H) ppm; ^{13}C-NMR (CD_3CN, 100 MHz) cannot be measured due to the low solubility. HR-FAB-MS (*m*/*z*): calculated for $C_{18}H_{17}N_2As$ $[M-2I]^+$: 336.0608; found: 336.0600.

2,7-dimethyl-9-Phenyl-9H-arsolo[2,3-c:5,4-c']dipyridium 1,1,1-trifluoromethanesulfonate (**4-TfO**)

To a CH_2Cl_2 solution of **1** (30.7 mg, 0.10 mmol) was added dropwise methyl triflate (0.10 mL, 0.95 mmol, 9.5 eq) at 0°C. Then the solution was stirred at room temperature for 5 h. Then the precipitate was isolated via vacuum filtration to obtain the title compound as light-yellow solids (82%, 51.7 mg, 0.0815 mmol).

^{1}H-NMR (CD_3CN, 400 MHz): δ 9.13 (s, 2H), 8.87 (d, J = 6.4 Hz, 2H), 8.77 (d, J = 6.4 Hz, 2H), 7.43-7.27 (m, 5H), 4.37 (s, 6H) ppm; ^{13}C-NMR (CD_3CN, 100 MHz): δ 155.85, 149.76, 149.37, 147.26, 134.33, 133.95, 131.70, 130.54, 125.20, 49.91 ppm; ^{19}F-NMR (CD_3CN,376 MHz): δ -80.42 (s) ppm; HR-FAB-MS (*m*/*z*): calculated for $C_{20}H_{17}N_2AsF_6O_6S_2Na$ $[M+Na]^+$: 656.9546; found: 656.9547.

*9-Phenyl-9H-phospholo[2,3-c:5,4-c']dipyridine (**5**)*

1.6 M *n*-hexane solution of *n*-BuLi (1.5 mL, 2.40 mmol, 2.0 eq) was added dropwise to a THF mixed solution (THF: 60mL) of 3,3'-dibromo-4,4'-bipyridine (0.379 g, 1.21 mmol, 1.0 eq) at -100 °C under N_2 atmosphere and the mixture was stirred at that temperature for 1 h. Then, dichlorophenylphosphine (1.0 eq) was added dropwise into the mixture. The mixture was heated to 40 °C and stirring for 40 min. Distilled water was poured into the reaction mixture, and the organic layer was concentrated in vacuo. The aqueous layer was extracted with $CHCl_3$, and the combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified through the silica column chromatography (eluent: *n*-hexane/EtOAc = 1/9). The title compound was obtained as light-yellow solids (25%, 78.1 mg, 0.298 mmol). The single crystal of **6** was obtained by slow evaporation of saturated solution in CH_2Cl_2.

^{1}H-NMR (acetone-d_6, 400 MHz): δ 9.08 (s, 12), 8.80 (d, J = 4.8 Hz, 2H), 8.21 (d, J = 5.2 Hz, 2H), 7.35-7.34 (m, 5H) ppm; ^{13}C-NMR (acetone-d_6, 100 MHz): δ 152.83, (d, J = 22.6 Hz), 150.75, 149.64 (d, J = 1.5 Hz), 139.32 (d, J = 10.0 Hz), 134.30 (d, J = 18.2 Hz), 1333.30 (d, J = 20.6 Hz), 130.93, 130.03 (d, J = 7.8 Hz), 118.37 ppm; ^{31}P-NMR (acetone-d_6, 162 MHz): δ -16.40 Hz; HR-FAB-MS (*m*/*z*): calculated for $C_{16}H_{12}N_2P$ $[M]^+$: 263.0675; found: 263.0743.

2,7-Dimethyl-9-Phenyl-9H-phospholo[2,3-c:5,4-c']dipyridium 1,1,1-trifluoromethanesulfonate (**7**)

To a CH_2Cl_2 solution of **6** (27.5 mg, 0.11 mmol) was added dropwise methyl triflate (0.10 mL, 0.95 mmol, 9.5 eq) at 0 °C. Then the solution was stirred at ambient temperature. Then the precipitate was collected via vacuum filtration to obtain the title compound as yellow solids (96%, 59.1 mg, 0.100 mmol).

^{1}H-NMR (CD_3CN, 400 MHz): δ 9.15 (s, 2H), 8.85 (d, 4H), 7.54 (m, 1H), 7.42-7.37 (m. ,4H), 4.37 (s, 6H) ppm; ^{19}F-NMR (CD_3CN, 376 MHz): δ -80.42 (s) ppm; ^{31}P-NMR (CD_3CN, 162 MHz): δ -5.92 Hz; HR-ESI-MS (*m*/*z*): calcd. for $C_{19}H_{17}N_2PF_3O_3S$ $[M-TfO]^+$: 441.0650; found: 441.0632.

*9-Phenyl-2,7-bis(phenylmethyl)-9H-arsolo[2,3-c:5,4-c']dipyridium bromide (**8-Br**)*

A neat mixture of **1** (38.4 mg, 0.125 mmol) and benzylbromide (5.0 mL, excess) was heated at 50 °C for 3 d while stirring. The mixture was allowed to cool to room temperature and the precipitate vacuum filtration and washed with a mixture of MeOH:diethyl ether:$CHCl_3$ (1:10:2). The title compound was obtained as orange solids (93%, 75.3 mg, 0.116 mmol).

^{1}H-NMR (CD_3CN, 400 MHz): δ 9.66 (s, 2H), 9.15 (d, J = 6.8 Hz, 2H), 8.92 (d, J = 6.4 Hz, 2H), 7.55-7.26 (m, 15H), 5.85 (s, 4H) ppm; ^{13}C-NMR CD_3CN, 100 MHz) cannot be measured due to the low solubility. HR-FAB-MS (*m*/*z*): calculated for $C_{30}H_{25}N_2AsBr$ [M-Br]$^+$: 488.1234; found: 488.1236.

9-Phenyl-2,7-bis(phenylmethyl)-9H-arsolo[2,3-c:5,4-c']dipyridium1,1,1-trifluoromethanesulfonate (**8-TfO**)

To a suspension of **5-Br** (39.6 mg, 0.0611 mmol) in CH_2Cl_2 (20.0 mL) was added dropwise methyl triflate (0.03 mL, 0.3 mmol, 5 eq) at 0 °C. The mixture was stirred at ambient temperature for 10 hours. The solution was concentrated under reduced pressure. Then the crude crystal was washed with CH_2Cl_2 to afford the title compound as yellow crystals (84%, 40.4 mg, 0.0514 mmol).

^{1}H-NMR (CD_3CN, 400 MHz): δ 9.26 (s, 2H), 9.02 (d, J = 6.0 Hz, 2H), 8.82 (d, J = 6.4 Hz, 2H), 7.48 (s, 10H), 7.43-7.92 (m, 5H), 5.79 (s, 4H) ppm; ^{13}C-NMR (CD_3CN, 100 MHz): δ 156.41, 150.72, 148.39, 146.52, 134.33, 134.01, 133.55, 131.64, 131.14, 130.61, 130.53, 130.49, 125.82, 66.06 ppm; ^{19}F-NMR (CD_3CN,376 MHz): δ -80.47 (s) ppm; HR-FAB-MS (*m*/*z*): calculated for $C_{32}H_{25}N_2AsO_6F_6S_2Na$ [M+Na]$^+$: 809.0172; found: 809.1082.

5. NMR spectra

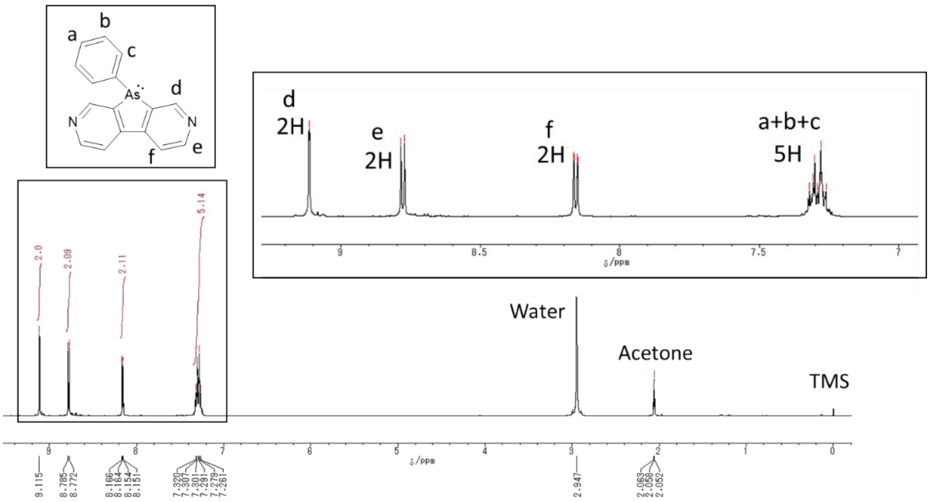


Figure S1. ^{1}H-NMR spectrum (400 MHz) of **1** in acetone-d_6.

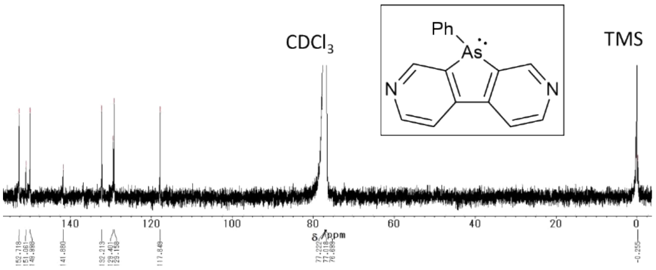


Figure S2. ^{13}C-NMR spectrum (100 MHz) of **1** in CDCl$_3$.

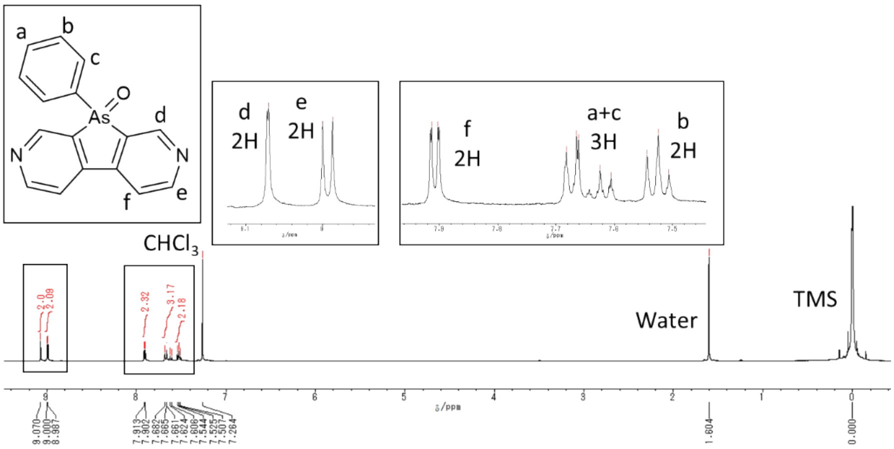


Figure S3. ^{1}H-NMR spectrum (400 MHz) of **2** in acetone-d_6.

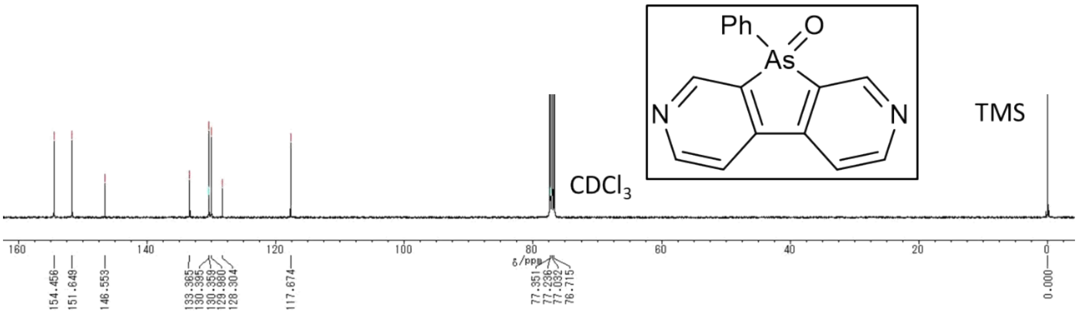


Figure S4. ^{13}C-NMR spectrum (100 MHz) of **2** in CDCl$_3$.

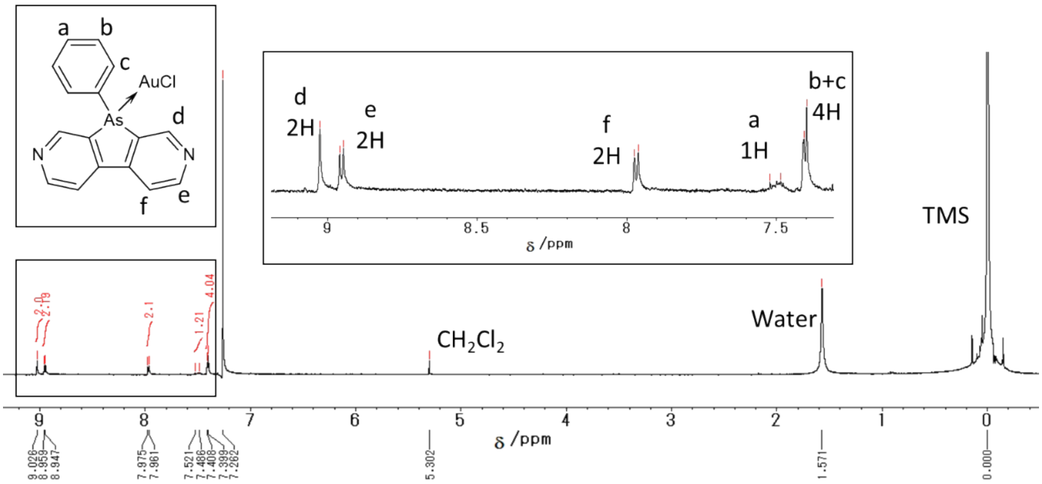


Figure S5. ^{1}H-NMR spectrum (400 MHz) of **3** in CDCl$_3$.

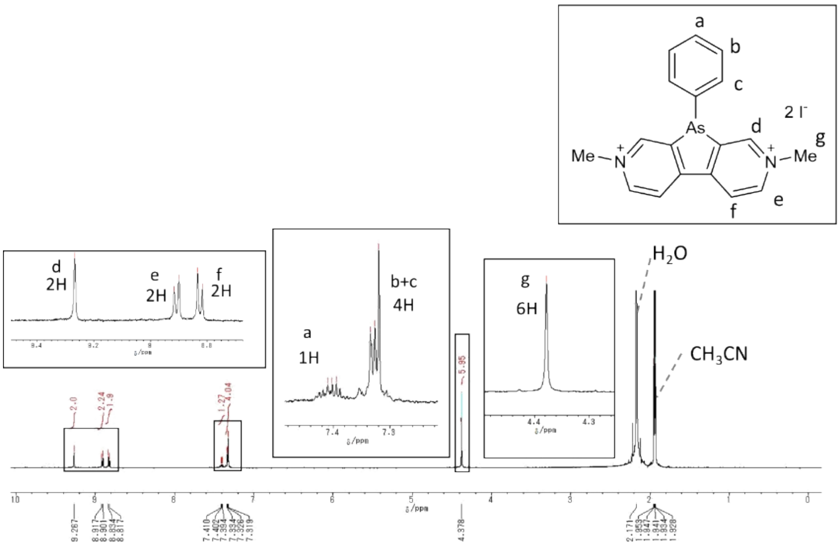


Figure S6. ^{1}H-NMR spectrum (400 MHz) of **4-I** in CD$_3$CN.

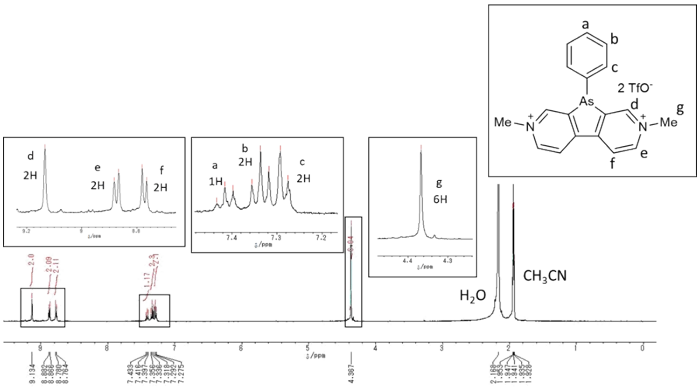


Figure S7. ^{1}H-NMR spectrum (400 MHz) of **4-TfO** in CD_3CN.

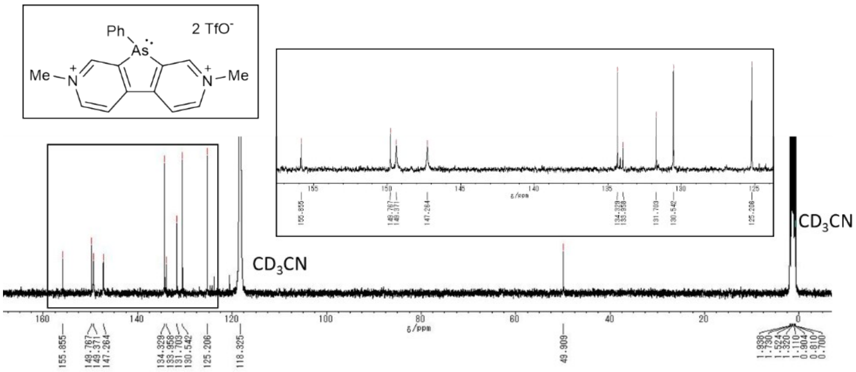


Figure S8. ^{13}C-NMR spectrum (100 MHz) of **4-TfO** in CD_3CN.

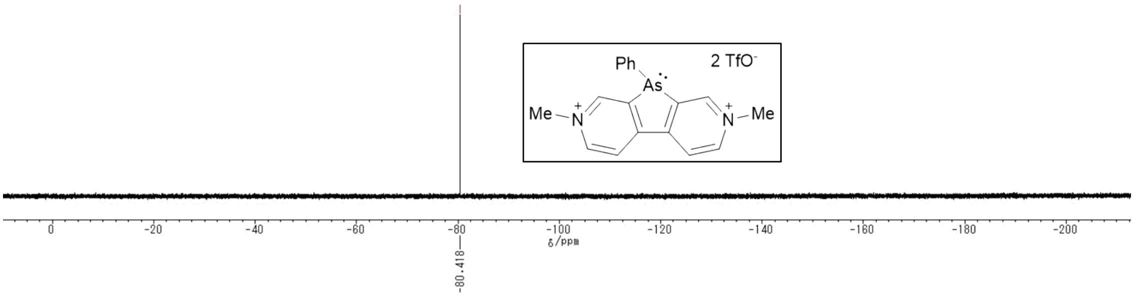


Figure S9. ^{19}F-NMR spectrum (376 MHz) of **4-TfO** in CD_3CN.

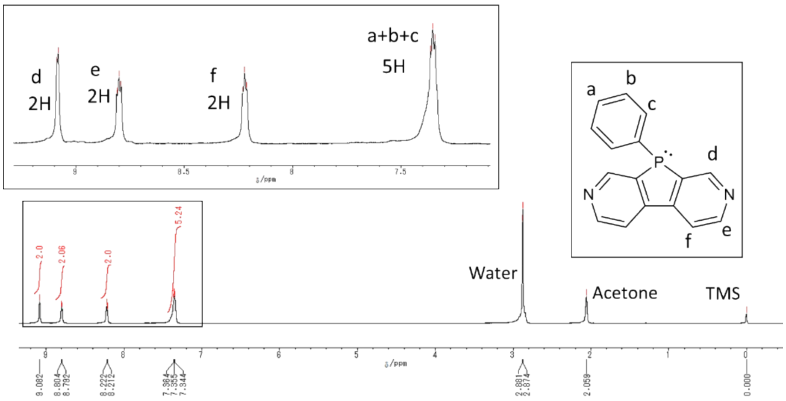


Figure S10. ^{1}H-NMR spectrum (400 MHz) of **5** in acetone-d_6.

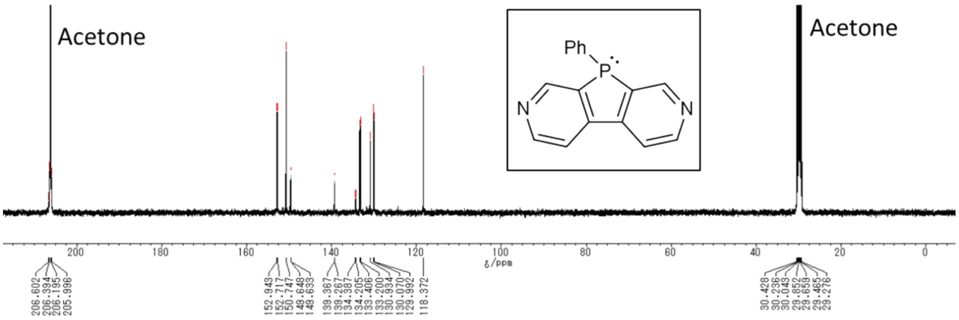


Figure S11. ^{13}C-NMR spectrum (100 MHz) of **5** in acetone-d_6.

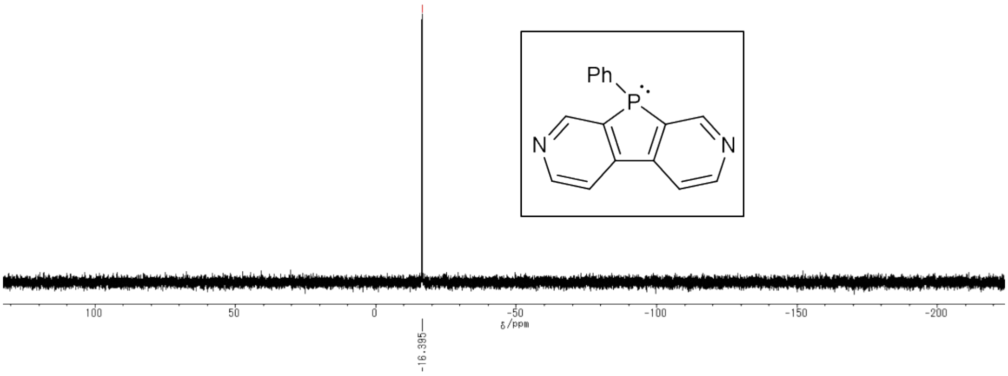


Figure S12. ^{31}P-NMR spectrum (376 MHz) of **5** in acetone-d_6.

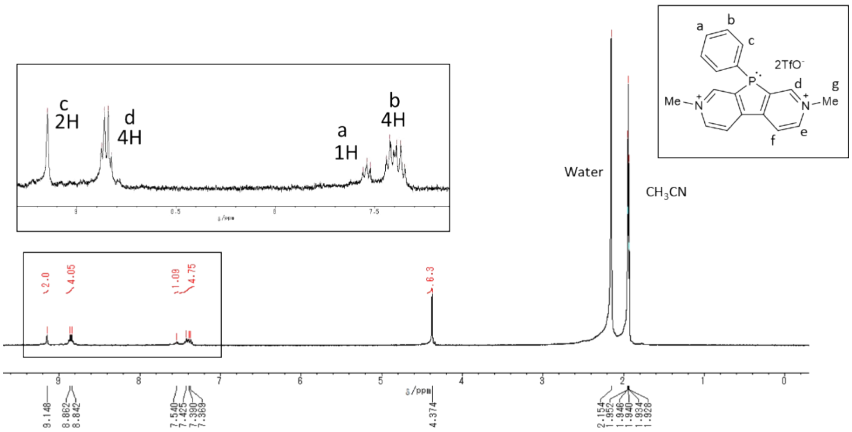


Figure S13. ^{1}H-NMR spectrum (400 MHz) of **7** in CD$_3$CN.

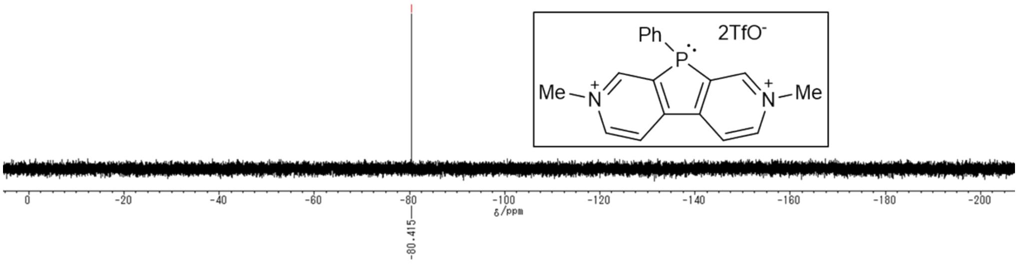


Figure S14. ^{19}F-NMR spectrum (100 MHz) of **7** in CD$_3$CN.

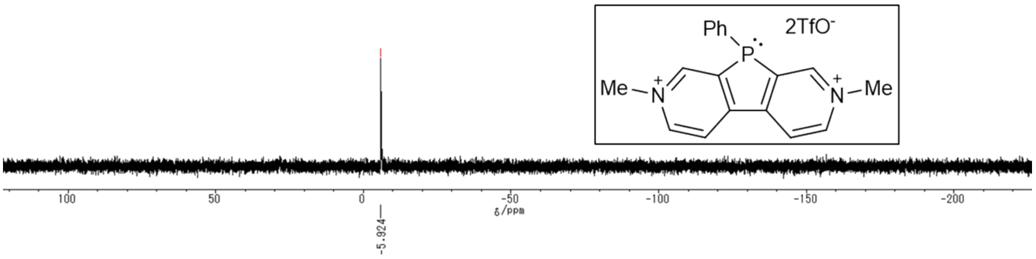


Figure S15. ^{31}P-NMR spectrum (376 MHz) of **7** in CD_3CN.

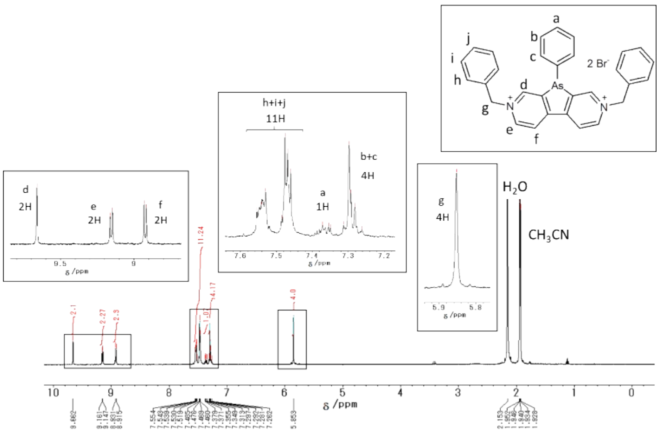


Figure S16. ^{1}H-NMR spectrum (400 MHz) of **8-Br** in CD_3CN.

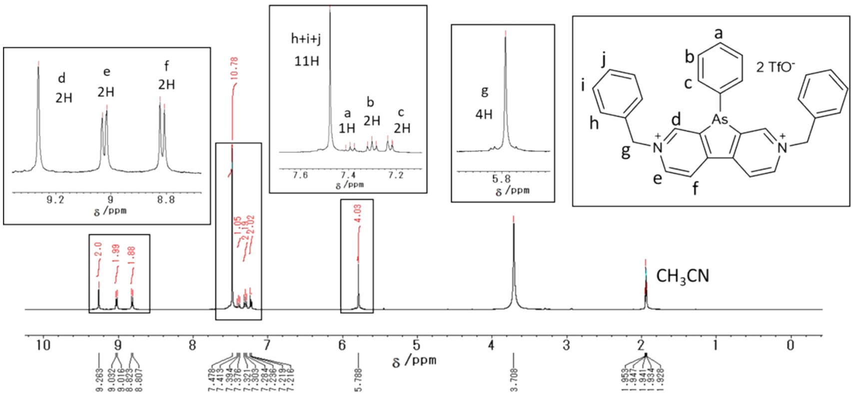


Figure S17. ^{1}H-NMR spectrum (400 MHz) of **8-TfO** in CD_3CN

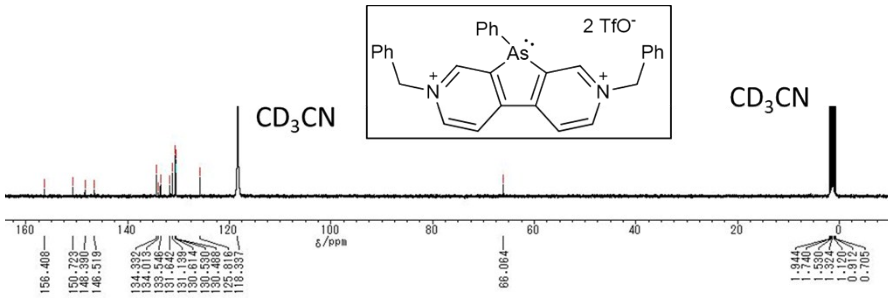


Figure S18. ^{13}C-NMR spectrum (100 MHz) of **8-TfO** in CD_3CN.

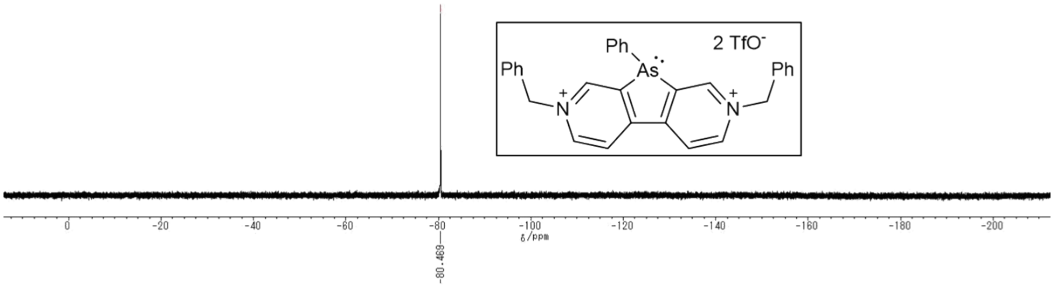


Figure S19. ^{19}F-NMR spectrum (376 MHz) of **8-TfO** in CD_3CN.

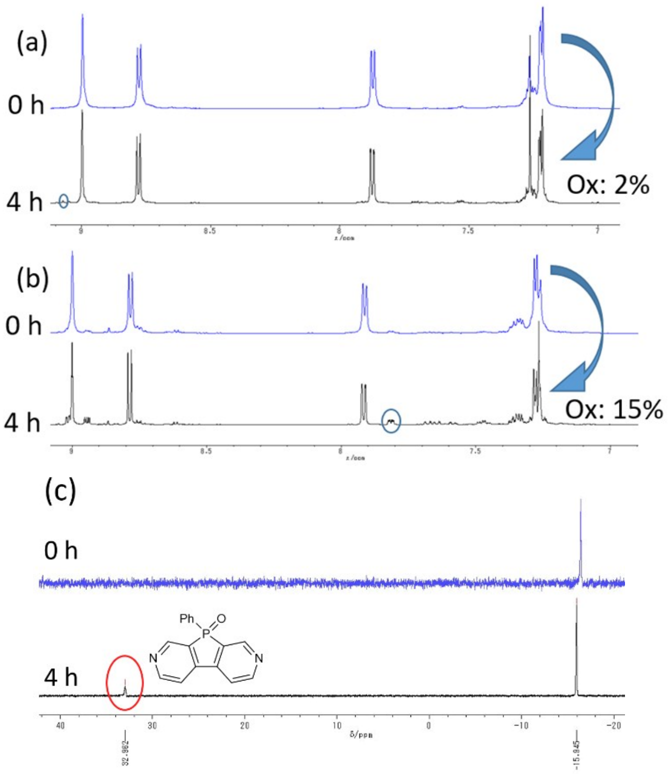


Figure S20. ^{1}H NMR spectra of (a) **1** and (b) **5** and (c) ^{31}P NMR spectra of **5** before and after air-bubbling for 4 h in $CDCl_3$. Solid circle indicates the new signal.

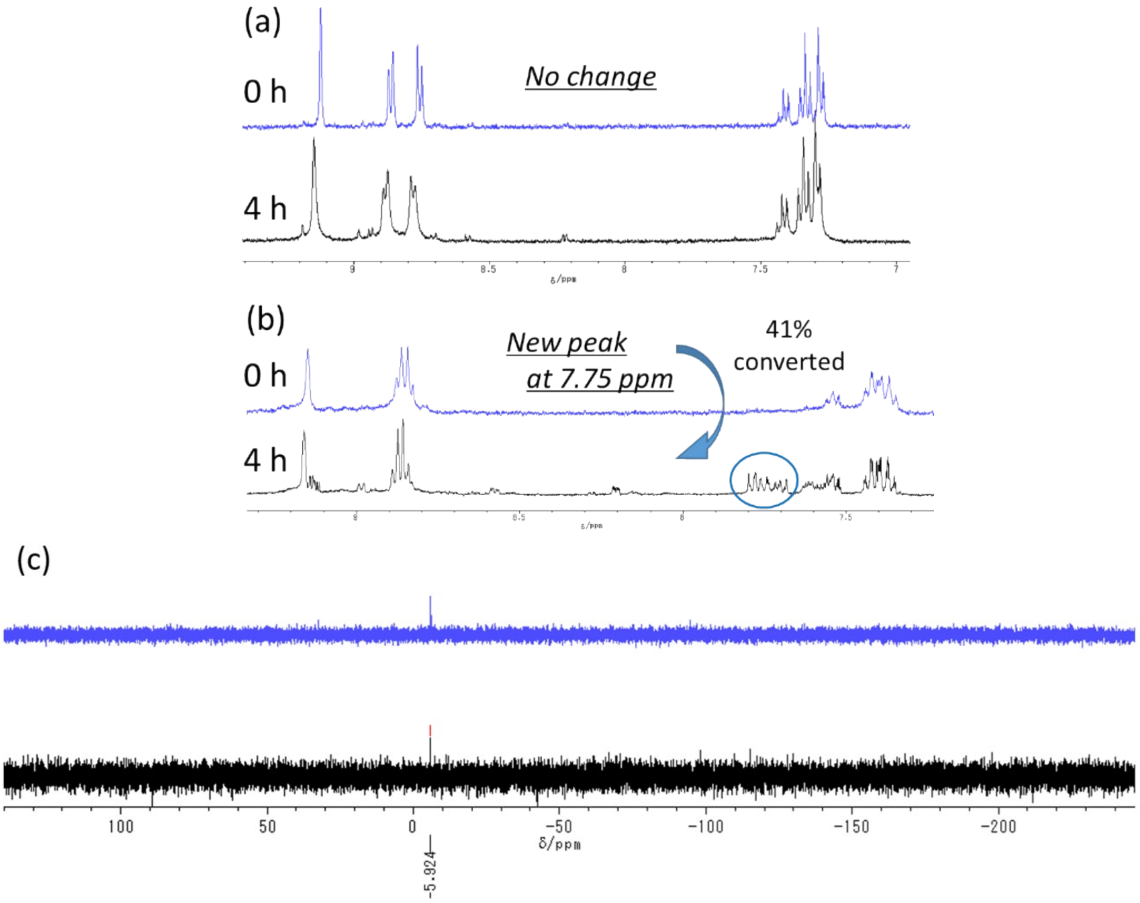


Figure S21. ^{1}H NMR spectra of (a) **4-TfO** and (b) **7** and (c) ^{31}P NMR spectra of **7** before and after air-bubbling for 4 h in CD_3CN. Solid circle indicates new signals. The conversion of **7** was estimated by using 2-methoxynaphthalene as a standard material.

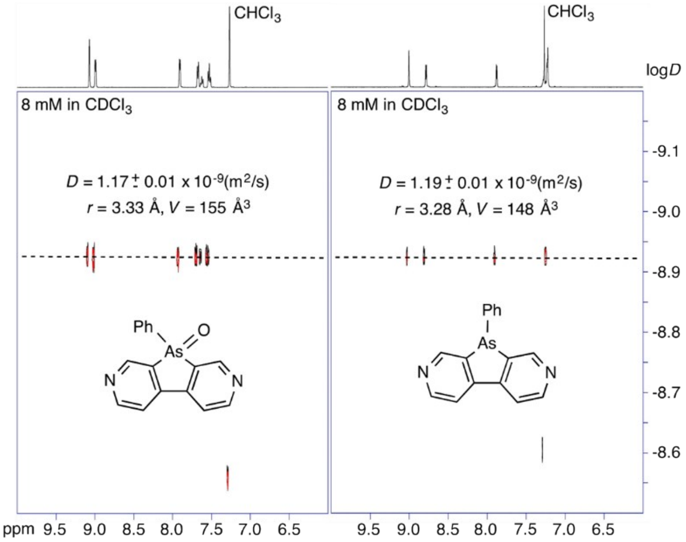


Figure S22. ^{1}H DOSY spectra (8.0 mM in $CDCl_3$, 298 K, diffusion time Δ = 200 ms) of **2** (left) and **1** (right). Diffusion coefficient were recorded at 298 K in $CDCl_3$ (diffusion time Δ = 200 ms), and the molecular radii were calculated using the Stokes-Einstein equation.

6. Crystallographic data

Table S1. Crystallographic data of **1** and **2**.

	1	**2**
Crystal data		
Experimental Formula	$C_{16}H_{11}AsN_2$	$C_{32}H_{22}As_2N_4O_2$
Formula Weight	306.20	644.39
Crystal Dimension, mm^3	0.200 × 0.200 × 0.200	0.250 X 0.180 X 0.050
Crystal System	monoclinic	triclinic
Space Group	$P2_1/c$	P-1
a, Å	13.672(9)	8.366(3)
b, Å	11.334(8)	8.971(3)
c, Å	8.756(6)	9.981(4)
α, deg	-	70.613(13)
β, deg	104.051(9)	73.295(15)
γ, deg	-	74.157(14)
Volume, Å^3	1316.2(16)	663.5(4)
D_{calcd}, g cm^{-3}	1.545	1.613
Z	4	1
F(000)	616.00	324.00
Data Collection		
Temperature, deg	25.0	25.0
2θmax, deg	54.9	55.0
Tmin/Tmax	0.497 – 0.598	0.742 - 0.880
Refinement		
No. of Observed Data	3012	3030
No. of Parameters	172	181
R1[a], wR2[b]	0.0366, 0.0841	0.0311, 0.0820
Goodness of Fit Indicator	1.070	1.063

[a]$R1 = \Sigma \mid |Fo| - |Fc| \mid / \Sigma |Fo|$ [b]$wR2 = [\Sigma w ((Fo^2-Fc^2)^2 / \Sigma w (Fo^2)^2]^{1/2}$ $w = [\sigma^2(Fo^2)]^{-1}$

CCDC #1994425 (**1**) and 1994422 (**2**).

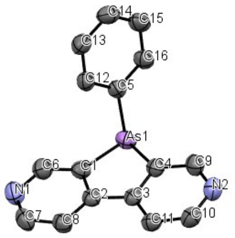
Table S2. Crystallographic data of **3**, **5**, and **6**.

	3	**5**	**6**
Crystal data			
Experimental Formula	$C_{17}H_{13}AsAuCl_3N_2$	$C_{16}H_{11}N_2P$	$C_{16}H_{11}N_2OP$
Formula Weight	623.55	262.25	278.25
Crystal Dimension, mm^3	0.320 X 0.160 X 0.130	0.550 X 0.080 X 0.060	0.280 X 0.260 X 0.150
Crystal System	orthorhombic	monoclinic	triclinic
Space Group	Fdd2	$P2_1/c$	P-1
a, Å	16.402(5)	13.597(4)	7.692(4)
b, Å	47.390(13)	11.204(3)	9.588(6)
c, Å	9.844(3)	8.645(2)	10.081(7)
α, deg	-	-	88.33(2)
β, deg	-	103.655(14)	72.47(2)
γ, deg	-	-	67.903(14)
Volume, Å^3	7652(4)	1279.8(6)	653.9(7)
D_{calcd}, g cm^{-3}	2.165	1.361	1.413
Z	16	4	2
F(000)	4672.00	544.00	288.00
Data Collection			
Temperature, deg	25.0	25.0	25.0
2θmax, deg	54.9	55.4	55.0
Tmin/max	0.199 - 0.278	0.928 - 0.988	0.881 - 0.970
Refinement			
No. of Observed Data	4311	2995	2925
No. of Parameters	217	172	181
R1[a], wR2[b]	0.0384, 0.0984	0.0666, 0.1913	0.0411, 0.1105
Goodness of Fit Indicator	1.020	1.054	1.035

[a]$R1 = \Sigma \mid |Fo| - |Fc| \mid / \Sigma |Fo|$ [b]$wR2 = [\Sigma w ((Fo^2-Fc^2)^2 / \Sigma w (Fo^2)^2]^{1/2}$ $w = [\sigma^2(Fo^2)]^{-1}$

CCDC #1994426 (**3**), 1994424 (**5**), and 1994423 (**6**).

Table S3. ORTEP drawing (ellipsoids at 50% probability), selected angles (deg) and distances (Å) of **1**.

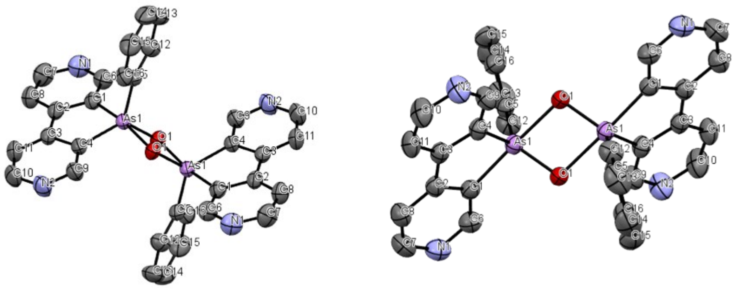


interplanar angle (°)	
C(1)C(2)C(8)C(7)N(1)C(6)- C(4)C(3)C(11)C(10)N(2)C(9)	2.34

distance (Å)	
As(1)-C(1)	1.942(3)
As(1)-C(4)	1.943(3)
As(1)-C(5)	1.953(3)
C(1)-C(2)	1.399(3)
C(2)-C(3)	1.469(4)
C(3)-C(4)	1.395(4)

angle (°)	
C(1)-As(1)-C(4)	85.2(1)
C(1)-As(1)-C(5)	101.5(1)
C(4)-As(1)-C(5)	101.3(1)
As(1)-C(1)-C(6)	128.7(2)
As(1)-C(4)-C(9)	129.2(2)
As(1)-C(1)-C(2)	112.7(2)
As(1)-C(4)-C(3)	112.5(2)
C(1)-C(2)-C(3)	114.3(2)
C(2)-C(3)-C(4)	114.7(2)
C(1)-C(2)-C(8)	118.2(2)
C(2)-C(1)-C(6)	118.4(2)
C(4)-C(3)-C(11)	118.6(2)
C(3)-C(4)-C(9)	118.0(2)
C(2)-C(3)-C(11)	126.7(2)
C(3)-C(2)-C(8)	127.5(2)

Table S4. ORTEP drawing (ellipsoids at 50% probability), selected angles (deg) and distances (Å) of **2**.

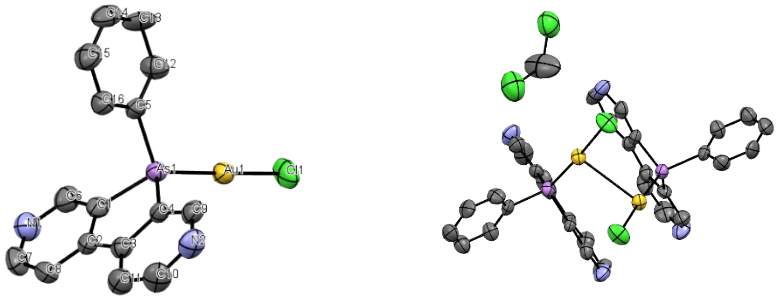


interplanar angle (°)	
C(1)C(2)C(8)C(7)N(1)C(6)- C(4)C(3)C(11)C(10)N(2)C(9)	5.49

distance (Å)	
As(1)-C(1)	1.966(3)
As(1)-C(4)	1.936(2)
As(1)-C(5)	1.923(3)
C(1)-C(2)	1.398(3)
C(2)-C(3)	1.484(4)
C(3)-C(4)	1.395(5)
As(1)-O(1)	2.100(2)
	1.706(2)

angle (°)	
C(1)-As(1)-C(4)	85.9(1)
C(1)-As(1)-C(5)	100.9(1)
C(4)-As(1)-C(5)	113.3(1)
As(1)-C(1)-C(6)	129.7(2)
As(1)-C(4)-C(9)	128.2(2)
As(1)-C(1)-C(2)	111.7(2)
As(1)-C(4)-C(3)	112.4(2)
C(1)-C(2)-C(3)	114.4(2)
C(2)-C(3)-C(4)	115.3(2)
C(1)-C(2)-C(8)	119.2(3)
C(2)-C(1)-C(6)	118.5(3)
C(4)-C(3)-C(11)	118.1(3)
C(3)-C(4)-C(9)	119.5(3)
C(2)-C(3)-C(11)	126.5(3)
C(8)-C(2)-C(3)	127.5(2)
O(1)-As(1)-C(1)	171.87(9)
	98.8(1)
O(1)-As(1)-C(4)	88.74(9)
	126.3(1)
O(1)-As(1)-C(5)	86.87(9)
	118.1(1)
As(1)-O(1)-As(1)	100.44(8)
O(1)-As(1)-O(1)	79.56(8)

Table S5. ORTEP drawing (ellipsoids at 50% probability), selected angles (deg) and distances (Å) of **3**.

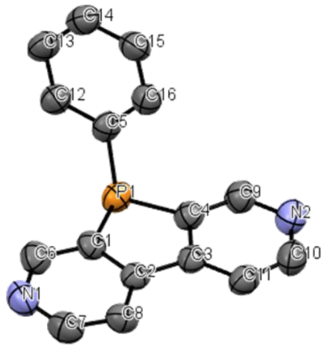


interplanar angle (°)	
C(1)C(2)C(8)C(7)N(1)C(6)- C(4)C(3)C(11)C(10)N(2)C(9)	3.96

distance (Å)	
As(1)-C(1)	1.94(1)
As(1)-C(4)	1.93(1)
As(1)-C(5)	1.91(1)
C(1)-C(2)	1.39(2)
C(2)-C(3)	1.47(1)
C(3)-C(4)	1.41(2)
As(1)-Au(1)	2.337(1)
Au(1)-Cl(1)	2.288(4)
Au(1)-Au(1)	3.077(2)

angle (°)	
C(1)-As(1)-C(4)	87.6(5)
C(1)-As(1)-C(5)	106.8(5)
C(4)-As(1)-C(5)	107.0(4)
As(1)-C(1)-C(6)	128.4(9)
As(1)-C(4)-C(9)	129.4(9)
As(1)-C(1)-C(2)	110.3(8)
As(1)-C(4)-C(3)	110.9(7)
C(1)-C(2)-C(3)	117(1)
C(2)-C(3)-C(4)	114.5(9)
C(1)-C(2)-C(8)	117(1)
C(2)-C(1)-C(6)	121(1)
C(4)-C(3)-C(11)	119(1)
C(3)-C(4)-C(9)	120(1)
C(2)-C(3)-C(11)	127(1)
C(3)-C(2)-C(8)	126(1)
As(1)-Au(1)-Cl(1)	176.9(1)
Au(1)-Au(1)-Cl(1)	90.1(1)
Au(1)-Au(1)-As(1)	92.88(3)

Table S6. ORTEP drawing (ellipsoids at 50% probability), selected angles (deg) and distances (Å) of **5**.

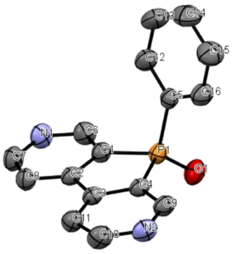


interplanar angle (°)	
C(1)C(2)C(8)C(7)N(1)C(6)- C(4)C(3)C(11)C(10)N(2)C(9)	1.97

distance (Å)	
P(1)-C(1)	1.813(4)
P(1)-C(4)	1.799(3)
P(1)-C(5)	1.824(3)
C(1)-C(2)	1.385(5)
C(2)-C(3)	1.459(4)
C(3)-C(4)	1.399(5)

angle (°)	
C(1)-P(1)-C(4)	89.1(1)
C(1)-P(1)-C(5)	103.3(1)
C(4)-P(1)-C(5)	104.0(1)
P(1)-C(1)-C(6)	129.0(3)
P(1)-C(4)-C(9)	130.1(3)
P(1)-C(1)-C(2)	112.5(2)
P(1)-C(4)-C(3)	112.6(2)
C(1)-C(2)-C(3)	112.9(3)
C(2)-C(3)-C(4)	112.5(3)
C(1)-C(2)-C(8)	119.2(3)
C(2)-C(1)-C(6)	118.3(3)
C(4)-C(3)-C(11)	118.9(3)
C(3)-C(4)-C(9)	117.0(3)
C(2)-C(3)-C(11)	128.6(3)
C(3)-C(2)-C(8)	127.9(3)

Table S7. ORTEP drawing (ellipsoids at 50% probability), distances (Å) and selected angles (deg) of **6**.



interplanar angle (°)	
C(1)C(2)C(8)C(7)N(1)C(6)-C(4)C(3)C(11)C(10)N(2)C(9)	3.00

distance (Å)	
P(1)-C(1)	1.811(2)
P(1)-C(4)	1.810(2)
P(1)-C(5)	1.797(2)
C(1)-C(2)	1.403(2)
C(2)-C(3)	1.481(2)
C(3)-C(4)	1.405(3)
P(1)-O(1)	1.480(1)

angle (°)	
C(1)-P(1)-C(4)	91.37(7)
C(1)-P(1)-C(5)	107.43(7)
C(4)-P(1)-C(5)	105.58(8)
P(1)-C(1)-C(6)	130.5(1)
P(1)-C(4)-C(9)	130.2(1)
P(1)-C(1)-C(2)	111.0(1)
P(1)-C(4)-C(3)	111.1(1)
C(1)-C(2)-C(3)	113.4(1)
C(2)-C(3)-C(4)	113.2(1)
C(1)-C(2)-C(8)	119.0(2)
C(2)-C(1)-C(6)	118.6(2)
C(4)-C(3)-C(11)	119.1(2)
C(3)-C(4)-C(9)	118.7(2)
C(2)-C(3)-C(11)	127.7(2)
C(3)-C(2)-C(8)	127.6(2)
O(1)-P(1)-C(1)	117.55(8)
O(1)-P(1)-C(4)	117.16(8)
O(1)-P(1)-C(5)	114.85(8)

7. Optical properties

Table S8. Optical properties of **1**, **2**, **5**, and **6**.[a]

	λ_{abs}[b] [nm]	λ_{ex}[c] [nm]	λ_{em}[d] [nm]	τ[g] [μs]	Φ_{PL}
1	302	297	497	7.99	ND[i]
2	272[e]	258[h]	437[h]	7.88	ND[i]
5	322	260	488	7.45	0.12
6	275[f]	257	444	7.86	ND[i]

[a]Measured in $CHCl_3$ (10^{-4} M). [b]Longest absorption maximum. [c]Excitation maximum (emission at the λ_{em}). [d]Emission maximum (excitation at the λ_{ex}). [e]Measured in 2×10^{-5} M. [f] Measured in 10^{-5} M. [g]Excited at 280 nm. [h]Measured in 2×10^{-4} M. [i]Not determined.

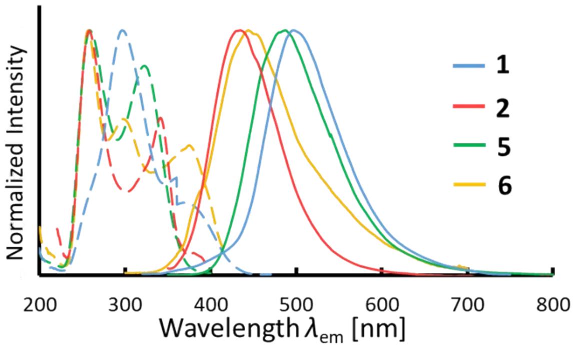


Figure S23. Emission and excitation spectra of **1**, **2**, **5** and **6** in the solid-state at 77K.

Table S9. Optical properties of **1**, **2**, **5**, and **6** in the solid state at 77K.

	λ_{ex} [nm][a]	λ_{em} [nm][b]	Φ[c]
1	353	487	0.10
2	310	515	0.14
5	355	456	0.14
6	312	498	0.16

[a]Excitation maximum (emission at the λ_{em}). [b]Emission maximum (excitation at the λ_{ex}). [c]Absolute quantum yield.

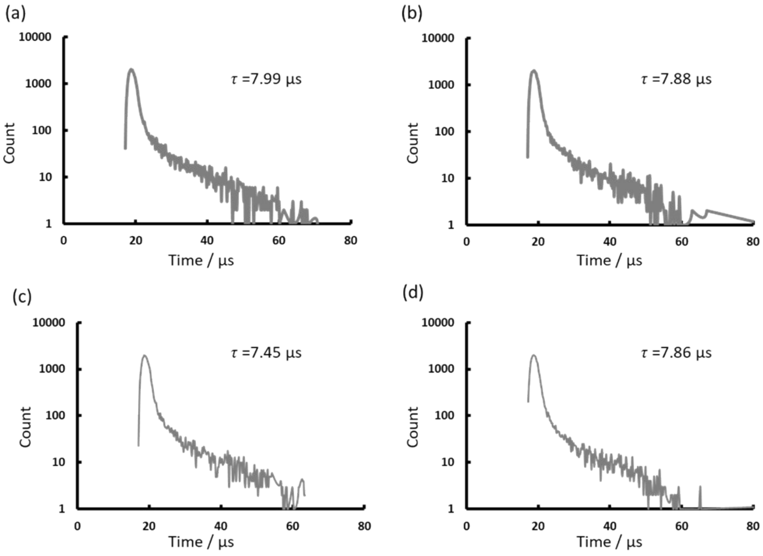
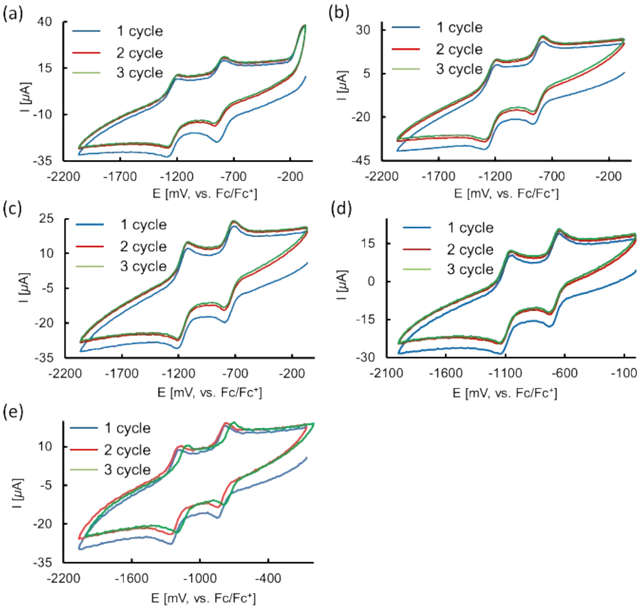


Figure S24. The emission decay kinetics of (a) **1** (b) **2**, (c) **5**, and (d) **6** in $CHCl_3$ (**1**, **5**, **6**: 10^{-4} M, **2**: 2×10^{-4} M) on excitation at 280 nm (monitoring: λ_{em} shown in Table S8).

8. Cyclic voltammetric analysis



FigureS25. Cyclic voltammograms of (a) **4-I**, (b) **4-TfO**, (c) **8-Br**, (d) **8-TfO**, and (e) **7** for 3 cycles (solvent: DMF (1 mM) under N_2, supporting electrolyte: NBu_4PF_6 (0.1 M), scan rate: 100 mV/s, working electrode: glassy carbon, counter electrode: platinum wire). Potential *E* was referenced to Fc/Fc^+.

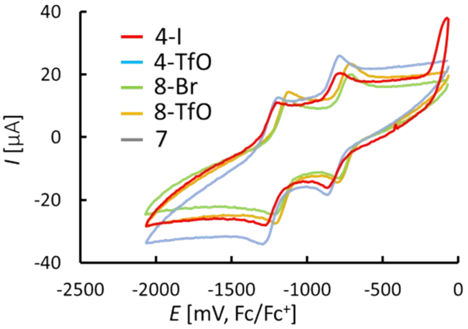


Figure S26. Cyclic voltammograms of **4-I**, **4-TfO**, **8-Br**, **8-TfO**, and **7** (solvent: DMF (1 mM) under N_2, supporting electrolyte: NBu_4PF_6 (0.1 M), scan rate: 100 mV/s, working electrode: glassy carbon, counter electrode: platinum wire). Potential *E* was referenced to Fc/Fc^+.

Table S10. Reduction potential (E_{red}) of **4**, **8**, and **7**.

	$E_{red1,c}$ [mV] ^{a}	$E_{red2,c}$ [mV] ^{a}
4-I	-865	-1275
4-TfO	-865	-1295
8-Br	-790	-1210
8-TfO	-805	-1215
7	-855	-1255

^{a}CV in DMF (10^{-3} M) with $^nBu_4NPF_6$ (0.1 M), as refered to Fc/Fc^+.

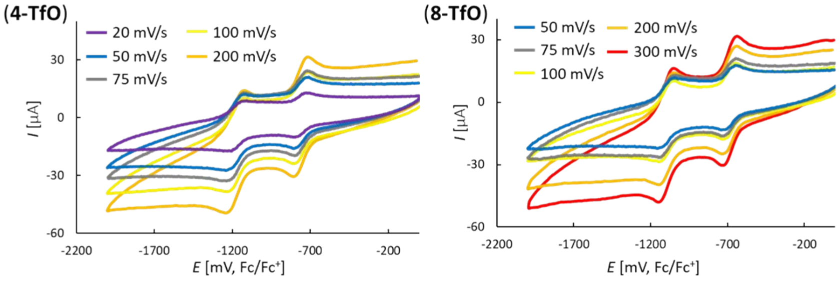
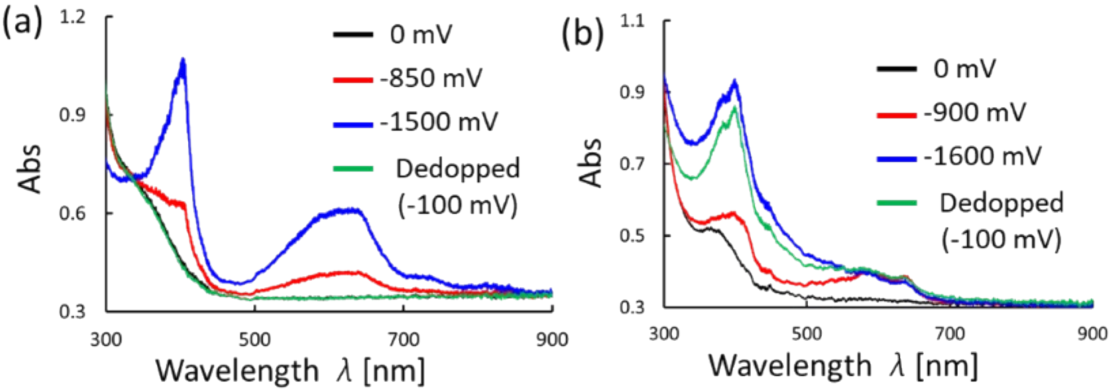


Figure S27. Cyclic voltammograms of **4-TfO** and **8-TfO** at different scan rates (solvent: DMF (1 mM) under N_2, supporting electrolyte: NBu_4PF_6 (0.1 M)).

Table S11. Diffusion coefficient of **4-TfO** and **8-TfO.**[8]

	D [10^{-3} cm^2 s^{-1}]
4-TfO	3.37
8-TfO	2.17

9. Spectroelectrochemistry



FigureS28. Spectroelectrochemistry of (a) **4-TfO** and (b) **7** (solvent: DMF (1 g/L), supporting electrolyte: NBu_4PF_6 (0.1 M), working electrode: Pt mesh, counter electrode: platinum wire).

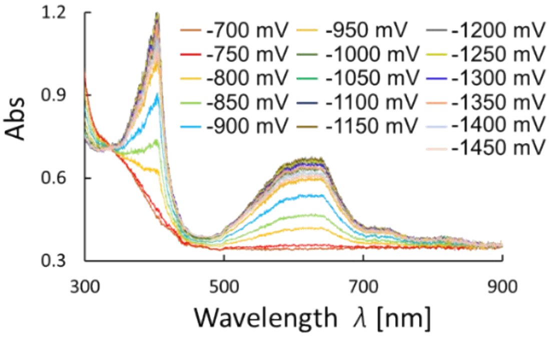


Figure S29. Spectroelectrochemistry of **4-TfO** (solvent: DMF (1 g/L), supporting electrolyte: NBu_4PF_6 (0.1 M), working electrode: Pt mesh, counter electrode: platinum wire).

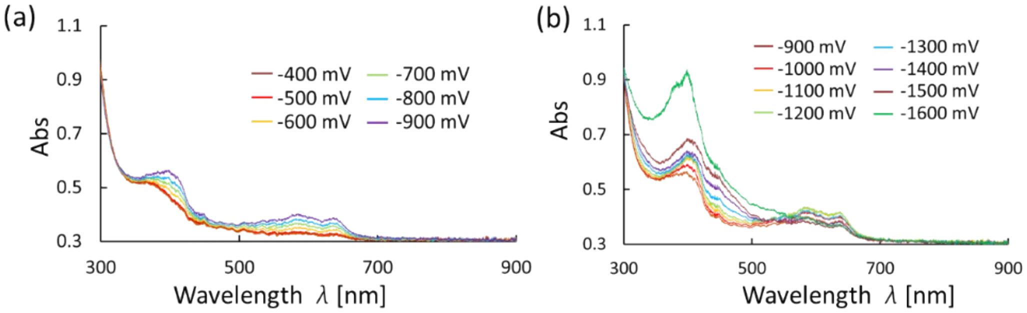


Figure S30. Spectroelectrochemistry of **7** for (a) the first reduction and (b) the second reduction (solvent: DMF (1 g/L), supporting electrolyte: NBu_4PF_6 (0.1 M) working electrode: Pt mesh, counter electrode: platinum wire).

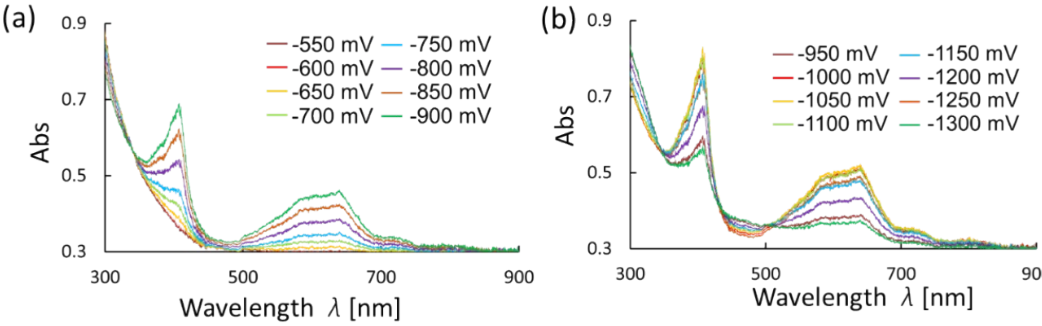


Figure S31. Spectroelectrochemistry of **8-TfO** for (a) the first reduction and (b) the second reduction (solvent: DMF (1 g/L), supporting electrolyte: NBu_4PF_6 (0.1 M) working electrode: Pt mesh, counter electrode: platinum wire).

10. Theoretical calculation

Computational methods

Density functional theory (DFT) calculations were carried out to investigate the frontier orbitals of the synthesized compounds. In addition, the vertical excitation energies (*ΔE*) and oscillator strengths (*f*) were obtained for the three lowest $S_0 \rightarrow S_1$ transitions at the optimized ground state equilibrium geometries by using the time-dependent density functional theory (TD-DFT). These calculations employed B3LYP/6-31G+(d,p). Also, natural bonding orbital (NBO) analysis was performed by B3LYP/6-1G+(d,p).[10] Nucleus-independent chemical shift (NICS) values were calculated by GIAO-B3LYP/6-311G+(d,p) based on the optimized structures shown in Tables S13 and S18.[11] NICS(1)$_{zz}$ values were employed for the evaluation of aromaticity; the ring centers of the arsole rings were determined by the average of the coordinates of atoms 1-5 in Tables S13 and S18. For the open-shell systems (radical cation species), unrestricted Kohn-Sham (UKS) calculations have been performed. No spin contamination has been found for the open shell system being the $\langle S^2 \rangle$ value equal to 0.75. When we conducted calculations for viologen-analogues in DMF, the Polarized Continuum Model (PCM)[9] as a self-consistent reaction field (SCRF) was used. For all the calculation, Gaussian 09 code was employed.[12]

Table S12. WBI of **1**, **2**, **5**, and **6**.[a]

	1	**2**	**5**	**6**
C1-C2	1.3521	1.3677	1.3446	1.3456
C2-C3	1.0698	1.0471	1.0733	1.0546
C3-C4	1.3508	1.3589	1.3332	1.3476

[a] Level of theory: B3LYP/6-31G+(d,p). Geometries were based on their structures measured by single crystal X-ray diffraction analysis.

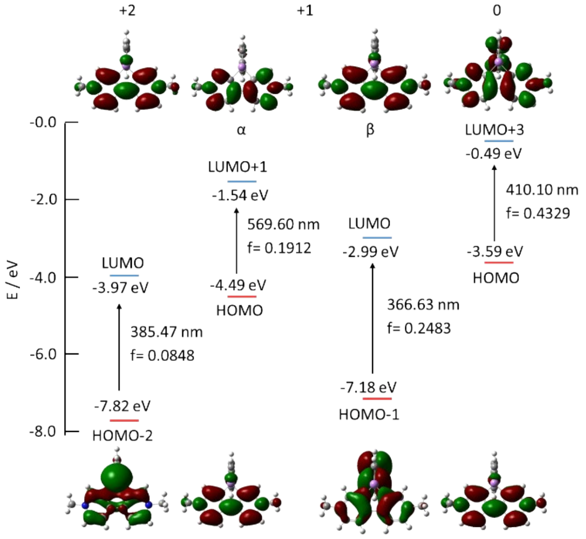


Figure S32. Frontier orbitals of **4** by DFT calculations (B3LYP/6-31G+(d,p)).

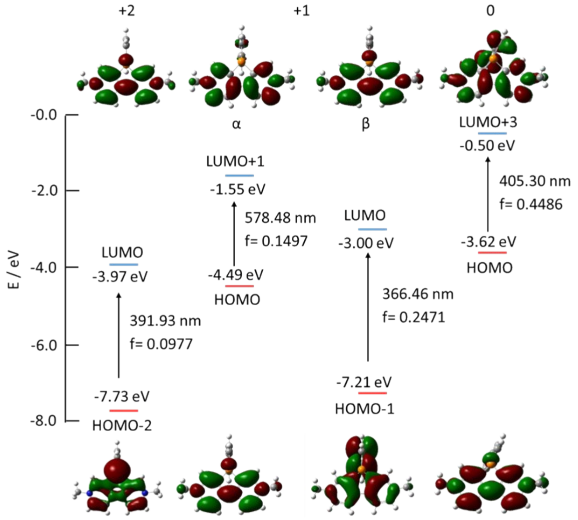


Figure S33. Frontier orbitals of **7** by DFT calculations (B3LYP/6-31G+(d,p)).

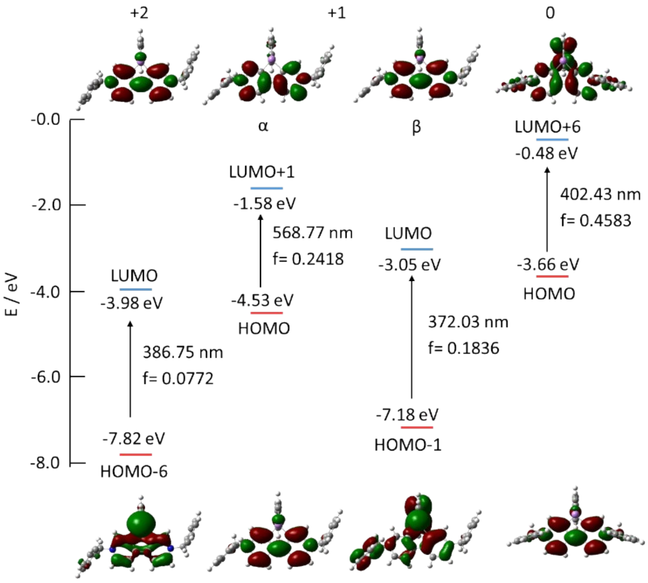


Figure S34. Frontier orbitals of **8** by DFT calculations (B3LYP/6-31G+(d,p)).

Table S13. Atom coordinates and absolute energy levels for **1** optimized in the S_0 state.

1 (S_0 state): *E*(B3LYP) = -2959.68061579 A.U.

Center Number	Atomic Number	Atomic Type	Coordinate		
			X	Y	Z
1	33	0	0.357415	0.000024	1.319846
2	7	0	-1.58353	-3.52835	-0.08281
3	7	0	-1.58345	3.528404	-0.08301
4	6	0	1.924837	-6.7E-05	0.137043
5	6	0	-1.85708	-0.73712	-0.25431
6	6	0	-1.85705	0.737173	-0.25436
7	6	0	-0.77473	1.321294	0.433166
8	6	0	-0.69982	-2.71136	0.508096
9	6	0	-2.60111	-2.9618	-0.74967
10	6	0	-2.79022	-1.58338	-0.86223
11	6	0	-0.6997	2.711424	0.507868
12	6	0	-2.6011	2.961843	-0.74974
13	6	0	-2.79022	1.583412	-0.86225
14	6	0	3.189052	0.000193	0.737947
15	6	0	4.348554	0.000192	-0.04538
16	6	0	4.249694	-6.4E-05	-1.43776
17	6	0	2.988806	-0.00033	-2.04526
18	6	0	1.835589	-0.00032	-1.26041
19	6	0	-0.77482	-1.32123	0.433316
20	1	0	0.108163	-3.19898	1.050082
21	1	0	-3.30483	-3.64863	-1.21456
22	1	0	-3.64527	-1.19588	-1.40785
23	1	0	0.108323	3.199065	1.049775
24	1	0	-3.30488	3.648656	-1.21455
25	1	0	-3.64536	1.195902	-1.40772
26	1	0	3.27358	0.000364	1.821705
27	1	0	5.323713	0.000386	0.433229
28	1	0	5.148173	-6.6E-05	-2.04808
29	1	0	2.905494	-0.00055	-3.12842
30	1	0	0.862925	-0.00055	-1.74415

Table S14. Atom coordinates and absolute energy levels for **2** optimized in the S_0 state.

2 (S_0 state): *E*(B3LYP) = -3034.88140751 A.U.

Center Number	Atomic Number	Atomic Type	Coordinate		
			X	Y	Z
1	6	0	0.77124	-2.73099	0.352906
2	7	0	1.719351	-3.53713	-0.14969
3	6	0	2.776919	-2.95744	-0.73399
4	6	0	2.956319	-1.57476	-0.84159
5	6	0	1.966576	-0.74162	-0.31699
6	6	0	0.841823	-1.34432	0.272953
7	6	0	1.965841	0.743225	-0.31661
8	6	0	0.84056	1.344501	0.273778
9	33	0	-0.36701	-0.0007	0.978131
10	6	0	2.954641	1.577568	-0.84107
11	6	0	2.773693	2.96002	-0.73314
12	7	0	1.715656	3.538394	-0.14838
13	6	0	0.768536	2.731068	0.354201
14	8	0	-0.65034	-0.00155	2.604606
15	6	0	-1.99233	-0.00082	-0.05756
16	6	0	-1.97677	-0.00046	-1.45564
17	6	0	-3.17899	-0.00013	-2.16361
18	6	0	-4.3955	-0.00038	-1.47199
19	6	0	-4.40875	-0.00093	-0.07445
20	6	0	-3.20517	-0.00083	0.636076
21	1	0	-0.0731	-3.22411	0.828586
22	1	0	3.527943	-3.63486	-1.13409
23	1	0	3.848613	-1.18	-1.31691
24	1	0	3.847174	1.183923	-1.31687
25	1	0	3.523951	3.638382	-1.13309
26	1	0	-0.07633	3.223144	0.830034
27	1	0	-1.03519	-0.00017	-1.99812
28	1	0	-3.16805	0.000417	-3.24952
29	1	0	-5.33121	-0.00028	-2.02346
30	1	0	-5.35254	-0.00107	0.462749
31	1	0	-3.19411	-0.00086	1.722342

Table S15. Atom coordinates and absolute energy levels for **4**$^{2+}$ optimized in the S_0 state.

4^{2+} (S_0 state): *E*(B3LYP) = -3039.20085508 A.U.

Center Number	Atomic Number	Atomic Type	coordinate		
			X	Y	Z
1	6	0	-1.30021	-0.64052	-0.45374
2	6	0	-0.71747	-1.74543	0.198371
3	6	0	0.752776	-1.73747	0.188919
4	6	0	1.315605	-0.61747	-0.45621
5	33	0	-0.00316	0.533933	-1.33402
6	6	0	-2.67791	-0.52245	-0.47684
7	7	0	-3.45638	-1.44786	0.128897
8	6	0	-2.91253	-2.51983	0.758146
9	6	0	-1.54302	-2.69784	0.807906
10	6	0	1.596258	-2.69262	0.767191
11	6	0	2.963164	-2.49334	0.712665
12	7	0	3.486631	-1.39985	0.10518
13	6	0	2.69059	-0.47715	-0.48319
14	6	0	-0.02077	2.07553	-0.12921
15	6	0	-0.04162	3.338021	-0.73463
16	6	0	-0.05616	4.493729	0.054235
17	6	0	-0.04912	4.388719	1.447059
18	6	0	-0.02732	3.1268	2.053789
19	6	0	-0.01331	1.973982	1.267688
20	6	0	-4.93368	-1.32527	0.064835
21	6	0	4.957	-1.20301	0.108414
22	1	0	-3.19656	0.293801	-0.96337
23	1	0	-3.60711	-3.21402	1.212729
24	1	0	-1.15106	-3.56365	1.32745
25	1	0	1.221519	-3.58199	1.258528
26	1	0	3.669966	-3.18809	1.14661
27	1	0	3.194943	0.354888	-0.95849
28	1	0	-0.04675	3.426326	-1.81717
29	1	0	-0.07271	5.469762	-0.42096
30	1	0	-0.06045	5.284982	2.05984
31	1	0	-0.02162	3.041204	3.136217
32	1	0	0.003748	1.003272	1.754163
33	1	0	-5.19143	-0.30273	-0.20191
34	1	0	-5.31048	-2.01688	-0.69037
35	1	0	-5.35046	-1.56936	1.040856
36	1	0	5.442373	-2.17458	0.036165
37	1	0	5.231643	-0.58814	-0.7461
38	1	0	5.24331	-0.70697	1.037456

Table S16. Atom coordinates and absolute energy levels for **4**$^{1+}$ optimized in the S_0 state.

4^{1+} (S_0 state): *E*(UB3LYP) = -3039.35628620 A.U.

Center Number	Atomic Number	Atomic Type	Coordinate		
			X	Y	Z
1	6	0	-1.33002	-0.60378	-0.46851
2	6	0	-0.73743	-1.69749	0.247789
3	6	0	0.682967	-1.72371	0.239189
4	6	0	1.305983	-0.64852	-0.47971
5	33	0	0.003501	0.522801	-1.35261
6	6	0	-2.68741	-0.46566	-0.52581
7	7	0	-3.51773	-1.35335	0.118189
8	6	0	-2.97854	-2.41065	0.808889
9	6	0	-1.62615	-2.60608	0.892789
10	6	0	1.545653	-2.67042	0.863889
11	6	0	2.903555	-2.52304	0.765389
12	7	0	3.47197	-1.48595	0.068489
13	6	0	2.666385	-0.55864	-0.55151
14	6	0	0.034624	2.0624	-0.13161
15	6	0	0.049844	3.3382	-0.70851
16	6	0	0.070661	4.4816	0.099489
17	6	0	0.076659	4.352999	1.490589
18	6	0	0.06164	3.0793	2.073289
19	6	0	0.040522	1.9418	1.264289
20	6	0	-4.97633	-1.23392	-0.01941
21	6	0	4.932873	-1.32837	0.028989
22	1	0	-3.1838	0.335049	-1.06091
23	1	0	-3.68955	-3.07504	1.283489
24	1	0	-1.26216	-3.45418	1.460989
25	1	0	1.15854	-3.51632	1.420289
26	1	0	3.595244	-3.21705	1.225789
27	1	0	3.186096	0.226652	-1.08721
28	1	0	0.045245	3.4462	-1.78991
29	1	0	0.082176	5.466299	-0.35841
30	1	0	0.092773	5.238399	2.119189
31	1	0	0.066138	2.9741	3.154389
32	1	0	0.028508	0.9601	1.729589
33	1	0	-5.23461	-0.19102	-0.20211
34	1	0	-5.32994	-1.84832	-0.85251
35	1	0	-5.45433	-1.56212	0.904189
36	1	0	5.403058	-2.30458	0.144989
37	1	0	5.223179	-0.90528	-0.93321
38	1	0	5.265283	-0.66628	0.833789

Table S17. Atom coordinates and absolute energy levels for **4^0** optimized in the S_0 state.

4^0 (S_0 state): *E*(B3LYP) = -3039.47667534 A.U.

Center Number	Atomic Number	Atomic Type	Coordinate		
			X	Y	Z
1	6	0	-1.37237	-0.5365	-0.46001
2	6	0	-0.7874	-1.60965	0.346367
3	6	0	0.589048	-1.69455	0.325361
4	6	0	1.276442	-0.702	-0.50345
5	33	0	0.008355	0.51585	-1.3567
6	6	0	-2.7118	-0.37867	-0.56885
7	7	0	-3.60553	-1.18275	0.142823
8	6	0	-3.08466	-2.21976	0.913515
9	6	0	-1.751	-2.44279	1.043936
10	6	0	1.463901	-2.6367	1.000562
11	6	0	2.807575	-2.6003	0.802378
12	7	0	3.417805	-1.69478	-0.06123
13	6	0	2.618219	-0.73009	-0.67807
14	6	0	0.128182	2.05871	-0.12938
15	6	0	0.186868	3.340713	-0.69002
16	6	0	0.270069	4.476622	0.125636
17	6	0	0.29507	4.336403	1.515576
18	6	0	0.236986	3.058154	2.086218
19	6	0	0.153555	1.930415	1.266545
20	6	0	-5.0215	-1.17411	-0.20414
21	6	0	4.868166	-1.55084	-0.06611
22	1	0	-3.17389	0.391702	-1.17731
23	1	0	-3.82266	-2.83007	1.422086
24	1	0	-1.42654	-3.255	1.686967
25	1	0	1.063119	-3.39296	1.668257
26	1	0	3.481204	-3.29257	1.294742
27	1	0	3.153145	-0.02352	-1.30371
28	1	0	0.168027	3.459425	-1.77088
29	1	0	0.315252	5.464447	-0.32463
30	1	0	0.359732	5.214844	2.151345
31	1	0	0.25608	2.943068	3.166614
32	1	0	0.10844	0.943507	1.719179
33	1	0	-5.33236	-0.1546	-0.44425
34	1	0	-5.23789	-1.82062	-1.06658
35	1	0	-5.60903	-1.52072	0.649257
36	1	0	5.333861	-2.53076	0.062111
37	1	0	5.190484	-1.14046	-1.02591
38	1	0	5.219241	-0.8865	0.736256

Table S18. Atom coordinates and absolute energy levels for **5** optimized in the S_0 state.

5 (S_0 state): *E*(B3LYP) = -1067.22696357 A.U.

Center Number	Atomic Number	Atomic Type	Coordinate		
			X	Y	Z
1	7	0	1.469373	-3.5138	-0.06998
2	7	0	1.469343	3.513808	-0.06998
3	6	0	-1.89422	-7E-06	-0.31919
4	6	0	1.825281	-0.73531	0.099952
5	6	0	1.825275	0.735324	0.099952
6	6	0	0.706955	1.284372	-0.56314
7	6	0	0.584431	-2.67483	-0.62551
8	6	0	2.531659	-2.97769	0.552893
9	6	0	2.763121	-1.60584	0.66369
10	6	0	0.584408	2.67483	-0.62551
11	6	0	2.531632	2.977708	0.552898
12	6	0	2.763107	1.605857	0.663692
13	6	0	-3.12318	0.000001	-0.99525
14	6	0	-4.32713	0	-0.28224
15	6	0	-4.31082	-0.00001	1.113089
16	6	0	-3.0889	-0.00002	1.796318
17	6	0	-1.8888	-1.8E-05	1.085764
18	6	0	0.706965	-1.28437	-0.56315
19	1	0	-0.25761	-3.1393	-1.13474
20	1	0	3.235387	-3.68621	0.983812
21	1	0	3.646778	-1.24107	1.178628
22	1	0	-0.25763	3.139293	-1.13474
23	1	0	3.235354	3.686236	0.983819
24	1	0	3.646767	1.241095	1.178631
25	1	0	-3.13904	0.000008	-2.08189
26	1	0	-5.27189	0.000007	-0.81812
27	1	0	-5.24396	-1.1E-05	1.668986
28	1	0	-3.07245	-2.8E-05	2.8825
29	1	0	-0.94652	-2.6E-05	1.626097
30	15	0	-0.35233	-3E-06	-1.35192

Table S19. Atom coordinates and absolute energy levels for **6** optimized in the S_0 state.

6 (S_0 state): *E*(B3LYP) = -1142.47263083 A.U.

Center Number	Atomic Number	Atomic Type	coordinate		
			X	Y	Z
1	6	0	0.750415	-1.30129	0.42856
2	6	0	1.862511	-0.74138	-0.22807
3	6	0	1.862551	0.741304	-0.22803
4	6	0	0.750488	1.301239	0.428646
5	15	0	-0.35597	-1.8E-05	1.096428
6	6	0	0.64298	-2.68732	0.519216
7	7	0	1.555044	-3.52254	-0.00378
8	6	0	2.604813	-2.97836	-0.63465
9	6	0	2.812598	-1.60178	-0.77721
10	6	0	2.812674	1.60169	-0.77713
11	6	0	2.604961	2.978266	-0.63448
12	7	0	1.555226	3.522472	-0.00357
13	6	0	0.643126	2.687265	0.519383
14	6	0	-1.88777	0.000065	0.101919
15	6	0	-3.10532	-0.00017	0.796015
16	6	0	-4.3109	-0.00015	0.088525
17	6	0	-4.30343	0.000112	-1.30815
18	6	0	-3.08891	0.000359	-2.00341
19	6	0	-1.88333	0.000338	-1.30158
20	8	0	-0.6329	-0.00008	2.57298
21	1	0	-0.19671	-3.15282	1.029724
22	1	0	3.324679	-3.68102	-1.04839
23	1	0	3.691607	-1.2344	-1.29749
24	1	0	3.691658	1.234293	-1.29744
25	1	0	3.324858	3.680922	-1.04819
26	1	0	-0.19653	3.152777	1.029925
27	1	0	-3.09316	-0.00036	1.881712
28	1	0	-5.25277	-0.00034	0.62918
29	1	0	-5.24089	0.000129	-1.85672
30	1	0	-3.08208	0.00057	-3.08938
31	1	0	-0.94456	0.000538	-1.84913

Table S20. Atom coordinates and absolute energy levels for **7**$^{2+}$ optimized in the S_0 state.

7^{2+} (S_0 state): *E*(B3LYP) = -1146.74523692 A.U.

Center Number	Atomic Number	Atomic Type	coordinate		
			X	Y	Z
1	6	0	-1.27208	-0.551	-0.51174
2	6	0	-0.732	-1.70345	0.099471
3	6	0	0.73356	-1.69982	0.105715
4	6	0	1.272986	-0.54828	-0.50782
5	15	0	0.000465	0.529659	-1.28864
6	6	0	-2.65001	-0.40586	-0.57461
7	7	0	-3.4589	-1.34771	-0.04218
8	6	0	-2.95463	-2.46907	0.536558
9	6	0	-1.59219	-2.67991	0.615946
10	6	0	1.594189	-2.66566	0.640665
11	6	0	2.956516	-2.45178	0.564785
12	7	0	3.460366	-1.33677	-0.02629
13	6	0	2.650623	-0.39993	-0.56668
14	6	0	-0.00091	2.08109	-0.29256
15	6	0	-0.00068	3.286457	-1.01188
16	6	0	-0.00176	4.508896	-0.33197
17	6	0	-0.00314	4.530797	1.064156
18	6	0	-0.00341	3.330206	1.785466
19	6	0	-0.00226	2.108157	1.112945
20	6	0	-4.93193	-1.16969	-0.07793
21	6	0	4.934407	-1.18004	-0.10676
22	1	0	-3.13755	0.44423	-1.03467
23	1	0	-3.67785	-3.17415	0.925164
24	1	0	-1.23085	-3.58897	1.080736
25	1	0	1.2333	-3.56726	1.120086
26	1	0	3.679609	-3.15054	0.964762
27	1	0	3.13666	0.448657	-1.03117
28	1	0	0.000315	3.272583	-2.09776
29	1	0	-0.00158	5.437326	-0.89443
30	1	0	-0.00403	5.479404	1.592363
31	1	0	-0.00448	3.346157	2.871035
32	1	0	-0.00245	1.185772	1.685564
33	1	0	-5.16615	-0.2813	-0.65956
34	1	0	-5.38063	-2.04749	-0.5425
35	1	0	-5.29665	-1.05419	0.943384
36	1	0	5.362351	-1.37508	0.875723
37	1	0	5.323058	-1.8919	-0.83641
38	1	0	5.165919	-0.1635	-0.41601

Table S21. Atom coordinates and absolute energy levels for **7^{1+}** optimized in the S_0 state.

7^{1+} (S_0 state): *E*(UB3LYP) = -1146.90061921 A.U.

Center Number	Atomic Number	Atomic Type	coordinate		
			X	Y	Z
1	6	0	-1.25973	-0.59609	-0.57742
2	6	0	-0.65121	-1.6832	0.140258
3	6	0	0.766101	-1.63421	0.146333
4	6	0	1.304995	-0.50921	-0.56829
5	15	0	-0.01028	0.514968	-1.36412
6	6	0	-2.62155	-0.51183	-0.67987
7	7	0	-3.43277	-1.45038	-0.08535
8	6	0	-2.87566	-2.49573	0.610361
9	6	0	-1.51994	-2.64383	0.732751
10	6	0	1.693303	-2.52845	0.754081
11	6	0	3.036424	-2.28717	0.644598
12	7	0	3.526571	-1.20208	-0.04118
13	6	0	2.658867	-0.3307	-0.65688
14	6	0	-0.06786	2.039994	-0.30884
15	6	0	-0.14509	3.275119	-0.97008
16	6	0	-0.19451	4.468741	-0.24024
17	6	0	-0.16569	4.434714	1.155437
18	6	0	-0.0876	3.205558	1.822947
19	6	0	-0.03902	2.015008	1.096394
20	6	0	-4.89335	-1.28547	-0.1265
21	6	0	4.97847	-1.02571	-0.19374
22	1	0	-3.1322	0.277409	-1.21845
23	1	0	-3.5758	-3.19574	1.048317
24	1	0	-1.13833	-3.49568	1.283787
25	1	0	1.365379	-3.39682	1.313644
26	1	0	3.779341	-2.93499	1.092211
27	1	0	3.118367	0.490649	-1.19322
28	1	0	-0.16662	3.306817	-2.05596
29	1	0	-0.25481	5.418567	-0.76322
30	1	0	-0.2036	5.359441	1.723629
31	1	0	-0.06491	3.175789	2.908443
32	1	0	0.021725	1.068761	1.626353
33	1	0	-5.17586	-0.81427	-1.06822
34	1	0	-5.36799	-2.2644	-0.06203
35	1	0	-5.22796	-0.66239	0.708004
36	1	0	5.481	-1.37867	0.70718
37	1	0	5.339777	-1.5897	-1.05858
38	1	0	5.19842	0.032699	-0.33229

Table S22. Atom coordinates and absolute energy levels for **7**^{0} optimized in the S_0 state.

7^{0} (S_0 state): *E*(B3LYP) = -1147.02147650 A.U.

Center Number	Atomic Number	Atomic Type	Coordinate		
			X	Y	Z
1	6	0	-1.13443	-0.79115	-0.60792
2	6	0	-0.35539	-1.64795	0.293664
3	6	0	0.998752	-1.39351	0.281931
4	6	0	1.397387	-0.30579	-0.61966
5	15	0	-0.06461	0.483089	-1.41717
6	6	0	-2.45934	-0.99597	-0.80669
7	7	0	-3.14825	-2.01474	-0.14509
8	6	0	-2.45763	-2.77951	0.792957
9	6	0	-1.12453	-2.64243	1.017148
10	6	0	2.089414	-2.0475	0.98035
11	6	0	3.375011	-1.66717	0.761251
12	7	0	3.719512	-0.63522	-0.11049
13	6	0	2.702636	0.007724	-0.81373
14	6	0	-0.37803	1.975265	-0.33674
15	6	0	-1.21516	2.978276	-0.8528
16	6	0	-1.51652	4.118686	-0.10007
17	6	0	-0.97227	4.276052	1.177936
18	6	0	-0.12618	3.289227	1.69695
19	6	0	0.170338	2.1485	0.945027
20	6	0	-4.60664	-2.03236	-0.16395
21	6	0	5.111573	-0.44395	-0.5001
22	1	0	-3.05959	-0.39836	-1.48443
23	1	0	-3.05809	-3.5121	1.320234
24	1	0	-0.65287	-3.2965	1.743923
25	1	0	1.901154	-2.84482	1.692583
26	1	0	4.209977	-2.13863	1.267042
27	1	0	3.031631	0.788379	-1.49165
28	1	0	-1.63228	2.871187	-1.85152
29	1	0	-2.16568	4.884464	-0.51556
30	1	0	-1.19927	5.162732	1.762952
31	1	0	0.303213	3.407476	2.688198
32	1	0	0.831776	1.392297	1.356674
33	1	0	-4.96266	-1.72645	-1.15034
34	1	0	-4.96221	-3.0468	0.030249
35	1	0	-5.03593	-1.35774	0.590251
36	1	0	5.761172	-0.62875	0.358638
37	1	0	5.405584	-1.11909	-1.31582
38	1	0	5.260435	0.587279	-0.82818

Table S23. Atom coordinates and absolute energy levels for **8**$^{2+}$ optimized in the S_0 state.

8^{2+} (S_0 state): *E*(B3LYP) = -3501.33323666 A.U.

Center Number	Atomic Number	Atomic Type	Coordinate		
			X	Y	Z
1	6	0	-1.3128	-0.15206	0.358708
2	6	0	-0.43422	-0.83079	1.22918
3	6	0	0.986762	-0.53107	0.99867
4	6	0	1.2186	0.384216	-0.04702
5	33	0	-0.40225	0.903528	-1.01762
6	6	0	-2.67369	-0.34853	0.487946
7	7	0	-3.16178	-1.16345	1.452482
8	6	0	-2.33319	-1.82321	2.296657
9	6	0	-0.95954	-1.68317	2.20523
10	6	0	2.074569	-1.04773	1.713652
11	6	0	3.347685	-0.62858	1.380892
12	7	0	3.552496	0.261123	0.377372
13	6	0	2.518744	0.757686	-0.33893
14	6	0	-0.68144	2.72065	-0.34317
15	6	0	-1.03691	3.686425	-1.29277
16	6	0	-1.25628	5.010447	-0.89661
17	6	0	-1.12007	5.369002	0.446644
18	6	0	-0.76475	4.403602	1.396852
19	6	0	-0.54663	3.082831	1.002791
20	6	0	-4.65466	-1.31314	1.606095
21	6	0	4.960408	0.693457	0.065002
22	6	0	-5.34354	-1.66273	0.308416
23	6	0	5.848839	-0.46636	-0.32282
24	6	0	-6.15926	-0.72028	-0.33186
25	6	0	-6.80998	-1.04492	-1.52663
26	6	0	-6.64579	-2.31303	-2.08891
27	6	0	-5.83436	-3.25968	-1.45207
28	6	0	-5.18949	-2.93857	-0.25699
29	6	0	6.891849	-0.8656	0.523349
30	6	0	7.72724	-1.92751	0.161503
31	6	0	7.521444	-2.59839	-1.04623
32	6	0	6.483065	-2.20118	-1.89709
33	6	0	5.652259	-1.13869	-1.53937
34	1	0	-3.40768	0.124864	-0.15187
35	1	0	-2.80037	-2.45793	3.037574
36	1	0	-0.33637	-2.23507	2.897878
37	1	0	1.957918	-1.75889	2.522069
38	1	0	4.229093	-0.98688	1.895582
39	1	0	2.772245	1.451231	-1.13067
40	1	0	-1.14368	3.413389	-2.33865
41	1	0	-1.53179	5.755352	-1.63685
42	1	0	-1.28972	6.396271	0.754691
43	1	0	-0.65853	4.679148	2.44173
44	1	0	-0.27323	2.345624	1.751809
45	1	0	-4.80068	-2.08744	2.35916
46	1	0	-5.02071	-0.36727	2.010582
47	1	0	4.879988	1.42666	-0.73773
48	1	0	5.335664	1.201336	0.955173
49	1	0	-6.29252	0.265813	0.104774
50	1	0	-7.44221	-0.30851	-2.01295

51	1	0	-7.15033	-2.56653	-3.01636
52	1	0	-5.71038	-4.24865	-1.88254
53	1	0	-4.56834	-3.68138	0.236231
54	1	0	7.058607	-0.34369	1.461827
55	1	0	8.534616	-2.22682	0.822692
56	1	0	8.168827	-3.42335	-1.32781
57	1	0	6.324928	-2.71488	-2.84039
58	1	0	4.85473	-0.83126	-2.21039

Table S24. Atom coordinates and absolute energy levels for **8^{1+}** optimized in the S_0 state.

8^{1+} (S_0 state): *E*(UB3LYP) = -3501.48962697 A.U.

Center Number	Atomic Number	Atomic Type	Coordinate		
			X	Y	Z
1	6	0	-1.35025	0.035266	0.343127
2	6	0	-0.48701	-0.5799	1.311852
3	6	0	0.901633	-0.36467	1.10215
4	6	0	1.228594	0.430279	-0.04705
5	33	0	-0.35498	0.956591	-1.06853
6	6	0	-2.70407	-0.11227	0.42647
7	7	0	-3.2763	-0.82939	1.453684
8	6	0	-2.47635	-1.42011	2.398891
9	6	0	-1.11062	-1.32234	2.355518
10	6	0	1.988915	-0.83682	1.894514
11	6	0	3.273046	-0.52416	1.542628
12	7	0	3.557015	0.236221	0.432699
13	6	0	2.531388	0.699453	-0.35739
14	6	0	-0.55139	2.824674	-0.48356
15	6	0	-0.86397	3.770431	-1.46769
16	6	0	-1.01985	5.120175	-1.12938
17	6	0	-0.86254	5.529521	0.197089
18	6	0	-0.54906	4.587657	1.185228
19	6	0	-0.39503	3.242623	0.844342
20	6	0	-4.75316	-0.94495	1.526057
21	6	0	4.967548	0.530897	0.094052
22	6	0	-5.35375	-1.62926	0.313674
23	6	0	5.762138	-0.70489	-0.28517
24	6	0	-6.24685	-0.93873	-0.5152
25	6	0	-6.81822	-1.56948	-1.6262
26	6	0	-6.49507	-2.89635	-1.91928
27	6	0	-5.6016	-3.59255	-1.09588
28	6	0	-5.03674	-2.96374	0.014887
29	6	0	6.965384	-0.99084	0.371759
30	6	0	7.726153	-2.10749	0.007712
31	6	0	7.28372	-2.95242	-1.01279
32	6	0	6.079773	-2.67454	-1.67126
33	6	0	5.324134	-1.55748	-1.31062
34	1	0	-3.39678	0.316968	-0.28708
35	1	0	-2.99006	-1.96842	3.178168
36	1	0	-0.53461	-1.81674	3.129087
37	1	0	1.82947	-1.43849	2.781784
38	1	0	4.128683	-0.86068	2.114115
39	1	0	2.829076	1.288358	-1.21638
40	1	0	-0.98748	3.459067	-2.50154
41	1	0	-1.26249	5.845627	-1.9004
42	1	0	-0.98254	6.575891	0.462014
43	1	0	-0.42565	4.901296	2.21785
44	1	0	-0.15177	2.523435	1.621166
45	1	0	-4.97775	-1.50067	2.438639
46	1	0	-5.16693	0.06095	1.640689
47	1	0	4.948845	1.249703	-0.72841
48	1	0	5.426494	1.029075	0.952416
49	1	0	-6.49898	0.094925	-0.29292
50	1	0	-7.51002	-1.02253	-2.25984

51	1	0	-6.93567	-3.38746	-2.78182
52	1	0	-5.34948	-4.62547	-1.31696
53	1	0	-4.34729	-3.51287	0.650808
54	1	0	7.31185	-0.33926	1.16975
55	1	0	8.657514	-2.31684	0.525443
56	1	0	7.870512	-3.82159	-1.29475
57	1	0	5.73098	-3.32681	-2.46642
58	1	0	4.391758	-1.35087	-1.82939

Table S25. Atom coordinates and absolute energy levels for **8^0** optimized in the S_0 state.

8^0 (S_0 state): *E*(B3LYP) = -3501.61307078 A.U.

Center Number	Atomic Number	Atomic Type	Coordinate		
			X	Y	Z
1	6	0	-1.32668	0.625279	0.023699
2	6	0	-0.6892	-0.00388	1.182932
3	6	0	0.689368	-0.00392	1.183053
4	6	0	1.327088	0.625215	0.023938
5	33	0	0.000338	1.364833	-1.2048
6	6	0	-2.66877	0.607021	-0.14542
7	7	0	-3.51662	0.036116	0.806371
8	6	0	-2.94705	-0.54733	1.938035
9	6	0	-1.60722	-0.57559	2.152204
10	6	0	1.607176	-0.57571	2.152477
11	6	0	2.947043	-0.54752	1.938557
12	7	0	3.516863	0.035991	0.807037
13	6	0	2.669211	0.606908	-0.14491
14	6	0	0.000314	3.257873	-0.62688
15	6	0	0.000363	4.239484	-1.62549
16	6	0	0.000321	5.600303	-1.29283
17	6	0	0.000239	5.98829	0.049573
18	6	0	0.000208	5.013289	1.055801
19	6	0	0.000233	3.658294	0.716638
20	6	0	-4.9324	-0.16422	0.522974
21	6	0	4.932579	-0.16483	0.523652
22	6	0	-5.29628	-1.55632	0.016578
23	6	0	5.295959	-1.55689	0.016775
24	6	0	-6.58521	-2.05804	0.248328
25	6	0	-6.96247	-3.3132	-0.2378
26	6	0	-6.04903	-4.0894	-0.95872
27	6	0	-4.75986	-3.59937	-1.18898
28	6	0	-4.38616	-2.34132	-0.70529
29	6	0	6.584822	-2.059	0.248053
30	6	0	6.961648	-3.31412	-0.23853
31	6	0	6.047831	-4.0899	-0.95943
32	6	0	4.758713	-3.59948	-1.1892
33	6	0	4.385459	-2.34147	-0.70508
34	1	0	-3.17037	1.043758	-1.00261
35	1	0	-3.65426	-0.97231	2.64149
36	1	0	-1.24236	-1.03283	3.066629
37	1	0	1.242114	-1.03297	3.066817
38	1	0	3.654107	-0.97258	2.642117
39	1	0	3.17099	1.04364	-1.002
40	1	0	0.000437	3.945116	-2.67246
41	1	0	0.000363	6.350638	-2.0787
42	1	0	0.00022	7.04231	0.312537
43	1	0	0.000154	5.310426	2.101093
44	1	0	0.000191	2.910286	1.504444
45	1	0	-5.50705	0.052283	1.430697
46	1	0	-5.22729	0.588034	-0.21705
47	1	0	5.227823	0.587572	-0.21607
48	1	0	5.50725	0.051117	1.431489
49	1	0	-7.29844	-1.4652	0.816478
50	1	0	-7.96444	-3.68683	-0.04637

51	1	0	-6.33748	-5.06754	-1.33242
52	1	0	-4.04155	-4.19602	-1.74419
53	1	0	-3.38107	-1.97388	-0.88863
54	1	0	7.298345	-1.46649	0.816181
55	1	0	7.963576	-3.68804	-0.04746
56	1	0	6.335938	-5.06801	-1.33347
57	1	0	4.040113	-4.19581	-1.74438
58	1	0	3.380419	-1.97373	-0.88808

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