Electronic Supplementary Information (ESI)

Synthesis and Structural Evaluation of Closed-Shell Folded and Open-Shell Twisted Hexabenzo[5.6.7]quinarene

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General information

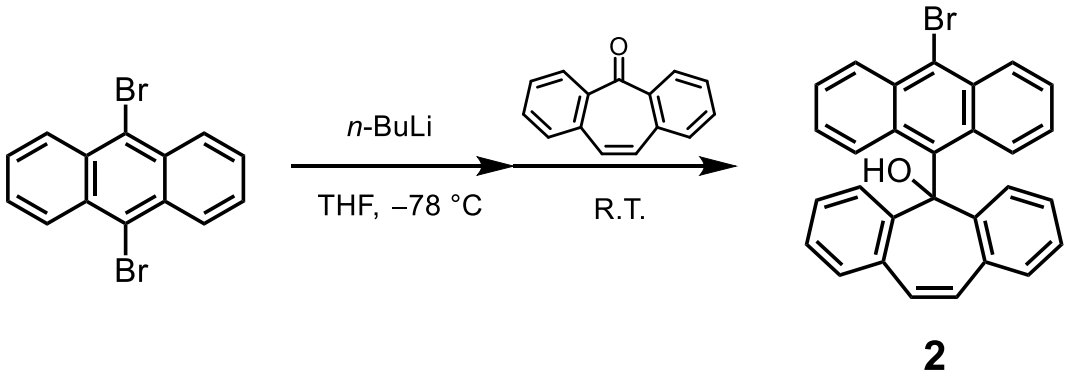
All experiments with moisture- or air-sensitive compounds were performed in anhydrous solvents under nitrogen atmosphere in well-dried glassware. Dried solvents (THF and dichloromethane) were purchased from KANTO CHEMICAL. Column chromatography was performed with silica gel [Silica gel 60N (KANTO CHEMICAL)]. ^{1}H and ^{13}C NMR spectra were recorded on JEOL lambda-500 spectrometer or Bruker AVANCENEO600 spectrometer. Positive EI mass spectra were taken by using Shimadzu QP-5050. MALDI TOF MS spectra were taken by KRATOS AXIMA-PERFORMANCE (Shimazu). Dithranol was used for the matrix. Data collection for X-ray crystal analysis was performed on Rigaku XtaLAB Synaergy Custom (Detector is Hypix-6000HE. Mo-Kα (λ = 0.71069 Å)). The structure was solved with direct methods and refined with full-matrix least squares. UV-vis absorption spectra were measured in anhydrous dichloromethane, DMF, and toluene with a JASCO V-570 spectrometer. Cyclic voltammetric measurement was performed with a BAS CV-50W electrochemical analyzer under the nitrogen atmosphere. Cyclic voltammograms were recorded with a grassly carbon working electrode, an $Ag/AgNO_3$ reference electrode, and a Pt counter electrode in DCM containing 0.1 M $^{n}Bu_4NPF_6$ as a supporting electrolyte.

Computational Methods. All DFT calculations were performed with the Gaussian 16 program. Structure optimization in both ground states were performed by (U)ωB97XD/6-31G**. TD-DFT calculations of **1** and $\mathbf{1}^{2+}$ were performed by a (U)CAM-B3LYP/6-31G** method with a tuned-parameter method (μ = 0.150, α = 0.0799, β = 0.9201 [α + β = 1.0])[S1], using optimized structures by (U)ωB97XD/6-31G** method.

Reference:
[S1] K. Okubo, Y. Shigeta, R. Kishi, M. Nakano, *Chem. Phys. Lett*. **2013**, *585*, 201.

Synthesis

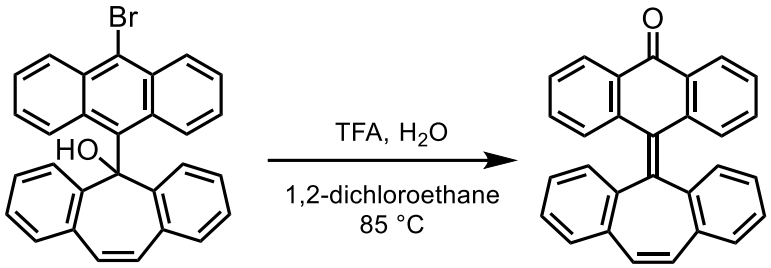
5-(10-Bromoanthracen-9-yl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (2)



2

To a suspension of 9,10-dibromoanthracene (2.7 g, 7.9 mmol) in THF (70 mL) was added ^{n}BuLi (1.6 M, 7.9 mmol) at −78 °C under nitrogen atmosphere. After stirring for 1 hour, to the solution was added a solution of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (1.5 g, 7.2 mmol) in THF (20 mL). After the reaction mixture was stirred at room temperature for 14 hours, aqueous ammonium chloride was added for quenching. The reaction mixture was extracted with ether, and the organic layer was separated and washed with brine, dried over anhydrous sodium sulfate. After filtration, the filtrate was evaporated, and the residual solid was washed with DCM/hexane to give **2** as a pale yellow solid (2.4 g, 73%). Mp > 115 °C (decomp.); R_f = 0.47 (DCM/hexane 50%); ^{1}H NMR (500 MHz, Acetone-d_6) δ 8.54 (dd, J = 8.0 Hz, 1.0 Hz, 2H), 8.35 (ddd, J = 8.5 Hz, 1.0 Hz, 0.5 Hz, 2H), 7.72 (dt, J = 9.0 Hz, 0.5 Hz, 2H), 7.58 (ddd, J = 8.5 Hz, 7.0 Hz, 1.0 Hz, 2H), 7.31 (ddd, J = 8.5 Hz, 6.5 Hz, 1.0 Hz, 2H), 7.16 (td, J = 7.5 Hz, 1.5 Hz, 2H), 6.94 (dd, J = 7.5 Hz, 1.5 Hz, 2H), 6.78 (ddd, J = 9.0 Hz, 6.5 Hz, 1.0 Hz, 2H), 6.71 (s, OH), 5.95 (s, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 147.59, 138.58, 132.89, 131.73, 131.15, 130.91, 128.95, 128.54, 127.69, 127.58, 126.72, 126.15, 123.68, 123.30, 122.92, 79.72; EI-MS *m/z* 464 ($[M+1]^+$), 462 ($[M-1]^+$); Anal. Calcd for $C_{29}H_{19}BrO$: C, 75.17; H, 4.13. Found: C, 74.91; H, 4.09.

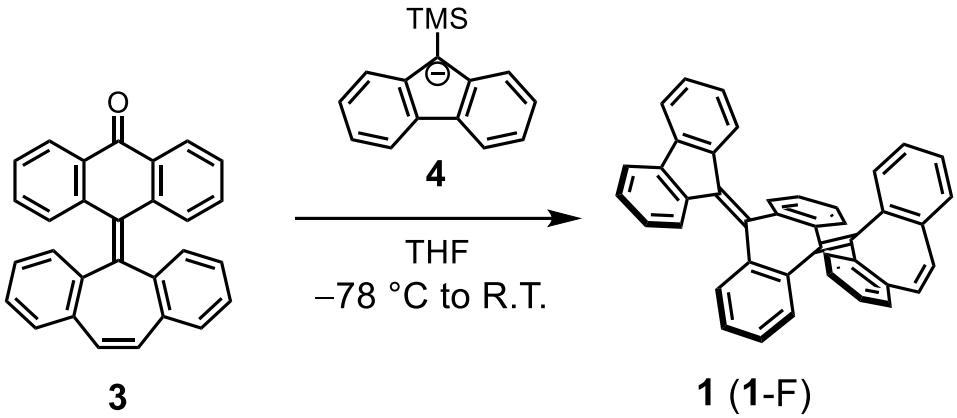
10-(5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylidene)anthracen-9(10*H*)-one (3)



2 **3**

To a solution of **2** (0.60 g, 1.3 mmol) in 1,2-dichloroethane (24 mL) was added trifluoroacetic acid (6 mL) and water (6 mL), and then the reaction mixture was stirred for 48 hours at 85 °C. After the solution was cooled to room temperature, the organic layer was separated, washed with aqueous sodium carbonate, and dried over anhydrous sodium sulfate. After filtration, the filtrate was evaporated and the residue was purified by column chromatography on silica gel (DCM/hexane 50%) to give **3** as a pale yellow solid (0.45 g, 91%). Mp 282–283 °C; R_f = 0.27 (DCM/hexane 50%); ^{1}H NMR (500 MHz, dichloromethane-d_2) δ 8.06 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.32-7.27 (m, 6H), 7.12 (t, J = 8.0 Hz, 2H), 7.02 (t, J = 8.0 Hz, 2H), 6.81 (d, J = 7.5 Hz, 2H), 6.55 (d, J = 8.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.14, 142.12, 138.95, 138.46, 134.95, 133.44, 131.25, 130.09, 129.33, 129.24, 128.84, 128.03, 127.97, 127.14, 127.11, 126.24; EI-MS *m/z* 382 ([M]$^+$); Anal. Calcd for $C_{29}H_{18}O$: C, 91.07; H, 4.74. Found: C, 91.07; H, 4.72.

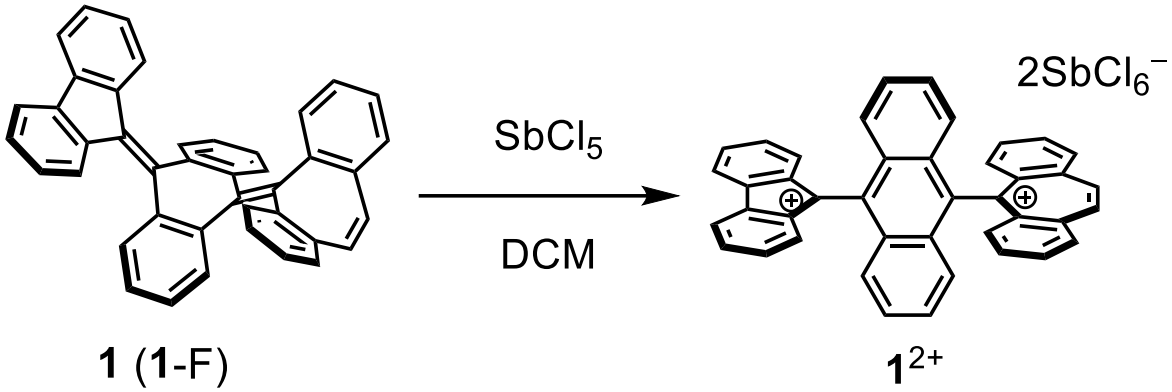
5-(10-(9*H*-fluoren-9-ylidene)anthracen-9(10*H*)-ylidene)-5*H*-dibenzo[*a*,*d*]heptene (1)



3 **1** (**1**-F)

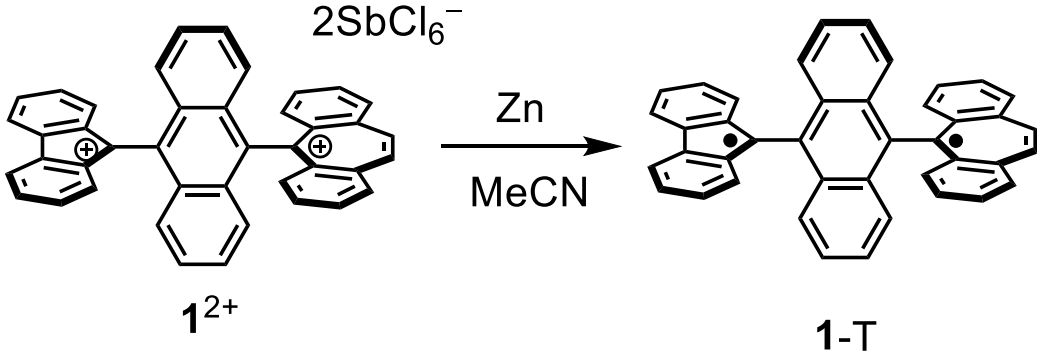
To a solution of (9*H*-fluoren-9-yl)trimethylsilane (0.23 g, 0.95 mmol) in THF (10 mL) was added ^{n}BuLi (1.6 M, 0.95 mmol) at −78 °C under nitrogen atmosphere, and the solution was stirred for 1 hour. To the solution was added **3** (0.31 g, 0.81 mmol) in THF (10 mL), and then the reaction mixture was stirred at room temperature. After 18 hours stirring, aqueous ammonium chloride was added for quenching. The reaction mixture was extracted with DCM, and the organic layer was separated, washed with brine, dried over sodium sulfate. After filtration, the filtrate was evaporated and the residue was purified by column chromatography on silica gel (DCM/hexane 10%) to give **1** (**1**-F) as a pale yellow solid (0.32 g, 74%). Mp > 300 °C; R_f = 0.27 (DCM/hexane 20%); ^{1}H NMR (600 MHz, dichloromethane-d_2) δ 7.87 (d, J = 8.4 Hz, 2H), 7.82 (dd, J = 7.2 Hz, 0.6 Hz, 2H), 7.78 (d, J = 7.2 Hz, 2H), 7.45 (dd, J = 7.8 Hz, 1.2 Hz, 2H), 7.36 (td, J = 7.2 Hz, 1.2 Hz, 2H), 7.28 (td, J = 7.2 Hz, 1.2 Hz, 2H), 7.20 (s, 2H), 7.14-7.09 (m, 6H), 6.98 (dd, J = 7.8 Hz, 1.2 Hz, 2H), 6.91 (td, J = 7.2 Hz, 1.2 Hz, 2H), 6.58 (dd, J = 7.8 Hz, 0.6 Hz, 2H); ^{13}C NMR (126 MHz, dichloromethane-d_2) δ 140.48, 138.95, 138.43, 138.35, 138.31, 138.22, 137.01, 135.09, 135.06, 130.98, 130.06, 129.16, 128.21, 128.11, 127.84, 127.75, 127.13, 126.71, 126.07, 125.93, 124.92, 124.71, 119.10; EI-MS *m/z* 530 ([M]$^+$); Anal. Calcd for $C_{42}H_{26}$: C, 95.06; H, 4.94. Found: C, 95.11; H, 5.01.

Dication salt of 5-(10-(9*H*-fluoren-9-ylidene)anthracen-9(10*H*)-ylidene)-5*H*-dibenzo[*a*,*d*]heptene ($\mathbf{1}^{2+}$)



To a solution of **1** (53 mg, 0.094 mmol) in DCM (10 mL) was added antimony(V) chloride (1.0 M, 0.37 mmol) at 0 °C under nitrogen atmosphere. After the reaction mixture was stirred for 30 min., hexane (10 mL) was added. The precipitate of $\mathbf{1}^{2+}$ salt that appeared after the addition of hexane was collected and washed with hexane. The crude product was purified by the reprecipitation from DCM/hexane to give $\mathbf{1}^{2+}\cdot 2SbCl_6^-$ as a dark red solid (115 mg, 96%). ^{1}H NMR (500 MHz, dichloromethane-d_2) δ 9.54 (s, 2H), 8.97 (d, J = 8.5 Hz, 2H), 8.82 (d, J = 9.0 Hz, 2H), 8.67 (t, J = 7.5 Hz, 2H), 8.18 (t, J = 7.5 Hz, 2H), 8.05 (d, J = 9.0 Hz, 2H), 7.84 (t, J = 8.5 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.42 (d, J = 7.5 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.03 (d, J = 7.0 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 6.87 (t, J = 7.5 Hz, 2H); Anal. Calcd for $C_{42}H_{26}Cl_{12}Sb_2$: C, 42.05; H, 2.18. Found: C, 41.91; H, 2.33.

Diradical of 5-(10-(9*H*-fluoren-9-ylidene)anthracen-9(10*H*)-ylidene)-5*H*-dibenzo[*a*,*d*]heptene (1-T)



To a solution of $\mathbf{1}^{2+}$ (13 mg, 0.010 mmol) in MeCN (3 mL) was added zinc powder (13 mg 0.20 mmol) at –40 °C under nitrogen atmosphere. After the reaction mixture was stirred for 1 hour, brown to black precipitate was collected by filtration. After dried the precipitate under vacumm, this precipitate (2~3 mg) was used for the measurement of ESR and UV-vis spectra.

Reference data of 9-anthryl substituted fluorenyl and dibenzosuberenyl radicals

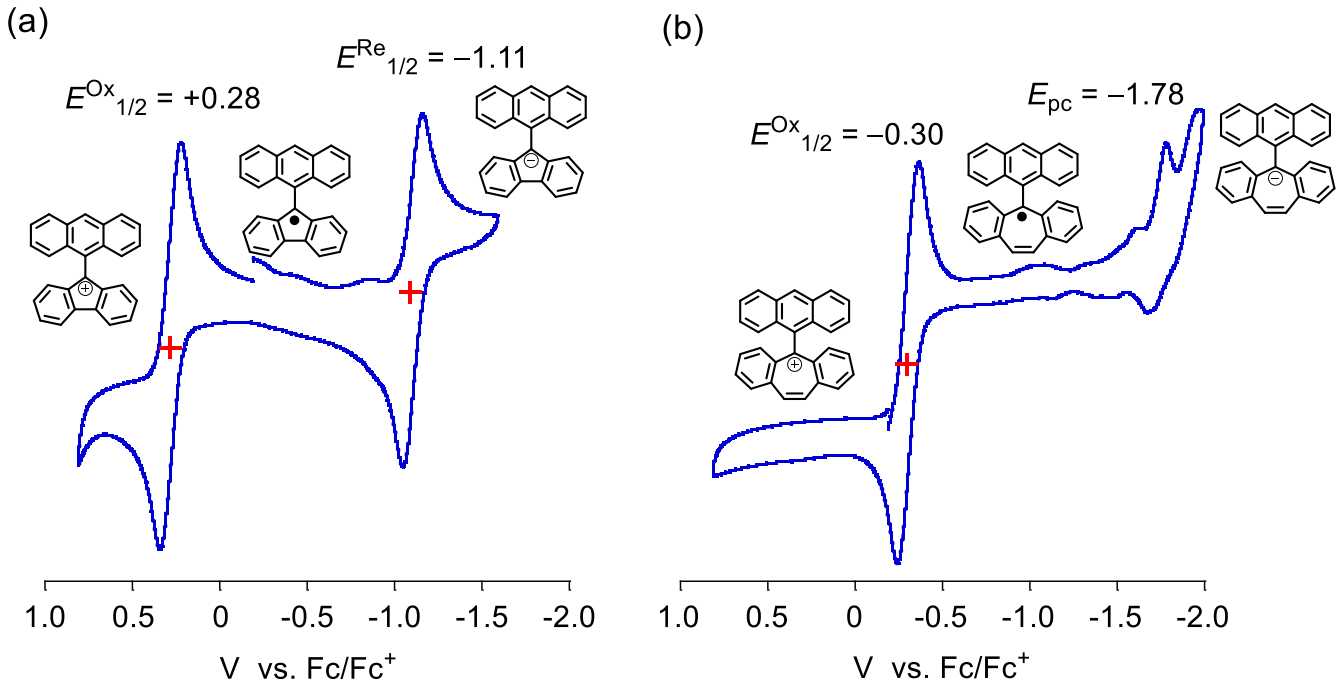


Figure S1. (a) Cyclic voltammogram of 9-anthryl substituted fluorenyl radical. (b) Cyclic voltammogram of 9-anthryl substituted dibenzosuberenyl radical. Due to high reactivity of 8π-electron antiaromatic system in the seven-membered ring of dibenzosuberenyl anion, irreversible wave was observed at E_{pc} = −1.78 V. Measurement condition: 0.1 m nBu$_4$PF$_6$ in CH_2Cl_2, scan rate = 100 mV s^{-1}, room temperature.

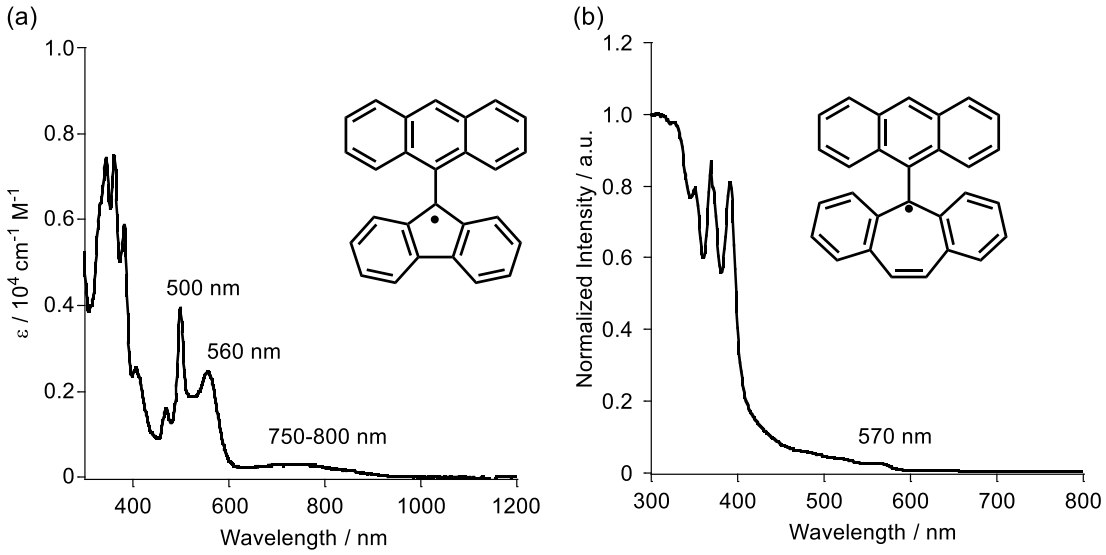


Figure S2. (a) UV-vis spectrum of 9-anthryl substituted fluorenyl radical in CH_2Cl_2. (b) UV-vis spectrum of 9-anthryl substituted dibenzosuberenyl radical in CH_2Cl_2.

X-ray crystallographic data

Crystal data for 1-F. CCDC 2256324. $C_{42}H_{26}$, *M*w =530.63 g/mol, monoclinic, space group *C*2/c (no. 15), *a* = 26.2349(11) Å, *b* = 10.4272(3) Å, *c* = 24.3603(10) Å, β = 123.766(6)°, *V* = 5539.8(5) Å^3, Z = 8, *T* = 120.15 K, μ(Mo Kα) = 0.072 mm^{-1}, D_{calc} = 1.272 g/cm^3, 45228 reflections measured (3.664° ≤ 2*θ* ≤ 61.528°), 7363 unique (R_{int} = 0561, R_{sigma} = 0.0450) which were used in all calculations. The final R_1 was 0.0456 (I > 2σ(I)) and wR_2 was 0.1080 (all data), *GOF* = 1.061.

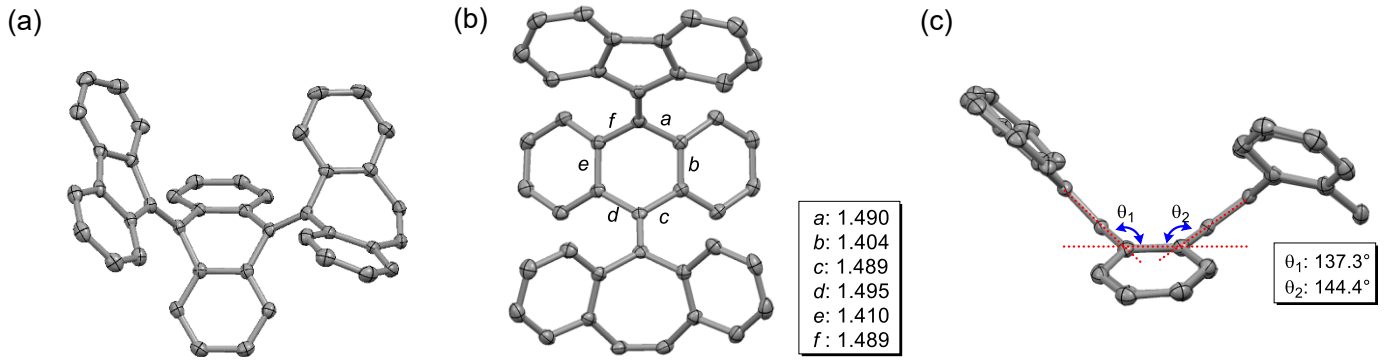


Figure S3. X-ray crystal structure of **1**-F. (a) Side view 1, (b) top view with C-C bond length (Å) of the central anthracene core., and (c) side view 2 with bent angles θ_1 and θ_2 of the central anthraquinodimethane core. Protons are omitted for clarity.

Crystal data for $\mathbf{1}^{2+}$. CCDC 2256323. $C_{43}H_{28}Cl_{14}Sb_2$, *M*w =1284.45 g/mol, monoclinic, space group $P2_1/n$ (no. 14), *a* = 10.6573(2) Å, *b* = 34.0386(6) Å, *c* = 14.0166(2) Å, β = 97.905(2)°, *V* = 5036.34(15) Å^3, *Z* = 4, *T* = 120.15 K, μ(Mo Kα) = 1.846 mm^{-1}, D_{calc} = 1.694 g/cm^3, 111156 reflections measured (3.786° ≤ 2*θ* ≤ 61.47°), 13835 unique (R_{int} = 0.0750, R_{sigma} = 0.0536) which were used in all calculations. The final R_1 was 0.0456 (I > 2σ(I)) and wR_2 was 0.1177 (all data)., *GOF* = 1.042.

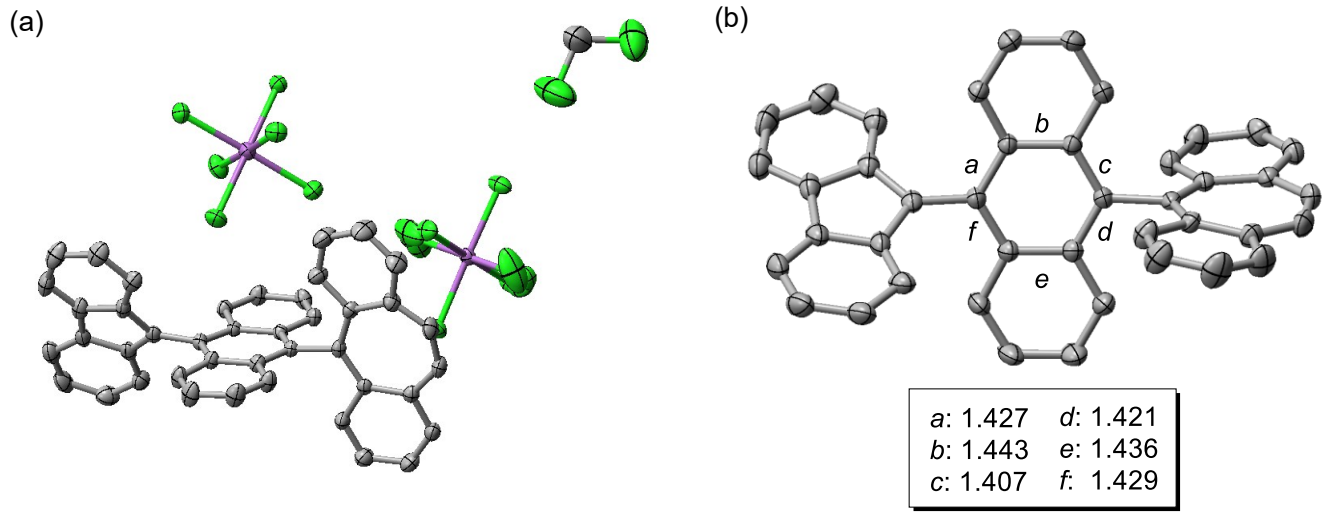


Figure S4. X-ray crystal structure of $\mathbf{1}^{2+}$. (a) Whole structure of $\mathbf{1}^{2+}$ with counter anions of $SbCl_6^-$ and dichloromethane. (b) Bond length (Å) of the central anthracene core. Protons are omitted for clarity.

2D NMR data

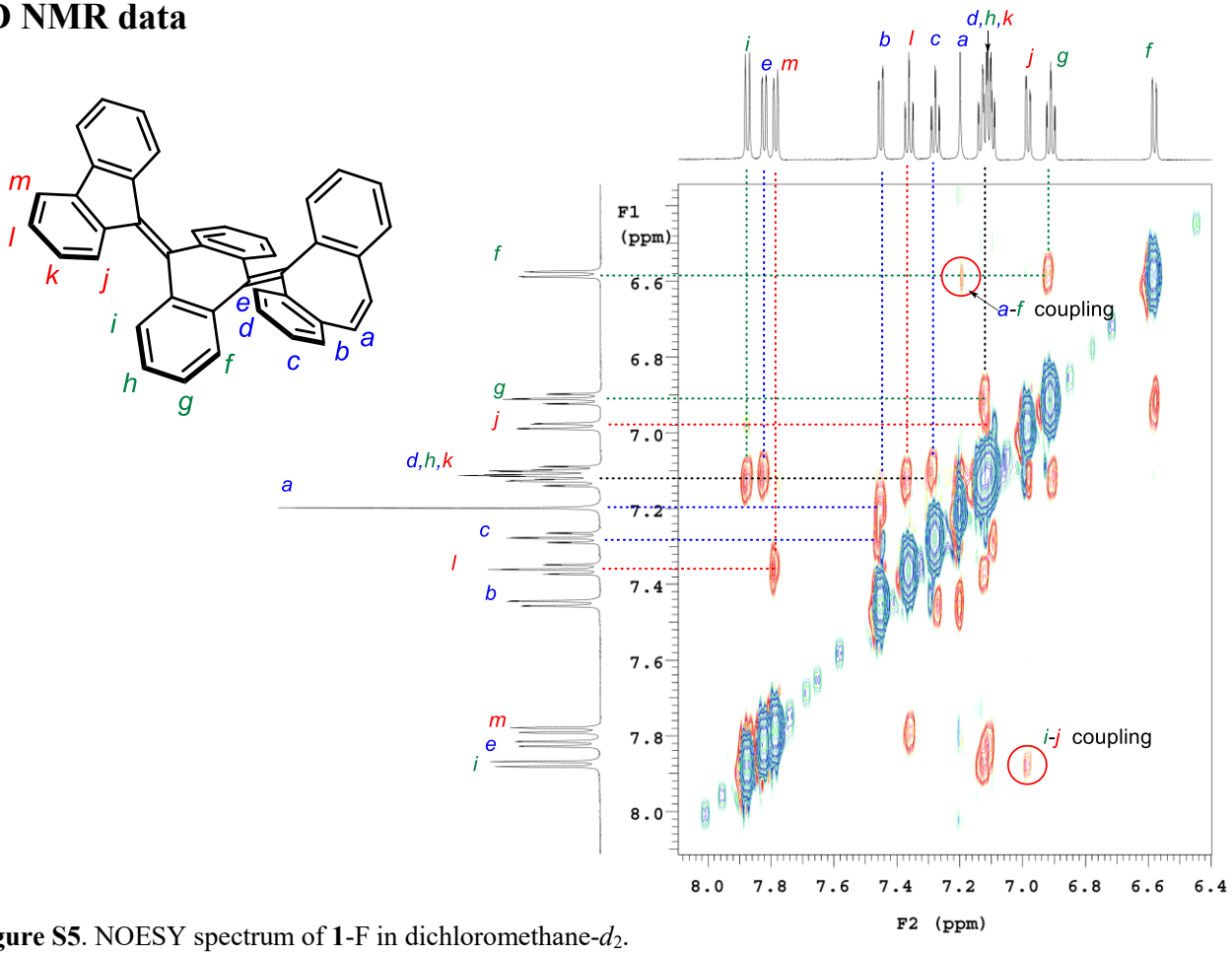


Figure S5. NOESY spectrum of **1**-F in dichloromethane-d_2.

UV-vis spectra of 1-F

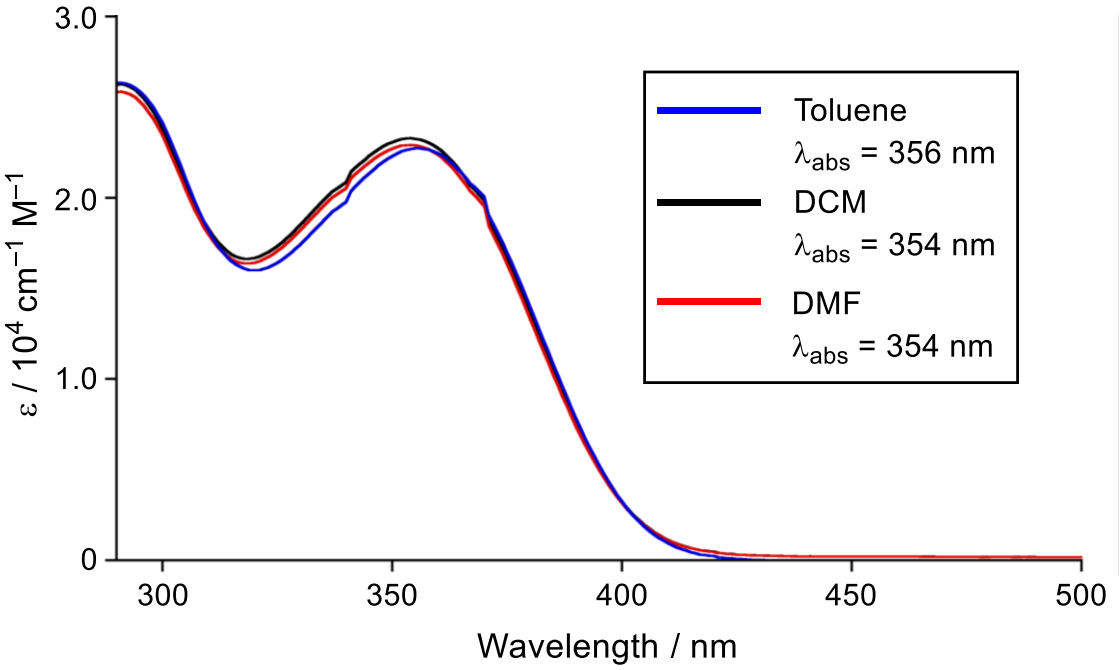
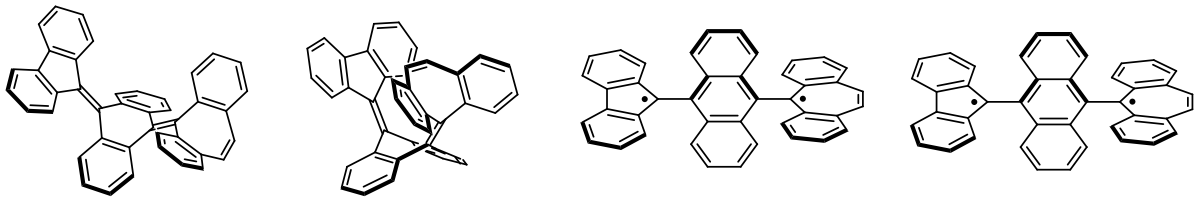


Figure S6. UV-vis spectra of **1**-F in toluene (blue line), DCM (black line), and DMF (red line).

Relative energy differences of 1 conformers

(a)



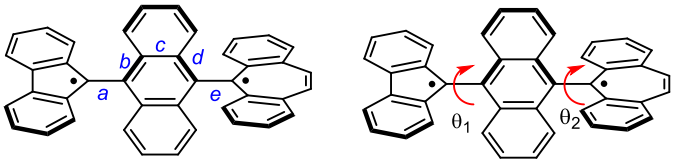
1-F (*exo*-form) 0.00 kcal mol^{-1}

1-F (*endo*-form) +2.27 kcal mol^{-1}

1-T (open-shell singlet) +20.07 kcal mol^{-1}

1-T (triplet) +20.13 kcal mol^{-1}

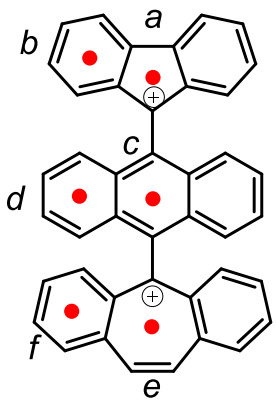
(b)



	a / Å	*b* / Å	*c* / Å	*d* / Å	*e* / Å	θ_1 / °	θ_2 / °
1-T (open-shell singlet)	1.470	1.412	1.434	1.406	1.503	64.4	90.3
1-T (triplet)	1.470	1.411	1.434	1.405	1.503	64.7	90.3

Figure S7. (a) Energy differences of **1**-F (*exo*-form), **1**-F (*endo*-form), **1**-T (open-shell singlet), and **1**-T (triplet). (b) Bond length and twist angles of **1**-T (open-shell singlet and triplet). ((U)ωB97X-D/6-31G**).

NICS calculations of 1^{2+}



	NICS(0) / ppm
a	+25.7
b	+5.35
c	–7.27
d	–6.71
e	–4.27
f	–8.54

Figure S8. (a) NICS(0) values of $\mathbf{1}^{2+}$ at each aromatic rings (*a* to *f*). (CAM-B3LYP-D3/6-311+G**//ωB97X-D/6-31G**)

Charge distribution of 1^{2+}

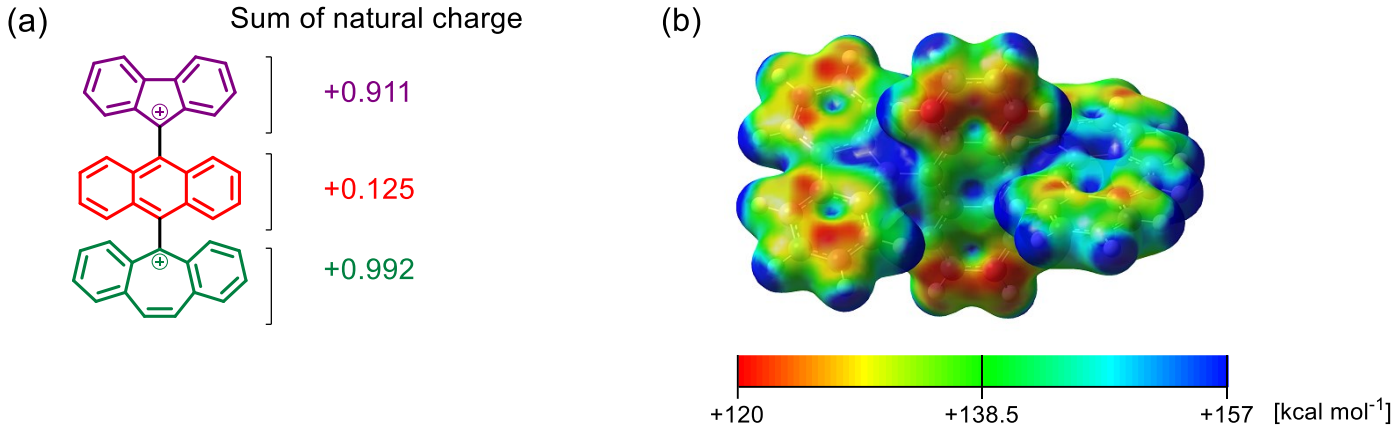


Figure S9. (a) Charge distribution on fluorenyl, anthryl, and dibenzosuberenyl units of $\mathbf{1}^{2+}$ calculated using natural population analysis. The dibenzosuberenyl cation unit has a positive charge of +0.992 and the fluorenyl cation unit has a lesser positive charge of +0.911. The residual positive charge localizes in the central anthryl unit (+0.125). (b) Electrostatic potential surface of $\mathbf{1}^{2+}$ shows positive π-surface (The color bar of energy ranges from +120 (red) to +157 (blue) kcal mol^{-1}). (ωB97X-D/6-311+G**//ωB97X-D/6-31G**).

UV-vis spectra of 1^{2+}

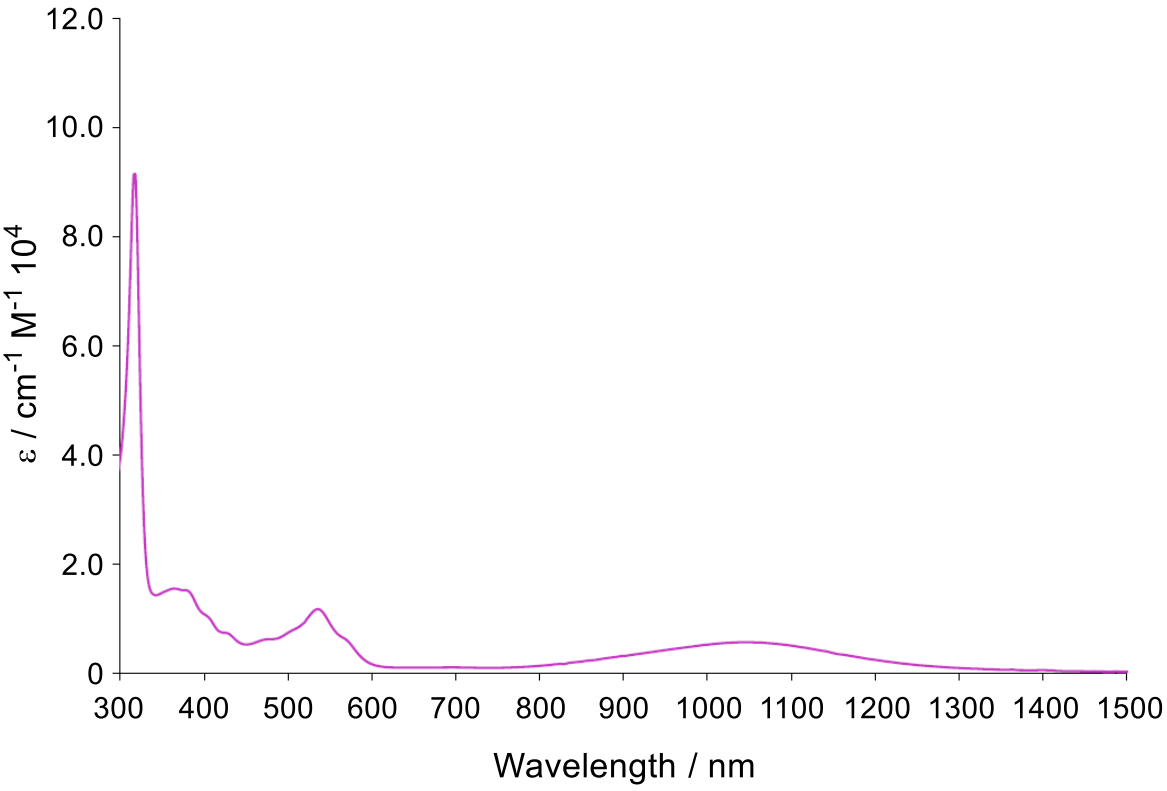


Figure S10. UV-vis spectra of $\mathbf{1}^{2+}\cdot 2SbCl_6^-$ in DCM.

Kohn-Sham molecular orbitals and TD-DFT calculations of $\mathbf{1}^{2+}$

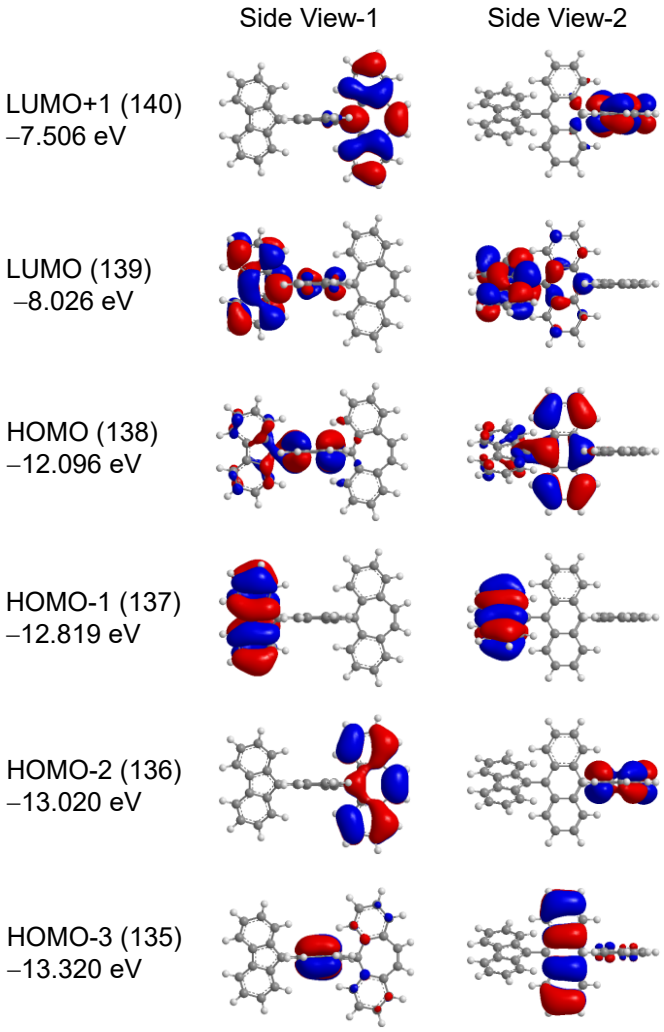
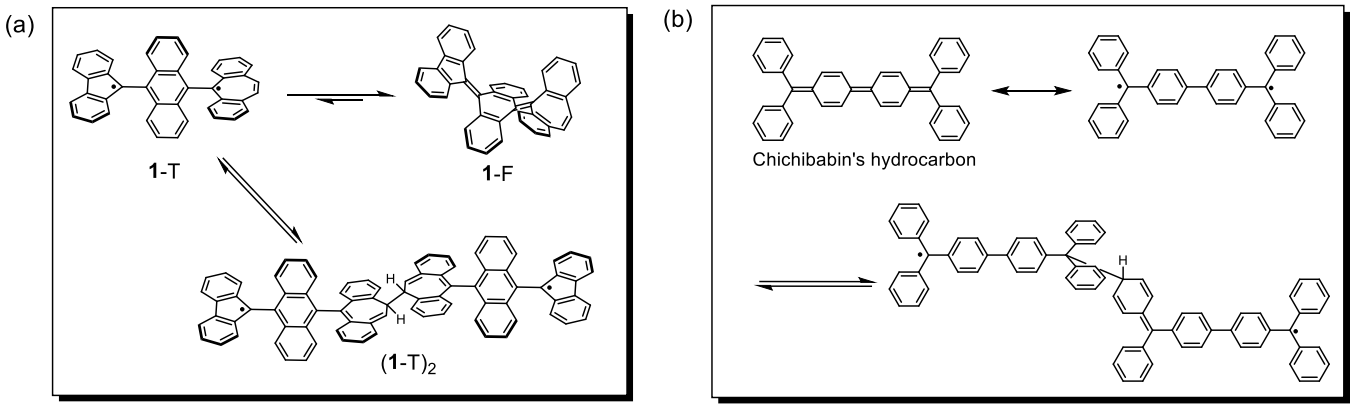


Figure S11. Kohm-Sham molecular orbitals and its energy of $\mathbf{1}^{2+}$ (CAM-B3LYP/6-31G**//ωB97X-D/6-31G**).

Table S1. TD-DFT calculation result (nstate=5) of $\mathbf{1}^{2+}$ (CAM-B3LYP/6-31G**//ωB97X-D/6-31G**).

Excited State 1:	Singlet-A	1.3817 eV	897.35 nm	*f*=0.1502
138 ->139	0.70393 (99%)			
Excited State 2:	Singlet-A	1.4390 eV	861.61 nm	*f*=0.0021
137 ->139	0.70267 (99%)			
Excited State 3:	Singlet-A	1.8685 eV	663.53 nm	*f*=0.0002
138 ->140	0.69947 (98%)			
Excited State 4:	Singlet-A	2.4885 eV	498.24 nm	*f*=0.0151
133 ->139	0.10314 (2%)			
134 ->139	0.15759 (5%)			
135 ->139	0.67523 (91%)			
Excited State 5:	Singlet-A	2.5158 eV	492.83 nm	*f*=0.0644
136 ->140	0.69850 (98%)			

Plausible competitive equilibrium of 1-T



Scheme S1. (a) Plausible competitive equilibriums of intramolecular isomerization of **1**-T to **1**-F and intermolecular dimerization of **1**-T to (**1**-T)$_2$. (b) Typical example of the intermolecular dimerization of biradicaloid observed in Chichibabin's hydrocarbon.

UV-vis spectra of 1-T with different solvents

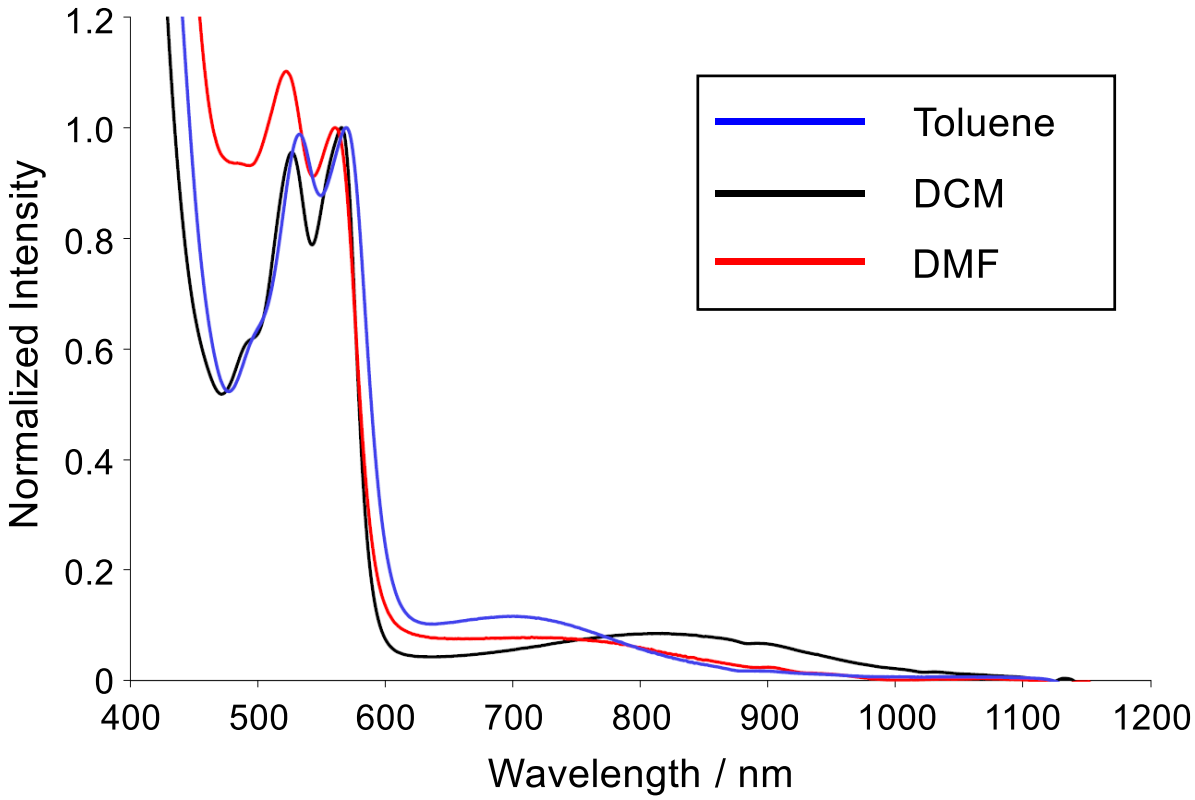


Figure S12. UV-vis spectra of **1**-T in toluene (blue line), DCM (black line), and DMF (red line).

Kohn-Sham molecular orbitals and TD-DFT calculations of 1-T

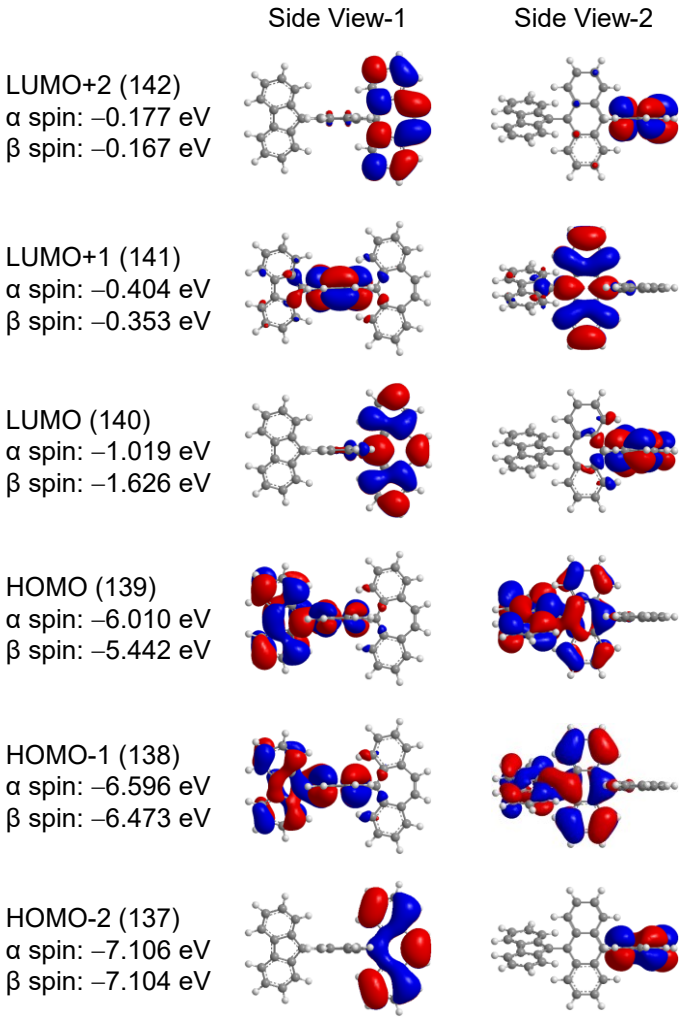


Figure S13. Kohm-Sham molecular orbitals and its energy of **1**-T (UCAM-B3LYP/6-31G**//UωB97X-D/6-31G**).

Table S2. TD-DFT calculation result (nstate=5) of **1-T** (CAM-B3LYP/6-31G**//ωB97X-D/6-31G**).

Excited State 1: 2.402-A 1.6221 eV 764.34 nm *f*=0.0005 <S**2>=1.193
137A ->142A -0.12683 (2%)
136B ->142B -0.10570 (1%)
139B ->142B 0.97491 (95%)

Excited State 2: 2.976-A 1.7063 eV 726.61 nm f=0.0123 <S**2>=1.964
138A ->141A 0.35873 (13%)
139A ->141A 0.36772 (14%)
138B ->140B 0.73371 (54%)
138B ->141B -0.40542 (16%)

Excited State 3: 1.569-A 1.7402 eV 712.48 nm f=0.0001 <S**2>=0.366
139B ->140B 0.88326 (78%)
139B ->141B -0.43372 (19%)

Excited State 4: 2.329-A 1.8181 eV 681.95 nm f=0.0007 <S**2>=1.106
137B ->140B 0.97751 (96%)
137B ->141B 0.10859 (1%)

Excited State 5: 2.927-A 2.0980 eV 590.97 nm f=0.0473 <S**2>=1.892
138A ->141A -0.38030 (14%)
139A ->141A -0.38996 (15%)
138B ->140B 0.65581 (43%)
138B ->141B 0.48818 (24%)

Electrostatic potential surface of 1-T

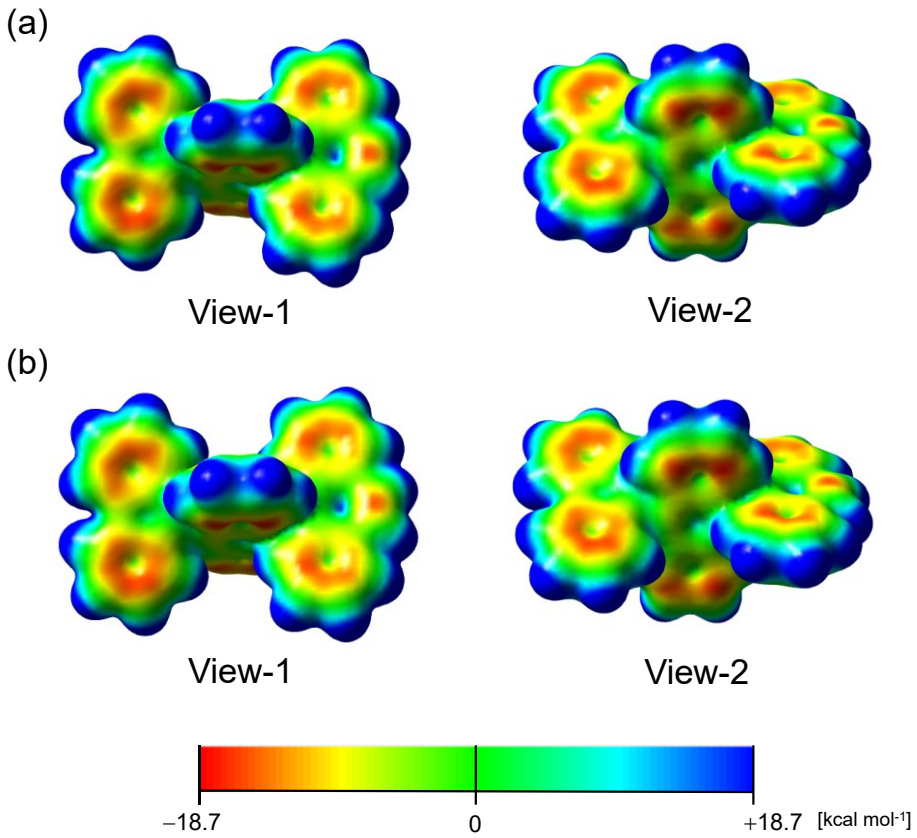


Figure S14. (a) Electrostatic potential surface of **1**-T (open-shell singlet, biradical character y_0 = 99%). (b) Electrostatic potential surface of **1**-T (triplet). The color bar of energy ranges from −18.7 (red) to +18.7 (blue) kcal mol^{-1}). Computations were performed using UωB97X-D/6-31G** level of theory.

Spin density of 1-T

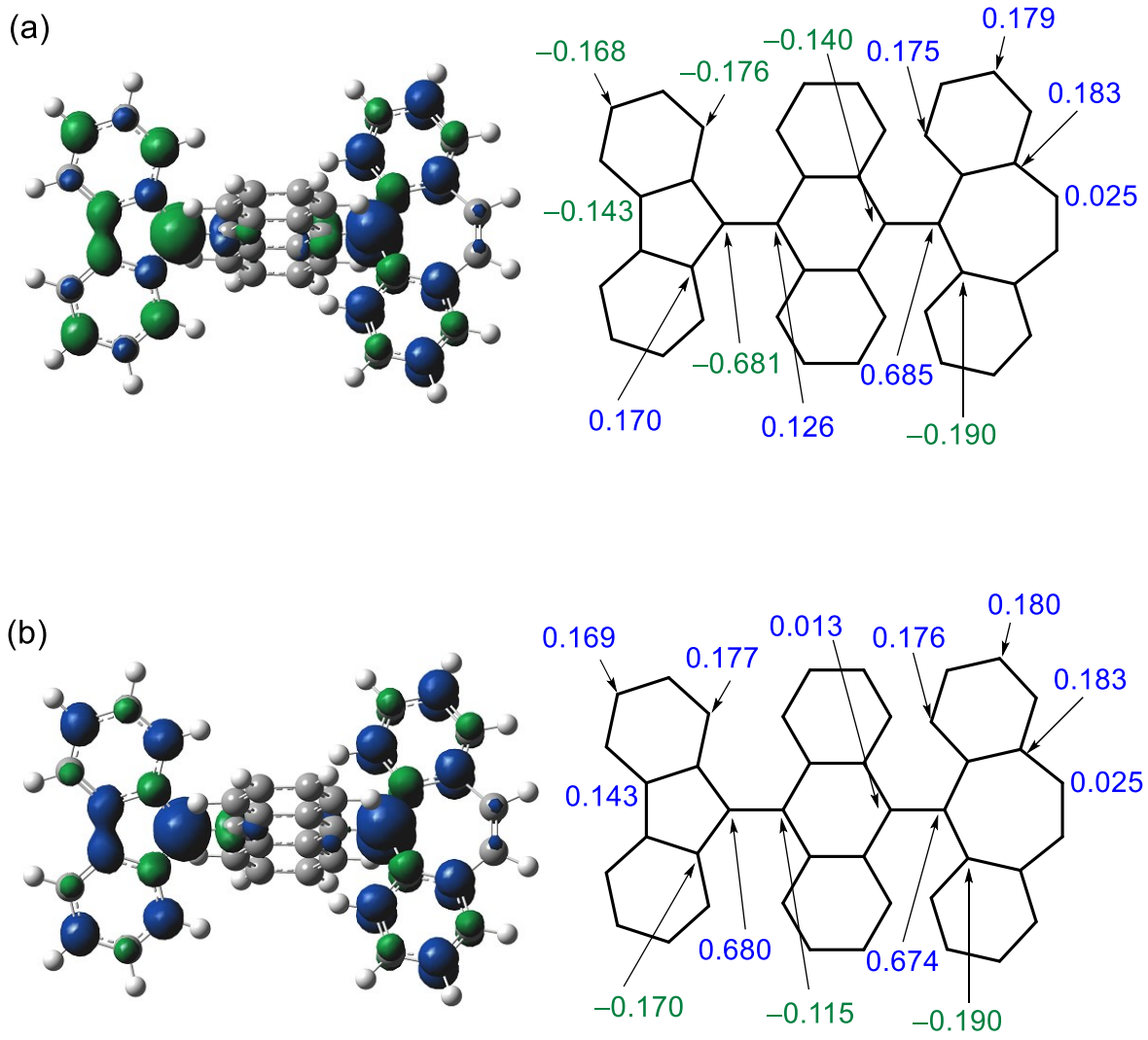
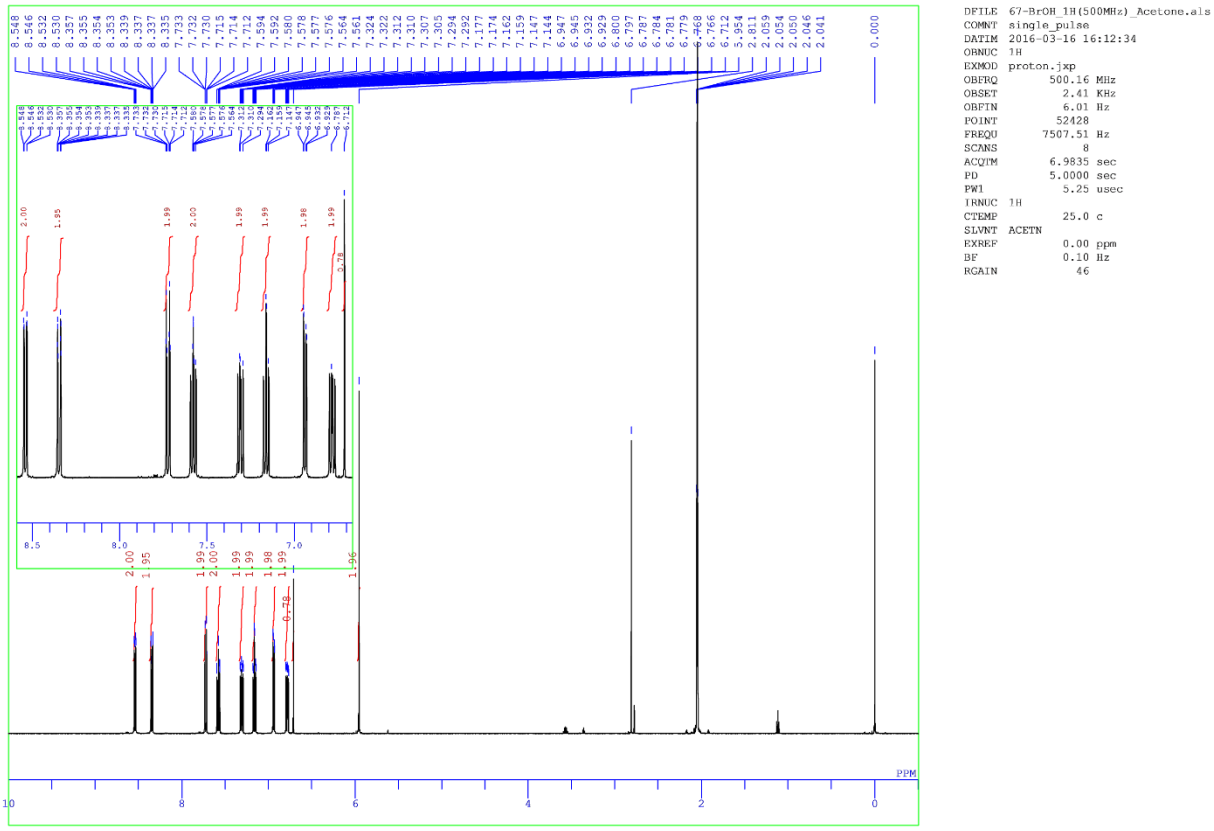


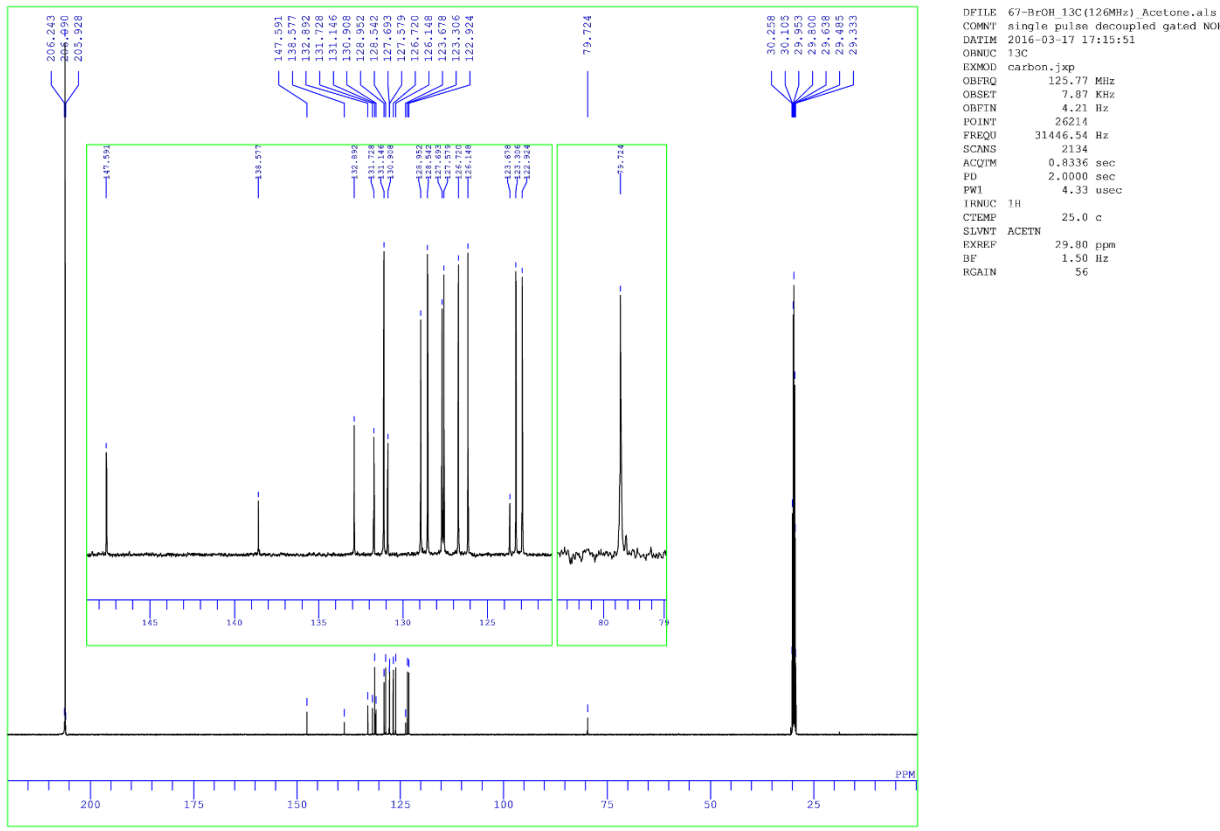
Figure S15. (a) Spin density map of **1**-T (open-shell singlet) (left) and its values on significant positions (right). (b) Spin density map of **1**-T (triplet) (left) and its values on significant positions (right). (UωB97X-D/6-31G**).

NMR Chart



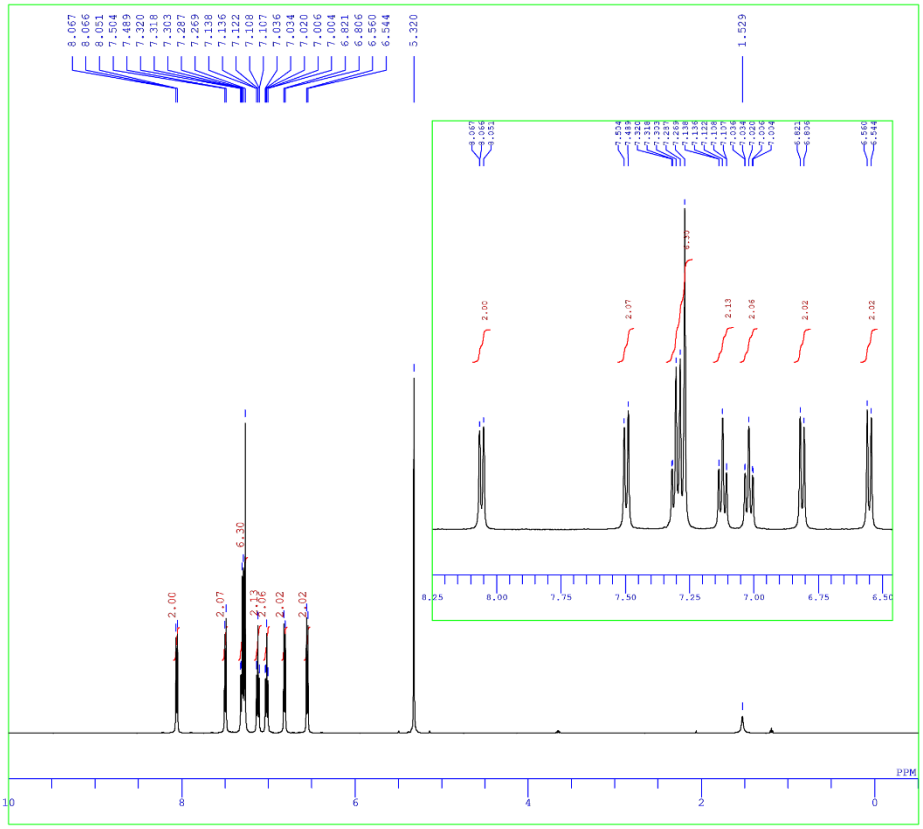
```
DFILE  67-BrOH_1H(500MHz)_Acetone.als
COMNT  single_pulse
DATIM  2016-03-16 16:12:34
ONUC   1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         52428
FREQU       7507.51 Hz
SCANS             8
ACQTM        6.9835 sec
PD           5.0000 sec
PW1            5.25 usec
IRNUC  1H
CTEMP         25.0 c
SLVNT  ACETN
EXREF          0.00 ppm
BF             0.10 Hz
RGAIN            46
```

Figure S16. ^{1}H NMR (500 MHz) of compound **2** (Acetone-d_6).



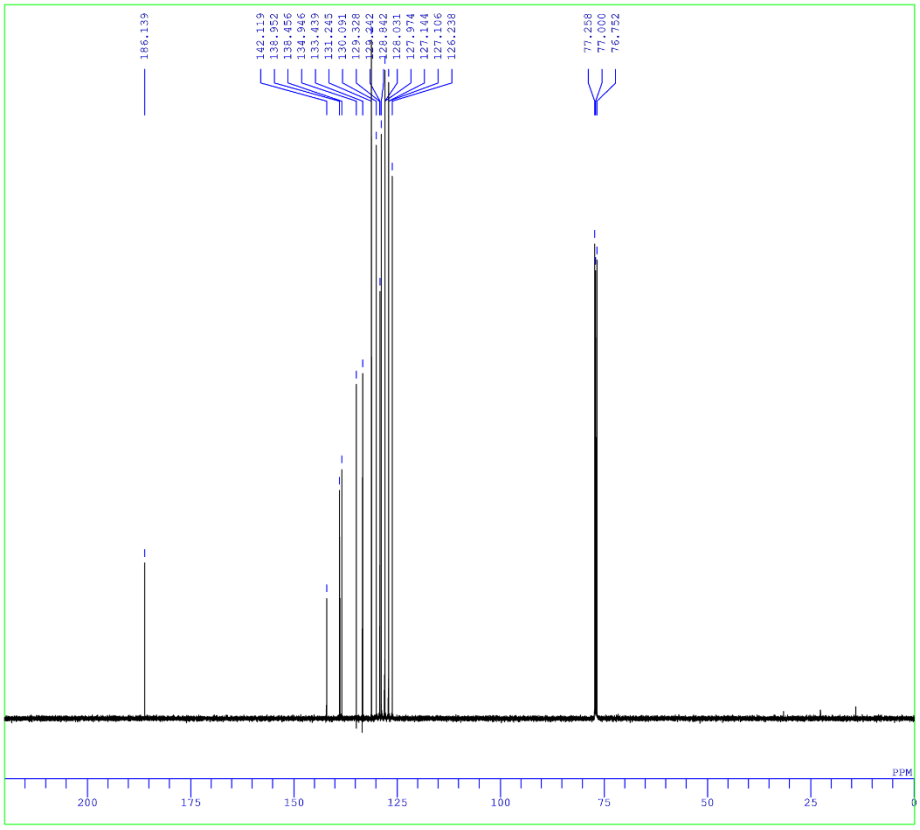
```
DFILE  67-BrOH_13C(126MHz)_Acetone.als
COMNT  single pulse decoupled gated NOE
DATIM  2016-03-17 17:15:51
ONUC   13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.54 Hz
SCANS          2134
ACQTM        0.8336 sec
PD           2.0000 sec
PW1            4.33 usec
IRNUC  1H
CTEMP         25.0 c
SLVNT  ACETN
EXREF         29.80 ppm
BF             1.50 Hz
RGAIN            56
```

Figure S17. ^{13}C NMR (126 MHz) of compound **2** (Acetone-d_6).



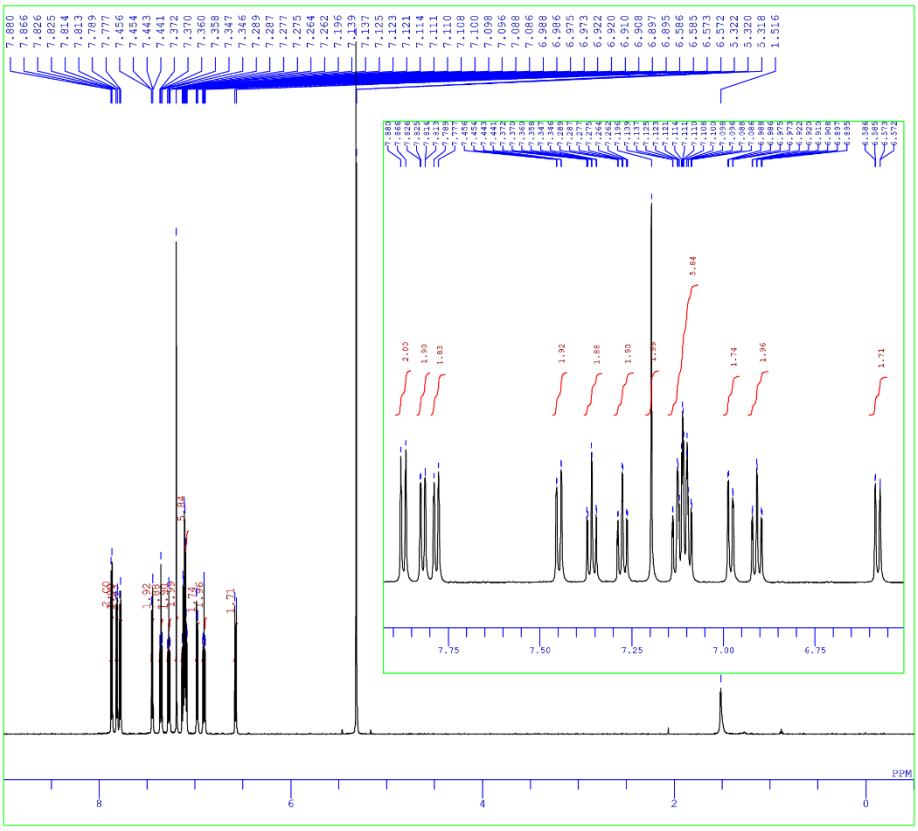
```
DFILE  67-C-O_1H(500MHz)_CD2Cl2.als
COMNT  single_pulse
DATIM  2016-03-25 17:09:42
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         52428
FREQU       7507.51 Hz
SCANS             8
ACQTM         6.9835 sec
PD            5.0000 sec
PW1           5.25 usec
IRNUC  1H
CTEMP         25.0 c
SLVNT  CD2CL2
EXREF         5.32 ppm
BF            1.50 Hz
RGAIN           50
```

Figure S18. ^{1}H NMR (500 MHz) of compound **3** (CD_2Cl_2).



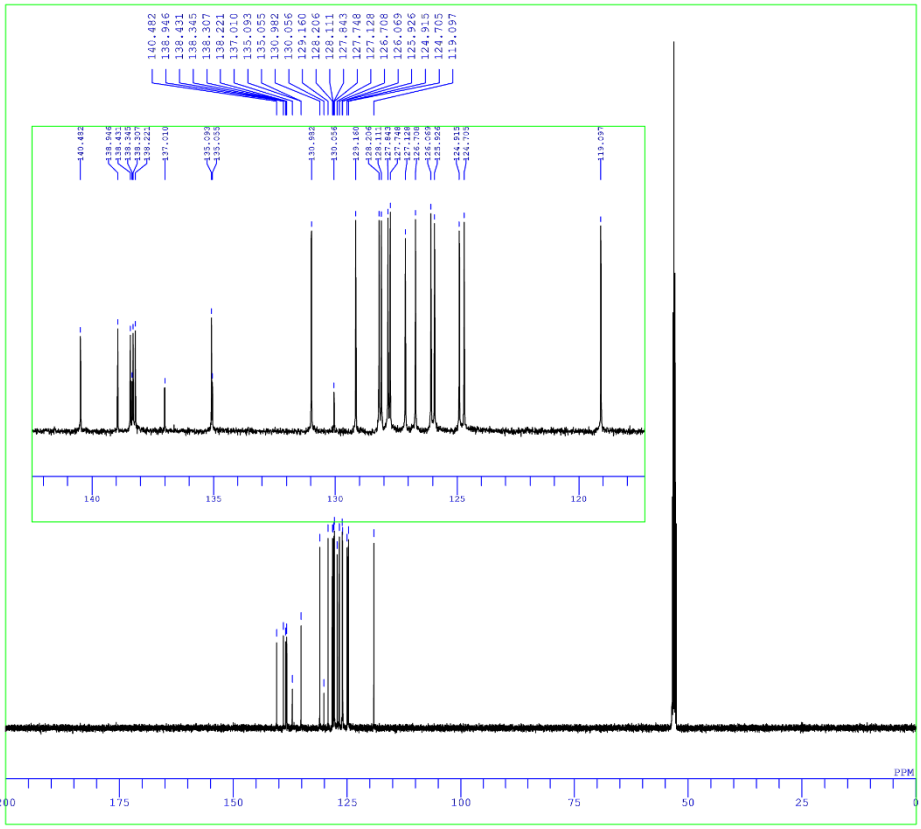
```
DFILE  67-C-O_13C(126MHz)_CDCl3.als
COMNT  single pulse decoupled gated NOE
DATIM  2016-03-03 19:14:22
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU       31446.54 Hz
SCANS          2202
ACQTM         0.8336 sec
PD            2.0000 sec
PW1           4.33 usec
IRNUC  1H
CTEMP         25.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF            0.12 Hz
RGAIN           58
```

Figure S19. ^{13}C NMR (126 MHz) of compound **3** ($CDCl_3$).



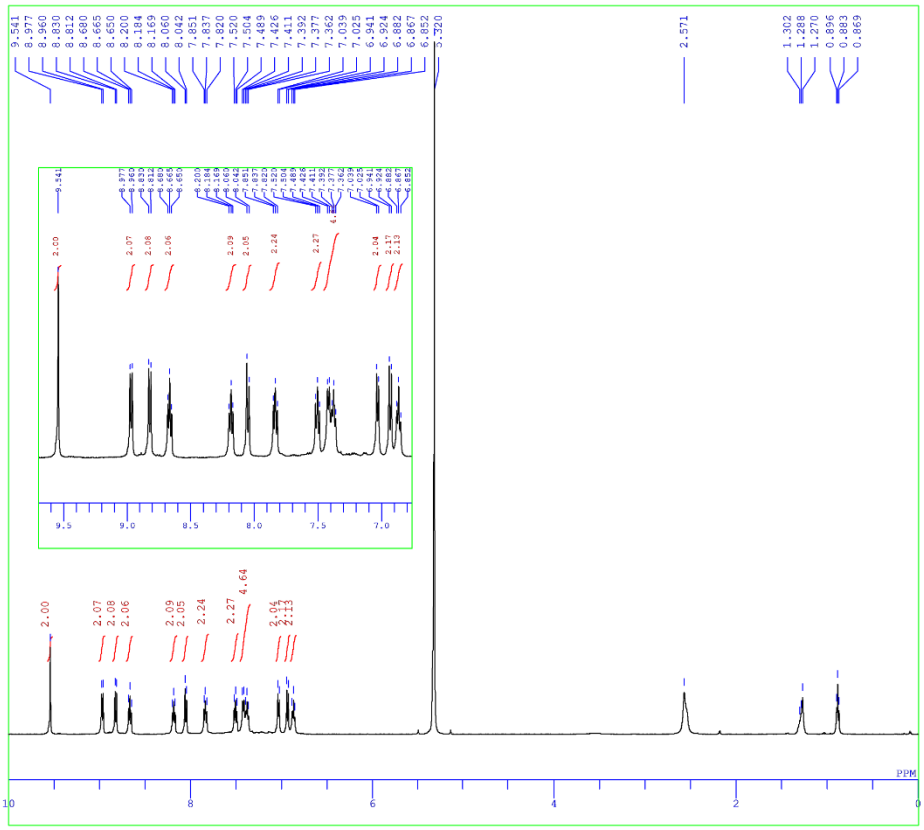
```
DFILE  567_1H(600MHz)_DCM.als
COMNT  new experiment
DATIM  2016-02-22 16:00:22
ONUC   H1
EXMOD  s2pul
OBFRQ        599.91 MHz
OBSET          5.39 KHz
OBFIN          2.00 Hz
POINT         32768
FREQU       9615.38 Hz
SCANS             1
ACQTM          3.4000 sec
PD             1.6000 sec
PW1              7.20 usec
IRNUC
CTEMP          25.0 c
SLVNT  cd2cl2
EXREF          5.32 ppm
BF             0.10 Hz
RGAIN            48
```

Figure S20. ^{1}H NMR (600 MHz) of compound **1**-F (CD_2Cl_2).



```
DFILE  567_13C(126MHz)_DCM.als
COMNT  single pulse decoupled gated NOE
DATIM  2016-03-02 19:03:38
ONUC   13C
EXMOD  carbon.jxp
OBFRQ        125.77 MHz
OBSET          7.87 KHz
OBFIN          4.21 Hz
POINT         26214
FREQU      31446.54 Hz
SCANS          2400
ACQTM          0.8336 sec
PD             2.0000 sec
PW1              4.33 usec
IRNUC  1H
CTEMP          25.0 c
SLVNT  CD2CL2
EXREF         53.10 ppm
BF             0.10 Hz
RGAIN            58
```

Figure S21. ^{13}C NMR (126 MHz) of compound **1**-F (CD_2Cl_2).




```
DFILE  567(2+)_1H(500MHz)_DCM.als
COMNT  single_pulse
DATIM  2016-02-25 17:25:48
ONNUC  1H
EXMOD  proton.jxp
OBSFRQ       500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT         52428
FREQU       7507.51 Hz
SCANS            64
ACQTM         6.9835 sec
PD            5.0000 sec
PW1              5.25 usec
IRNUC  1H
CTEMP         25.0 c
SLVNT  CD2CL2
EXREF            5.32 ppm
BF               1.50 Hz
RGAIN              50
```

Figure S22. ^{1}H NMR (500 MHz) of compound $\mathbf{1}^{2+}\cdot 2SbCl_6^-$ (CD_2Cl_2).

Calculated Cartesian coordination

Table S3. Cartesian Coordinates of **1**-F (*exo* form) ($C_{42}H_{26}$, total 68 atoms) (ωB97X-D/6-31G**).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.967751	4.254578	0.732377	35	6	0	1.322002	-4.393616	2.817179
2	6	0	0.967751	4.254578	-0.732377	36	6	0	1.866504	-3.471144	3.696899
3	6	0	0.257956	3.125454	-1.184007	37	6	0	1.897944	-2.120776	3.352270
4	6	0	-0.324729	2.423802	0.000000	38	6	0	1.362236	-1.707531	2.141695
5	6	0	0.257956	3.125454	1.184007	39	6	0	1.362236	-1.707531	-2.141695
6	6	0	0.268533	2.824774	2.545459	40	6	0	1.897944	-2.120776	-3.352270
7	6	0	0.923900	3.678887	3.430607	41	6	0	1.866504	-3.471144	-3.696899
8	6	0	1.573195	4.825328	2.977041	42	6	0	1.322002	-4.393616	-2.817179
9	6	0	1.608804	5.112760	1.616065	43	1	0	-0.209773	1.934307	2.929403
10	6	0	1.608804	5.112760	-1.616065	44	1	0	0.929449	3.440394	4.489502
11	6	0	1.573195	4.825328	-2.977041	45	1	0	2.070722	5.482106	3.683548
12	6	0	0.923900	3.678887	-3.430607	46	1	0	2.146193	5.982549	1.250203
13	6	0	0.268533	2.824774	-2.545459	47	1	0	2.146193	5.982549	-1.250203
14	6	0	-1.207504	1.399507	0.000000	48	1	0	2.070722	5.482106	-3.683548
15	6	0	-1.701297	0.688695	-1.211285	49	1	0	0.929449	3.440394	-4.489502
16	6	0	-1.482586	-0.698648	-1.224740	50	1	0	-0.209773	1.934307	-2.929403
17	6	0	-0.859870	-1.275176	-0.000000	51	1	0	-1.760430	-2.527322	2.315774
18	6	0	-1.482586	-0.698648	1.224740	52	1	0	-2.981181	-1.442135	4.177426
19	6	0	-1.701297	0.688695	1.211285	53	1	0	-3.440318	0.995776	4.108769
20	6	0	-1.936250	-1.456959	2.303272	54	1	0	-2.613012	2.357412	2.205730
21	6	0	-2.623978	-0.844851	3.344786	55	1	0	-2.613012	2.357412	-2.205730
22	6	0	-2.879283	0.524493	3.308258	56	1	0	-3.440318	0.995776	-4.108769
23	6	0	-2.423167	1.289502	2.240597	57	1	0	-2.981181	-1.442135	-4.177426
24	6	0	-2.423167	1.289502	-2.240597	58	1	0	-1.760430	-2.527322	-2.315774
25	6	0	-2.879283	0.524493	-3.308258	59	1	0	-0.051756	-5.942426	-1.163638
26	6	0	-2.623978	-0.844851	-3.344786	60	1	0	-0.051756	-5.942426	1.163638
27	6	0	-1.936250	-1.456959	-2.303272	61	1	0	1.306602	-5.447717	3.080503
28	6	0	0.161739	-2.150862	-0.000000	62	1	0	2.270146	-3.802549	4.648189
29	6	0	0.795777	-2.628847	-1.255661	63	1	0	2.325957	-1.391130	4.031818
30	6	0	0.804224	-3.998436	-1.574389	64	1	0	1.354645	-0.654730	1.876418
31	6	0	0.288378	-5.033055	-0.672148	65	1	0	1.354645	-0.654730	-1.876418
32	6	0	0.288378	-5.033055	0.672148	66	1	0	2.325957	-1.391130	-4.031818
33	6	0	0.804224	-3.998436	1.574389	67	1	0	2.270146	-3.802549	-4.648189
34	6	0	0.795777	-2.628847	1.255661	68	1	0	1.306602	-5.447717	-3.080503

Zero-point correction= 0.549341 (Hartree/Particle)
Thermal correction to Energy= 0.578983
Thermal correction to Enthalpy= 0.579928
Thermal correction to Gibbs Free Energy= 0.488294
Sum of electronic and zero-point Energies= -1615.091363
Sum of electronic and thermal Energies= -1615.061720
Sum of electronic and thermal Enthalpies= -1615.060776
Sum of electronic and thermal Free Energies= -1615.152409

Table S4. Cartesian Coordinates of **1**-F (*endo* form) ($C_{42}H_{26}$, total 68 atoms) (ωB97X-D/6-31G**).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.734255	-3.458578	0.179364	35	1	0	-2.305159	3.435788	-1.294032
2	6	0	0.729121	-3.459739	0.179362	36	1	0	2.310245	3.432551	-1.293783
3	6	0	1.183194	-2.344441	-0.550001	37	1	0	4.158363	2.742085	-2.789240
4	6	0	-0.001090	-1.618249	-1.098286	38	1	0	4.089554	0.536029	-3.916765
5	6	0	-1.186577	-2.342598	-0.550070	39	1	0	2.194224	-1.015705	-3.489667
6	6	0	-2.549962	-2.050721	-0.552398	40	1	0	-4.490560	-2.648745	0.130855
7	6	0	-3.431442	-2.886053	0.131250	41	1	0	-3.678462	-4.649139	1.341094
8	6	0	-2.974832	-4.009064	0.818227	42	1	0	3.671543	-4.655076	1.340726
9	6	0	-1.613881	-4.297283	0.851518	43	1	0	4.486741	-2.655861	0.130645
10	6	0	1.607483	-4.299893	0.851369	44	6	0	0.001461	2.048167	0.606217
11	6	0	2.968888	-4.013829	0.817980	45	6	0	-1.251971	1.995903	1.402161
12	6	0	3.427244	-2.891478	0.131088	46	6	0	-2.120924	3.083243	1.488387
13	6	0	2.547029	-2.054691	-0.552400	47	1	0	-1.839285	4.018979	1.015128
14	6	0	-0.000195	-0.481628	-1.826505	48	1	0	-4.006296	3.824231	2.203366
15	6	0	-1.208788	0.330436	-2.140041	49	6	0	-3.335387	2.972682	2.153392
16	6	0	-1.222343	1.598317	-1.530666	50	6	0	-3.694687	1.758865	2.734672
17	6	0	0.001462	1.900839	-0.729748	51	1	0	-4.650399	1.656427	3.238599
18	6	0	1.224890	1.596601	-1.530530	52	6	0	-2.824293	0.680503	2.675284
19	6	0	1.209606	0.328722	-2.139885	53	1	0	-3.098645	-0.264006	3.136665
20	6	0	-2.227912	-0.039459	-3.010245	54	6	0	-1.577762	0.784438	2.042522
21	6	0	-3.290590	0.830954	-3.240612	55	6	0	-0.672966	-0.369162	2.083463
22	6	0	-3.326036	2.070176	-2.608869	56	6	0	1.254697	1.994283	1.402346
23	6	0	-2.290011	2.458223	-1.762053	57	6	0	2.125064	3.080488	1.488664
24	6	0	2.293776	2.455014	-1.761821	58	1	0	1.844743	4.016558	1.015281
25	6	0	3.329323	2.065537	-2.608562	59	6	0	3.339241	2.968357	2.153931
26	6	0	3.292192	0.826377	-3.240311	60	1	0	4.011270	3.819016	2.204006
27	6	0	2.228279	-0.042555	-3.010019	61	6	0	3.696806	1.754086	2.735343
28	1	0	-2.939407	-1.174539	-1.049672	62	1	0	4.652274	1.650419	3.239480
29	1	0	-1.244660	-5.151444	1.411313	63	6	0	2.825018	0.676848	2.675806
30	1	0	1.236980	-5.153536	1.411109	64	1	0	3.098044	-0.267996	3.137284
31	1	0	2.937737	-1.179045	-1.049642	65	6	0	1.578765	0.782401	2.042778
32	1	0	-2.195197	-1.012687	-3.489827	66	6	0	0.672455	-0.370025	2.083551
33	1	0	-4.088316	0.541713	-3.917112	67	1	0	1.162407	-1.333744	2.205016
34	1	0	-4.154116	2.747872	-2.789636	68	1	0	-1.164179	-1.332244	2.204878

Zero-point correction= 0.549208 (Hartree/Particle)
Thermal correction to Energy= 0.578779
Thermal correction to Enthalpy= 0.579724
Thermal correction to Gibbs Free Energy= 0.488994
Sum of electronic and zero-point Energies= -1615.087734
Sum of electronic and thermal Energies= -1615.058163
Sum of electronic and thermal Enthalpies= -1615.057219
Sum of electronic and thermal Free Energies= -1615.147948

Table S5. Cartesian Coordinates of $\mathbf{1}^{2+}$ ($C_{42}H_{26}$, total 68 atoms) (ωB97X-D/6-31G**).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.153857	-0.735127	-0.097168	35	6	0	5.241350	2.726572	-1.172743
2	6	0	-5.153835	0.735215	0.097285	36	6	0	4.341124	3.674964	-1.583666
3	6	0	-3.799355	1.149412	0.182255	37	6	0	2.962561	3.414020	-1.472662
4	6	0	-2.951396	0.000010	0.000067	38	6	0	2.529241	2.223552	-0.958256
5	6	0	-3.799389	-1.149373	-0.182097	39	6	0	2.529249	-2.223910	0.957462
6	6	0	-3.463762	-2.499124	-0.308664	40	6	0	2.962571	-3.414564	1.471435
7	6	0	-4.496363	-3.432354	-0.384050	41	6	0	4.341136	-3.675355	1.582783
8	6	0	-5.822848	-3.014618	-0.316543	42	6	0	5.241359	-2.726575	1.172752
9	6	0	-6.169181	-1.655570	-0.162955	43	1	0	-2.426062	-2.812153	-0.356006
10	6	0	-6.169127	1.655693	0.163061	44	1	0	-4.269173	-4.486358	-0.491019
11	6	0	-5.822747	3.014727	0.316680	45	1	0	-6.614452	-3.754437	-0.373576
12	6	0	-4.496250	3.432414	0.384231	46	1	0	-7.211290	-1.364643	-0.091123
13	6	0	-3.463680	2.499147	0.308859	47	1	0	-7.211245	1.364805	0.091205
14	6	0	-1.497637	0.000002	0.000032	48	1	0	-6.614327	3.754573	0.373708
15	6	0	-0.795980	-0.470323	-1.143219	49	1	0	-4.269024	4.486408	0.491220
16	6	0	0.638498	-0.474595	-1.131967	50	1	0	-2.425969	2.812136	0.356228
17	6	0	1.321999	-0.000012	-0.000022	51	1	0	2.425807	0.957313	2.278004
18	6	0	0.638550	0.474587	1.131952	52	1	0	1.217214	1.692756	4.272483
19	6	0	-0.795931	0.470329	1.143255	53	1	0	-1.271124	1.580754	4.338773
20	6	0	1.341734	0.939706	2.288003	54	1	0	-2.532175	0.796462	2.419342
21	6	0	0.671986	1.345223	3.402354	55	1	0	-2.532255	-0.796424	-2.419270
22	6	0	-0.746075	1.289381	3.435826	56	1	0	-1.271255	-1.580707	-4.338743
23	6	0	-1.453149	0.857517	2.351551	57	1	0	1.217082	-1.692740	-4.272515
24	6	0	-1.453228	-0.857493	-2.351507	58	1	0	2.425730	-0.957311	-2.278045
25	6	0	-0.746184	-1.289353	-3.435803	59	1	0	6.894209	-1.043316	0.449154
26	6	0	0.671878	-1.345210	-3.402369	60	1	0	6.894206	1.044405	-0.446617
27	6	0	1.341656	-0.939707	-2.288029	61	1	0	6.303806	2.926063	-1.257878
28	6	0	2.833960	-0.000011	-0.000013	62	1	0	4.689497	4.617650	-1.991006
29	6	0	3.425120	-1.194979	0.513310	63	1	0	2.241763	4.156148	-1.795963
30	6	0	4.834913	-1.479395	0.635744	64	1	0	1.464448	2.059814	-0.889544
31	6	0	5.908454	-0.624401	0.268890	65	1	0	1.464454	-2.060310	0.888435
32	6	0	5.908452	0.625101	-0.267254	66	1	0	2.241776	-4.156954	1.794141
33	6	0	4.834908	1.479577	-0.635305	67	1	0	4.689511	-4.618208	1.989732
34	6	0	3.425117	1.194929	-0.513394	68	1	0	6.303816	-2.925891	1.258283

Zero-point correction= 0.549893 (Hartree/Particle)
Thermal correction to Energy= 0.579931
Thermal correction to Enthalpy= 0.580876
Thermal correction to Gibbs Free Energy= 0.487973
Sum of electronic and zero-point Energies= -1614.544218
Sum of electronic and thermal Energies= -1614.514180
Sum of electronic and thermal Enthalpies= -1614.513236
Sum of electronic and thermal Free Energies= -1614.606138

Table S6. Cartesian Coordinates of **1**-T (open-shell singlet, $C_{42}H_{26}$, total 68 atoms) (UωB97X-D/6-31G**).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.174425	-0.729908	-0.075382
2	6	0	-5.174447	0.729888	0.075403
3	6	0	-3.819773	1.153252	0.125390
4	6	0	-2.963667	0.000022	0.000031
5	6	0	-3.819739	-1.153237	-0.125316
6	6	0	-3.507519	-2.509508	-0.253476
7	6	0	-4.547916	-3.428767	-0.339178
8	6	0	-5.880081	-3.007940	-0.292947
9	6	0	-6.201763	-1.654198	-0.158749
10	6	0	-6.201811	1.654152	0.158741
11	6	0	-5.880167	3.007900	0.292969
12	6	0	-4.548014	3.428760	0.339260
13	6	0	-3.507591	2.509529	0.253585
14	6	0	-1.493611	0.000039	0.000015
15	6	0	-0.785640	-0.405594	-1.151939
16	6	0	0.648088	-0.415667	-1.143807
17	6	0	1.351445	0.000029	-0.000017
18	6	0	0.648123	0.415747	1.143788
19	6	0	-0.785611	0.405683	1.151946
20	6	0	1.339840	0.840708	2.323163
21	6	0	0.660691	1.212019	3.443397
22	6	0	-0.760855	1.172180	3.463765
23	6	0	-1.457426	0.779013	2.360923
24	6	0	-1.457470	-0.778907	-2.360913
25	6	0	-0.760912	-1.172057	-3.463770
26	6	0	0.660635	-1.211899	-3.443428
27	6	0	1.339795	-0.840610	-2.323194
28	6	0	2.854332	0.000006	0.000018
29	6	0	3.457902	-1.240056	0.457286
30	6	0	4.853035	-1.532758	0.563972
31	6	0	5.942133	-0.628728	0.231218
32	6	0	5.942167	0.628731	-0.230766
33	6	0	4.853117	1.532704	-0.563830
34	6	0	3.457970	1.239992	-0.457364
35	6	0	5.262664	2.792225	-1.027431
36	6	0	4.371181	3.784796	-1.394678
37	6	0	3.008515	3.516341	-1.297941
38	6	0	2.575388	2.285938	-0.844490
39	6	0	2.575267	-2.286069	0.844108
40	6	0	3.008332	-3.516505	1.297530
41	6	0	4.370985	-3.784922	1.394560
42	6	0	5.262518	-2.792300	1.027573
43	1	0	-2.471680	-2.832327	-0.291767
44	1	0	-4.324173	-4.485685	-0.442128
45	1	0	-6.675849	-3.742900	-0.360547
46	1	0	-7.240380	-1.339312	-0.119591
47	1	0	-7.240418	1.339241	0.119547
48	1	0	-6.675956	3.742839	0.360548
49	1	0	-4.324302	4.485683	0.442232
50	1	0	-2.471761	2.832372	0.291920
51	1	0	2.424026	0.856427	2.307829
52	1	0	1.202418	1.530046	4.328260
53	1	0	-1.292607	1.450691	4.367900
54	1	0	-2.540039	0.740381	2.390252
55	1	0	-2.540083	-0.740275	-2.390229
56	1	0	-1.292680	-1.450556	-4.367900
57	1	0	1.202344	-1.529904	-4.328310
58	1	0	2.423982	-0.856323	-2.307857
59	1	0	6.926867	-1.062418	0.390627
60	1	0	6.926925	1.062463	-0.389917
61	1	0	6.329181	2.986221	-1.097683
62	1	0	4.730088	4.745211	-1.748558
63	1	0	2.276620	4.267383	-1.577035
64	1	0	1.509099	2.119437	-0.785473
65	1	0	1.508985	-2.119613	0.784840
66	1	0	2.276399	-4.267610	1.576355
67	1	0	4.729844	-4.745339	1.748484
68	1	0	6.329025	-2.986269	1.098045

Zero-point correction= 0.546304 (Hartree/Particle)
Thermal correction to Energy= 0.576407
Thermal correction to Enthalpy= 0.577351
Thermal correction to Gibbs Free Energy= 0.483368
Sum of electronic and zero-point Energies= -1615.059381
Sum of electronic and thermal Energies= -1615.029278
Sum of electronic and thermal Enthalpies= -1615.028334
Sum of electronic and thermal Free Energies= -1615.122317

Table S7. Cartesian Coordinates of **1**-T (triplet, $C_{42}H_{26}$, total 68 atoms) (UωB97X-D/6-31G**).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.174372	-0.730030	-0.074242
2	6	0	-5.174377	0.730036	0.074342
3	6	0	-3.819611	1.153417	0.123280
4	6	0	-2.963737	0.000018	-0.000024
5	6	0	-3.819603	-1.153391	-0.123282
6	6	0	-3.507127	-2.509715	-0.250149
7	6	0	-4.547422	-3.429181	-0.334974
8	6	0	-5.879633	-3.008420	-0.289342
9	6	0	-6.201549	-1.654534	-0.156779
10	6	0	-6.201561	1.654525	0.156947
11	6	0	-5.879656	3.008417	0.289475
12	6	0	-4.547448	3.429198	0.335006
13	6	0	-3.507145	2.509748	0.250112
14	6	0	-1.493379	0.000020	-0.000035
15	6	0	-0.785688	-0.402474	-1.152948
16	6	0	0.648081	-0.412405	-1.144965
17	6	0	1.351314	0.000001	-0.000070
18	6	0	0.648118	0.412428	1.144847
19	6	0	-0.785656	0.402512	1.152860
20	6	0	1.339684	0.834203	2.325511
21	6	0	0.660332	1.202994	3.446409
22	6	0	-0.761327	1.163970	3.466268
23	6	0	-1.457780	0.773752	2.362374
24	6	0	-1.457831	-0.773706	-2.362454
25	6	0	-0.761396	-1.163915	-3.466362
26	6	0	0.660264	-1.202945	-3.446533
27	6	0	1.339633	-0.834172	-2.325640
28	6	0	2.854292	-0.000028	-0.000066
29	6	0	3.457811	-1.241480	0.453282
30	6	0	4.852973	-1.534598	0.558899
31	6	0	5.942063	-0.629556	0.228913
32	6	0	5.942089	0.629431	-0.228890
33	6	0	4.853034	1.534533	-0.558829
34	6	0	3.457862	1.241416	-0.453358
35	6	0	5.262586	2.795588	-1.018202
36	6	0	4.371115	3.789378	-1.382187
37	6	0	3.008455	3.520550	-1.286472
38	6	0	2.575305	2.288636	-0.837156
39	6	0	2.575215	-2.288696	0.837003
40	6	0	3.008319	-3.520566	1.286487
41	6	0	4.370969	-3.789358	1.382441
42	6	0	5.262476	-2.795603	1.018452
43	1	0	-2.471204	-2.832328	-0.288066
44	1	0	-4.323599	-4.486189	-0.436816
45	1	0	-6.675305	-3.743546	-0.356264
46	1	0	-7.240229	-1.339764	-0.118359
47	1	0	-7.240240	1.339741	0.118603
48	1	0	-6.675334	3.743531	0.356449
49	1	0	-4.323633	4.486210	0.436824
50	1	0	-2.471225	2.832375	0.287958
51	1	0	2.423884	0.849611	2.310476
52	1	0	1.201917	1.518667	4.332201
53	1	0	-1.293133	1.440945	4.370843
54	1	0	-2.540470	0.735987	2.390963
55	1	0	-2.540522	-0.735946	-2.391025
56	1	0	-1.293221	-1.440886	-4.370927
57	1	0	1.201829	-1.518603	-4.332344
58	1	0	2.423833	-0.849578	-2.310608
59	1	0	6.926800	-1.063821	0.386735
60	1	0	6.926843	1.063643	-0.386745
61	1	0	6.329103	2.989826	-1.087768
62	1	0	4.730032	4.750969	-1.732850
63	1	0	2.276562	4.272487	-1.563154
64	1	0	1.509008	2.121977	-0.778886
65	1	0	1.508924	-2.122076	0.778523
66	1	0	2.276397	-4.272503	1.563092
67	1	0	4.729850	-4.750895	1.733287
68	1	0	6.328987	-2.989832	1.088152

Zero-point correction= 0.546349 (Hartree/Particle)
Thermal correction to Energy= 0.576447
Thermal correction to Enthalpy= 0.577391
Thermal correction to Gibbs Free Energy= 0.482423
Sum of electronic and zero-point Energies= -1615.059285
Sum of electronic and thermal Energies= -1615.029187
Sum of electronic and thermal Enthalpies= -1615.028243
Sum of electronic and thermal Free Energies= -1615.123212