Electronic Supplementary Material (ESI) for Chemical Science.

# Isomerism Tunes the Diradical Character of DifluorenoPyrroles at Constant Hückel-level Antiaromaticity

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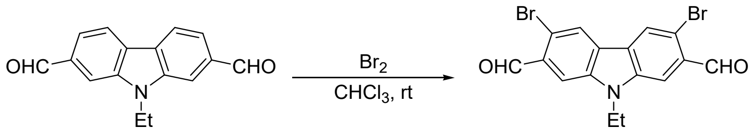
## Experimental Details: Synthesis of Compounds

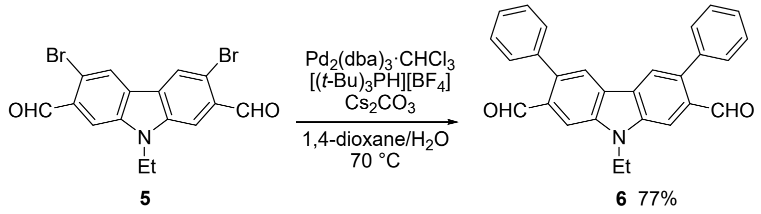
**General procedures.** All air-sensitive manipulations were carried out under inert nitrogen gas. Compound **9** was synthesized according to the literature procedures.[1] An oil bath was used as the heat source. Column chromatography was carried out using $SiO_2$. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with $SiO_2$ 60 $F_{254}$. Recycling gel-permeation chromatography (JAIGEL LC-918 and LaboACE LC-5060) was performed with UV detectors using 1H and 2H polystyrene columns eluted with $CHCl_3$. Melting points (M.p.) were measured with a capillary tube (Stanford Research Systems OPTiMelt MPA100). $^1$H and $^{13}$C NMR spectra were recorded on a spectrometer (JEOL JNM-ECS400) at 400 MHz for $^1$H and 100 MHz for $^{13}$C. $CDCl_3$ and $CD_2Cl_2$ were used as a solvent, and the residual solvent signal in the $^1$H and $^{13}$C NMR spectra was used as an internal reference. To avoid the effect of DCl on spectral broadening, $Et_3N$ was included in $CDCl_3$. HRMS (Thermo Fisher Scientific LTQ Orbitrap XL) spectrometric analyses were conducted in a positive mode. Electronic absorption (JASCO V-670 or JV-550) spectra were measured in a cuvette of 1 cm at room temperature.



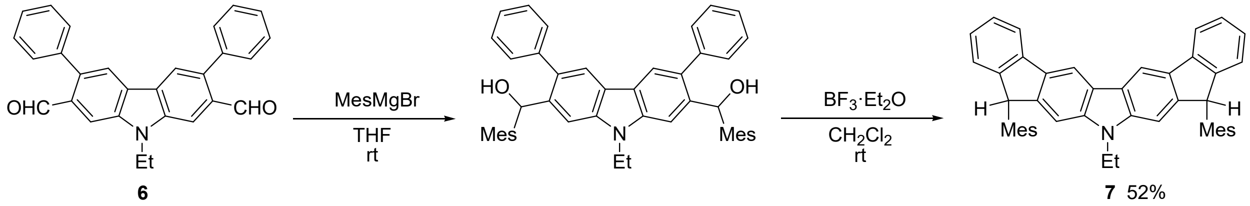
**8**

**5** *ca.* 91%

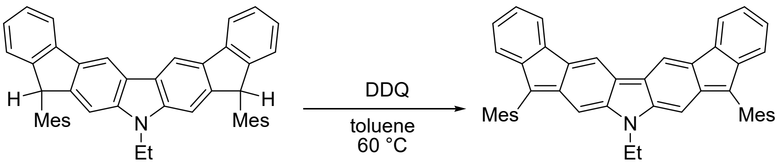
**Preparation of dibromide 5.** Bromine (0.30 mL, 3.87 mmol, 3.0 equiv) was added to a solution of diformylcarbazole **8** (1.0 g, 3.98 mmol, 1.0 equiv) in $CHCl_3$ (5 mL) under a nitrogen atmosphere. After the mixture was stirred at room temperature for 0.5 h, the resulting mixture was evaporated under reduced pressure. The residue was suspended with saturated aqueous $Na_2S_2O_3$ (100 mL), and the precipitate was collected by filtration and washed with $CH_3OH$ to give **5** (1.47 g, 3.62 mmol, *ca.* 91 %) including some impurities as a yellow solid. Dibromide **5** was used without further purification. M.p. 120-122 °C. $^1$H NMR ($CDCl_3/Et_3N$, 400 MHz): $\delta$ 10.2 (s, 2H), 8.34 (s, 2H), 8.05 (s, 2H), 4.51 (q, 2H, $J = 7.4$ Hz), 1.50 (t, 3H, $J = 7.4$ Hz) ppm. $^{13}$C NMR ($CDCl_3/Et_3N$, 100 MHz, 50 °C): $\delta$ 192.50, 141.09, 132.43, 127.29, 126.77, 116.96, 111.07, 38.91, 14.40 ppm (9 signals out of 9 expected). UV–vis ($CH_2Cl_2$): $\lambda^{abs}$ (relative intensity) 281 (1.0), 316 (0.67), 358 (0.58), 430 (0.08), 454 (0.07) nm. HRMS (APCI, positive): $m/z$ calcd for $C_{16}H_{11}Br_2NO_2$ 408.9151, found 408.9132 [$M^+$].



**Preparation of dialdehyde 6**. A solution of dibromide **5** (1.0 g, 2.46 mmol, 1.0 equiv), phenylboronic acid (900 mg, 7.38 mmol, 3.0 equiv), $Cs_2CO_3$ (2.4 g, 7.38 mmol, 3.0 equiv), $Pd_2(dba)_3·CHCl_3$ (120 mg, 0.12 mmol, 0.05 equiv) and $[(t\text{-Bu})_3PH][BF_4]$ (71 mg, 0.25 mmol, 0.1 equiv) in degassed 1,4-dioxane/$H_2O$ (10:1, 33 mL) was stirred at 70 °C for 12 h under a nitrogen atmosphere. The resulting mixture was evaporated under reduced pressure. The residue was suspended with $CH_2Cl_2$ and the suspension was filtered through a bed of Celite. The filtrate was evaporated under reduced pressure. The residue was purified by column chromatography ($SiO_2$; $CH_2Cl_2$) to give **6** (758 mg, 1.88 mmol, 77 %) as a yellow solid. M.p. 151–153 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 10.2 (s, 2H), 8.18 (d, 4H, $J$ = 8.0 Hz), 7.52–7.44 (m, 10H), 4.51 (q, 2H, $J$ = 7.4 Hz), 1.50 (t, 3H, $J$ = 7.4 Hz) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 192.88, 141.03, 138.59, 137.78, 132.88, 130.76, 128.55, 127.83, 126.48, 123.59, 108.10, 38.40, 14.24 ppm (13 signals out of 13 expected). UV–vis ($CH_2Cl_2$): $\lambda^{abs}$ (relative intensity): 284 (1.00), 310 (0.97), 348 (0.78), 429 (0.13), 440 (0.13) nm. HRMS (APCI, positive): $m/z$ calcd for $C_{28}H_{21}NO_2$ 403.1566, found 403.1571 [$M^+$].



**Preparation of dihydrodifluorenopyrrole 7**. A $Et_2O$ solution of mesitylmagnesium bromide (1.0 M, 12.0 mL, 12.0 mmol, 6.0 equiv) was added to a solution of dialdehyde **6** (700 mg, 1.98 mmol, 1.0 equiv) in THF (30 mL) at room temperature under a nitrogen atmosphere, and the mixture was stirred for 4 h. After addition of $H_2O$ (1.0 mL, 5.56 mmmol, 2.8 equiv), the organic layer was separated and concentrated under reduced pressure; the aqueous layer was extracted with $CH_2Cl_2$. The residue was diluted with the $CH_2Cl_2$ solution, and the resulting solution was washed with brine, dried over anhydrous $Na_2SO_4$, and evaporated under reduced pressure. The residue was purified by column chromatography ($SiO_2$; $CH_2Cl_2$/hexane 1:5 → pure $CH_2Cl_2$ → $CH_2Cl_2$/EtOAc 5:1) to give diol (881 mg, 1.37 mmol) as a white solid. $BF_3·OEt_2$ (2.20 mL, 18.3 mmol, 10 equiv) was added to a solution of the diol (881 mg, 1.37 mmol, 1.0 equiv) in $CH_2Cl_2$ (30 mL) at room temperature under a nitrogen atmosphere. After the mixture was stirred for 0.5 h, aqueous $NaHSO_3$ (5 %) was added. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (30 mL × 3). The combined organic layer was dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The residue was purified by recycling GPC to give **7** (613 mg, 1.01 mmol, 51 %) as a pale yellow solid. M.p. 170-172 °C. $^1$H NMR ($CDCl_3$, 400 MHz, diastereomer mixture): $\delta$ 8.61, 8.60 (2s, 2H), 7.96 (d, 2H, $J$ = 7.0 Hz), 7.42 (t, 2H, $J$ = 7.0 Hz), 7.20 (t, 2H, $J$ = 7.0 Hz), 7.19 (s, 4H), 7.06 (s, 2H), 6.67 (s, 2H), 5.64 (s, 2H), 4.22 (q, 2H, $J$ = 7.3 Hz), 2.74 (s, 6H), 2.30 (s, 6H), 1.11 (s, 6H), 1.29 (t, 3H, $J$ = 7.3 Hz) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 146.65, 146.29, 141.77, 141.73, 140.96, 138.36, 137.86, 136.29, 134.99, 133.17, 133.14, 130.73, 128.84, 127.02, 126.11, 124.13, 122.75, 119.26, 111.51, 104.32, 104.28, 49.87, 37.76, 22.80, 21.04, 19.07, 13.98, 13.89 ppm (28 signals out of 48 expected). UV–vis ($CH_2Cl_2$): $\lambda^{abs}$ (reactive intensity) 284 (0.90), 330 (1.00), 361 (0.36) nm. HRMS (APCI, positive): *m*/*z* calcd for $C_{46}H_{41}N$ 607.3233, found 607.3236 [$M^+$].

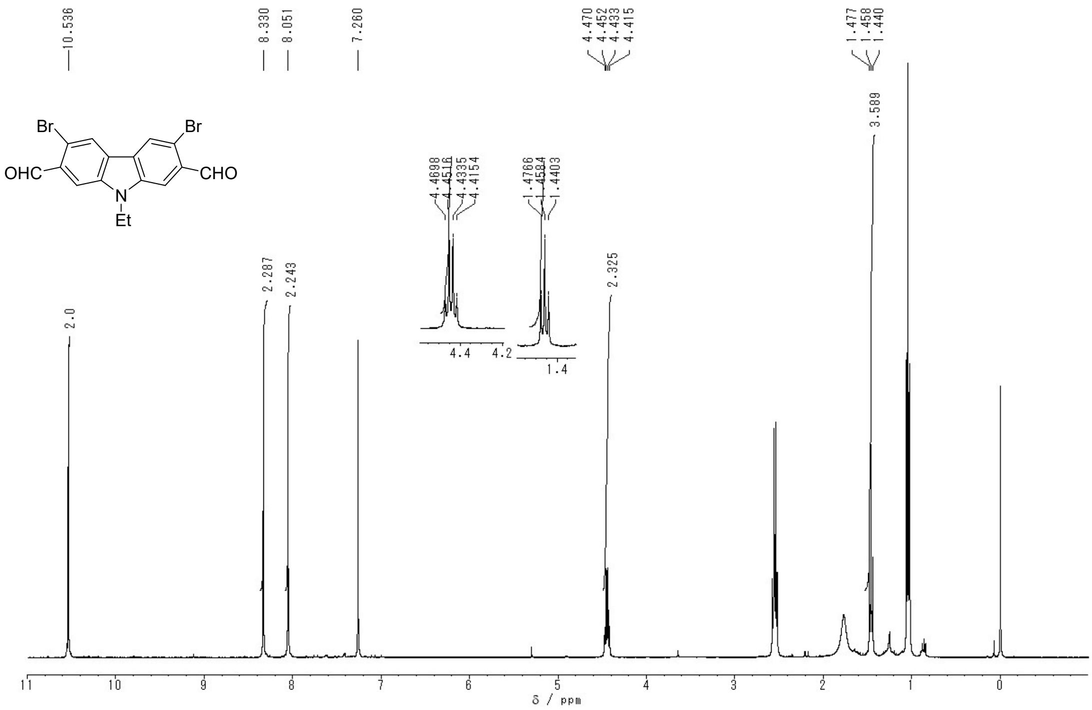


**7**

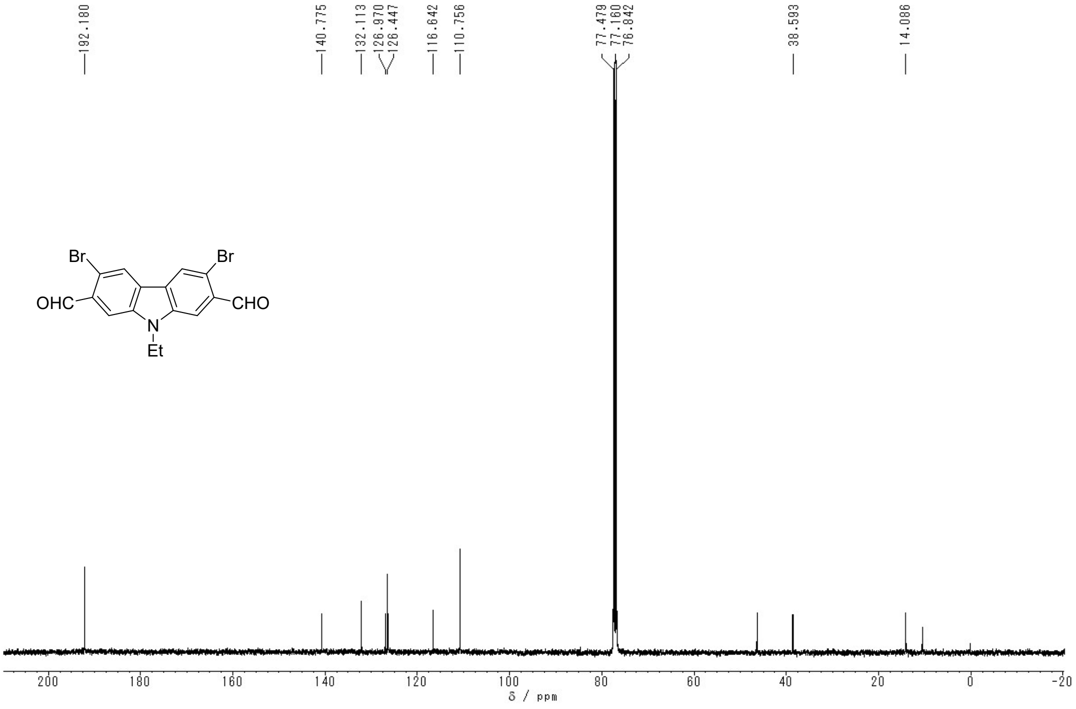
**DFPy-Iso** quant.

**Preparation of DFPy-Iso.** DDQ (28.0 mg, 0.123 mmol, 2.5 equiv) in degassed toluene (5 mL) was added into a degassed toluene (10 mL) of dihydrodifluorenopyrrole **7** (30 mg, 0.049 mmol, 1.0 equiv) under an argon atmosphere. The mixture was stirred at 60 °C for 1 h, and the resulting solution was evaporated under reduced pressure. The residue was purified by column chromatography ($SiO_2$; toluene/$Et_3N$ 100:1) to give DFPy-Iso (30 mg, 0.049 mmol, quant) as a bluish-purple solid; the solvents, namely toluene and $Et_3N$, were replaced with cyclohexane by evaporation followed by dilution, and the resulting cyclohexane solution of DFPy-Iso was evaporated to give its solid. M.p. 170-172 °C. $^1$H NMR ($CD_2Cl_2$/$Et_3N$, -80 °C, 400 MHz): $\delta$ 7.52 (s, 2H), 7.26 (d, 2H, $J$ = 7.6 Hz), 6.90 (s, 4H), 6.83-6.77 (m, 4H), 6.36 (br, 2H), 5.72 (s, 2H), 3.55 (br, 2H), 2.24 (s, 6H), 2.04 (s, 12H) ppm; the $CH_3$ protons in the Et group were not identified because their signals overlapped with those of cyclohexane and/or $Et_3N$. $^{13}$C NMR ($CD_2Cl_2$/$Et_3N$, -80 °C, 400 MHz): $\delta$ 167.56, 131.55 ppm (Only 2 signals were observed due to the relatively high diradical character). UV-vis (toluene/$Et_3N$ = 100:1): $\lambda^{abs}$ ($\varepsilon$) 398 (16300), 577 (34100), 829 (4750), 914 (5610), 1060 (3000) nm. HRMS (APCI, positive): *m*/*z* calcd for $C_{46}H_{39}N$ 605.3077, found 605.3081 [$M^+$].

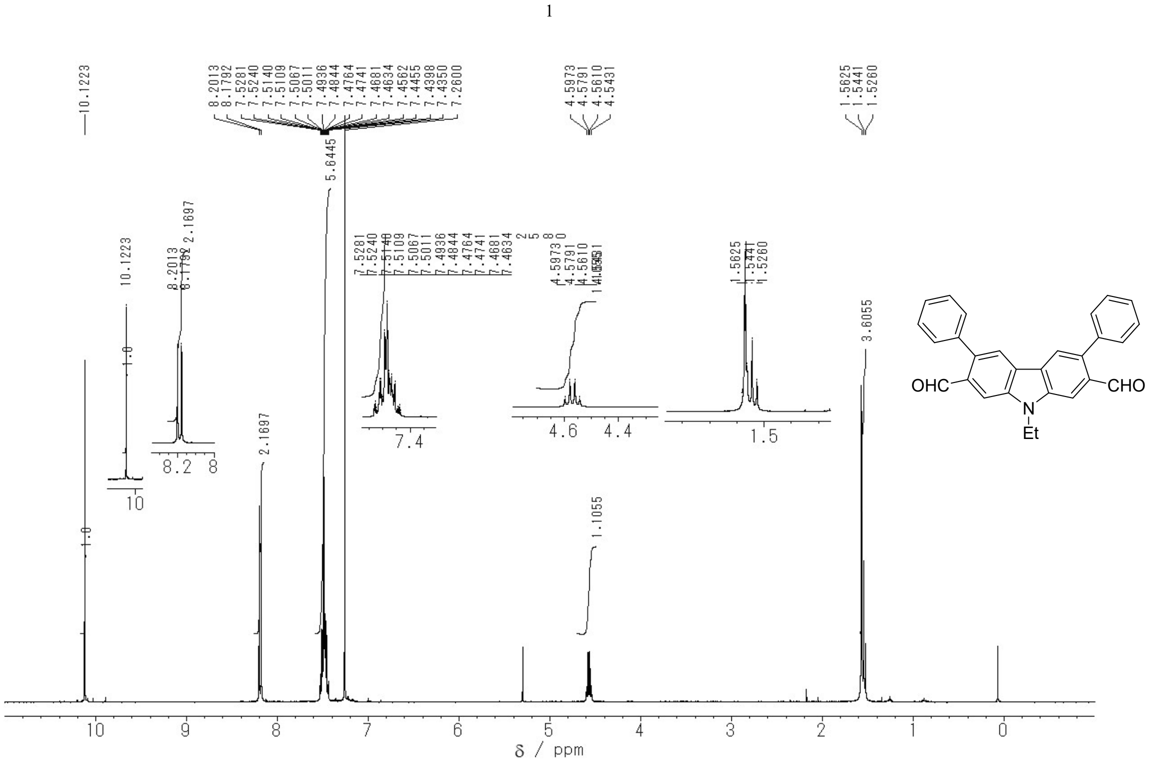
# Characterization of Compounds



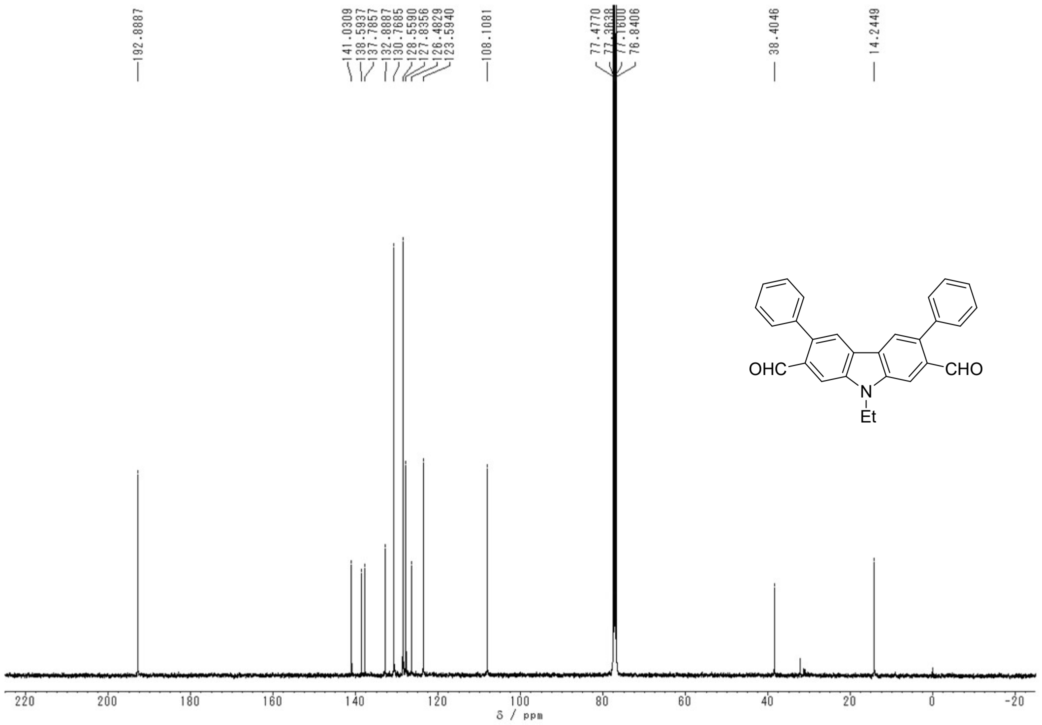
$^1$H NMR spectrum of **5** in $CDCl_3/Et_3N$ solution (400 MHz).



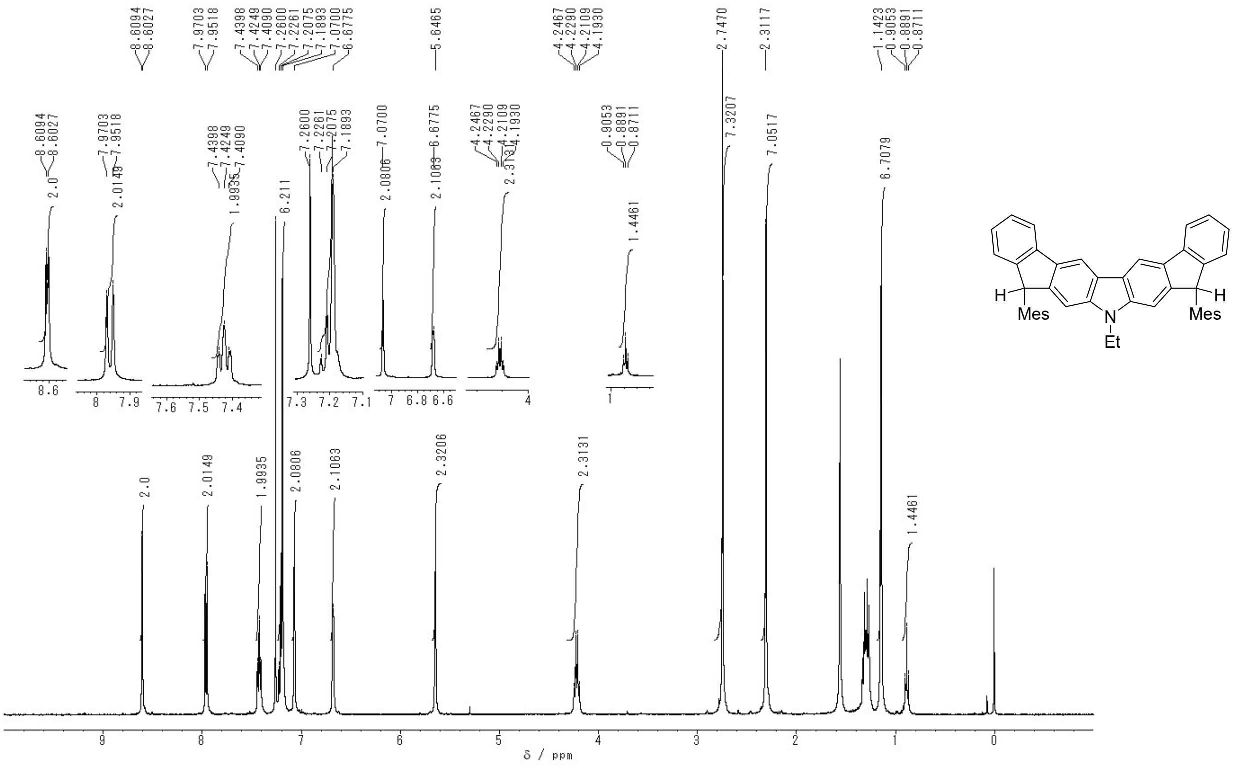
$^{13}$C NMR spectrum of **5** in $CDCl_3/Et_3N$ solution (100 MHz, 50 °C).



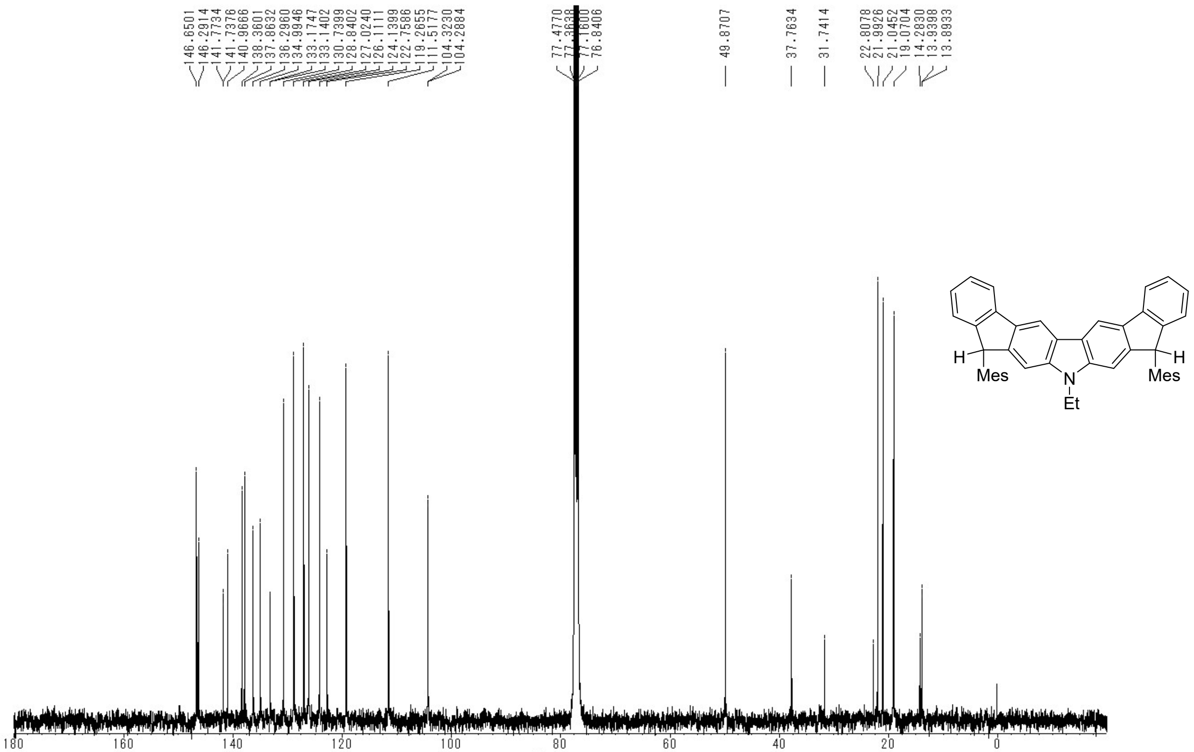
$^1$H NMR spectrum of **6** in CDCl$_3$ solution (400 MHz).



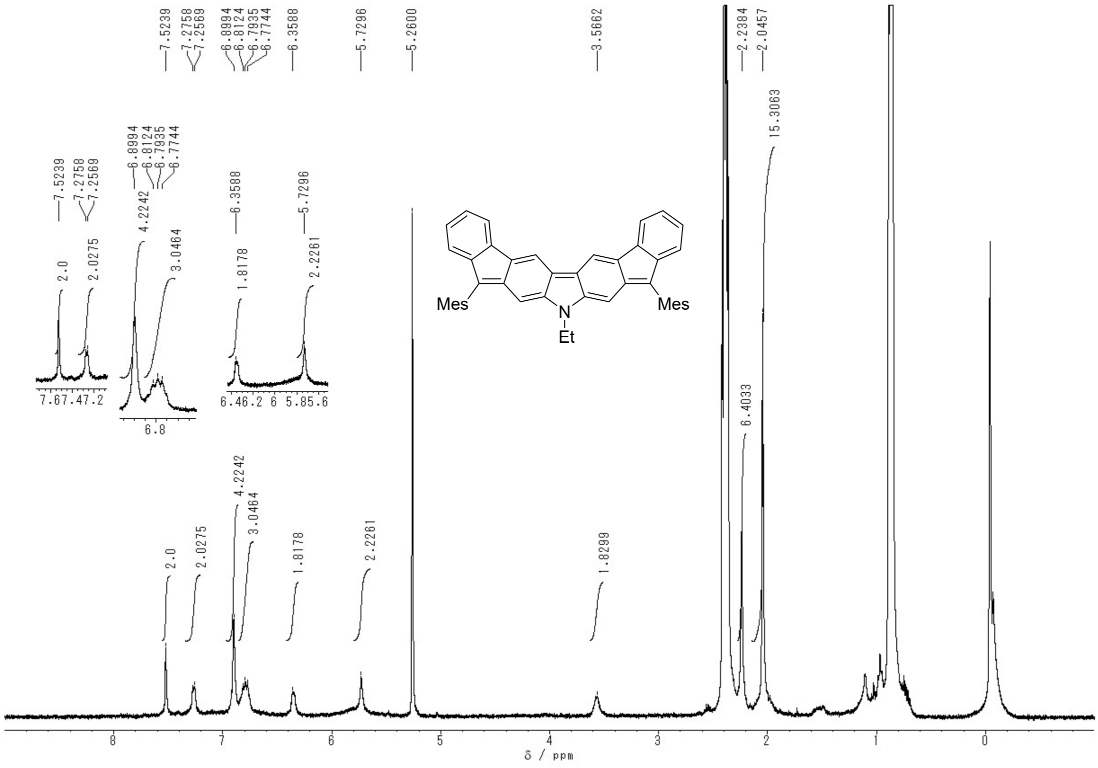
$^{13}$C NMR spectrum of **6** in CDCl$_3$ solution (100 MHz).



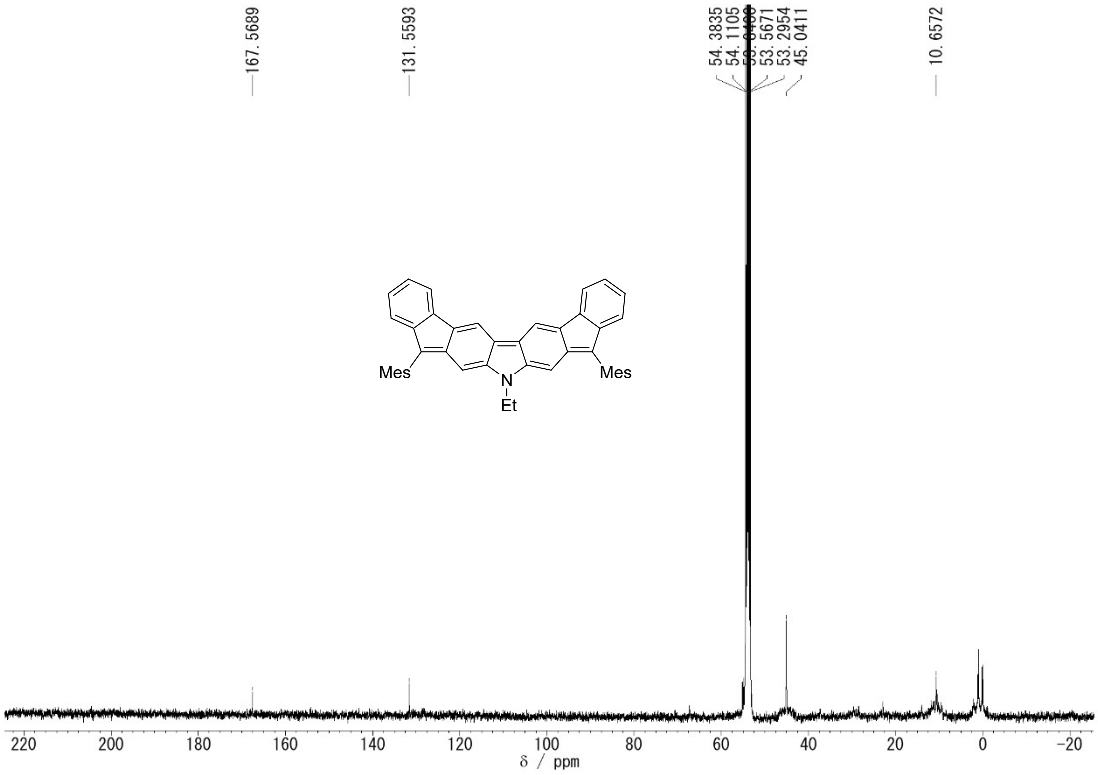
$^1$H NMR spectrum of **7** (diastereomer mixture) in CDCl$_3$ solution (400 MHz).



$^{13}$C NMR spectrum of **7** in CDCl$_3$ solution (100 MHz).



$^1$H NMR spectrum of DFPy-Iso **4** in $CD_2Cl_2/Et_3N$ solution (–80 °C, 400 MHz).



$^{13}$C NMR spectrum of DFPy-Iso **4** in $CD_2Cl_2/Et_3N$ solution (–80 °C, 400 MHz).
The signals at 45.04 and 10.65 ppm are ascribed to $Et_3N$.

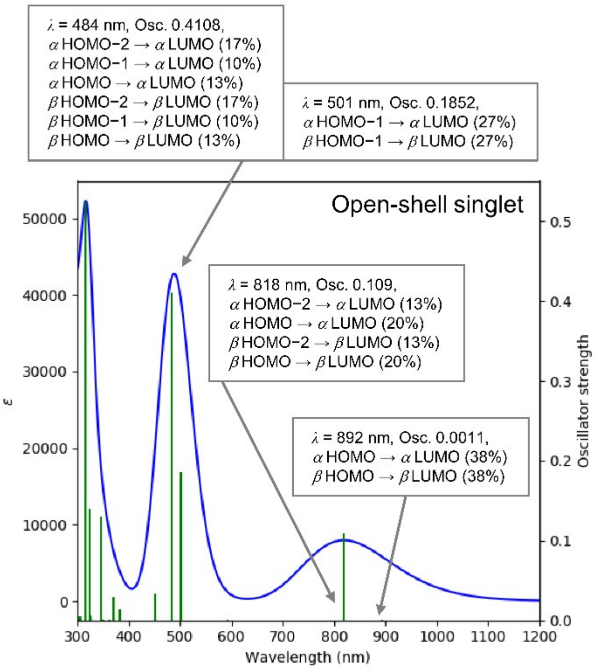
## Computational Details.

**General.** The gas-phase quantum chemical calculations were performed in order to investigate electronic structures of difluorenopyrrol isomers, i.e., DFPy-Iso-H and DFPy. In the first step, the optimized geometry was calculated by DFT methodology at the (U)B3LYP/6-311G* level of theory.

In this work, the Doehnert-Koutecký definition[2] has been used, $y_0$= $N_{LUMO}$, where $N_{LUMO}$ is the lowest unoccupied natural orbital occupation number.[2,3] In a second step, $N_{LUMO}$ were calculated in two ways, at (U)B3LYP/6-31G** level of theory and at the restricted active space spin-flip (RAS-SF) level of theory with 4 electrons in 4 orbitals in the active space and with the 6-31G** basis set. In order to investigate aromatic characters, we analyzed the nucleous-independent chemical shift values, NICS(1,7)[4], the aromaticity of induced current density (ACID) maps[5,6] and the magnetically induced current density analysis.[7] Magnetic responses were evaluated at the B3LYP/6-31G* level of theory.

## Time Dependent-DFT

Electronic excitation properties of neutrals were examined by the TD-UM06-2X/6-311+G** level of theory. The results are found to reproduce qualitatively the experimental UV-vis-NIR spectra of neutrals.


$\lambda$ = 484 nm, Osc. 0.4108,
$\alpha$ HOMO−2 → $\alpha$ LUMO (17%)
$\alpha$ HOMO−1 → $\alpha$ LUMO (10%)
$\alpha$ HOMO → $\alpha$ LUMO (13%)
$\beta$ HOMO−2 → $\beta$ LUMO (17%)
$\beta$ HOMO−1 → $\beta$ LUMO (10%)
$\beta$ HOMO → $\beta$ LUMO (13%)

$\lambda$ = 501 nm, Osc. 0.1852,
$\alpha$ HOMO−1 → $\alpha$ LUMO (27%)
$\beta$ HOMO−1 → $\beta$ LUMO (27%)

$\lambda$ = 818 nm, Osc. 0.109,
$\alpha$ HOMO−2 → $\alpha$ LUMO (13%)
$\alpha$ HOMO → $\alpha$ LUMO (20%)
$\beta$ HOMO−2 → $\beta$ LUMO (13%)
$\beta$ HOMO → $\beta$ LUMO (20%)

$\lambda$ = 892 nm, Osc. 0.0011,
$\alpha$ HOMO → $\alpha$ LUMO (38%)
$\beta$ HOMO → $\beta$ LUMO (38%)

**Figure S1.** Results of TD-DFT calculations for DFPy-Iso-H in the open-shell singlet ground states at the UM06-2X/6-311+G** level of theory.

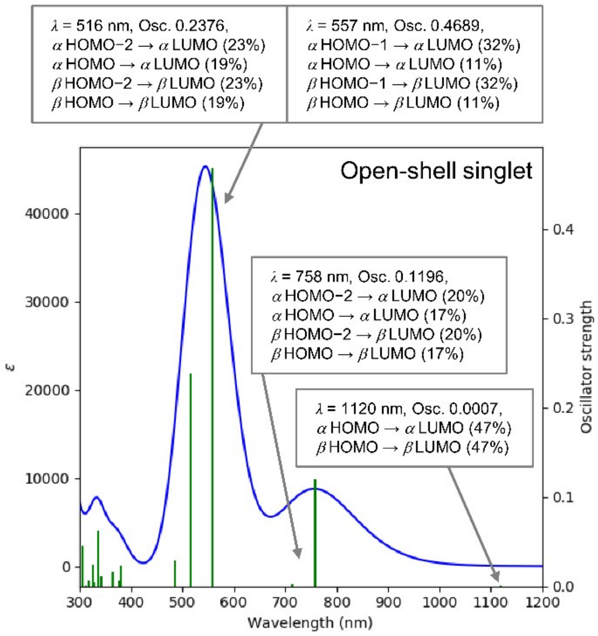


**Figure S2.** Results of TD-DFT calculations for DFPy in the open-shell singlet ground states at the UM06-2X/6-311+G** level of theory.

## Physicochemical Data

**Electrochemistry.** Cyclic voltammetry (EC Frontier ECstat-100) was performed using a cell equipped with a platinum wire working electrode, a platinum wire counter electrode, and an Ag/AgNO$_3$ reference electrode. All electrochemical measurements were performed in CH$_2$Cl$_2$ solution (*ca.* 0.5 mM) containing 0.1 M tetrabutyl ammonium hexafluorophosphate, [($n$-Bu)$_4$N][PF$_6$], at room temperature. All potentials are referenced to the ferrocenium/ferrocene (Fc$^+$/Fc) couple, which was used as a standard.

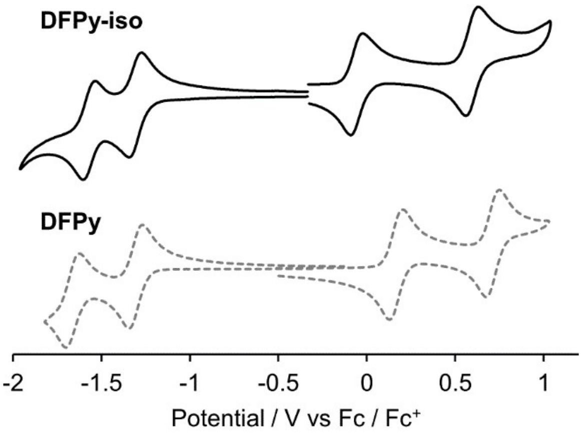


**Figure S3.** Cyclic voltammograms of DFPy-Iso as well as DFPy; scan rate: 100 mV s$^{-1}$; in CH$_2$Cl$_2$ with 0.1 M [($n$-Bu)$_4$N][PF$_6$].

Electrochemical experiments have been conducted in CH$_2$Cl$_2$ at room temperature by using 0.1 M [($n$-Bu)$_4$N][PF$_6$] as the supporting electrolyte. In situ UV-Vis-NIR spectroelectrochemical studies were conducted on the Varian Cary 5000 UV-Vis-NIR Spectrophotometer, respectively. A C3 epsilon potentiostat from BASi was used for the electrolysis using a thin layer cell from a demountable omni cell from Specac. In this cell, a three electrodes system was coupled to conduct in situ spectroelectrochemistry. A Pt gauze was used as the working electrode, a Pt wire was used as the counter electrode, and an Ag wire was used as the pseudo-reference electrode. The spectra were collected through a constant potential electrolysis and the potentials were changed in interval of 15 mV. The electrochemical medium used was 0.1 M [($n$-Bu)$_4$N][PF$_6$] in spectroscopic grade CH$_2$Cl$_2$, at room temperature with sample concentrations of 10$^{-3}$ M.

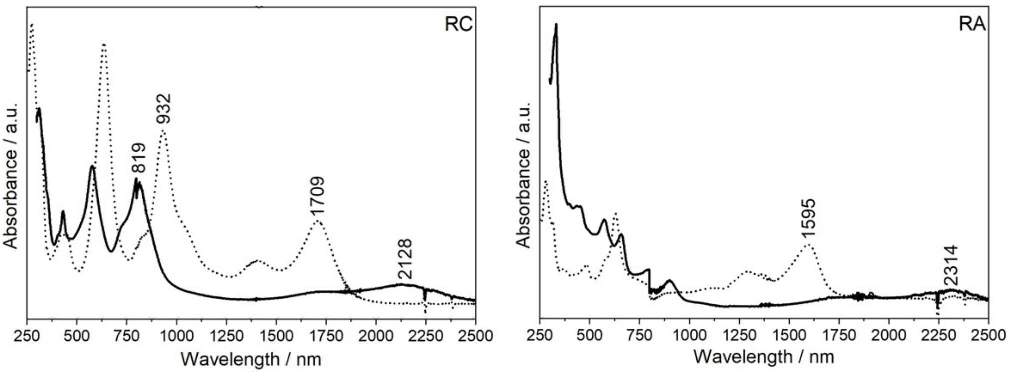


**Figure S4.** UV-Vis-NIR spectroelctrochemical reductions and oxidations in $CH_2Cl_2$ with 0.1 M $[(n\text{-Bu})_4N][PF_6]$ as the electrolyte at room temperature of DFPy **3** (broken lines) and and DFPy-Iso **4** (solid lines). RC: radical cation and RA: radical anion.

**Table S1.** Redox Potentials and Comproportionation Constants $K_c^{RC}$ and $K_c^{RA}$

| Cmpd. | $E_{ox}$ (V) [a] | $E_{red}$ (V) [a] | $\Delta E_{redox}$ (V) [b] | $K_c^{RC}$ [c] | $K_c^{RA}$ [d] |
|---|---|---|---|---|---|
| DFPy-Iso | –0.05<br>+0.60 | –1.32<br>–1.58 | 1.27 | $8.4 \times 10^{10}$ | $2.3 \times 10^4$ |
| DFPy | +0.17<br>+0.71 | –1.33<br>–1.66 | 1.50 | $1.2 \times 10^9$ | $7.6 \times 10^5$ |

[a] Scan rate 100 mV $s^{-1}$. [b] $\Delta E_{redox} = E^1_{ox} - E^1_{red}$. [c] Comproportionation constant for radical cation. [d] Comproportionation constant for radical anion.

## Temperature-dependent $^1$H NMR

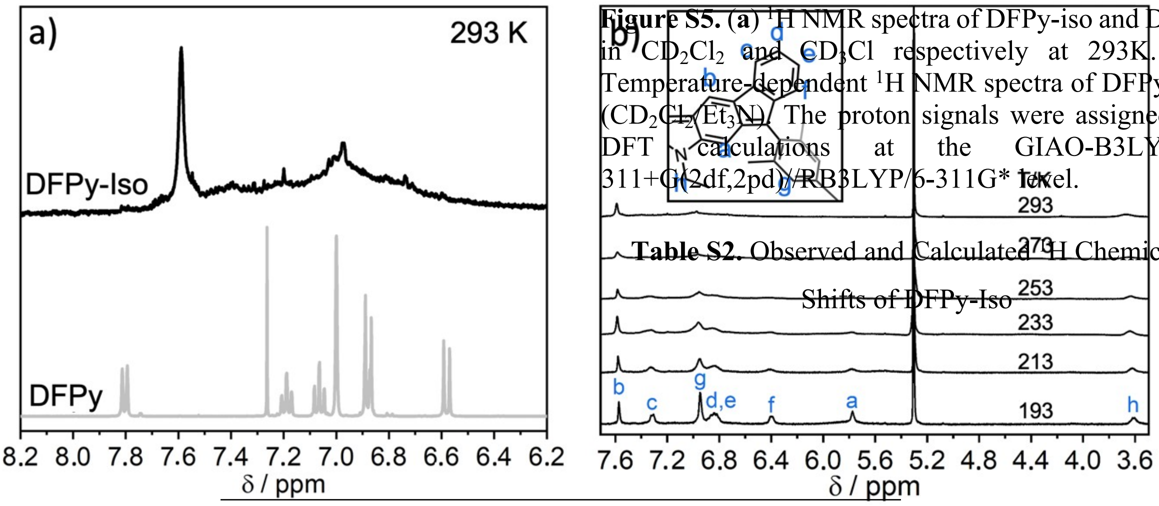


**Figure S5.** (**a**) $^1$H NMR spectra of DFPy-iso and DFPy in $CD_2Cl_2$ and $CD_3Cl$ respectively at 293K. (**b**) Temperature-dependent $^1$H NMR spectra of DFPy-Iso ($CD_2Cl_2$/$Et_3N$). The proton signals were assigned by DFT calculations at the GIAO-B3LYP/6-311+G(2df,2pd)//RB3LYP/6-311G* level.

**Table S2.** Observed and Calculated $^1$H Chemical Shifts of DFPy-Iso

| Positions | Observed [a] | Calculated [b]<br>B3LYP/6-311++G(2df,2pd) |
|---|---|---|
| a | 5.72 | 5.60 |
| b | 7.52 | 7.59 |
| c | 7.26 | 7.49 |
| d,e | 6.77–6.83 | 7.00, 7.02 |
| f | 6.36 | 6.51 |
| g | 6.90 | 7.29 |

[a] In $CD_2Cl_2$. [b] PCM model ($CH_2Cl_2$).

## Magnetic measurements

Variable temperature susceptibility measurements were carried out with a Quantum Design MPMS-XL-7 SQUID magnetometer, in the temperature range 4-400 K, with an applied magnetic field of 0.5 T, on polycrystalline samples of both compounds, sealed in glass capillaries under inert atmosphere. The samples were measured in heating and cooling scans at a scan rate of 2 K/min. The data (and the fits) were very similar in the cooling and heating scans. The susceptibility data were corrected for the empty glass capillary previously measured using the same conditions and for the diamagnetic contribution of the samples as deduced by using Pascal´s constant tables.[7]

## Geometry optimizations

Quantum chemical calculations were performed by Gaussian 16 package of ab initio MO calculations.[8]

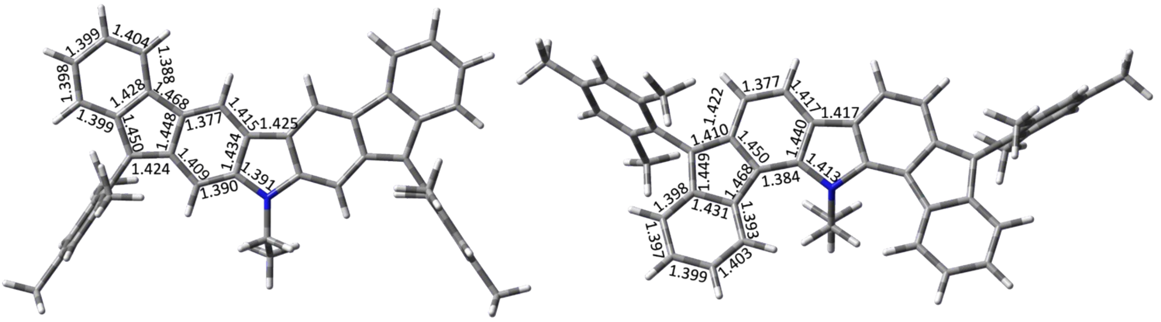
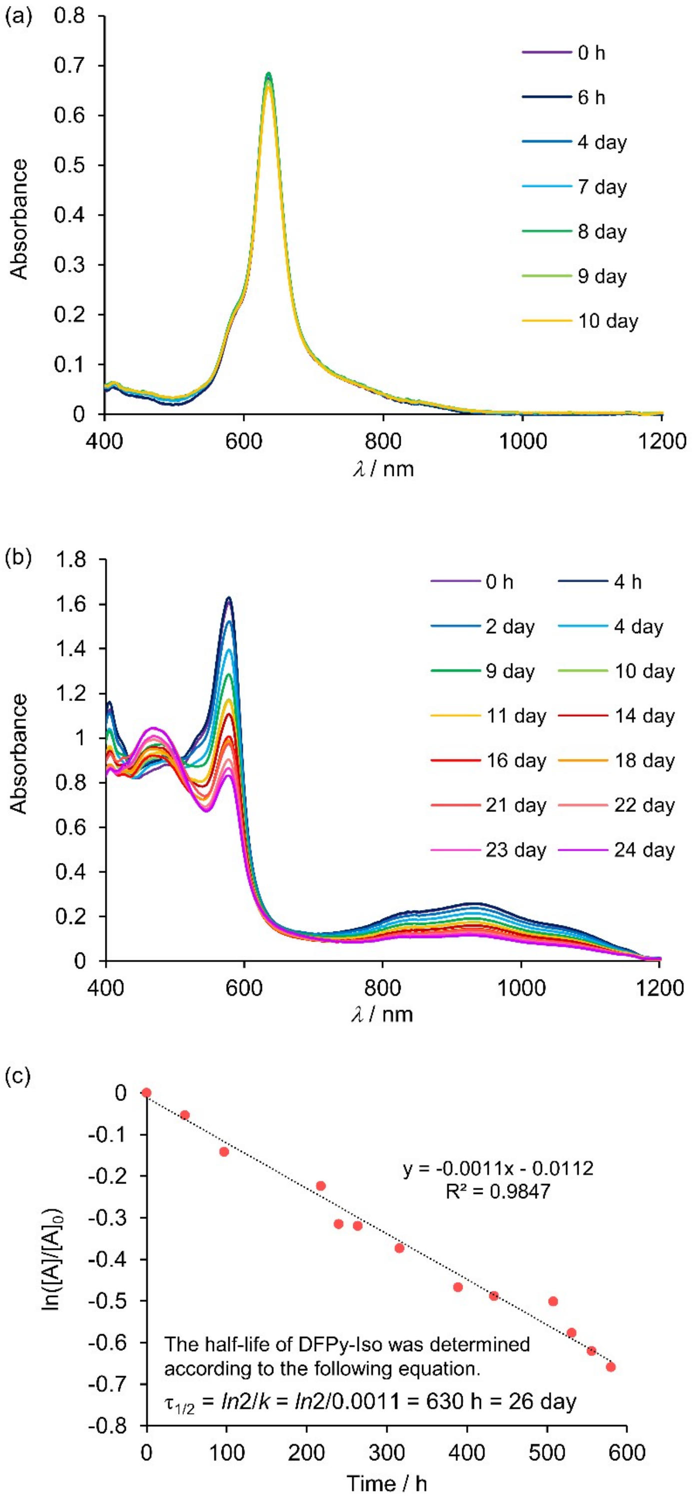


**Figure S6.** Optimized structures of DFPy-Iso (left) and DFPy (right) at the UB3LYP/6-31G** level of theory. Bond lengths (Å) from the calculated structures are in black.

# Stability studies



The half-life of DFPy-Iso was determined according to the following equation.

$\tau_{1/2} = ln2/k = ln2/0.0011 = 630$ h = 26 day

**Figure S7.** Absorbance–time profiles of (**a**) DFPy and (**b**) DFPy-Iso under protection from light in air-saturated $CH_2Cl_2$ at room temperature. (c) Time dependence of the electronic absorption of DFPy-Iso at 577 nm.

**Thermal gravimetric analysis.** Thermogravimetric analysis (TGA) was performed from 25–450 °C on samples of DFPy-Iso using a Rigaku Thermo Plus TG 8120 instrument. The measurements were performed under an oxygen-free dry $N_2$ flow.

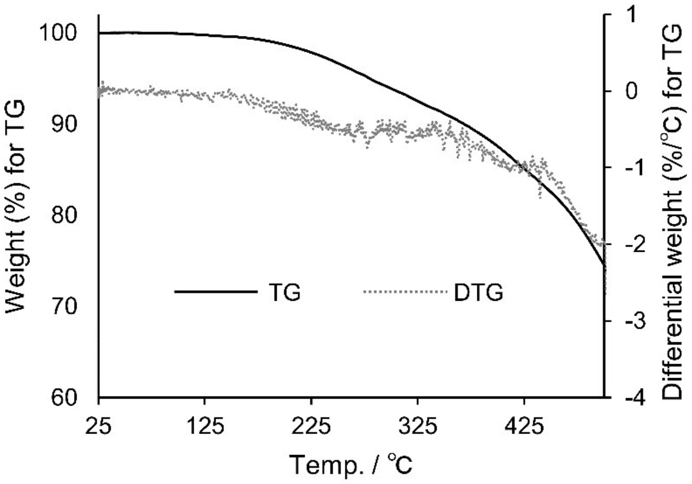


**Figure S8.** TGA plot for DFPy-Iso.

## ACID calculations

The anisotropy of current-induced density (ACID) plots were analyzed by the ACID 2.0.1 program provided by Prof. Rainer Herges (Institut für Organische Chemie, Universität Kiel).[5,6]

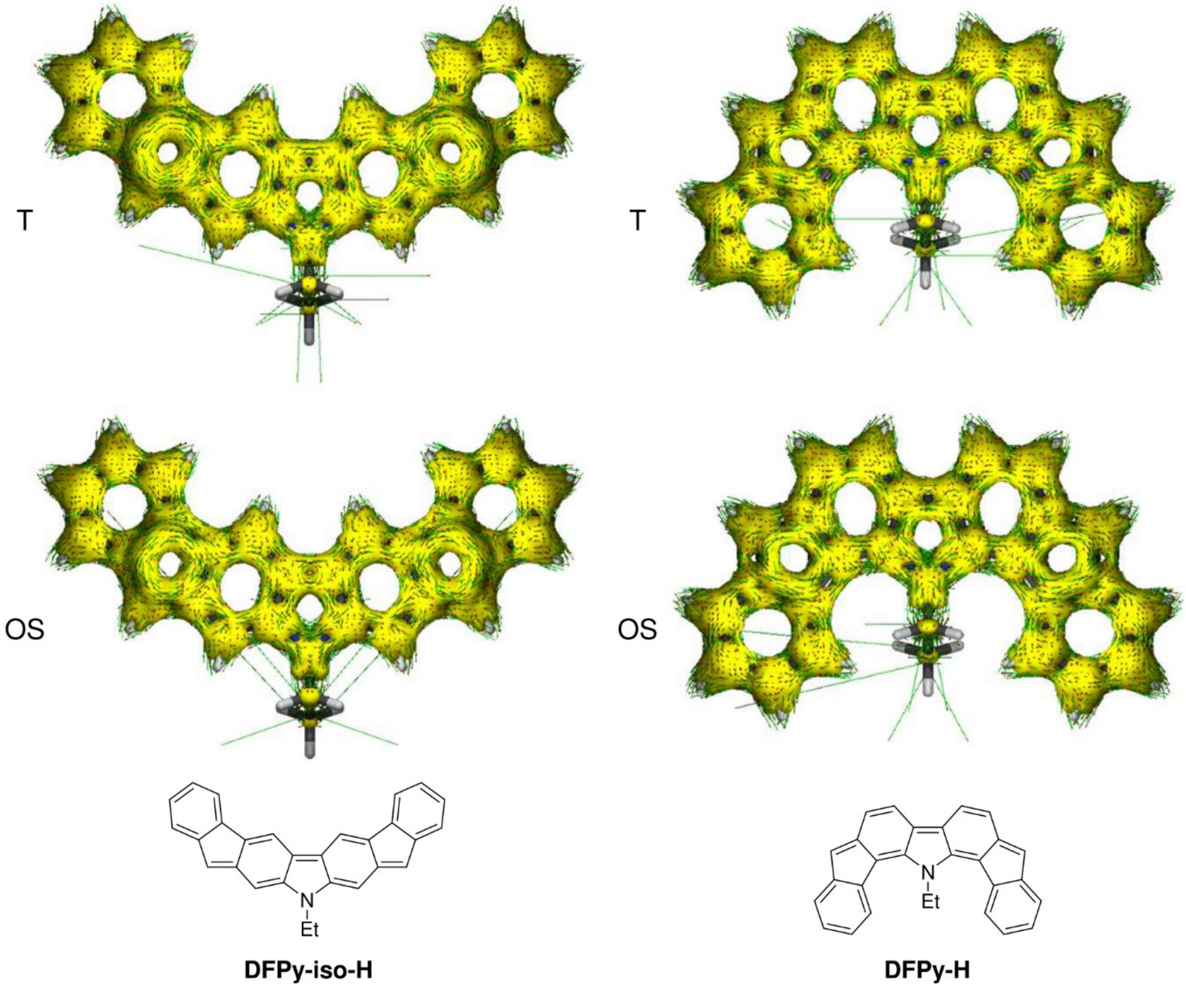


**Figure S9.** ACID plots for **DFPy-Iso-H** as well as **DFPy-H** in the open-shell singlet (OS) and the triplet states (T) calculated at the B3LYP/6-31G* level of theory.

## Magnetically induced current density calculations

The magnetically induced current density calculations[7] were performed with the GIMIC program[8] at the PBE0[9]/def2-TZVP[10] level of theory. This level of theory performs well in the ring current calculations, as shown in previous works.[11,12] For the calculations, the external magnetic field was oriented perpendicular to the molecular plane. The plots of the current density vectors were generated in planes at 0.0 and 0.5 Å above the molecular plane, commonly used in GIMIC calculations.[6] At 0.5 Å, local sigma contributions are minimized, making the π-circuits more visible. The Paraview5.10.0[13] program was employed to visualize the current density paths. Ring current strengths (RCS), a measure of the net current intensity around the molecular ring, were obtained for selected integration planes. The integration planes correspond to cut-off planes perpendicular to the selected bonds. The two-dimensional Gauss-Lobatto algorithm[8] was used to integrate the current passing through an integration plane. The current density analysis on the archetypal benzene molecule was also included for comparative purposes.

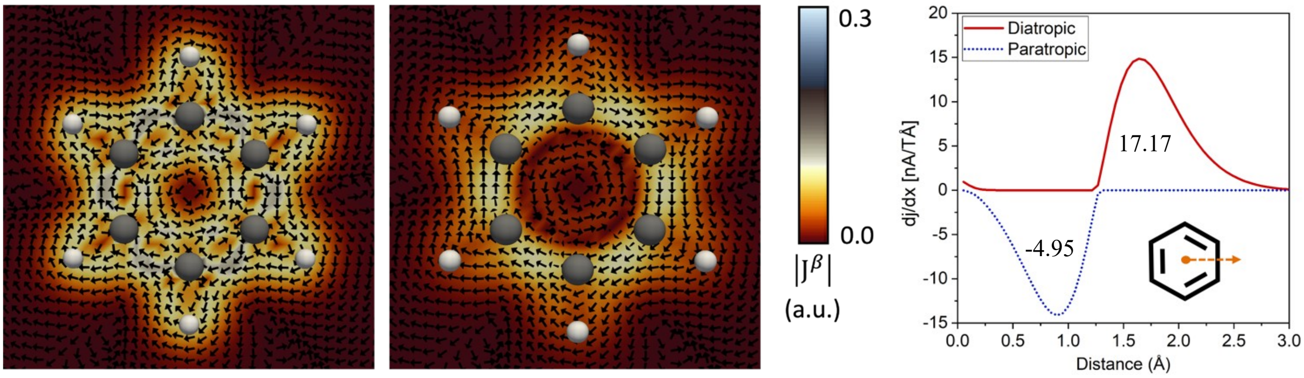
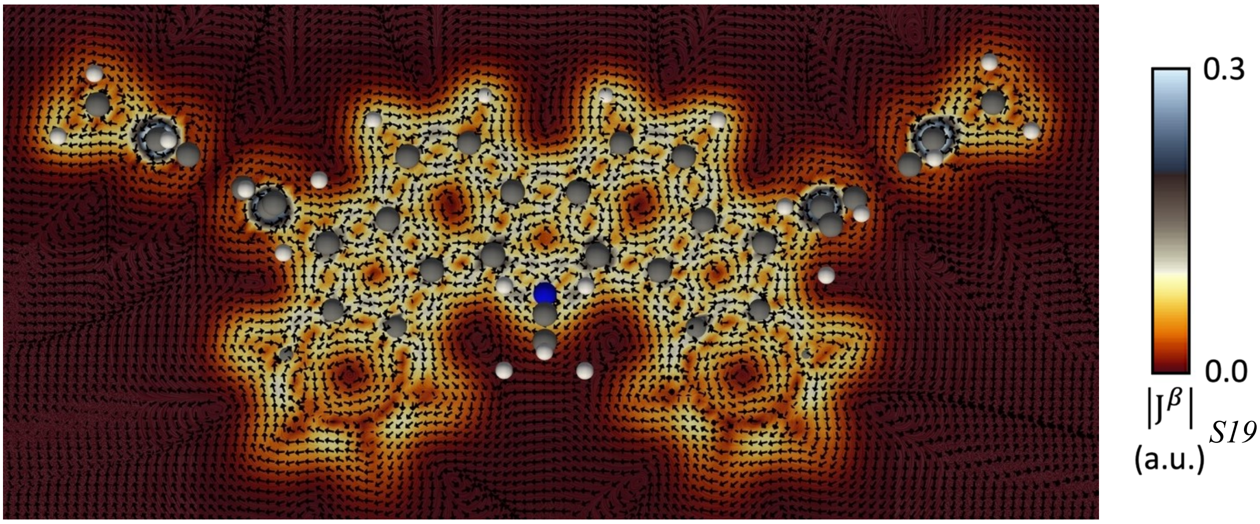


**Figure S10.** Current density vector plots at 0.0 (left) and 0.5Å (center) above the molecular plane for benzene. Current density values ($|J^{\beta}|$) values are given in atomic units (1 a.u. = 100.63 nA/T/Å$^2$). On the left, current strength profiles for the selected integration plane in bencene (right). A net RCS of 12.22 nA/T is obtained for benzene in line with previous studies.[6]

**3** SOS 0Å



**3** SOS 0.5Å

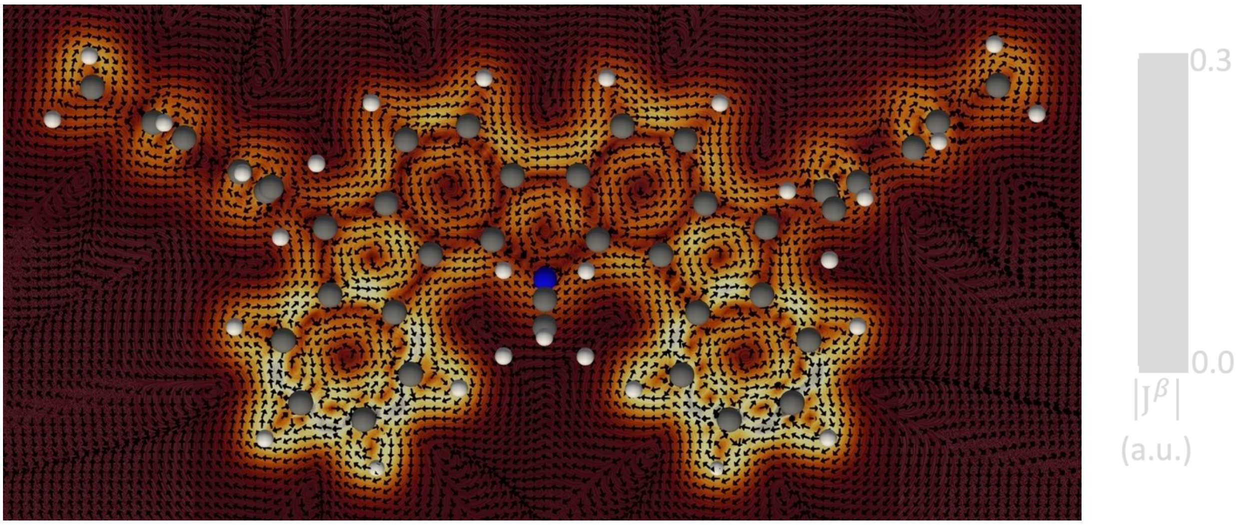
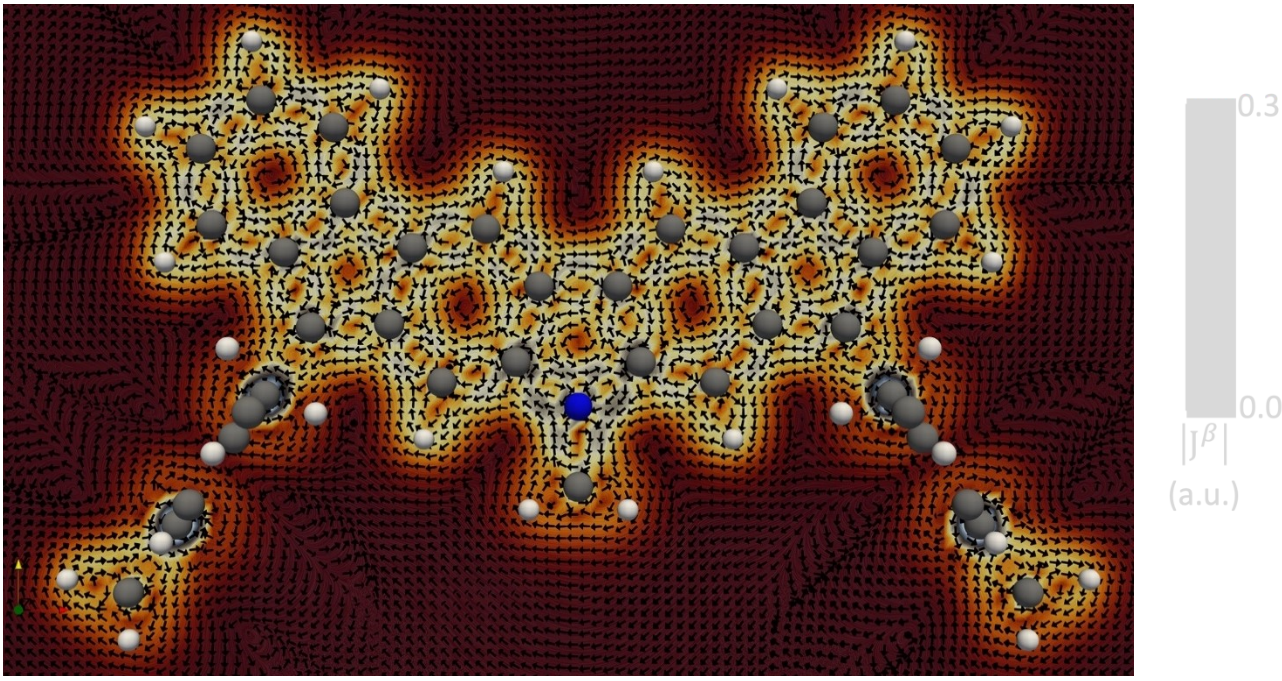


**Figure S11.** Current density vector plots at 0.0 (top) and 0.5 Å (bottom) above the molecular plane for the DFPy (**3**) isomer computed for the singlet open-shell configuration. Current density values ($|J^{\beta}|$) values are given in atomic units (1 a.u. = 100.63 nA/T/Å$^2$).

**4** SOS 0Å


0.3
0.0
|J$^\beta$|
(a.u.)

**4** SOS 0.5Å

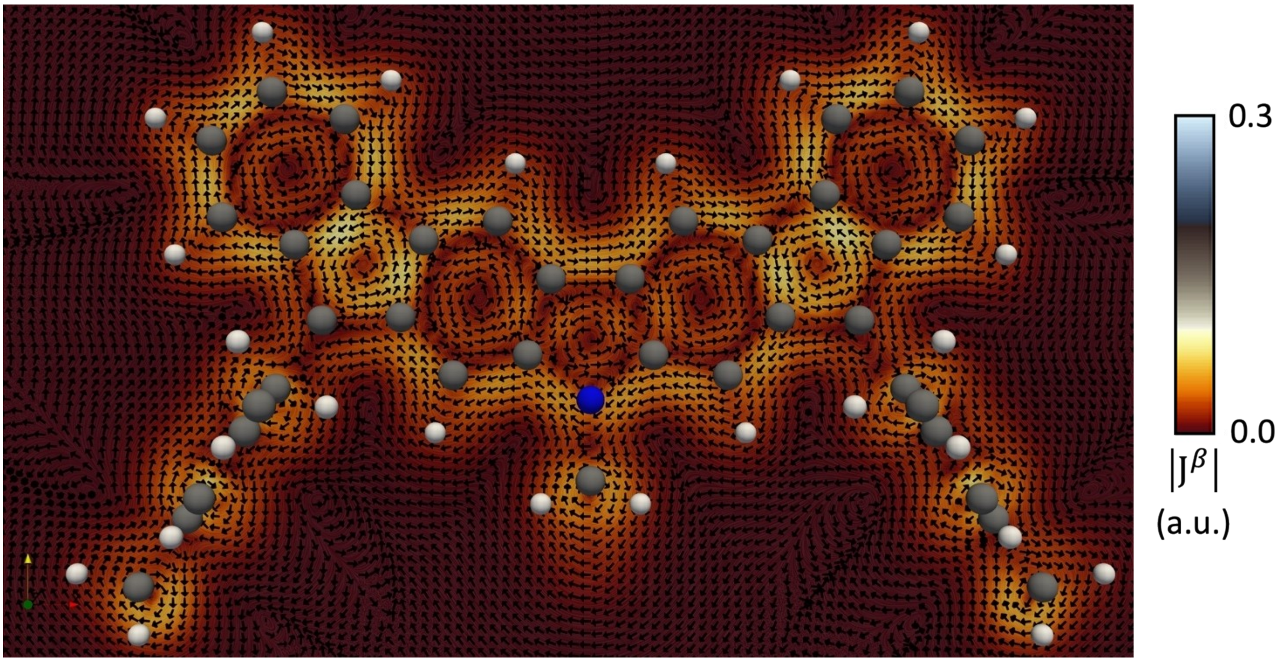

0.3
0.0
$|J^{\beta}|$
(a.u.)

**Figure S12.** Current density vector plots at 0.0 (top) and 0.5 Å (bottom) above the molecular plane for the DFPy-Iso (**4**) isomer computed for the singlet open-shell configuration. Current density values ($|J^{\beta}|$) values are given in atomic units (1 a.u. = 100.63 nA/T/Å²).

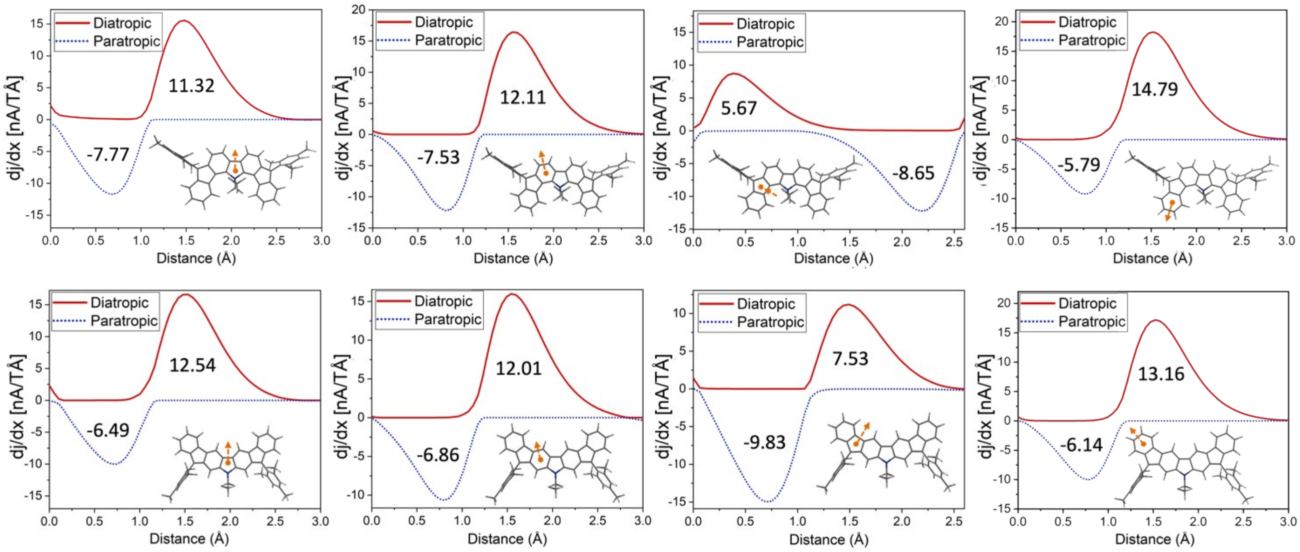


**Figure S13.** Profiles of the current strength corresponding to the selected planes to assess the RCS associated to selected bonds of the ring fused structure of DFPy (**3**) and DFPy-Iso (**4**). Insert: structures of **3** a **4** with the selected plane highlighted.

# Cartesian Coordinates

Cartesian Coordinates of DFPy-Iso at the B3LYP/6-311G* level.

| Center number | Atomic number | Atomic type | Coordinates (Å) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 6 | 0 | 0.291368 | -0.060902 | 1.135482 |
| 2 | 6 | 0 | -1.092472 | -0.053390 | 0.696545 |
| 3 | 6 | 0 | -1.092472 | -0.053390 | -0.696545 |
| 4 | 6 | 0 | 0.291368 | -0.060902 | -1.135482 |
| 5 | 7 | 0 | 1.095533 | -0.080649 | -0.000000 |
| 6 | 6 | 0 | 0.639773 | -0.049561 | 2.460352 |
| 7 | 6 | 0 | -0.419883 | -0.046275 | 3.418095 |
| 8 | 6 | 0 | -1.816904 | -0.040482 | 2.979919 |
| 9 | 6 | 0 | -2.146569 | -0.042843 | 1.658384 |
| 10 | 6 | 0 | -2.146569 | -0.042843 | -1.658384 |
| 11 | 6 | 0 | -1.816904 | -0.040482 | -2.979919 |
| 12 | 6 | 0 | -0.419883 | -0.046275 | -3.418095 |
| 13 | 6 | 0 | 0.639773 | -0.049561 | -2.460352 |
| 14 | 6 | 0 | 3.144118 | 1.347359 | -0.000000 |
| 15 | 6 | 0 | 2.548311 | -0.062794 | -0.000000 |
| 16 | 6 | 0 | -0.379032 | -0.032863 | 4.804516 |
| 17 | 6 | 0 | -1.755650 | -0.021377 | 5.301631 |
| 18 | 6 | 0 | -2.644895 | -0.027281 | 4.192617 |
| 19 | 6 | 0 | -2.644895 | -0.027281 | -4.192617 |
| 20 | 6 | 0 | -1.755650 | -0.021377 | -5.301631 |
| 21 | 6 | 0 | -0.379032 | -0.032863 | -4.804516 |
| 22 | 6 | 0 | -2.257719 | -0.022540 | 6.600200 |
| 23 | 6 | 0 | -3.645478 | -0.020885 | 6.788624 |
| 24 | 6 | 0 | -4.515027 | -0.022461 | 5.699737 |
| 25 | 6 | 0 | -4.015135 | -0.027737 | 4.388248 |
| 26 | 6 | 0 | -4.015135 | -0.027737 | -4.388248 |
| 27 | 6 | 0 | -4.515027 | -0.022461 | -5.699737 |
| 28 | 6 | 0 | -3.645478 | -0.020885 | -6.788624 |
| 29 | 6 | 0 | -2.257719 | -0.022540 | -6.600200 |
| 30 | 6 | 0 | 0.833837 | -0.035979 | 5.657810 |
| 31 | 6 | 0 | 1.541042 | -1.235184 | 5.880652 |
| 32 | 6 | 0 | 2.678266 | -1.213273 | 6.690962 |
| 33 | 6 | 0 | 3.136764 | -0.040124 | 7.289864 |
| 34 | 6 | 0 | 2.424401 | 1.136389 | 7.055071 |
| 35 | 6 | 0 | 1.281622 | 1.161377 | 6.254000 |

| | | | | | |
|---|---|---|---|---|---|
| 36 | 6 | 0 | 0.556668 | 2.465368 | 6.015800 |
| 37 | 6 | 0 | 1.079389 | -2.537438 | 5.268446 |
| 38 | 6 | 0 | 4.349304 | -0.047396 | 8.189083 |
| 39 | 6 | 0 | 0.833837 | -0.035979 | -5.657810 |
| 40 | 6 | 0 | 1.541042 | -1.235184 | -5.880652 |
| 41 | 6 | 0 | 2.678266 | -1.213273 | -6.690962 |
| 42 | 6 | 0 | 3.136764 | -0.040124 | -7.289864 |
| 43 | 6 | 0 | 2.424401 | 1.136389 | -7.055071 |
| 44 | 6 | 0 | 1.281622 | 1.161377 | -6.254000 |
| 45 | 6 | 0 | 0.556668 | 2.465368 | -6.015800 |
| 46 | 6 | 0 | 1.079389 | -2.537438 | -5.268446 |
| 47 | 6 | 0 | 4.349304 | -0.047396 | -8.189083 |
| 48 | 1 | 0 | 1.671676 | -0.033525 | 2.792596 |

Cartesian Coordinates of DFPy-Iso at the B3LYP/6-311G* level (Contin.).

| **Center number** | **Atomic number** | **Atomic type** | **Coordinates (Å)** | | |
|---|---|---|---|---|---|
| | | | **X** | **Y** | **Z** |
| 49 | 1 | 0 | -3.181545 | -0.034395 | 1.329969 |
| 50 | 1 | 0 | -3.181545 | -0.034395 | -1.329969 |
| 51 | 1 | 0 | 1.671676 | -0.033525 | -2.792596 |
| 52 | 1 | 0 | 4.236796 | 1.299842 | -0.000000 |
| 53 | 1 | 0 | 2.828928 | 1.906711 | -0.883755 |
| 54 | 1 | 0 | 2.828928 | 1.906711 | 0.883755 |
| 55 | 1 | 0 | 2.889978 | -0.623489 | 0.874154 |
| 56 | 1 | 0 | 2.889978 | -0.623489 | -0.874154 |
| 57 | 1 | 0 | -1.586245 | -0.027720 | 7.453113 |
| 58 | 1 | 0 | -4.048425 | -0.020338 | 7.796546 |
| 59 | 1 | 0 | -5.587382 | -0.022100 | 5.865547 |
| 60 | 1 | 0 | -4.702007 | -0.034216 | 3.546752 |
| 61 | 1 | 0 | -4.702007 | -0.034216 | -3.546752 |
| 62 | 1 | 0 | -5.587382 | -0.022100 | -5.865547 |
| 63 | 1 | 0 | -4.048425 | -0.020338 | -7.796546 |
| 64 | 1 | 0 | -1.586245 | -0.027720 | -7.453113 |
| 65 | 1 | 0 | 3.217573 | -2.141866 | 6.861638 |
| 66 | 1 | 0 | 2.769429 | 2.064421 | 7.504574 |
| 67 | 1 | 0 | 1.073385 | 3.295608 | 6.501546 |
| 68 | 1 | 0 | 0.481536 | 2.693068 | 4.948736 |
| 69 | 1 | 0 | -0.466524 | 2.437537 | 6.401240 |
| 70 | 1 | 0 | 1.157609 | -2.524837 | 4.177417 |
| 71 | 1 | 0 | 1.676116 | -3.374999 | 5.635602 |
| 72 | 1 | 0 | 0.031345 | -2.742373 | 5.503435 |
| 73 | 1 | 0 | 4.892499 | 0.899713 | 8.140246 |
| 74 | 1 | 0 | 4.065239 | -0.202851 | 9.235923 |
| 75 | 1 | 0 | 5.044745 | -0.846552 | 7.921276 |
| 76 | 1 | 0 | 3.217573 | -2.141866 | -6.861638 |
| 77 | 1 | 0 | 2.769429 | 2.064421 | -7.504574 |
| 78 | 1 | 0 | 0.481536 | 2.693068 | -4.948736 |
| 79 | 1 | 0 | 1.073385 | 3.295608 | -6.501546 |
| 80 | 1 | 0 | -0.466524 | 2.437537 | -6.401240 |
| 81 | 1 | 0 | 1.157609 | -2.524837 | -4.177417 |
| 82 | 1 | 0 | 0.031345 | -2.742373 | -5.503435 |
| 83 | 1 | 0 | 1.676116 | -3.374999 | -5.635602 |
| 84 | 1 | 0 | 4.892499 | 0.899713 | -8.140246 |
| 85 | 1 | 0 | 5.044745 | -0.846552 | -7.921276 |
| 86 | 1 | 0 | 4.065239 | -0.202851 | -9.235923 |

Cartesian Coordinates of DFPy at the B3LYP/6-311G* level.

| Center number | Atomic number | Atomic type | Coordinates (Å) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 7 | 0 | 1.110048 | 0.021781 | 0.000000 |
| 2 | 6 | 0 | 0.266383 | -0.034147 | 1.129124 |
| 3 | 6 | 0 | 0.575566 | -0.112747 | 2.460574 |
| 4 | 6 | 0 | 1.800333 | -0.286716 | 3.240518 |
| 5 | 6 | 0 | 3.115113 | -0.590882 | 2.903461 |
| 6 | 6 | 0 | 4.062480 | -0.755026 | 3.921096 |
| 7 | 6 | 0 | 3.700203 | -0.638504 | 5.265382 |
| 8 | 6 | 0 | 2.375062 | -0.384333 | 5.622515 |
| 9 | 6 | 0 | 1.425196 | -0.217893 | 4.615989 |
| 10 | 6 | 0 | -0.015145 | -0.054781 | 4.707381 |
| 11 | 6 | 0 | -0.523369 | -0.022695 | 3.416899 |
| 12 | 6 | 0 | -1.882654 | 0.060654 | 2.981296 |
| 13 | 6 | 0 | -2.178745 | 0.036061 | 1.648736 |
| 14 | 6 | 0 | -1.116412 | -0.003206 | 0.696855 |
| 15 | 6 | 0 | 2.174455 | 1.056273 | 0.000000 |
| 16 | 6 | 0 | -0.783022 | 0.010924 | 5.968092 |
| 17 | 6 | 0 | -0.738700 | 1.178183 | 6.755952 |
| 18 | 6 | 0 | -1.461025 | 1.219100 | 7.948578 |
| 19 | 6 | 0 | -2.223870 | 0.134846 | 8.384652 |
| 20 | 6 | 0 | -2.247172 | -1.014245 | 7.594041 |
| 21 | 6 | 0 | -1.540953 | -1.097918 | 6.392839 |
| 22 | 6 | 0 | 0.060806 | 2.377065 | 6.304586 |
| 23 | 6 | 0 | -3.023845 | 0.214545 | 9.661923 |
| 24 | 6 | 0 | -1.570508 | -2.371384 | 5.580619 |
| 25 | 6 | 0 | 0.266383 | -0.034147 | -1.129124 |
| 26 | 6 | 0 | 0.575566 | -0.112747 | -2.460574 |
| 27 | 6 | 0 | 1.800333 | -0.286716 | -3.240518 |
| 28 | 6 | 0 | 3.115113 | -0.590882 | -2.903461 |
| 29 | 6 | 0 | 4.062480 | -0.755026 | -3.921096 |
| 30 | 6 | 0 | 3.700203 | -0.638504 | -5.265382 |
| 31 | 6 | 0 | 2.375062 | -0.384333 | -5.622515 |
| 32 | 6 | 0 | 1.425196 | -0.217893 | -4.615989 |
| 33 | 6 | 0 | -0.015145 | -0.054781 | -4.707381 |
| 34 | 6 | 0 | -0.523369 | -0.022695 | -3.416899 |
| 35 | 6 | 0 | -1.882654 | 0.060654 | -2.981296 |
| 36 | 6 | 0 | -2.178745 | 0.036061 | -1.648736 |
| 37 | 6 | 0 | -1.116412 | -0.003206 | -0.696855 |
| 38 | 6 | 0 | -0.783022 | 0.010924 | -5.968092 |
| 39 | 6 | 0 | -0.738700 | 1.178183 | -6.755952 |
| 40 | 6 | 0 | -1.461025 | 1.219100 | -7.948578 |
| 41 | 6 | 0 | -2.223870 | 0.134846 | -8.384652 |
| 42 | 6 | 0 | -2.247172 | -1.014245 | -7.594041 |
| 43 | 6 | 0 | -1.540953 | -1.097918 | -6.392839 |
| 44 | 6 | 0 | 0.060806 | 2.377065 | -6.304586 |
| 45 | 6 | 0 | -3.023845 | 0.214545 | -9.661923 |
| 46 | 6 | 0 | -1.570508 | -2.371384 | -5.580619 |
| 47 | 6 | 0 | 1.616603 | 2.479766 | 0.000000 |
| 48 | 1 | 0 | 3.407063 | -0.742349 | 1.871002 |

Cartesian Coordinates of DFPy at the B3LYP/6-311G* level (contin.).

| **Center number** | **Atomic number** | **Atomic type** | **Coordinates (Å)** | | |
|---|---|---|---|---|---|
| | | | **X** | **Y** | **Z** |
| 49 | 1 | 0 | 5.089448 | -0.988865 | 3.659766 |
| 50 | 1 | 0 | 4.451079 | -0.770398 | 6.037755 |
| 51 | 1 | 0 | 2.077225 | -0.337124 | 6.665324 |
| 52 | 1 | 0 | -2.668112 | 0.122533 | 3.727403 |
| 53 | 1 | 0 | -3.206556 | 0.069194 | 1.303962 |
| 54 | 1 | 0 | 2.798358 | 0.900122 | 0.875991 |
| 55 | 1 | 0 | 2.798358 | 0.900122 | -0.875991 |
| 56 | 1 | 0 | -1.430274 | 2.123084 | 8.551878 |
| 57 | 1 | 0 | -2.824124 | -1.874071 | 7.925485 |
| 58 | 1 | 0 | 1.131234 | 2.156232 | 6.266081 |
| 59 | 1 | 0 | -0.083492 | 3.226255 | 6.975453 |
| 60 | 1 | 0 | -0.228153 | 2.687255 | 5.296324 |
| 61 | 1 | 0 | -4.024985 | 0.618269 | 9.474078 |
| 62 | 1 | 0 | -2.545312 | 0.866233 | 10.397328 |
| 63 | 1 | 0 | -3.152330 | -0.769625 | 10.119283 |
| 64 | 1 | 0 | -2.115422 | -2.240471 | 4.641450 |
| 65 | 1 | 0 | -2.049968 | -3.181139 | 6.134315 |
| 66 | 1 | 0 | -0.561535 | -2.694260 | 5.310508 |
| 67 | 1 | 0 | 3.407063 | -0.742349 | -1.871002 |
| 68 | 1 | 0 | 5.089448 | -0.988865 | -3.659766 |
| 69 | 1 | 0 | 4.451079 | -0.770398 | -6.037755 |
| 70 | 1 | 0 | 2.077225 | -0.337124 | -6.665324 |
| 71 | 1 | 0 | -2.668112 | 0.122533 | -3.727403 |
| 72 | 1 | 0 | -3.206556 | 0.069194 | -1.303962 |
| 73 | 1 | 0 | -1.430274 | 2.123084 | -8.551878 |
| 74 | 1 | 0 | -2.824124 | -1.874071 | -7.925485 |
| 75 | 1 | 0 | 1.131234 | 2.156232 | -6.266081 |
| 76 | 1 | 0 | -0.083492 | 3.226255 | -6.975453 |
| 77 | 1 | 0 | -0.228153 | 2.687255 | -5.296324 |
| 78 | 1 | 0 | -4.024985 | 0.618269 | -9.474078 |
| 79 | 1 | 0 | -2.545312 | 0.866233 | -10.397328 |
| 80 | 1 | 0 | -3.152330 | -0.769625 | -10.119283 |
| 81 | 1 | 0 | -2.115422 | -2.240471 | -4.641450 |
| 82 | 1 | 0 | -2.049968 | -3.181139 | -6.134315 |
| 83 | 1 | 0 | -0.561535 | -2.694260 | -5.310508 |
| 84 | 1 | 0 | 1.004602 | 2.662258 | -0.886317 |
| 85 | 1 | 0 | 1.004602 | 2.662258 | 0.886317 |
| 86 | 1 | 0 | 2.437182 | 3.202213 | 0.000000 |

Cartesian Coordinates of DFPy-Iso-H at the UB3LYP/6-311G* level (open-shell singlet)

| Center number | Atomic number | Atomic type | Coordinates (Å) | | |
|---|---|---|---|---|---|
| | | | X | Y | Z |
| 1 | 6 | 0 | -0.709879 | 0.230588 | -0.093608 |
| 2 | 6 | 0 | -1.131782 | 1.598674 | -0.186442 |
| 3 | 6 | 0 | 1.131699 | 1.598713 | -0.186428 |
| 4 | 6 | 0 | 0.709841 | 0.230612 | -0.093599 |
| 5 | 6 | 0 | -1.670233 | -0.806607 | -0.022967 |
| 6 | 6 | 0 | -2.999880 | -0.468200 | -0.041480 |
| 7 | 6 | 0 | -3.418875 | 0.918337 | -0.130578 |
| 8 | 6 | 0 | -2.470187 | 1.959156 | -0.201278 |
| 9 | 6 | 0 | 2.470093 | 1.959239 | -0.201246 |
| 10 | 6 | 0 | 3.418815 | 0.918452 | -0.130534 |
| 11 | 6 | 0 | 2.999865 | -0.468099 | -0.041443 |
| 12 | 6 | 0 | 1.670229 | -0.806551 | -0.022947 |
| 13 | 7 | 0 | -0.000055 | 2.402835 | -0.255286 |
| 14 | 6 | 0 | -0.000128 | 4.527479 | 1.057336 |
| 15 | 6 | 0 | -0.000081 | 3.855139 | -0.317929 |
| 16 | 6 | 0 | 4.827106 | 0.956910 | -0.124663 |
| 17 | 6 | 0 | 5.331316 | -0.388007 | -0.034003 |
| 18 | 6 | 0 | 4.219781 | -1.283439 | 0.018768 |
| 19 | 6 | 0 | -4.219769 | -1.283581 | 0.018719 |
| 20 | 6 | 0 | -5.331334 | -0.388187 | -0.034067 |
| 21 | 6 | 0 | -4.827167 | 0.956747 | -0.124723 |
| 22 | 6 | 0 | 6.635729 | -0.887159 | 0.006626 |
| 23 | 6 | 0 | 6.830133 | -2.266512 | 0.099601 |
| 24 | 6 | 0 | 5.740603 | -3.138755 | 0.151291 |
| 25 | 6 | 0 | 4.426655 | -2.649591 | 0.110847 |
| 26 | 6 | 0 | -4.426597 | -2.649740 | 0.110801 |
| 27 | 6 | 0 | -5.740529 | -3.138948 | 0.151231 |
| 28 | 6 | 0 | -6.830088 | -2.266742 | 0.099527 |
| 29 | 6 | 0 | -6.635730 | -0.887382 | 0.006548 |
| 30 | 1 | 0 | -1.350505 | -1.842200 | 0.045474 |
| 31 | 1 | 0 | -2.789239 | 2.994289 | -0.259916 |
| 32 | 1 | 0 | 2.789111 | 2.994383 | -0.259879 |
| 33 | 1 | 0 | 1.350535 | -1.842154 | 0.045489 |
| 34 | 1 | 0 | -0.000147 | 5.615941 | 0.949864 |
| 35 | 1 | 0 | 0.882959 | 4.243128 | 1.634018 |
| 36 | 1 | 0 | -0.883232 | 4.243093 | 1.633975 |
| 37 | 1 | 0 | -0.873370 | 4.165577 | -0.897400 |
| 38 | 1 | 0 | 0.873226 | 4.165610 | -0.897355 |
| 39 | 1 | 0 | 5.435391 | 1.851629 | -0.179662 |
| 40 | 1 | 0 | -5.435482 | 1.851446 | -0.179732 |
| 41 | 1 | 0 | 7.487485 | -0.214645 | -0.033165 |
| 42 | 1 | 0 | 7.838638 | -2.666258 | 0.131979 |
| 43 | 1 | 0 | 5.911645 | -4.207973 | 0.223418 |
| 44 | 1 | 0 | 3.590690 | -3.341823 | 0.151997 |
| 45 | 1 | 0 | -3.590610 | -3.341943 | 0.151962 |
| 46 | 1 | 0 | -5.911536 | -4.208172 | 0.223360 |
| 47 | 1 | 0 | -7.838580 | -2.666522 | 0.131894 |
| 48 | 1 | 0 | -7.487508 | -0.214898 | -0.033254 |

Cartesian Coordinates of DFPy-H at the UB3LYP/6-311G* level (open-shell singlet)

| **Center number** | **Atomic number** | **Atomic type** | **Coordinates (Å)** | | |
|---|---|---|---|---|---|
| | | | **X** | **Y** | **Z** |
| 1 | 6 | 0 | -0.698243 | 2.131168 | 0.058171 |
| 2 | 6 | 0 | -1.149039 | 0.755238 | -0.016707 |
| 3 | 6 | 0 | 1.149006 | 0.755165 | -0.016703 |
| 4 | 6 | 0 | 0.698271 | 2.131125 | 0.058197 |
| 5 | 6 | 0 | -1.600100 | 3.224644 | 0.095187 |
| 6 | 6 | 0 | -2.938591 | 2.975674 | 0.046898 |
| 7 | 6 | 0 | -3.404418 | 1.632379 | -0.019891 |
| 8 | 6 | 0 | -2.514530 | 0.471689 | -0.033635 |
| 9 | 6 | 0 | 2.514496 | 0.471560 | -0.033652 |
| 10 | 6 | 0 | 3.404420 | 1.632227 | -0.019768 |
| 11 | 6 | 0 | 2.938647 | 2.975536 | 0.047076 |
| 12 | 6 | 0 | 1.600168 | 3.224560 | 0.095294 |
| 13 | 6 | 0 | 3.412487 | -0.716505 | -0.066778 |
| 14 | 6 | 0 | 4.757423 | -0.218723 | -0.102329 |
| 15 | 6 | 0 | 4.723606 | 1.211465 | -0.071735 |
| 16 | 6 | 0 | -4.723612 | 1.211636 | -0.071889 |
| 17 | 6 | 0 | -4.757452 | -0.218559 | -0.102347 |
| 18 | 6 | 0 | -3.412527 | -0.716357 | -0.066671 |
| 19 | 6 | 0 | 3.245409 | -2.100910 | -0.039792 |
| 20 | 6 | 0 | 4.356189 | -2.953423 | -0.072428 |
| 21 | 6 | 0 | 5.654935 | -2.451522 | -0.127533 |
| 22 | 6 | 0 | 5.858992 | -1.074806 | -0.138176 |
| 23 | 6 | 0 | -5.859021 | -1.074644 | -0.138137 |
| 24 | 6 | 0 | -5.654967 | -2.451361 | -0.127293 |
| 25 | 6 | 0 | -4.356226 | -2.953265 | -0.072030 |
| 26 | 6 | 0 | -3.245443 | -2.100752 | -0.039455 |
| 27 | 1 | 0 | -1.218025 | 4.237825 | 0.151924 |
| 28 | 1 | 0 | -3.661370 | 3.785162 | 0.063143 |
| 29 | 1 | 0 | 3.661459 | 3.784993 | 0.063410 |
| 30 | 1 | 0 | 1.218133 | 4.237756 | 0.152061 |
| 31 | 1 | 0 | 2.274910 | -2.564782 | 0.019896 |
| 32 | 1 | 0 | 4.193053 | -4.026221 | -0.051290 |
| 33 | 1 | 0 | 6.500988 | -3.130409 | -0.154644 |
| 34 | 1 | 0 | 6.864152 | -0.664887 | -0.168499 |
| 35 | 1 | 0 | -6.864179 | -0.664726 | -0.168564 |
| 36 | 1 | 0 | -6.501021 | -3.130247 | -0.154359 |
| 37 | 1 | 0 | -4.193098 | -4.026060 | -0.050714 |
| 38 | 1 | 0 | -2.274939 | -2.564604 | 0.020399 |
| 39 | 7 | 0 | -0.000047 | -0.040634 | -0.074917 |
| 40 | 6 | 0 | -0.000133 | -1.478446 | -0.281506 |
| 41 | 1 | 0 | 0.862979 | -1.719241 | -0.897564 |
| 42 | 1 | 0 | -0.863443 | -1.719167 | -0.897320 |
| 43 | 6 | 0 | -0.000011 | -2.263433 | 1.032771 |
| 44 | 1 | 0 | -0.000108 | -3.341812 | 0.845198 |
| 45 | 1 | 0 | 0.880123 | -2.024811 | 1.632125 |
| 46 | 1 | 0 | -0.879966 | -2.024683 | 1.632339 |
| 47 | 1 | 0 | 5.591015 | 1.860186 | -0.078826 |
| 48 | 1 | 0 | -5.591009 | 1.860371 | -0.079075 |

# References

1. D. Myśliwiec, M. Stępień, *Angew. Chem. Int. Ed.* **2013**, *52*, 1713.
2. D. Doehnert, J. Koutecký, *J. Am. Chem. Soc.* **1980**, *102*, 1789.
3. For a recent example for the use of $y_0$ for the teranthene diradical molecule, see: A. Konishi, Y. Hirao, M. Nakano, A. Shimizu, E. Botek, B. Champagne, D. Shiomi, K. Sato, T. Takui, K. Matsumoto, H. Kurata, T. Kubo, *J. Am. Chem. Soc.* **2010**, *132*, 11021.
4. Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842.
5. R. Herges, D. Geuenich, *J. Phys. Chem. A* **2001**, *105*, 3214.
6. D. Geuenich, K. Hess, F. Köhler, R. Herges, *Chem. Rev.* **2005**, *105*, 3758.
7. D. Sundholm, H. Fliegl, R. J. F. Berger, *WIREs Comput. Mol. Sci.* **2016**, *6*, 639.
8. J. Jusélius, D. Sundholm, J. Gauss, *J. Chem. Phys.* **2004**, *121*, 3952.
9. C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158.
10. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
11. S. Lehtola, M. Dimitrova, H. Fliegl, D. Sundholm, *J. Chem. Theory Comput.* **2021**, *17*, 1457.
12. D. Inostroza, V. García, O. Yañez, J. J. Torres-Vega, A. Vásquez-Espinal, R. Pino-Rios, R. Báez-Grez, W. Tiznado, *New J. Chem.* **2021**, *45*, 8345.
13. U. Ayachit, *The ParaView Guide: A Parallel Visualization Application*, Kitware, Inc., USA, **2015**.