

## *Electronic Supplementary Information (ESI)*

### **5,5'-Biindeno[2,1-*c*]fluorene: importance of C5-C5' linkage for an indeno[2,1-*c*]fluorene dimer exhibiting open-shell ground state**

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## 1. Experimental section

**1.1 General information:** Chemicals and reagents were purchased from commercial suppliers (Merck, GLR innovations, BLD pharm, Spectrochem) and used without further purification. Thin layer chromatography (TLC) was performed using pre-coated silica-plates purchased from Merck (silica gel 60 PF254, 0.25 mm). Column chromatography was performed using silica gel 100-200 mesh. NMR spectra were recorded either in  $\text{CDCl}_3$  or in  $\text{CDCl}_3+0.03\%$  TMS v/v at room temperature, on JEOL JNM-ECS400 spectrometer at operating frequencies of 400 MHz ( $^1\text{H}$ ) or 100 MHz ( $^{13}\text{C}$ ) as indicated in the individual spectrum. Chemical shifts ( $\delta$ ) are given in ppm relative to residual solvent (chloroform  $\delta = 7.26$ , toluene  $\delta = 7.10, 7.01, 6.98, 2.29$  for  $^1\text{H}$ , and  $\delta = 77.16$  for proton-decoupled  $^{13}\text{C}$  NMR), and coupling constants ( $J$ ) are expressed in hertz (Hz). Multiplicity is tabulated as s for singlet, d for doublet, dd for doublet of doublet, t for triplet, q for quartet and m for multiplet. Structural assignments were made with additional information from gCOSY, and gNOESY experiments. High-resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI) methods on Waters (XEVO G2-XS QTOF) mass spectrometer. UV-vis-NIR spectra were recorded in JASCO V-770 spectrophotometer. Cyclic voltammetry measurements of **4** (0.001 M) was performed using an electrochemical analyzer potentiostat model CHI-1115C from CH Instruments with a conventional three-electrode cell at 298 K under a nitrogen atmosphere at a scan rate of 50 mV/s. This electrochemical cell contains a platinum (Pt) disk (disk shaped with 2-mm diameter) as a working electrode, Pt wire as a counter electrode, and silver (Ag) wire as a pseudo-reference electrode. The Pt working electrode was polished with 1.0 micron  $\alpha$ -alumina polishing powder in a figure-eight motion. Electrolyte solution (0.1 M) was prepared by dissolving tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) in 5 mL dry dichloromethane (DCM). The DCM solution was degassed by bubbling nitrogen gas for 10 minutes prior to measurements. The direction of initial scan was chosen as reductive, with the initial potential values set at zero for **4** and switching between negative potential first and then going to positive potential, and finally returning to zero (vs Ag wire). The potential was finally referenced against the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) couple (0.43 V). Melting points were determined using Cole-Parmer MP 250D-P melting point analyzer. X-band electron paramagnetic resonance (EPR) spectra were recorded using an EMX MICRO X Bruker EPR instrument. Compound **5** was synthesized following the procedure outlined in the literature.<sup>1</sup>

## **1.2 Syntheses and characterization data**

**4,4'-dibromo-9,9'-bifluorenylidene (6):** 4-bromo-9H-fluoren-9-one **5** (2.2 g, 8.5 mmol) and Lawesson's reagent (4.63 g, 11.4 mmol) were refluxed for 12 h under argon atmosphere in anhydrous toluene (30 mL). The orange solution gradually turned red during the overnight stirring. A catalytic amount of copper powder (12.4 mg, 0.1 mmol) was then added to the reaction mixture. The mixture was kept refluxing for 3 h, allowed to cool down to room temperature, and got through the silica gel pad to remove the copper. The mixture was further washed with water, brine, and aqueous K<sub>2</sub>CO<sub>3</sub>. The combined organic layers were extracted with CHCl<sub>3</sub> for three times, dried over anhydrous MgSO<sub>4</sub>, and the solvent was evaporated under reduced pressure. The crude material was subjected to column chromatography (SiO<sub>2</sub>, CHCl<sub>3</sub>/hexanes 5:1) to give **6** as an orange solid as *E/Z* diastereomeric mixture. (1.1 g, 50% yield): *R<sub>f</sub>* = 0.33 (hexanes); mp = 207 – 209 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.60 (d, *J* = 7.8 Hz, 2H), 8.42 – 8.36 (m, 2H), 8.33 – 8.27 (m, 2H), 7.48 (dd, *J* = 7.8, 3.3 Hz, 2H), 7.39 (td, *J* = 7.7, 3.6 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.03 (td, *J* = 7.8, 5.1 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 141.1, 141.1, 140.9, 140.8, 140.7, 139.1, 139.0, 138.6, 138.6, 134.4, 134.3, 129.4, 129.3, 127.5, 127.5, 127.4, 126.7, 126.5, 125.8, 125.6, 123.7, 117.4, 117.3; HRMS (ESI) *m/z*: [M]<sup>+</sup> calcd for C<sub>26</sub>H<sub>14</sub>Br<sub>2</sub> 483.9462 found 483.9462 (error: 0 ppm).

**2,2'-(9,9'-bifluorenylidene)-4,4'-diyl)dibenzaldehyde (7):** An oven-dried thick-walled glass tube was charged with diastereomeric mixture **6** (1 g, 2.05 mmol), (2-formylphenyl)boronic acid **7** (1.23 g, 8.22 mmol), NaHCO<sub>3</sub> (3.45 g, 41.14 mmol), tetrahydrofuran (10 mL), distilled water (1 mL) and purged with N<sub>2</sub> for 30 mins. Pd<sub>2</sub>(dba)<sub>3</sub> (300 mg, 0.164 mmol), and [(*t*-Bu)<sub>3</sub>PH]BF<sub>4</sub> (356 mg, 0.658 mmol) were added subsequently and the resulting mixture was heated at 80 °C using an oil bath for 12 h. After cooling to room temperature, the THF was evaporated, water was added and the resultant mixture was extracted with DCM (3 x 50 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The residue was subjected to column chromatography (SiO<sub>2</sub>, DCM/hexane 70:30) to give dialdehyde **7** as a mixture of stereoisomers as an orange solid. (605 mg, 55% yield): *R<sub>f</sub>* = 0.20 (70% DCM/hexane); mp = 133 – 135 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.97 – 9.96 (m, 2H), 8.51 (dd, *J* = 10.5, 7.9 Hz, 2H), 8.39 (dd, *J* = 10.6, 7.8 Hz, 2H), 8.17 (d, *J* = 7.8 Hz, 2H), 7.78 (t, *J* = 7.4 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 2H), 7.55 (dd, *J* = 7.5, 3.9 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.22 – 7.06 (m, 4H), 7.01 – 6.92 (m, 2H), 6.42 (d, *J* = 7.8 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 193.4, 192.0, 191.3, 191.2, 144.4, 143.8, 142.7, 141.2, 140.7, 140.6, 139.3, 139.1, 138.9, 138.8, 136.7, 134.8, 134.5, 134.5, 134.5, 134.1, 133.5, 133.3, 132.7, 132.6, 131.8, 131.7, 130.8, 130.7, 129.8, 129.4, 129.2, 128.9, 128.8, 128.6, 128.2, 127.6, 127.0, 126.9, 126.8, 126.7,

126.4, 124.6, 124.2, 122.6; HRMS (ESI)  $m/z$ :  $[M]^+$  calcd for  $C_{40}H_{24}O_2$  536.1776, found 536.1776 (error: 0 ppm).

**8,8'-dimesityl-5,5'-biindeno[2,1-c]fluorene (4)**: 2-mesitylmagnesium bromide (1.0 M solution in THF, 1.13 mL, 5.11 mmol) was added dropwise in 10 mL dry THF solution of isomeric mixture **7** (550 mg, 1.02 mmol) under nitrogen atmosphere. The mixture was stirred at room temperature for 16 h. After removal of the solvent, the crude compound was quenched with  $NH_4Cl$  (20 mL) and extracted into DCM (3 x 40 mL), washed with brine, and dried over anhydrous sodium sulfate. The starting material **7** was consumed (monitored by TLC), so the crude **8** (657 mg) was used for next step without purification. To the solution of crude **8** (600 mg, 0.76 mmol) in anhydrous DCM (10 mL) at room temperature, 0.1 mL of  $BF_3 \cdot Et_2O$  was added dropwise under nitrogen, and the reaction mixture was stirred for 10 mins at room temperature. Completion of the reaction was monitored by TLC (partial formation of **4** was observed in TLC, likely due to air oxidation), and the mixture was extracted with DCM/water to afford **9** (400 mg, including the partly dehydrogenated **4**), which was used directly for next step. A 1,2-DCE (5 ml) solution of crude **9** (70 mg) was treated with DDQ (22.5 mg, 0.09 mmol, 1.1 equiv) for 15 mins at room temperature. After 15 mins, the solvent was removed in vacuo and the crude residue was purified on silica gel column chromatography (DCM/hexanes 1:20) to afford the final compound **4** as greenish-black solid (50 mg, 54% yield over three steps):  $R_f = 0.23$  (10% DCM/hexanes); mp = 102 – 106 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.12 (d,  $J = 7.4$  Hz, 2H), 8.08 (d,  $J = 7.4$  Hz, 2H), 7.23 (d,  $J = 7.4$  Hz, 2H), 7.15 (m, 6H), 7.05 (t,  $J = 7.4$  Hz, 2H), 6.95 (s, 4H), 6.69 (d,  $J = 7.3$  Hz, 2H), 6.60 (d,  $J = 9.4$  Hz, 2H), 6.17 (d,  $J = 9.2$  Hz, 2H), 2.34 (s, 6H), 2.15 (s, 6H), 2.14 (s, 6H);  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  146.0, 145.5, 145.2, 139.4, 139.2, 138.1, 137.6, 137.0, 136.9, 136.8, 136.7, 136.5, 136.4, 129.8, 129.3, 129.1, 128.3, 127.0, 126.8, 125.6, 125.3, 123.6, 122.2, 122.1, 121.3, 21.29, 20.40; HRMS (ESI)  $m/z$ :  $[M]^+$  calcd for  $C_{58}H_{42}$  738.3287, found 738.3284 (error: -0.40 ppm).

### 1.3 NMR spectra

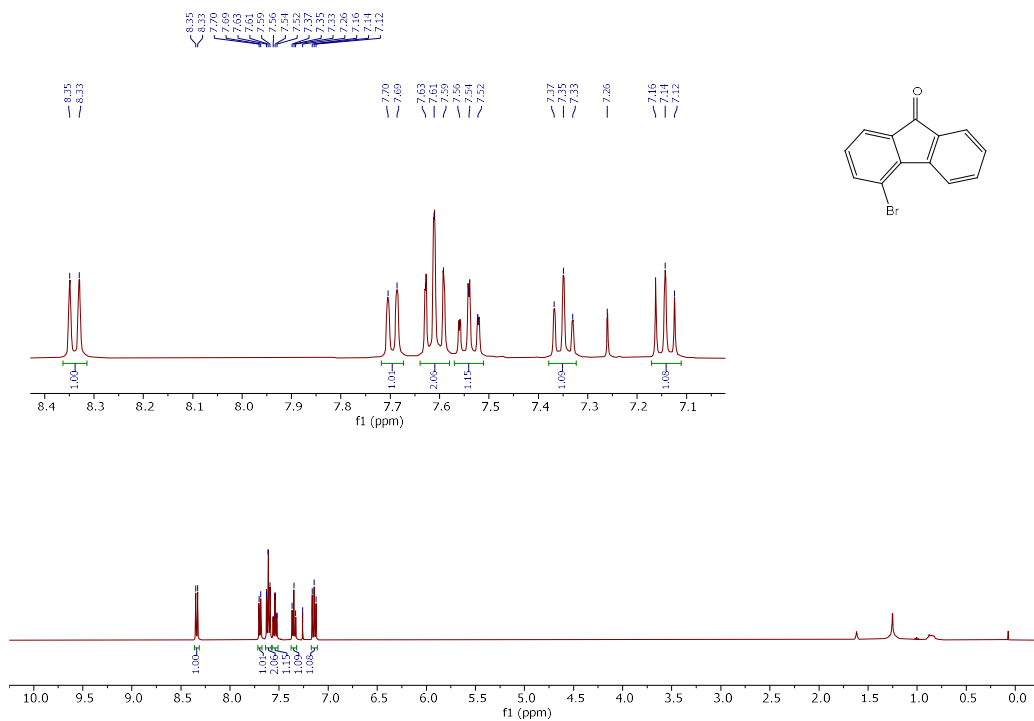


Fig. S1 <sup>1</sup>H NMR spectrum of 5 (in CDCl<sub>3</sub>, 400 MHz, 298 K).

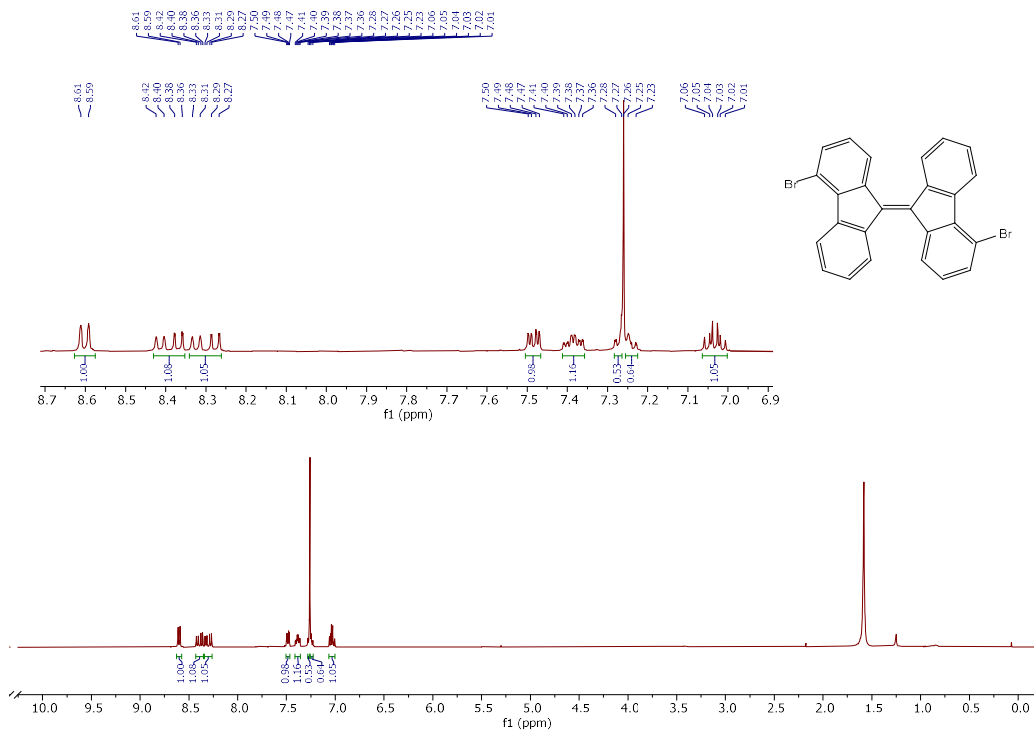


Fig. S2 <sup>1</sup>H NMR spectrum of 6 (in CDCl<sub>3</sub>, 400 MHz, 298 K).



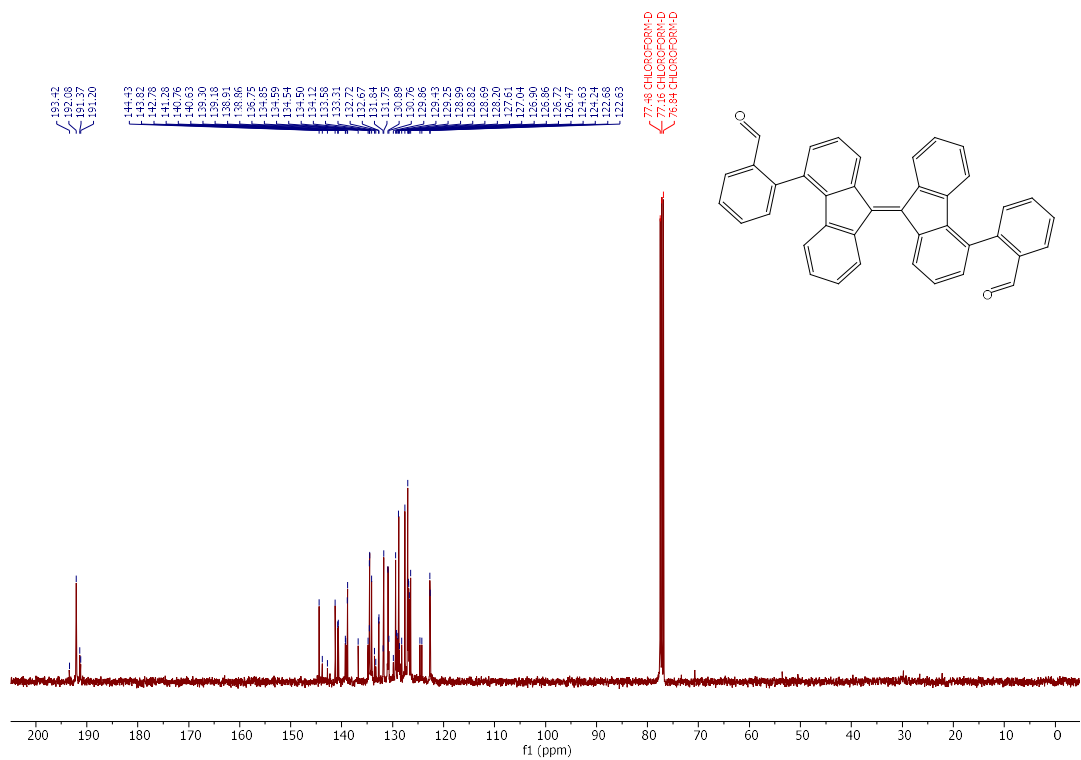


Fig. S5  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 7 (in  $\text{CDCl}_3$ , 100 MHz, 298 K).

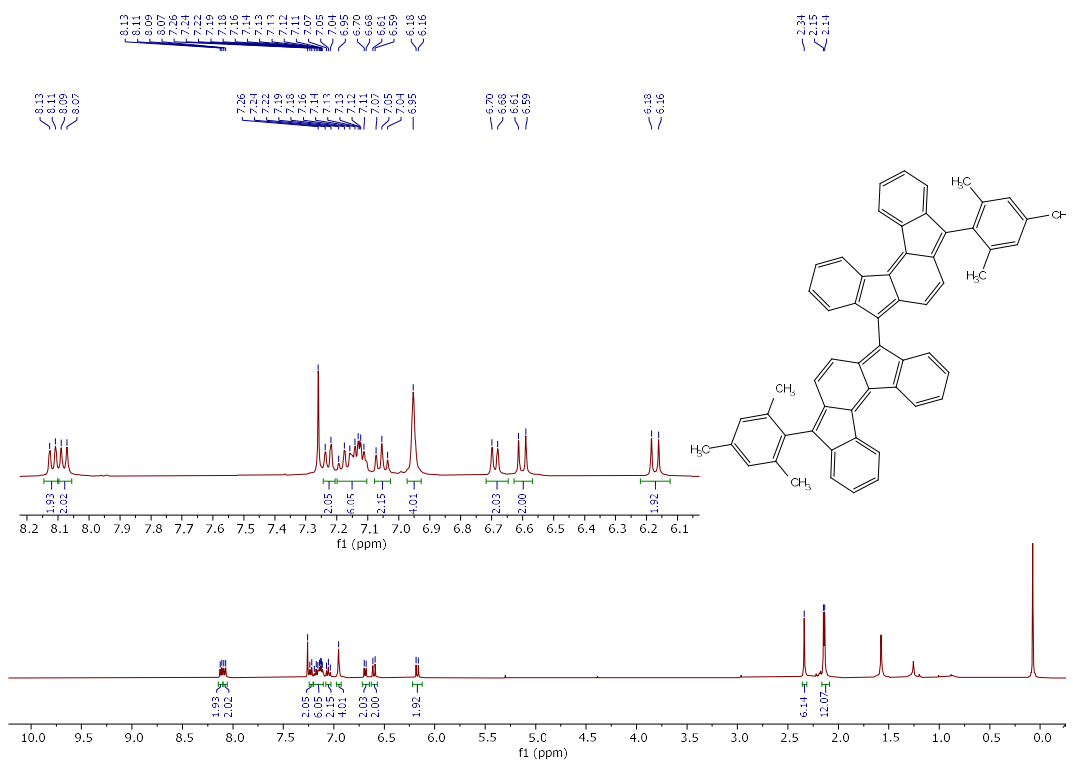
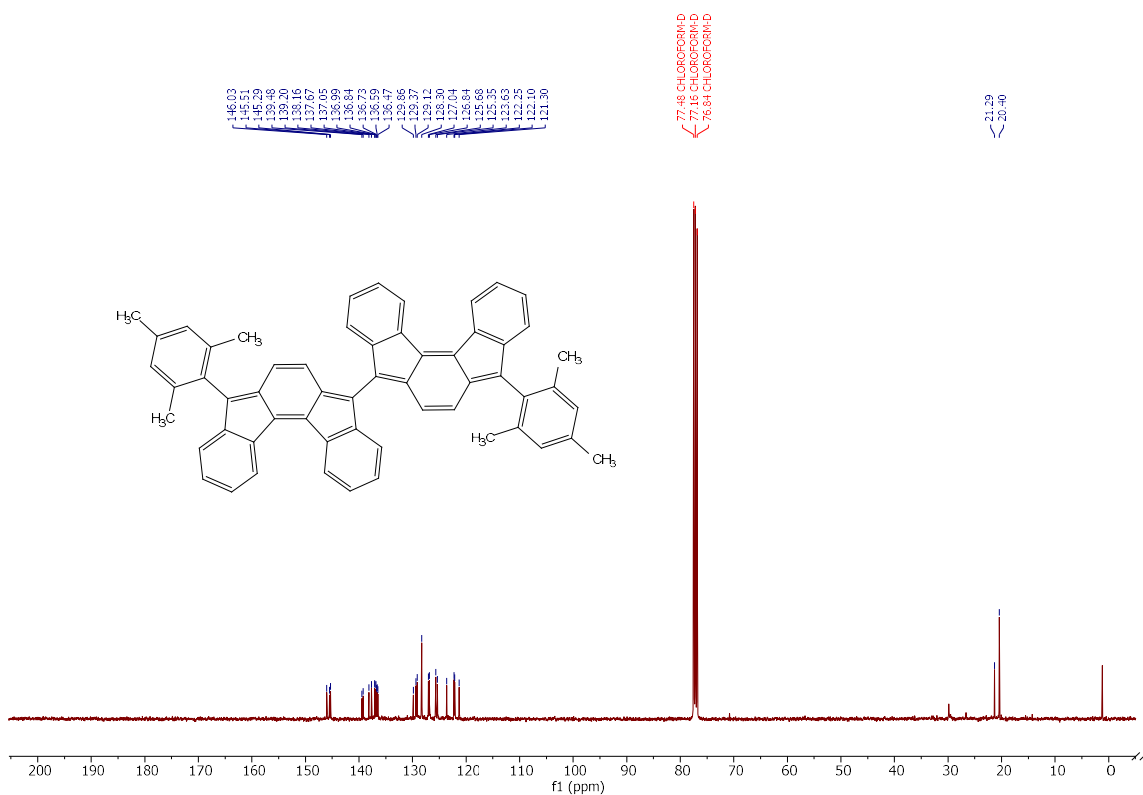
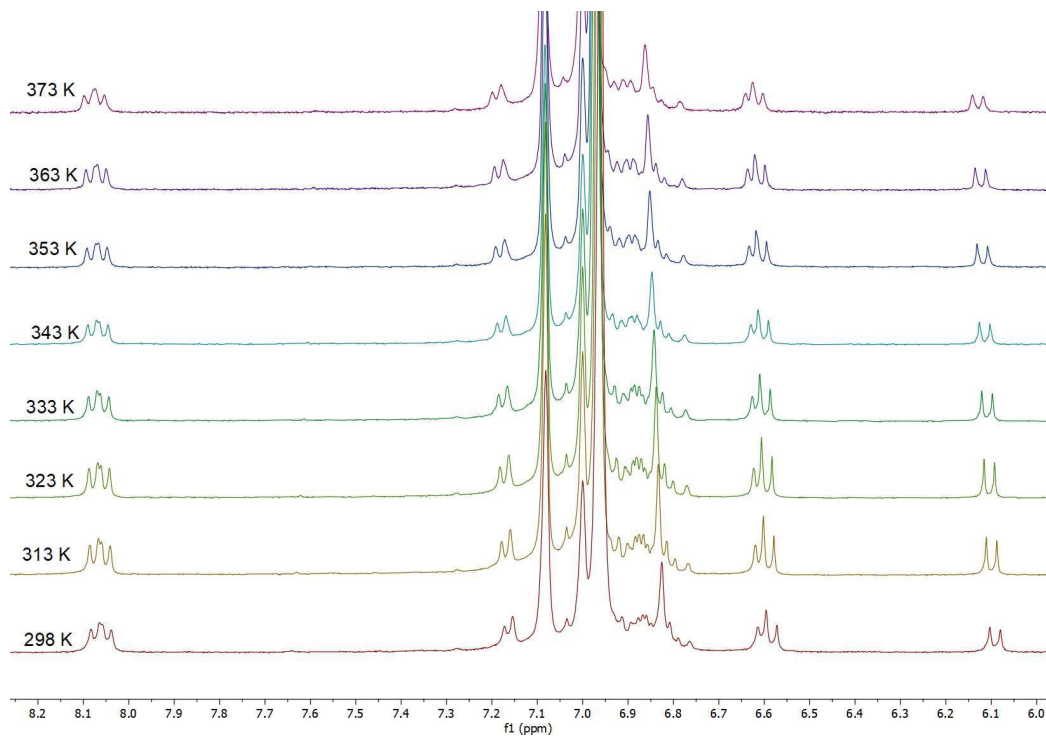


Fig. S6  $^1\text{H}$  NMR spectrum of 4 (in  $\text{CDCl}_3$ , 400 MHz, 298 K).



**Fig. S7**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4** (in  $\text{CDCl}_3$ , 100 MHz, 298 K).



**Fig. S8** Variable temperature  $^1\text{H}$  NMR spectra of **4** (in  $\text{toluene-}d_8$ , 400 MHz).



**VT-NMR discussion:** We tried to record the variable temperature  $^1\text{H}$  NMR of **4** in high-boiling solvents like  $\text{C}_2\text{D}_2\text{Cl}_4$  that can reach up to 400 K, but compound **4** decomposed in  $\text{C}_2\text{D}_2\text{Cl}_4$ . Hence, toluene- $d_8$  was chosen. There is only a slight broadening of  $^1\text{H}$  NMR signals for core protons observed at higher temperature (373 K). However, the spectral broadening for **4**, displaying a diradical character of only 26.4% with a low-lying closed-shell state, is not expected to be as large/prominent as other diradicaloid PHs showing larger diradical character.<sup>2</sup> Notably, an open-shell PH with large diradical character displays a large energy difference between its closed-shell singlet and open-shell singlet states, and a small energy difference between its open-shell singlet state and first excited triplet state,<sup>2b</sup> causing greater NMR line broadening unlike BIF **4** displaying a minor spectral broadening.

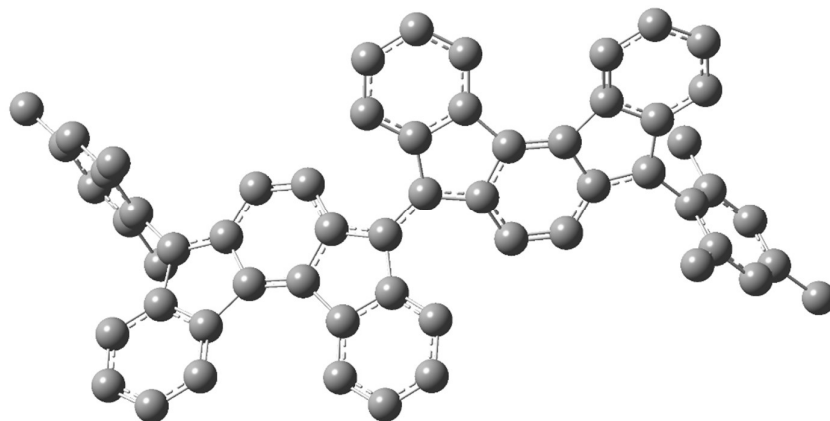
## 2. DFT calculations

Gas-phase density functional theory (DFT) calculations were performed with Gaussian 09 package using a high-performance computing cluster facility of IIT Ropar at the CAM-B3LYP level of theory with basis set 6-31G(d,p).<sup>3</sup> Optimization of the molecular geometries for **5**, was done by restricted CAM-B3LYP, and unrestricted CAM-B3LYP wave-functions using broken symmetry formalism.<sup>4</sup> The calculated NOON (natural orbital occupation number) value was based on the broken symmetry CAM-B3LYP method for ground state structure.<sup>5</sup> NICS (standard GIAO method)<sup>6</sup> values were calculated for the optimized structure at (U)BHandHLYP/6-31G(d,p) level, and the reported NICS(1)<sub>zz</sub> values are the average of two positions (1 Å above and below the plane). Molecular orbital contributions for TDDFT calculation were determined using the GaussSum 3.0 package.<sup>7</sup>

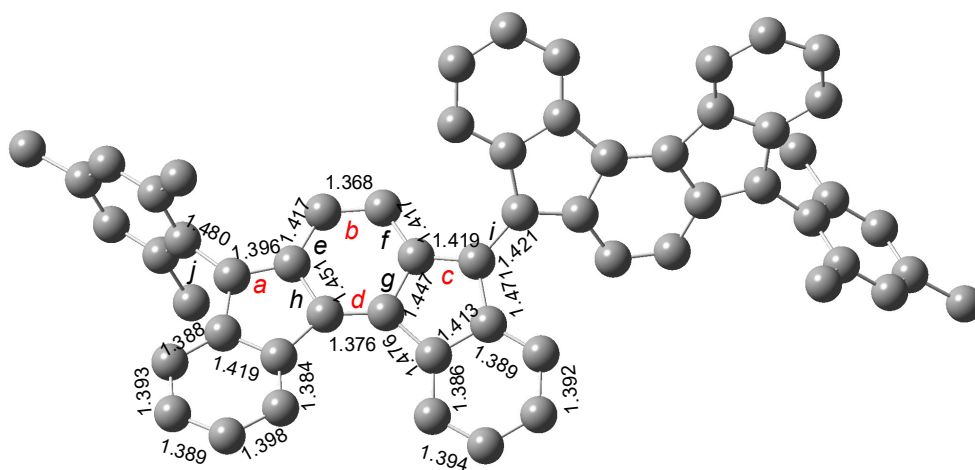
**Table S1.** Relative energies for the optimized structure **4**

State	Hartree	kcal/mol
Singlet Closed-Shell CAM-B3LYP/6-31G(d,p)	-2234.253983	-1401994.374
Singlet Open-Shell UCAM-B3LYP /6-31G(d,p)	-2234.256992	-1401996.262
Triplet biradical UCAM-B3LYP /6-31G(d,p)	-2234.2505	-1401992.189

**Compound 4** :  $\Delta E_{\text{Singlet(OS)-Triplet}} = -4.07$  kcal/mol;  $\Delta E_{\text{OS-CS}} = -1.88$  kcal/mol;  $\Delta E_{\text{CS-T}} = -2.18$  kcal/mol. Occupation numbers of HOMO-1 = 1.872, HOMO = 1.439, LUMO = 0.561, LUMO+1 = 0.128, affording a 26.4% diradical character (singlet diradical character index ( $y_0$ ) = 0.264) and 0.9% tetradical character (singlet tetradical character index ( $y_1$ ) = 0.009).

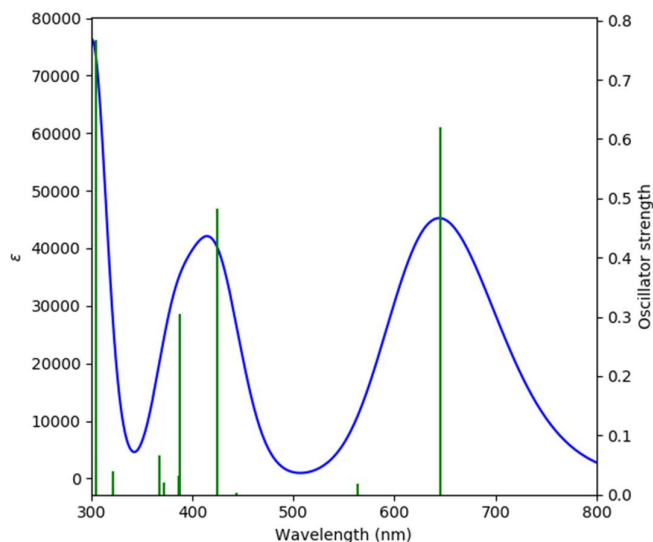


**Fig. S9** Optimized structure of **4** in the open-shell ground state.



**Fig. S10** DFT-optimized C-C bond lengths of ground state open-shell structure **4**.

## TDDFT computation of compound 4



**Fig. S11** Theoretical absorption of **4** at CAM-B3LYP/6-31G(d,p) level of theory.

**Table S2.** Summary of TDDFT calculation for **4**

Wavelength (nm)	Oscillator strength ( <i>f</i> )	Major contributions
644.9	0.6203	H-1->L+1 (11%), HOMO->LUMO (82%)
564.0	0.0177	H-1->LUMO (54%), HOMO->L+1 (30%)
443.9	0.0029	H-1->LUMO (32%), HOMO->L+1 (60%)
424.4	0.4817	H-2->LUMO (41%), H-1->L+1 (27%), HOMO->LUMO (13%)
387.2	0.3052	H-4->LUMO (46%), H-3->L+1 (11%), H-2->LUMO (16%), H-1->L+1 (11%)
385.9	0.0321	H-3->LUMO (58%), H-2->L+1 (13%)
372.0	0.0199	H-7->LUMO (28%), H-5->LUMO (34%), H-4->L+1 (18%)
367.5	0.0664	H-5->L+1 (10%), H-4->LUMO (16%), H-2->LUMO (13%), H-1->L+1 (42%)
321.6	0.0164	H-7->LUMO (36%), H-6->L+1 (21%), H-5->LUMO (33%)
321.5	0.0388	H-7->L+1 (12%), H-6->LUMO (65%), H-5->L+1 (10%)
303.8	0.0611	H-3->LUMO (13%), H-1->L+3 (10%), HOMO->L+2 (63%)
303.7	0.7662	H-2->LUMO (10%), H-1->L+2 (21%), HOMO->L+3 (53%)
294.9	0.0013	H-9->LUMO (18%), H-9->L+1 (14%), H-8->LUMO (58%)
294.9	0.0028	H-9->LUMO (55%), H-8->LUMO (19%), H-8->L+1 (14%)
290.2	0.0321	H-3->LUMO (16%), H-2->L+1 (60%)
289.3	0.278	H-3->L+1 (55%)
285.9	0.1192	H-11->L+1 (15%), H-10->LUMO (56%), H-3->L+1 (10%)
284.7	0.0027	H-11->LUMO (56%), H-10->L+1 (19%)
271.2	0.0003	H-7->LUMO (12%), H-5->LUMO (15%), H-4->L+1 (51%)

267.5	0.1847	H-12->LUMO (11%), H-7->L+1 (21%), H-5->L+1 (30%), H-4->LUMO (13%)
264.6	0.2515	H-13->L+1 (12%), H-12->LUMO (52%)
253.9	0.0854	H-13->LUMO (42%), H-12->L+1 (21%)
247.7	0.299	H-1->L+2 (48%), HOMO->L+3 (19%)
245.4	0.0008	H-1->L+3 (44%), HOMO->L+5 (11%)
244.0	0.1555	HOMO->L+4 (74%)
242.4	0.0401	H-14->LUMO (12%), H-2->L+2 (12%), HOMO->L+5 (33%)
240.4	0.0006	H-14->LUMO (25%), HOMO->L+5 (22%)
240.3	0.2384	H-15->LUMO (29%), H-14->L+1 (10%), H-3->L+2 (22%), H-2->L+3 (16%)
237.8	0.0001	H-7->LUMO (11%), H-6->L+1 (53%)
237.7	0.0004	H-7->L+1 (36%), H-6->LUMO (23%), H-5->L+1 (33%)

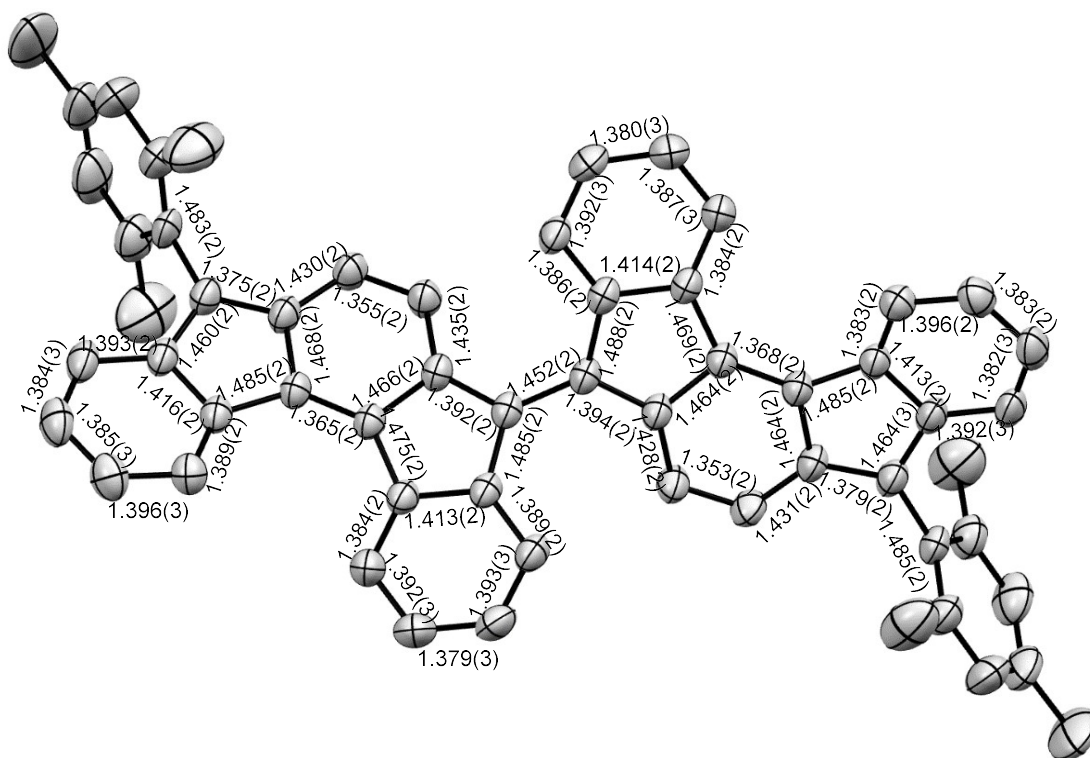
### 3. X-ray crystallographic analyses

Single crystals of **4** were selected using paratone oil and mounted on glass fiber with the help of gum. The intensity data and geometric parameters of these crystals were garnered with the help of Bruker D8 Venture X-ray diffractometer having a micro-focus sealed X-ray tube Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) source of X-rays along with a PHOTON 100 detector with inclining Phi and Omega (width of 0.5 for one frame) working at a scan speed of 10 s per frame. The crystal was kept at 298 K during data collection. Data acquisition as well as extraction of data was accomplished by utilizing Bruker Apex-3 and Bruker SAINT software packages using a narrow-frame algorithm.<sup>8</sup> By utilizing OLex2,<sup>9</sup> the crystal structure was solved with the help of olex2.solve<sup>10</sup> structure solution program by employing intrinsic Phasing methods and crystal structure refinement was done with the SHELXL<sup>11</sup> refinement package by putting into use Least Squares minimization. Refinement of all non-hydrogen atoms was completed with the help of anisotropic thermal parameters.

**Table S3.** X-ray crystallographic information of **4**

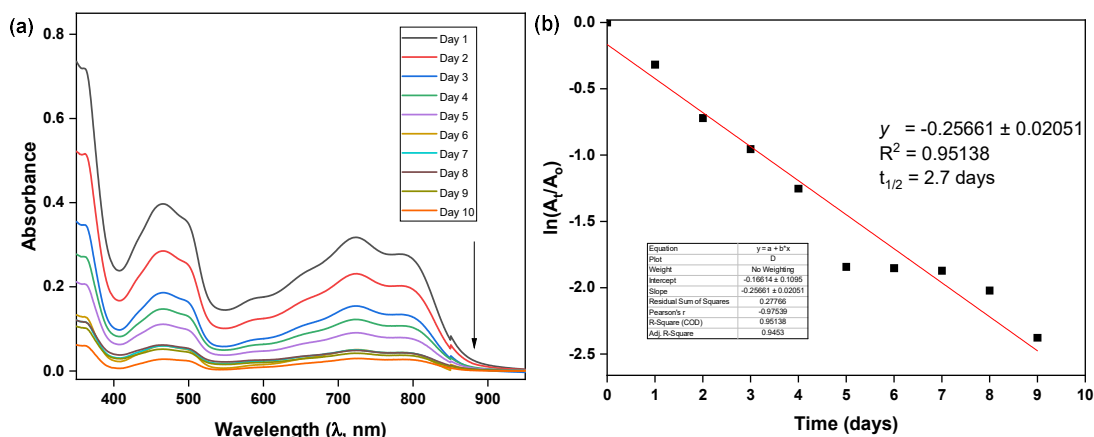
CCDC No.	2411678
Empirical formula	C <sub>58</sub> H <sub>42</sub>
Formula weight	738.91
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/ $\text{\AA}$	7.7801(16)
b/ $\text{\AA}$	12.750(3)
c/ $\text{\AA}$	21.284(6)

$\alpha/^\circ$	74.037(9)
$\beta/^\circ$	80.782(9)
$\gamma/^\circ$	86.993(7)
Volume/ $\text{\AA}^3$	2003.7(8)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.225
$\mu/\text{mm}^{-1}$	0.069
F(000)	780.0
Crystal size/ $\text{mm}^3$	0.215 $\times$ 0.156 $\times$ 0.125
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^\circ$	4.028 to 52.898
Index ranges	-9 $\leq h \leq$ 9, -15 $\leq k \leq$ 15, -24 $\leq l \leq$ 26
Reflections collected	17858
Independent reflections	8152 [ $R_{\text{int}} = 0.0426$ , $R_{\text{sigma}} = 0.0526$ ]
Data/restraints/parameters	8152/0/529
Goodness-of-fit on $F^2$	1.046
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0563$ , $wR_2 = 0.1426$
Final R indexes [all data]	$R_1 = 0.0694$ , $wR_2 = 0.1516$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.18/-0.16



**Fig. S12** Full crystallographic bond length analyses of **4** with e.s.d values.

#### 4. Photostability test



**Fig. S13** a) Absorption spectral changes under ambient light conditions for compound **4** in toluene (0 days to 9 days); b) Fitting with first-order kinetics.

The half-life ( $t_{1/2}$ ) of **4** was determined according to the following equation:

$$t_{1/2} = \frac{\ln 2}{0.03626} = 2.7 \text{ days}$$

To check the photostability of final compound **4**, solution of known concentration of **4** in toluene was exposed to ambient light (under normal lab light condition and temperature). It leads to the gradual decomposition of **4** in solution, resulting in the decrease of the absorbance at longer wavelength (720 nm) region.

#### 5. EPR measurement and Bleaney-Bowers plot

To have an assessment of the ground state spin multiplicity and an estimation of the energy gap between the singlet and triplet state, variable temperature electron paramagnetic resonance (VT-EPR) experiments were conducted with a solid sample of compound **4**. The EPR intensity ( $I$ ) at various temperatures ( $T$ ) was recorded, and the values of  $IT$  were plotted against the  $T$  following the modified Bleaney-Bowers equation (equation 1).

$$IT = \frac{2\rho N_A g^2 \beta^2}{k_b} * \frac{1}{3 + \exp\left(-\frac{2J}{k_b T}\right)} + \frac{(1-\rho) N_A g^2 \beta^2}{2k_b} \dots \dots \dots \text{equation 1}$$

In the equation, the parameter  $2J$  is the energy separation between singlet and triplet state,  $g$  is the  $g$  factor,  $N_A$  is the Avogadro constant,  $\beta$  is the Bohr magneton,  $k_b$  is the Boltzmann constant, and  $\rho$  is the paramagnetic purity. The energy gap ( $\Delta E_{S-T}$ ) between the singlet and triplet spin states of the diradicaloid compound **4** was obtained to be  $-4.12 \pm 0.26$  kcal/mol.

The  $IT$  vs.  $T$  data set was fitted according to the below equation using the Origin 2021 software package.

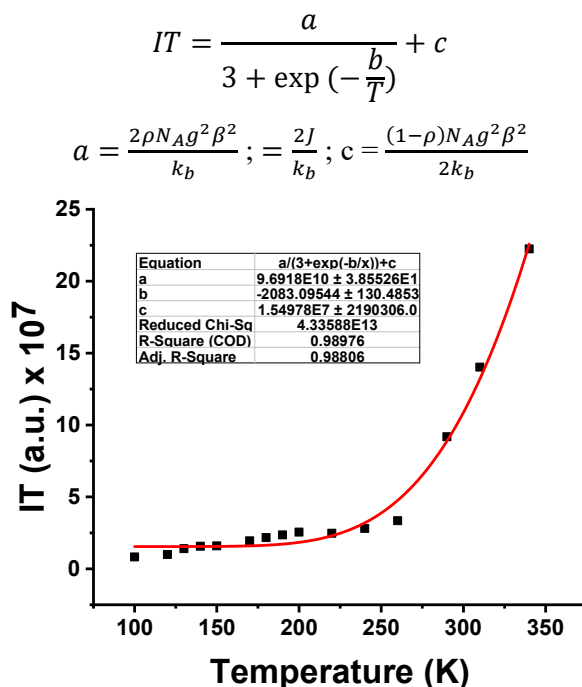


Fig. S14 Bleaney-Bowers plot for 4.

$$b = -2083.09 \pm 130.48; \quad 2J = b \times k_B = -4.12 \pm 0.26 \text{ kcal/mol}$$

## 6. Appendix

### Cartesian coordinates (in Angstroms) for the optimized structure:

#### Singlet closed-shell structure of 4

Atom type	x	y	z
C	9.12380600	3.41063700	3.51681600
H	10.17206000	3.09742900	3.46182400
H	8.84647800	3.43322200	4.57358900
H	9.06784500	4.43067900	3.12921300
C	8.23768600	2.47635500	2.73593200
C	7.94541500	2.71880900	1.39753700
H	8.34804800	3.60739500	0.91806700
C	7.15197500	1.85280300	0.64913500
C	6.62922500	0.70381900	1.26435600
C	5.78844500	-0.23852700	0.48950800
C	4.47673600	-0.09266100	0.15257600
C	4.01382600	-1.27480600	-0.59883900
C	2.70158600	-1.36174200	-0.93409300
C	1.82532000	-0.20095600	-0.68695600
C	0.57273600	-0.45183900	-1.17835200
C	-0.57274100	0.45176700	-1.17835400

C	-1.82532600	0.20090000	-0.68695400
C	-2.30565400	-0.95468800	0.02916400
H	-1.61765700	-1.76634500	0.23550800
C	-3.58317000	-0.99567800	0.45646600
H	-3.96340300	-1.83799800	1.02484000
C	-4.47672200	0.09264700	0.15261800
C	-5.78842200	0.23851700	0.48956500
C	-6.62921300	-0.70382300	1.26441800
C	-6.91206600	-0.44023700	2.61508600
C	-7.70853700	-1.33247100	3.32677600
H	-7.91754400	-1.12927300	4.37401600
C	-8.23779800	-2.47627800	2.73593600
C	-9.12395600	-3.41052700	3.51681900
H	-9.06871500	-4.43039400	3.12865300
H	-10.17208100	-3.09676700	3.46257900
H	-8.84604600	-3.43380800	4.57342700
C	6.87067700	2.15448500	-0.80091500
H	7.46306900	3.00618900	-1.14146000
H	5.81542300	2.39107600	-0.96579100
H	7.10608400	1.29838900	-1.43926400
C	6.91273600	0.43981900	2.61481700
C	6.34632200	-0.77854600	3.29725900
H	6.64841700	-0.81425200	4.34584100
H	6.68312100	-1.70134200	2.81595400
H	5.25322400	-0.78267500	3.25748800
C	7.70912100	1.33210000	3.32653500
H	7.91860500	1.12859500	4.37362000
C	6.26872800	-1.50140500	-0.08254400
C	5.20785400	-2.13008300	-0.77609000
C	3.58315100	0.99561800	0.45649100
H	3.96334900	1.83791900	1.02491600
C	2.30563200	0.95461700	0.02919500
H	1.61762000	1.76625100	0.23558000
C	1.84432700	-2.39124000	-1.55551900
C	0.56324400	-1.81856000	-1.72466400
C	-6.26870500	1.50140300	-0.08245900
C	-7.54142200	2.04653300	-0.06635100
H	-8.34297600	1.54834400	0.46995200
C	-7.77434900	3.22950300	-0.76889700
H	-8.76530700	3.67172600	-0.76730900
C	-6.75151800	3.82779600	-1.49214200
H	-6.94930300	4.72936800	-2.06233400
C	-5.46614900	3.27749000	-1.50730500
H	-4.70576600	3.73662800	-2.12247900
C	-5.20783400	2.13009400	-0.77600200
C	-4.01380700	1.27480300	-0.59878100
C	-2.70157200	1.36171000	-0.93406800
C	-1.84430200	2.39119000	-1.55551000
C	-2.04828900	3.71626600	-1.90636300
H	-2.98801400	4.21072800	-1.70773000
C	-1.00532100	4.44159800	-2.48613200
H	-1.16690200	5.47842100	-2.76168300
C	0.23142700	3.85048100	-2.70927200
H	1.02810700	4.42263600	-3.17344600
C	0.46424200	2.53155700	-2.32130200
H	1.43630900	2.07466400	-2.47002400



C	-0.56323200	1.81848500	-1.72467000
C	-7.15266400	-1.85235600	0.64895400
C	-7.94615500	-2.71833400	1.39732500
H	-8.34932000	-3.60658100	0.91767700
C	-6.34489100	0.77765000	3.29774900
H	-5.25177700	0.78094000	3.25824800
H	-6.64720300	0.81351400	4.34626300
H	-6.68086400	1.70073000	2.81641700
C	-6.87204200	-2.15351200	-0.80133400
H	-7.10859900	-1.29746100	-1.43933700
H	-7.46395100	-3.00562400	-1.14169400
H	-5.81669700	-2.38915100	-0.96693900
C	-0.46422400	-2.53166000	-2.32127600
H	-1.43630400	-2.07479200	-2.46998700
C	-0.23138600	-3.85058200	-2.70923500
H	-1.02806200	-4.42275800	-3.17339200
C	1.00537600	-4.44167400	-2.48610700
H	1.16697200	-5.47849600	-2.76165100
C	2.04833800	-3.71631600	-1.90636000
H	2.98807900	-4.21075200	-1.70773400
C	5.46616600	-3.27742800	-1.50747600
H	4.70576600	-3.73653300	-2.12265600
C	6.75154500	-3.82770900	-1.49239000
H	6.94933300	-4.72924300	-2.06264100
C	7.77439000	-3.22942600	-0.76915300
H	8.76536100	-3.67162000	-0.76763500
C	7.54146300	-2.04649800	-0.06653700
H	8.34303800	-1.54830500	0.46973000

#### Singlet open-shell structure of 4

Atom type	x	y	z
C	9.37001000	3.42223100	3.23042700
H	10.41374300	3.10022900	3.14746400
H	9.12948300	3.47354300	4.29517700
H	9.30708600	4.43248000	2.81900500
C	8.45163000	2.47477500	2.50467500
C	8.11501300	2.68507800	1.17117000
H	8.50707500	3.55777600	0.65514800
C	7.29042700	1.80624900	0.47345300
C	6.78202400	0.67658400	1.13536200
C	5.90624400	-0.27499000	0.41618400
C	4.55334800	-0.10754400	0.11547100
C	4.05042500	-1.28574800	-0.56602100
C	2.70634700	-1.35322600	-0.85072800
C	1.88355400	-0.18273500	-0.63184700
C	0.54835300	-0.45204800	-1.03223500
C	-0.54834900	0.45207800	-1.03224500
C	-1.88354600	0.18277000	-0.63184700
C	-2.39691900	-0.95816400	0.03259600
H	-1.73871600	-1.78866000	0.25601500
C	-3.70798000	-0.98696000	0.42222800
H	-4.11314000	-1.83581400	0.96314100
C	-4.55333600	0.10756700	0.11547500
C	-5.90624500	0.27498700	0.41615400

C	-6.78201800	-0.67660600	1.13529900
C	-7.11019600	-0.44547300	2.48193200
C	-7.93651300	-1.34995300	3.14230400
H	-8.18054900	-1.17212700	4.18657400
C	-8.45164000	-2.47482400	2.50457400
C	-9.36992200	-3.42230000	3.23042300
H	-9.30998700	-4.43165800	2.81640300
H	-10.41324300	-3.09808100	3.15104600
H	-9.12669600	-3.47665800	4.29442200
C	6.96381500	2.06923200	-0.97455300
H	7.53557400	2.91882900	-1.35334900
H	5.90129100	2.28830100	-1.11467600
H	7.19213000	1.20009100	-1.59790400
C	7.10985700	0.44564200	2.48209200
C	6.56008600	-0.75096000	3.21507500
H	6.87570200	-0.74683700	4.26027800
H	6.89715800	-1.68843800	2.76330600
H	5.46661100	-0.76355200	3.18977400
C	7.93617200	1.35012900	3.14249400
H	8.17992700	1.17247500	4.18685700
C	6.32486600	-1.55323100	-0.13079500
C	5.21760800	-2.17387900	-0.76556500
C	3.70801000	0.98701000	0.42217400
H	4.11318400	1.83588000	0.96305300
C	2.39694500	0.95821600	0.03255000
H	1.73875600	1.78872800	0.25595000
C	1.80632500	-2.41317400	-1.34765100
C	0.51142700	-1.85776600	-1.46558100
C	-6.32487200	1.55323200	-0.13082400
C	-7.58738000	2.13167500	-0.15507300
H	-8.42124200	1.64007900	0.33628500
C	-7.76430000	3.33233400	-0.83909000
H	-8.74348600	3.79891800	-0.86856100
C	-6.69749000	3.91842600	-1.50971800
H	-6.85117200	4.83425500	-2.07085300
C	-5.42478400	3.33874000	-1.48528500
H	-4.63295300	3.79110200	-2.06495700
C	-5.21761400	2.17389500	-0.76557200
C	-4.05043100	1.28575500	-0.56606300
C	-2.70635500	1.35323900	-0.85078400
C	-1.80633100	2.41319500	-1.34768600
C	-2.00536400	3.75390300	-1.64082300
H	-2.96136900	4.22630000	-1.47034500
C	-0.94448300	4.51655600	-2.12857400
H	-1.10222300	5.56539800	-2.35709800
C	0.30426000	3.94192600	-2.33204600
H	1.11495800	4.53730200	-2.73898900
C	0.52866600	2.60869800	-2.00011400
H	1.50737000	2.16830200	-2.14743100
C	-0.51143500	1.85778500	-1.46563300
C	-7.29008200	-1.80646500	0.47349300
C	-8.11468300	-2.68531600	1.17120300
H	-8.50648600	-3.55817100	0.65525800
C	-6.56075900	0.75133400	3.21483000
H	-5.46726700	0.76386000	3.19006500
H	-6.87688300	0.74751800	4.25988000

H	-6.89755100	1.68870000	2.76263200
C	-6.96318600	-2.06964900	-0.97441500
H	-7.19163900	-1.20068200	-1.59796000
H	-7.53468800	-2.91945700	-1.35312400
H	-5.90059400	-2.28848100	-1.11436400
C	-0.52868500	-2.60869400	-2.00002200
H	-1.50739600	-2.16830500	-2.14732100
C	-0.30428100	-3.94192600	-2.33194000
H	-1.11498600	-4.53730900	-2.73885900
C	0.94446800	-4.51654900	-2.12848900
H	1.10220100	-5.56539700	-2.35699200
C	2.00535700	-3.75388500	-1.64077300
H	2.96136400	-4.22628000	-1.47028400
C	5.42478000	-3.33871100	-1.48529700
H	4.63294900	-3.79107200	-2.06497000
C	6.69748300	-3.91841100	-1.50971200
H	6.85116300	-4.83423700	-2.07085100
C	7.76428600	-3.33234000	-0.83905800
H	8.74346700	-3.79893600	-0.86851500
C	7.58736700	-2.13168500	-0.15502700
H	8.42122600	-1.64010500	0.33635200

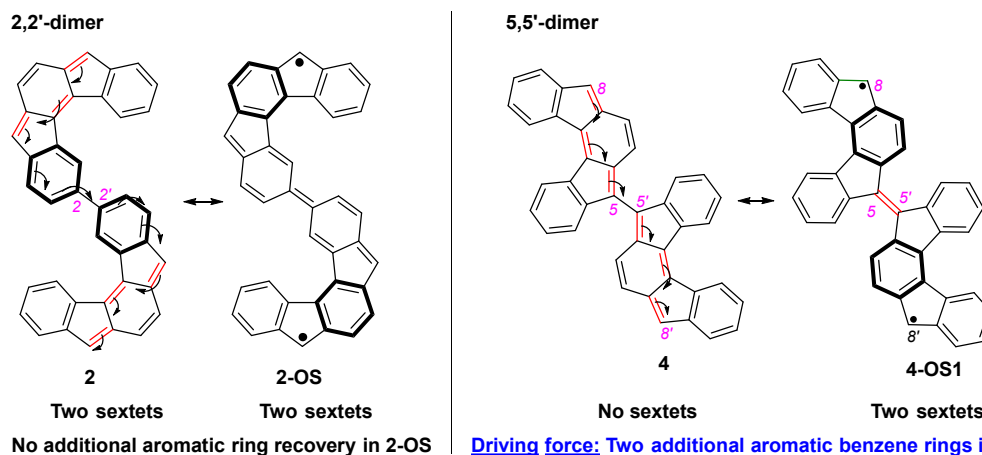
### Triplet structure of 4

Atom type	x	y	z
C	9.55233700	3.40241700	3.06153700
H	10.59307700	3.07781100	2.95482400
H	9.33810600	3.45922100	4.13165900
H	9.48112400	4.41076600	2.64697900
C	8.61477100	2.45322100	2.36313400
C	8.22592300	2.67106200	1.04514400
H	8.59155700	3.55061200	0.52143200
C	7.38211200	1.79102200	0.37258800
C	6.90850300	0.65153200	1.04400100
C	6.01038600	-0.29730300	0.35263400
C	4.61568900	-0.11722400	0.10135500
C	4.08935800	-1.27610700	-0.55484800
C	2.71970200	-1.33048200	-0.79023200
C	1.93152000	-0.16569100	-0.56076800
C	0.52240100	-0.44485600	-0.87869000
C	-0.52235700	0.44459200	-0.87877100
C	-1.93147500	0.16548000	-0.56086300
C	-2.46226200	-0.94540900	0.09915700
H	-1.82261500	-1.77685600	0.36619800
C	-3.80115700	-0.96450800	0.44935600
H	-4.22265400	-1.80675000	0.98838300

C	-4.61568200	0.11713400	0.10121000
C	-6.01032000	0.29734600	0.35259000
C	-6.90854900	-0.65134900	1.04397300
C	-7.28950100	-0.41276700	2.37565300
C	-8.13340200	-1.31887100	3.01102000
H	-8.41818600	-1.13533200	4.04392700
C	-8.61512300	-2.45275500	2.36314000
C	-9.55285100	-3.40180300	3.06152200
H	-9.48127400	-4.41032100	2.64743400
H	-10.59359600	-3.07742100	2.95417800
H	-9.33911000	-3.45810500	4.13176600
C	7.00123100	2.05884400	-1.06107400
H	7.53492600	2.92867200	-1.44927500
H	5.92863800	2.24637400	-1.16504000
H	7.23549100	1.20276400	-1.70026300
C	7.28898400	0.41334700	2.37588500
C	6.77745300	-0.79326400	3.12036700
H	7.11544700	-0.78256800	4.15851400
H	7.12226100	-1.72454600	2.66186400
H	5.68412100	-0.82665600	3.11890500
C	8.13273600	1.31959300	3.01123800
H	8.41715200	1.13638400	4.04430600
C	6.38343400	-1.56293000	-0.21049900
C	5.23934300	-2.16945600	-0.80516800
C	3.80115500	0.96443800	0.44937000
H	4.22264300	1.80675100	0.98829200
C	2.46225900	0.94527200	0.09914800
H	1.82258900	1.77673700	0.36607400
C	1.79447200	-2.40621500	-1.18658200
C	0.48371300	-1.87963200	-1.23054900
C	-6.38330300	1.56301700	-0.21057000
C	-7.64229000	2.15918700	-0.29482300
H	-8.50029000	1.68080400	0.16723600
C	-7.77783500	3.34943900	-0.99752700
H	-8.74913600	3.82679800	-1.07429100
C	-6.67463000	3.91552400	-1.63311900
H	-6.79682500	4.82403800	-2.21373400
C	-5.41014900	3.32612800	-1.54981200
H	-4.59233700	3.76354500	-2.10489200
C	-5.23921700	2.16937900	-0.80539300
C	-4.08929100	1.27594800	-0.55509300
C	-2.71963800	1.33027200	-0.79044900
C	-1.79438300	2.40595200	-1.18690300
C	-2.00682200	3.75336100	-1.45535800
H	-2.98380100	4.19546300	-1.32977400
C	-0.94242000	4.55029600	-1.86166500
H	-1.10937000	5.60216400	-2.06922700
C	0.32611700	4.00189000	-2.02174000
H	1.14341400	4.61928400	-2.37958800
C	0.55937600	2.66805300	-1.71072100
H	1.55094900	2.25430000	-1.83841900
C	-0.48363800	1.87933500	-1.23079500
C	-7.38184500	-1.79111200	0.37278200
C	-8.22580200	-2.67099700	1.04535200
H	-8.59119000	-3.55074900	0.52180800
C	-6.77822700	0.79403900	3.12000100

H	-5.68487800	0.82710300	3.11936500
H	-7.11700500	0.78385700	4.15789600
H	-7.12239300	1.72523400	2.66086200
C	-7.00057400	-2.05937200	-1.06069600
H	-7.23476600	-1.20351900	-1.70021700
H	-7.53411300	-2.92936700	-1.44873400
H	-5.92794900	-2.24684100	-1.16437500
C	-0.55927700	-2.66843800	-1.71039300
H	-1.55085800	-2.25472500	-1.83815400
C	-0.32598000	-4.00230300	-2.02125100
H	-1.14325700	-4.61976400	-2.37903000
C	0.94257200	-4.55066000	-1.86110100
H	1.10954600	-5.60254900	-2.06853600
C	2.00694900	-3.75365200	-1.45487800
H	2.98394000	-4.19570800	-1.32923600
C	5.41032200	-3.32630000	-1.54943100
H	4.59250700	-3.76388600	-2.10437200
C	6.67484900	-3.91559100	-1.63276000
H	6.79707800	-4.82417100	-2.21326400
C	7.77806200	-3.34933600	-0.99732100
H	8.74939200	-3.82663400	-1.07409700
C	7.64246900	-2.15901800	-0.29475200
H	8.50044800	-1.68051800	0.16722800

**Structural and electronic factors driving 5,5'-dimer to show open-shell traits:**



No additional aromatic ring recovery in 2-OS

**Driving force:** Two additional aromatic benzene rings in 4-OS1

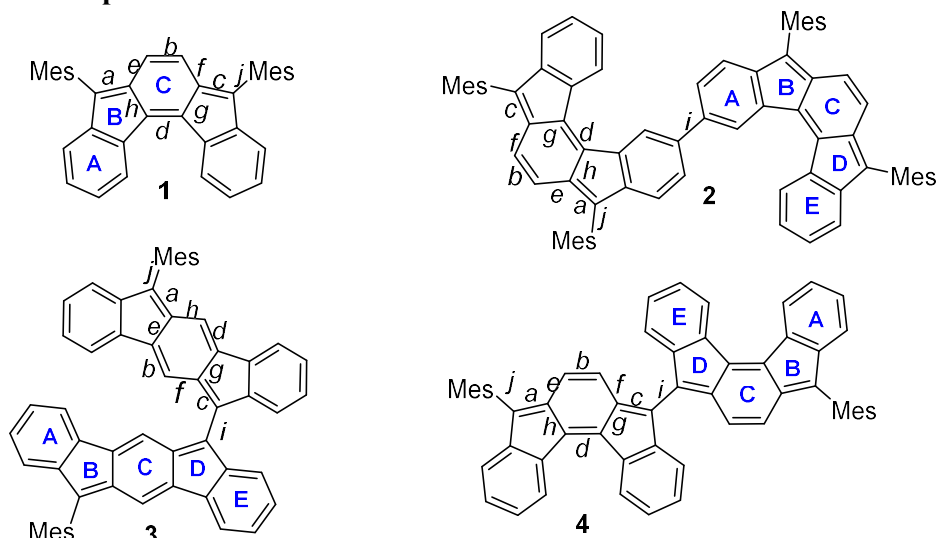
**Fig. S15** Closed-shell and open-shell resonance forms of parent isomers 2,2'-biindeno[2,1-*c*]fluorene (left) and 5,5'-biindeno[2,1-*c*]fluorene (right).

**Discussion:** Considering the effective  $\pi$ -delocalization path for parent isomeric IF dimers, shown in above Fig. S15, structurally, there is no net gain in Clar sextets (benzene aromaticity) for compound **2**, the 2,2'-dimer. While for **4**, it avoids two *as*-indacene antiaromaticities from **4** to **4-OS1** by recovering two additional Clar sextets. Therefore, compound **2** is closed-shell quinoidal while open-shell state of **4** is energetically more stable than the closed-shell form.

Electronically, the orbital coefficients of frontier molecular orbitals HOMO and LUMO are greater in 5,5'-positions in comparison to 2,2'-positions (Ref. 3b in main text). Therefore,

attaching an ambipolar [2,1-*c*]IF unit to C5 position of another [2,1-*c*]IF scaffold should influence the HOMO and LUMO energies greater than that could do for C2 substitution. A small HOMO-LUMO gap is the key to observe open-shell properties in the ground state. BIF **4** with more destabilized HOMO and stabilized LUMO (than those of BIF **2**) has a smaller HOMO-LUMO energy gap and exhibits ground state open-shell properties (as observed experimentally by EPR and SCXRD analyses).

**Structural comparison:**



**Fig. S16** Indeno[2,1-*c*]fluorene **1** and its dimers **2**, **4** including an OS [1,2-*b*]IF dimer **3**.

**Table S4.** Comparison of mean C-C bond lengths (Å) for quinoidal core of **1**, **2**, **3** & **4**

Bonds <sup>[a]</sup>	<b>4</b> <sup>X-ray</sup>	<b>4</b> <sup>DFT</sup>	<b>1</b> <sup>X-ray</sup>	<b>2</b> <sup>DFT</sup>	<b>3</b> <sup>X-ray</sup>	<b>3</b> <sup>DFT</sup>
<i>a</i>	1.377	1.396	1.371	1.379	1.392	1.403
<i>b</i>	1.354	1.368	1.357	1.359	1.364	1.368
<i>c</i>	1.393	1.419	1.374	1.378	1.392	1.429
<i>d</i>	1.367	1.376	1.366	1.369	1.367	1.371
<i>e</i>	1.431	1.417	1.434	1.436	1.456	1.441
<i>f</i>	1.432	1.417	1.434	1.436	1.415	1.416
<i>g</i>	1.465	1.447	1.470	1.476	1.459	1.436
<i>h</i>	1.466	1.451	1.470	1.476	1.416	1.414
<i>i</i>	1.451	1.421	-	1.481	1.452	1.414
<i>j</i>	1.484	1.480	1.486	1.485	1.501	1.480

**Table S5.** Comparison of NICS(1)<sub>zz</sub> (ppm) for **1**, **2**, **3** & **4**

Rings	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
A	-17.59	-14.32	-18.04	-17.11
B	17.62	14.77	5.40	5.59
C	8.16	6.92	-2.0	-2.73
D	-	15.78	5.55	8.60
E	-	-16.19	-18.90	-18.82

**Table S6.** Comparison of electronic properties including optical and electrochemical HOMO-LUMO gaps

Compounds	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
HOMO (eV)	-5.70	-5.06	-5.18	-4.98
LUMO (eV)	-3.63	-3.44	-3.80	-3.65
$E_{\text{gap}}^{\text{opt}}$ (eV)	1.60	1.50	1.50	1.33
$E_{\text{gap}}^{\text{ec}}$ (eV)	2.07	1.62	1.38	1.33

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