# Tailoring Diradicaloid Properties of Expanded Isophlorinoids with Systematic Core-Modification

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## **General information**

All reactions carried out in two necked round bottom flask under inert atmosphere. In addition, oxidation with DDQ carried out in open atmosphere. Dichloromethane dried prior to use with phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>). Chemicals bought from Sigma Aldrich, Alfa-Aesar and TCI. For column chromatography, aluminum oxide (basic) from Merck used. A size exclusion column performed if required using toluene bought from Spectrochem.

**Analytical information:** Column chromatography was performed on basic alumina in glass columns. Size exclusion chromatography with Bio-Beads S-X1 (BIO-RAD). <sup>1</sup>H-NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts reported as the delta scale in ppm relative to Chloroform-*d*, Dichloromethane-*d*<sub>2</sub>, Acetone-*d*<sub>6</sub>. Electronic spectra recorded on a Perkin-Elmer  $\lambda$ - 35 UV–Vis spectro-photometer. High Resolution Mass Spectrum (HRMS) obtained using WATERS G2 Synapt Mass Spectrometer. Single-crystal diffraction analysis data were collected at 100 K with a BRUKER KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite monochromatic Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structures were solved by direct methods and refined by least-squares against F2 utilizing the software packages SHELXL-2017,<sup>1a,b</sup> and WINGX.<sup>1c</sup> In case of disordered solvent molecules, the contributions to the scattering arising from the disordered solvents in the crystal were removed by use of the utility SQUEEZE in the PLATON software package.<sup>2</sup> More information on crystal

structures can also be obtained from the Cambridge Crystallographic Data Centre under CCDC deposition number **5** = 1940908, **7** = 2051833, **10** = 2051835.

#### **Computational Details**

Quantum mechanical calculations were performed with the Gaussian16 rev D program<sup>3</sup> suite using a High Performance Computing Cluster facility of IISER PUNE. All initial geometries optimization and HOMO-LUMO calculation were carried out by Density functional theory (DFT) with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (RB3LYP) and 6-31G (d, p) basis set for all the atoms were employed in the calculations. The global ring centers for the NICS (0) values were designated at the non-weighted mean centers of the macrocycles. The NICS (0)<sup>4</sup> value was obtained with gauge independent atomic orbital (GIAO) method based on the optimized geometries. ACID plots were calculated by using the method developed by Herges<sup>5</sup>. Singlet-triplet energies and NOON (natural orbital occupation number)<sup>6</sup> calculations were performed using DFT UCAM-B3LYP/631G(d) level. Diradical character (y0) were determined on the basis of the LUNO and LUNO+1 occupation number (*n*) in natural orbital analysis according to Yamaguchi's scheme: *yi* = 1 – (2*T*/(1 + *T*2)), where *T* =(*nHOMO-i* – *nLUMO+i*)/2. The molecular structures obtained from single crystal analysis were used to obtain the geometry optimized structures.

### **EXPERIMENTAL SECTION**

#### General Procedure for the synthesis of 5

Flame-dried 250-mL two neck round-bottomed flask was charged with biselenophene **4** (128mg,0.77mmol), and(phenylmethylene)bis(thiophene5,2diyl))bis((perfluorophenyl)methanol **3** (500mg, 0.77 mmol) in 200 ml of freshly distilled anhydrous dichloromethane under an nitrogen atmosphere and degassed with nitrogen for further ten minutes. BF<sub>3</sub>.OEt<sub>2</sub> (95.02 mml, 0.77 mmol) was added under dark using a syringe, and the resulting solution was stirred for one hour under an inert atmosphere. After adding DDQ (700 mg, 3.085 mmol), the solution was opened to air and stirred for one more hour. Few drops of triethylamine were added, and the reaction mixture was concentrated under reduced pressure. Purification through basic alumina column chromatography by using CH<sub>2</sub>Cl<sub>2</sub>/hexane as eluent followed by size exclusion column chromatogrphy using toluene gave desired macrocycle, as blue-colored band in 14% yield.

**HR-MS** (ESI-TOF): m/z = 1741.7310 (found), Calculated for (C<sub>74</sub>H<sub>26</sub>F<sub>20</sub>S<sub>4</sub>Se<sub>4</sub>), (1741.7279).

**UV-Vis:** (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> nm (ε, Lmol<sup>-1</sup>cm<sup>-1</sup>): 455 nm (24000), 579 (90000), 685(16500).

<sup>1</sup>**H NMR** (400 MHz, in Dichloromethane-*d*<sub>2</sub> at 253 K) δ: 8.32 (d, <sup>3</sup>*J* (H-H) = 5.2 Hz, 2H), 7.62-7.58 (m, 10H), 7.50 (d, <sup>3</sup>*J* (H-H) = 2.8, 2H), 7.38 (d, <sup>3</sup>*J* (H-H) = 5.2, 2H), 7.26 (d, <sup>3</sup>*J* (H-H) = 4.4 Hz, 2H), 6.74 (br s, 2H), 6.48(br s, 2H), 5.69 (br s, 2H), 5.58 (br s, 2H).

## Procedure for the synthesis of 7

(phenylmethylene)bis(thiophene5,2diyl)bis((perfluorophenyl)methanol **3** (500 mg, 0.90 mmol) and bifuran **6** (100 mg, 0.90 mmol) were reacted in presence of BF<sub>3</sub>.OEt<sub>2</sub> as described above to yield **7**, as green colored band in 4% yield.

**HR-MS** (ESI-TOF) : m/z = 1486.0386 (found), Calculated for (C<sub>74</sub>H<sub>26</sub>F<sub>20</sub>O<sub>4</sub>S<sub>4</sub>), (1486.0395).

**UV-Vis** (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> nm (ε, Lmol<sup>-1</sup>cm<sup>-1</sup>): 371(51000), 508 (36000), 637 (83000).

<sup>1</sup>**H NMR** (400 MHz, Acetone-*d*<sub>6</sub>, 233 K) δ: 7.72 (d, <sup>3</sup>*J* (H-H) = 4.4 Hz, 2H), 7.70 (d, <sup>3</sup>*J* (H-H) = 4.4 Hz, 2H), 7.60-7.40 (br s, 6H), 7.30 (d, <sup>3</sup>*J* (H-H) = 5.2, 2H), 7.21 (d, <sup>3</sup>*J* (H-H) = 4.8 Hz, 2H), 6.83 (br s, 4H), 6.80 (d, <sup>3</sup>*J* (H-H) = 4.4 Hz, 2H), 6.46 (d, <sup>3</sup>*J* (H-H) = 5.2 Hz, 2H), 5.84 (d, <sup>3</sup>*J* (H-H) = 5.2 Hz, 2H), 5.51 (d, <sup>3</sup>*J* (H-H) = 5.5 Hz, 2H).

#### Procedure for the synthesis of 10

Bithiophene **9** (150 mg, 0.90 mmol) and difuryl diol **8** (556 mg, 0.90 mmol) were reacted in presence of  $BF_3.OEt_2$  as described above to yield **10** in 16% yield.

**HR-MS** (ESI-TOF) : m/z = 1486.0381 (found), Calculated for (C<sub>74</sub>H<sub>26</sub>F<sub>20</sub>O<sub>4</sub>S<sub>4</sub>), (1486.0395).

**UV-Vis** (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> nm (ε, Lmol<sup>-1</sup>cm<sup>-1</sup>): 466 (23000), 593 (92000), 733 nm (18000).

<sup>1</sup>**H NMR** (400 MHz, Acetone- $d_6$ , 193K)  $\delta$ : 9.45 (d, <sup>3</sup>*J* (H-H) = 5.2 Hz, 1H), 9.34 (d, <sup>3</sup>*J* (H-H) = 5.6 Hz, 1H), 9.24 (d, <sup>3</sup>*J* (H-H) = 5.2, 1H), 9.06 (d, <sup>3</sup>*J* (H-H) = 3.6, 1H), 8.61 (d, <sup>3</sup>*J* (H-H) = 3.6 Hz, 1H), 8.49 (d, <sup>3</sup>*J* (H-H) = 4.8 Hz, 1H), 8.41 (d, <sup>3</sup>*J* (H-H) = 4.4 Hz, 1H), 8.25 (br s, 2H), 8.19 (d, <sup>3</sup>*J* (H-H) = 5.2 Hz, 1H), 8.13 (br s, 2H), 7.98 (br s, 2H), 7.69 (br s, 3H), 5.34 (m, 2H), 5.03 (m, 3H), 4.34 (br s, 1H) 4.15 (br s, 1H), 3.87 (br s, 1H), 3.37 (br s, 1H).

Crystal Data	5	7	10
Identification code	comp_5	comp_7	comp_10
Empirical formula	$C_{104}H_{56}F_{20}S_4Se_4$	$C_{78}H_{30}O_4F_{20}S_4CI_{12}$	$C_{77}H_{29}O_4F_{20}S_4Cl_9$
Formula weight	2129.56	1964.66	1845.29
Temperature/K	100(2)	100(2)	100(2)
Crystal system	triclinic	monoclinic	triclinic
Space group	P-1	C2/c	P-1
a/Å	13.490(5)	25.994(3)	13.895(6)
b/Å	18.005(6)	28.344(4)	15.650(7)
c/Å	19.696(7)	11.9777(15)	17.908(8)
α/°	90.718(8)	90	106.352(9)
β/°	109.418(7)	113.851(3)	94.537(9)
γ/°	98.519(8)	90	100.804(10)
Volume/Å <sup>3</sup>	4452(3)	8071.2(17)	3634(3)
Z	2	4	2
$\rho_{calc}g/cm^3$	1.589	1.617	1.686
µ/mm⁻¹	1.834	0.612	0.566
F(000)	2120.0	3912.0	1840.0
Crystal size/mm <sup>3</sup>	$0.21 \times 0.04 \times 0.030$	0.26 × 0.24 × 0.036	0.2 × 0.03 × 0.016
Radiation	ΜοΚ <sub>α</sub> (λ = 0.71073)	ΜοΚ <sub>α</sub> (λ = 0.71073)	ΜοΚ <sub>α</sub> (λ = 0.71073)
R(Reflections)	0.05 (10134)	0.059 (6320)	0.120 (6524)

 Table 1: Crystal information of octaphyrins 5, 7 and 10.



S1: High resolution mass spectrum (ESI-TOF) of 5



**S2:** Variable temperature <sup>1</sup>H NMR of **5** in Dichloromethane- $d_{2}$ .



.**S4:**  $\pi$ -stacking of **5** *meso*-substituents and solvents are omitted for clarity.



S5: A] Cyclic (Blue) and Differential pulse (red) voltammograms of 5 in dichloromethane containing 0.1M tetrabutylammonium perchlorate as the supporting electrolyte recorded at 50 mVs<sup>-1</sup>. B] Variable temperature EPR spectra of 5.



**S7:** Variable temperature <sup>1</sup>H NMR of spectra of **7** in Acetone- $d_6$ .



**S8**: <sup>1</sup>H NMR of spectra of **7** at 233K in Acetone- $d_{6}$ .



**S9**: <sup>1</sup>H NMR Spectrum for **7** at 233 K in acetone- $d_6$ .



**S10**: Cyclic (Blue) and Differential pulse (red) voltammograms of **7** in dichloromethane containing 0.1M tetrabutylammonium perchlorate as the supporting electrolyte recorded at 50 mVs<sup>-1</sup>.



S11: Variable temperature EPR spectra of 7.



S12: High resolution mass spectrum (ESI-TOF) of 10.



**S13:** Variable temperature <sup>1</sup>H NMR Spectrum of **10** in Acetone-*d*<sub>6</sub>.



**S14:** Partial <sup>1</sup>H-<sup>1</sup>H COSY spectrum of **10** at 193 K in Acetone- $d_6$ .



S15: A] Cyclic (Blue) and Differential pulse (red) voltammograms of 10 in dichloromethane containing 0.1M tetrabutylammonium perchlorate as the supporting electrolyte recorded at 50 mVs<sup>-1</sup>. B] Variable temperature EPR spectra of 10.

# **Computational Studies**

Macrocycle	NICS (ppm)	NOON	λ Max (nm)	ΔE(S-T)
5	-14.68	30.55	579	-5.31871
7	-18.23	24.20	593	-5.55903
10	-3.62	47.28	637	-3.50524

**S16**: Radical character and Singlet-Triplet Energies were calculated at DFT UCAM-B3LYP/6-31G (d) basis set and NICS (0) at RB3LYP/6-31G (d) basis set using Gaussian 16.



S17: Calculated spin density distribution using DFT UCAM-B3LYP/6-31G (d) for A = 5, B =

**10,** C = **7.** 



**S18:** Calculated UCAM-B3LYP/631G (d) frontier orbital profiles for  $\alpha$  and  $\beta$  electrons. (A = SOMO- $\alpha$  of **5**, B = SOMO- $\beta$  of **5**.)



**S19:** Calculated UCAM-B3LYP/631G (d) frontier orbital profiles for  $\alpha$  and  $\beta$  electrons. (A = SOMO- $\alpha$  of **10**, B = SOMO- $\beta$  of **10**, C = SOMO- $\alpha$  of **7**, D = SOMO- $\beta$  of **7**).



**S20:** ACID plot at iso value 0.05, ( $\sigma$  plus  $\pi$  electrons) for **5** the external magnetic field applied orthogonal to the plane of the macrocycle.



**S21:** ACID plot **10** ( $\sigma$  plus  $\pi$  electrons) at iso value 0.05, the external magnetic field applied orthogonal to the plane of the macrocycle.



**S22:** ACID plot **7** ( $\sigma$  plus  $\pi$  electrons) (left = top view, right = side view) at iso value 0.05, the external magnetic field applied orthogonal to the plane of the macrocycle.



**S23:** Optimized geometry for octaphyrin **5** at RB3LYP/6-31G (d, p).



**S24:** Optimized geometry for octaphyrin **10** at RB3LYP/6-31G (d, p).



**S25:** Optimized geometry for octaphyrin **7** at RB3LYP/6-31G (d, p).



# **Additional Figures:**

**S26:** Rmerge vs Resolution curve for **7**.











**S29**:  $I/\sigma(I)$  vs resolution for **10**.

For the compounds **7** and **10**, we obtained very poor diffraction data even with 50 sec exposure time and frame width of 1 degree. It could be reason behind at  $I/\sigma(I)$  value of 3.4 and the resolution is close to 40 degree (d ~ 1Å) in the case of compound **10**. Similarly, for compound **7** with the similar exposure time and frame width 1 degree the resolution of the data is close to 50 degree (d ~ 0.84 Å).

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