**Supplementary Materials**

**Contents**

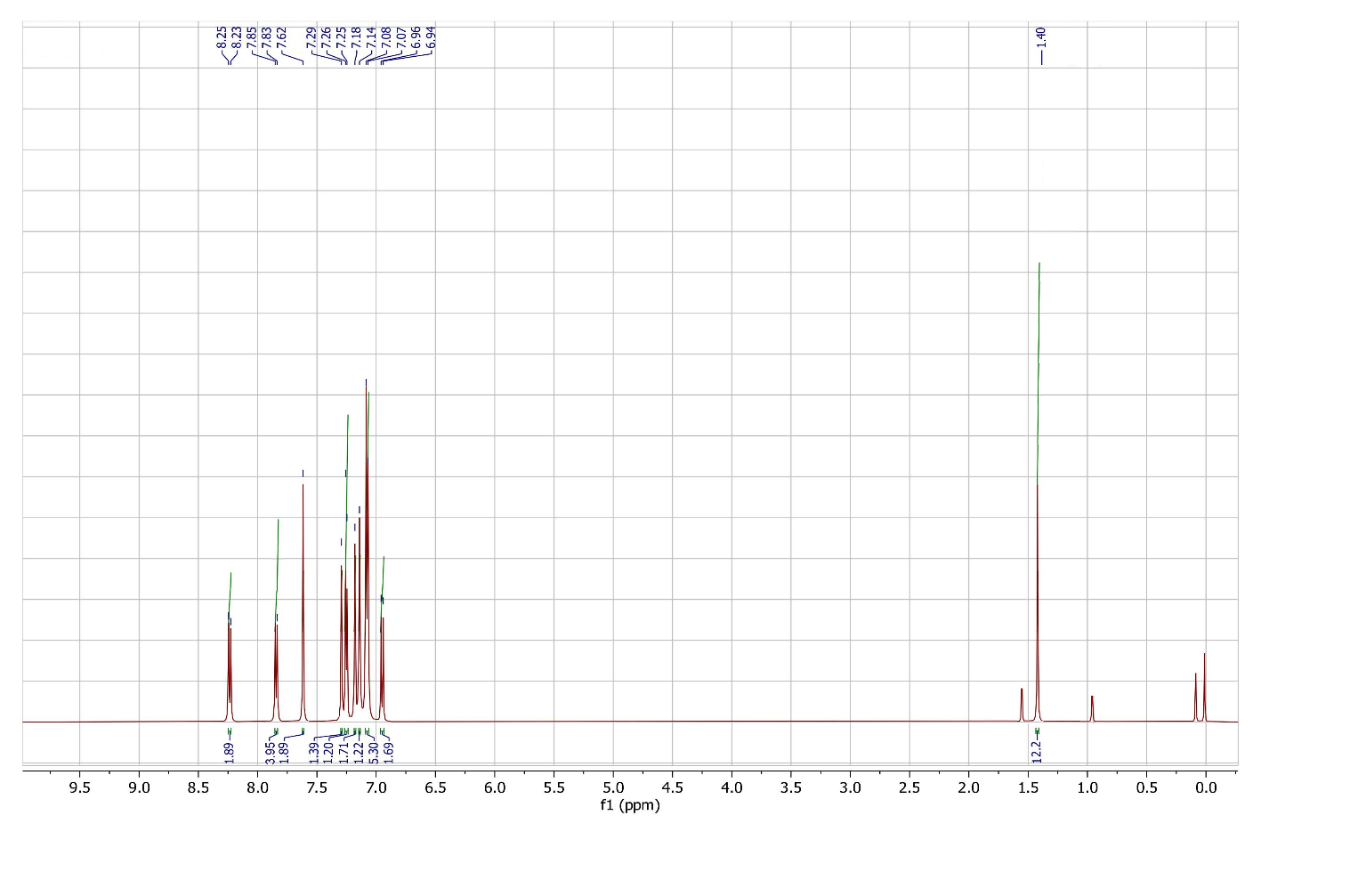
**1. Spectra of compounds**

**2.** **Thermal properties**

**3. Density Functional Theory (DFT) Calculations**

**4.** **Cyclic voltammetry studies**

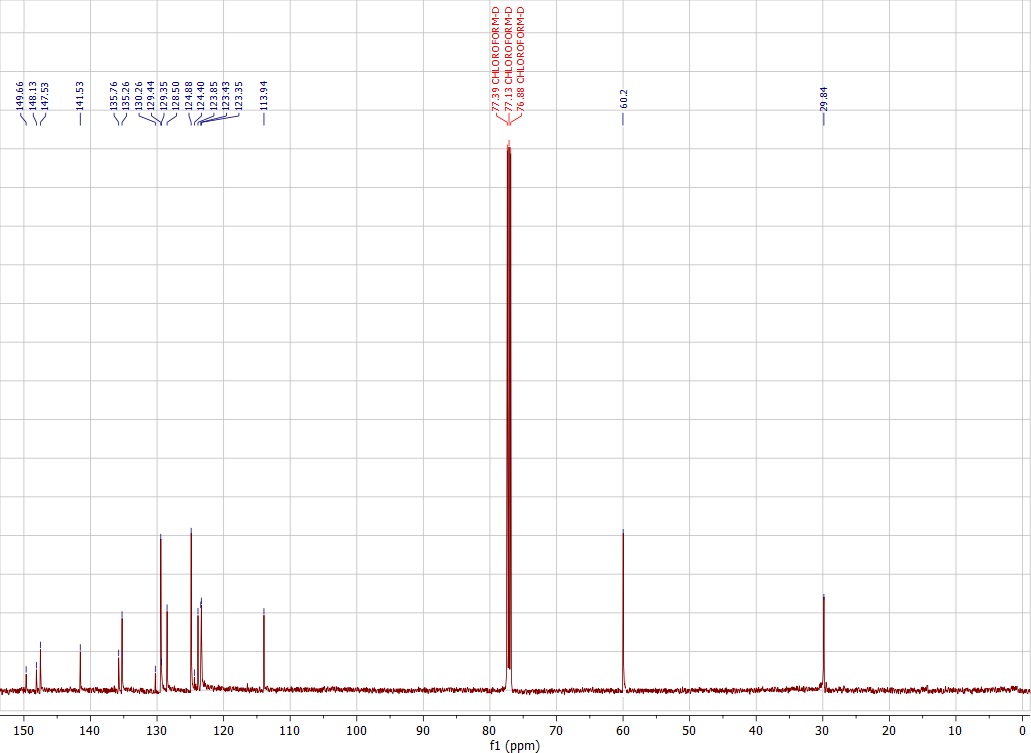
**1. Spectra of compounds**



**Figure S1.** 1H NMR spectra of 6-(N,N-diphenylaniline)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)-azulene **4**.

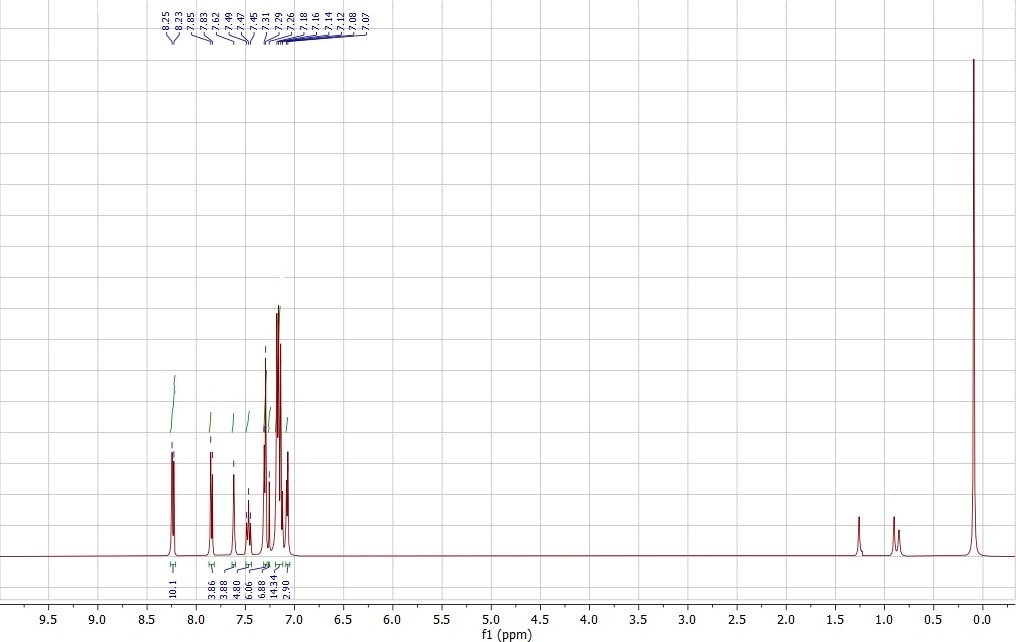
1H NMR: δ 8.25 (d, J = 9.40 Hz, 2H), 7.84 (d, J = 8.3 Hz, 4H), 7.62 (s, 2H), 7.29 – 6.94 (m, 12H), 1.40 (s, 12H).

In this spectrum, the proton signals at С-1 and С-3 (singlet at 7.62 δ) are consistent with the signals of the same protons of the initial molecule **2** [1], which confirms the structure of molecule **4**. In the case of substitution of the azulene position **2** with a diphenylaniline group, a significant shift of proton signals during C-1 and C-3 in a strong field would occur by an average of 1.0 δ due to an increase in electron density in the five-membered ring [2].



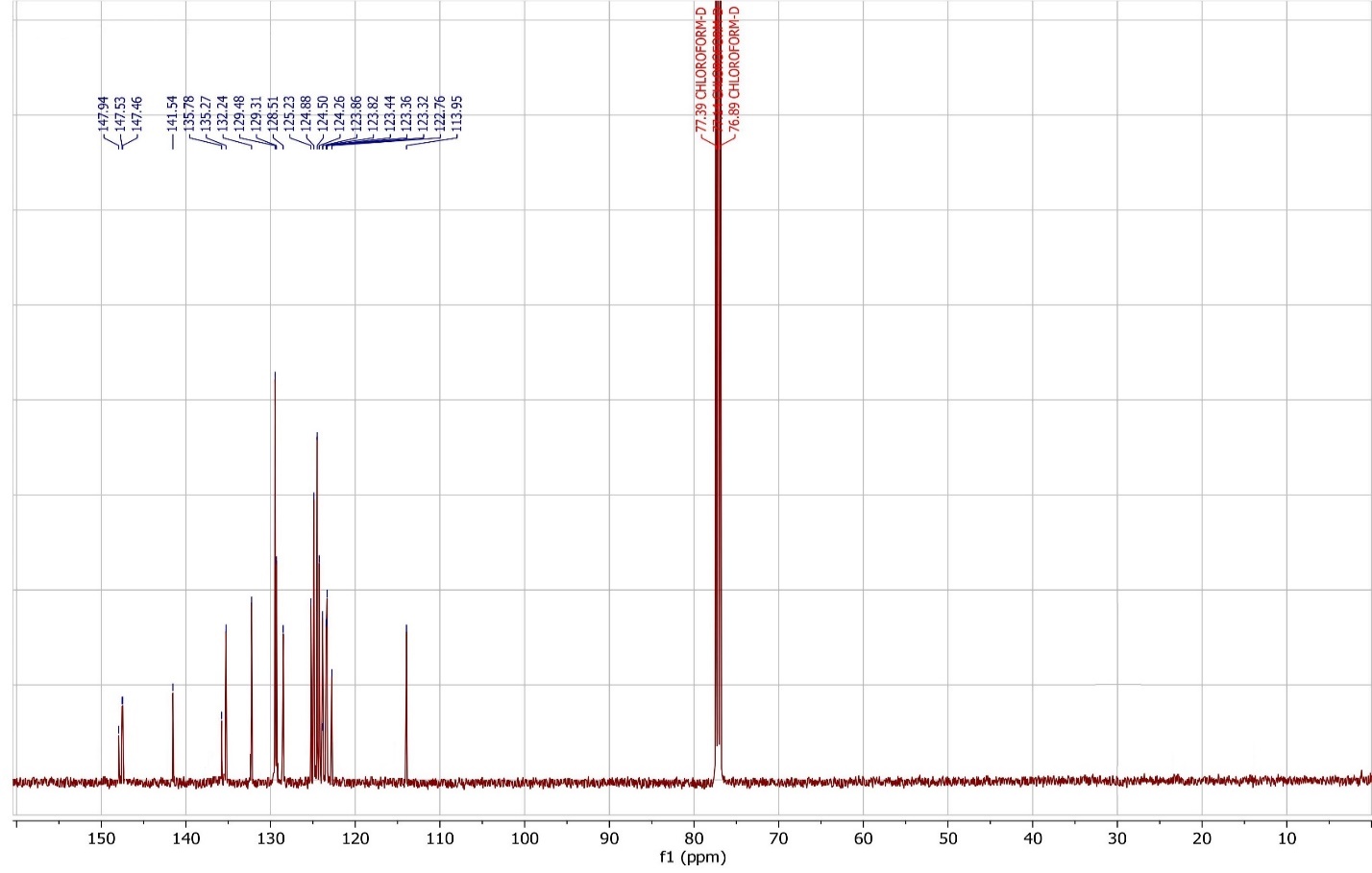
**Figure S2**. 13C NMR spectra of 6-(N,N-diphenylaniline)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)-azulene **4**.

13C NMR: δ 149.66, 148.13, 147.54, 141.53, 135.77, 135.26, 130.26, 129.44, 129.35, 128.50, 124.88, 124.40, 123.85, 123.43, 123.35, 113.94, 60.20, 29.84.



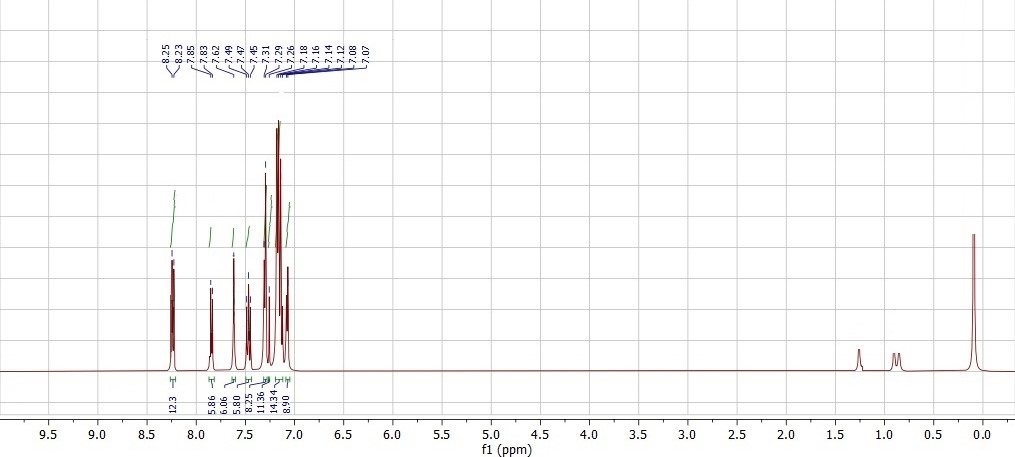
**Figure S3.** 1H NMR spectra of 6,6-Bis(N,N-diphenylaniline)- 2,2-(4-(diphenylamino)phenyl)-bis-azulene  **6**.

1H NMR: δ 8.24 (d, J = 9.4 Hz, 10H), 7.88 (d, J = 12.3 Hz, 4H), 7.62 (s, 4H), 7.47 (t, J = 9.9 Hz, 5H ),7.37 – 7.04 (m, 30H).



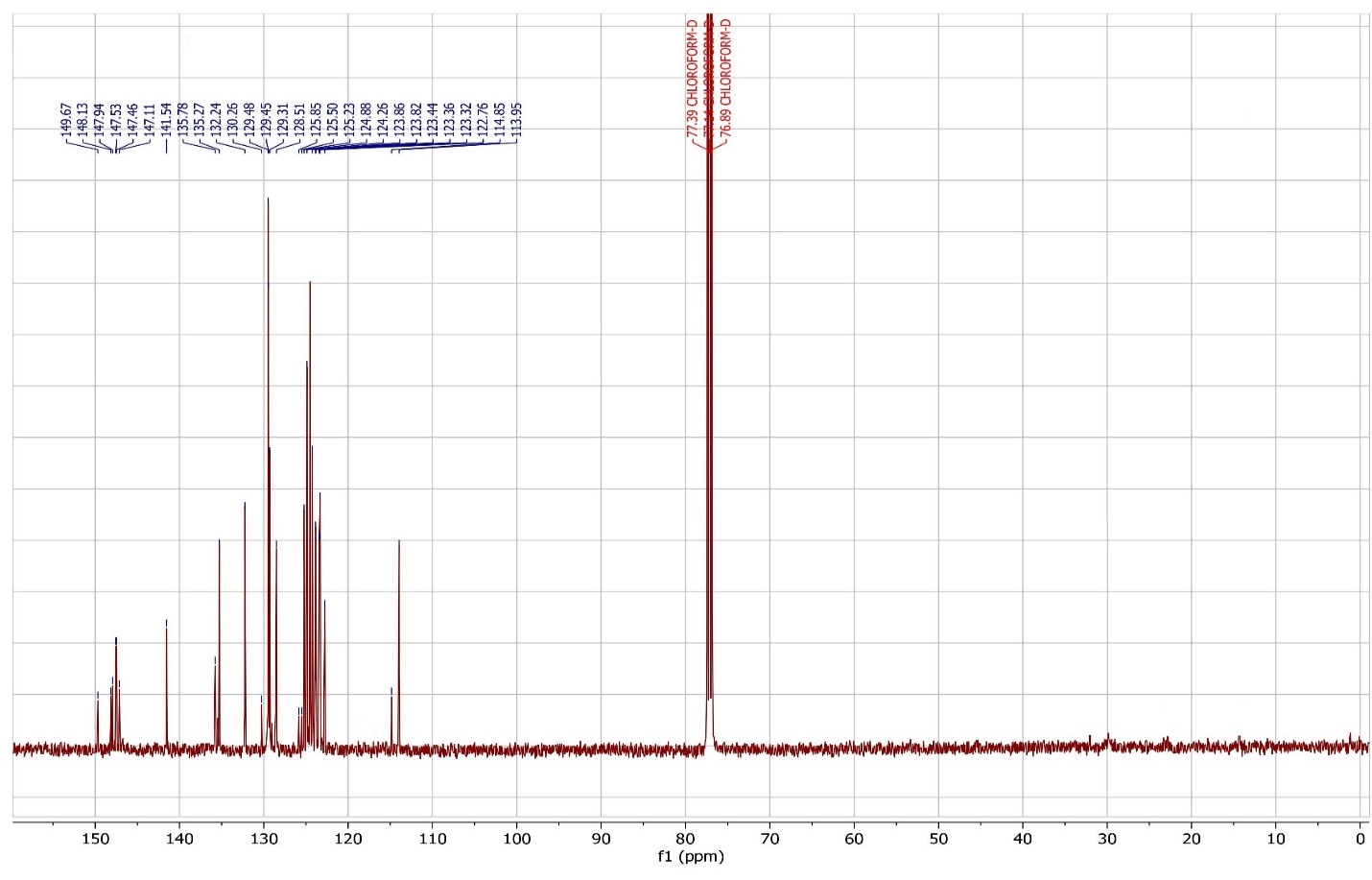
**Figure S4.** 13C NMR spectra of 6,6-Bis(N,N-diphenylaniline)- 2,2-(4-(diphenylamino)phenyl)-bis-azulene  **6**.

13C NMR: δ 147.84, 147.63, 147.44, 141.64, 135.88, 135.37, 132.44, 129.78, 129.21, 128.41, 125.33, 124.78, 124.47, 124.36, 123.76, 123.72, 123.34, 123.46, 123.22, 122.61, 113.84



**Figure S5.** 1H NMR spectra of 6,6,6-tris(N,N-diphenylaniline)- 2,2,2-(4-(triphenylamino)-tris-azulene **8**.

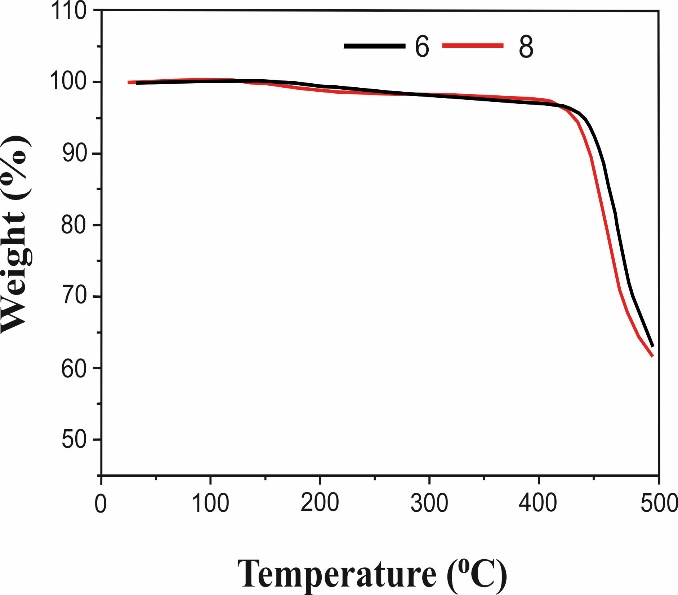
1H NMR: δ 8.24 (d, J = 9.4 Hz, 12H), 7.88 (d, J = 12.3 Hz, 6H), 7.62 (s, 6H), 7.47 (t, J = 9.9 Hz, 6H ),7.37 – 7.04 (m, 42H).



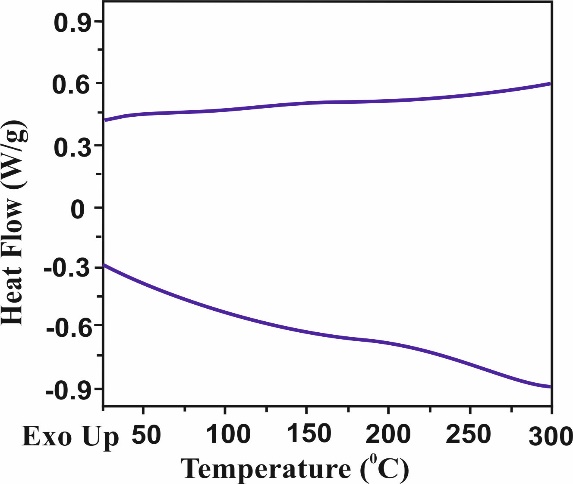
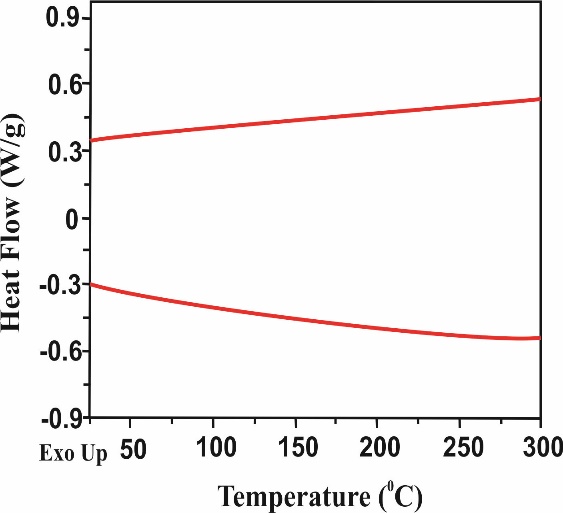
**Figure S6**. 13C NMR spectra of 6,6,6-tris(N,N-diphenylaniline)- 2,2,2-(4-(triphenylamino)-tris-azulene **8**.

13C NMR: δ 149.57, 148.23, 147.84, 147.43, 147.66, 147.21, 141.44, 135.68, 137.37, 132.14, 130.36, 129.58, 129.55, 129.21, 128.41, 125.75, 125.46, 125.32, 124.77, 124.46, 123.36, 13.52, 123.14, 123.66, 123.13, 122.36, 114.55, 113.25.

**2.** **Thermal properties**



**Figure S7**. Thermogravimetric measurements of co-oligomers **6** and **8**

**(a) (b)**

**Figure S8**. Differential scanning calorimetry measurements of co-oligomers **6** (a) and **8** (b)

**3. Density Functional Theory (DFT) Calculations**

To characterize the geometry and orbitals of HOMO-LUMO of co-oligomers **6** and **8**, DFT calculations based on the level of B3LYP/6-31G \* (d, p) Gaussian 16 were used. The geometry of the molecules was optimized in a singlet state using the keywords Opt and Freq, and the results were recorded in a .chk file to visualize the boundary orbitals.

After the correct completion of the calculations, the .chk file was opened in GaussView 6.0 and the HOMO-LUMO orbitals were visualized from it using the built-in GaussView tool. Then we obtained the energies of the boundary orbitals in Hartree units and recalculated them into eV, multiplying by the recalculation coefficient 27.2114.

**Table S1**. Atomic coordinates of optimized geometry of **6**

---------------------------------------------------------------------

Center Atomic Atomic Coordinates (Angstroms)

Number Number Type X Y Z

---------------------------------------------------------------------

1 7 0 0.000016 5.209712 -0.000009

2 6 0 0.000032 6.641096 0.000008

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4 6 0 -0.884358 8.750167 0.824065

5 6 0 0.000046 9.457247 0.000018

6 6 0 0.884443 8.750164 -0.824035

7 6 0 0.882501 7.353067 -0.833245

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9 6 0 -2.324929 4.956612 -0.772650

10 6 0 -3.534011 4.267328 -0.765797

11 6 0 -3.711757 3.090761 -0.005472

12 6 0 -2.610105 2.643332 0.756374

13 6 0 -1.400737 3.332112 0.765894

14 6 0 1.236836 4.500851 0.003087

15 6 0 2.324975 4.956620 0.772590

16 6 0 3.534029 4.267285 0.765791

17 6 0 3.711710 3.090617 0.005611

18 6 0 2.610005 2.643124 -0.756128

19 6 0 1.400663 3.331943 -0.765694

20 6 0 -9.616429 1.091014 -0.447769

21 6 0 -9.586557 -0.252657 -0.009380

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23 6 0 -7.118814 -0.553799 0.553948

24 6 0 -6.534148 0.682198 0.265004

25 6 0 -7.223288 1.893795 -0.280723

26 6 0 -8.584204 2.022735 -0.570988

27 6 0 -5.179407 1.022003 0.415473

28 6 0 -4.984971 2.365768 -0.006488

29 6 0 -6.239153 2.885059 -0.429519

30 6 0 8.446998 -0.965231 -0.429291

31 6 0 9.586482 -0.252830 0.009510

32 6 0 9.616369 1.090840 0.447894

33 6 0 8.584149 2.022569 0.571104

34 6 0 7.223229 1.893625 0.280862

35 6 0 6.534065 0.681997 -0.264777

36 6 0 7.118723 -0.554005 -0.553713

37 6 0 6.239108 2.884907 0.429608

38 6 0 4.984906 2.365597 0.006654

39 6 0 5.179323 1.021803 -0.415227

40 7 0 -14.599922 -3.099852 -0.009067

41 6 0 -15.309485 -3.309380 1.216062

42 6 0 -15.896771 -4.557781 1.492447

43 6 0 -16.600060 -4.755825 2.683379

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45 6 0 -16.125483 -2.481760 3.351606

46 6 0 -15.434747 -2.269421 2.155833

47 6 0 -15.144877 -3.600890 -1.233953

48 6 0 -16.517444 -3.461701 -1.510446

49 6 0 -17.049280 -3.963205 -2.701159

50 6 0 -16.222977 -4.594344 -3.639108

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52 6 0 -14.317742 -4.244037 -2.173385

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128 1 0 17.256888 -3.881108 -4.548537

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130 1 0 14.992166 -1.302291 -1.943659

------------------------------------------------------------------------------

Method: DFT B3LYP 6-31G\*

Key word: opt freq

E**total** (RB3LYP)= -3015.311973Hartree

**Table S2**. Atomic coordinates of optimized geometry of **8**

---------------------------------------------------------------------

Center Atomic Atomic Coordinates (Angstroms)

Number Number Type X Y Z

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1 7 0 0.002269 0.000027 -0.001192

2 6 0 0.717952 -1.234013 0.008182

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5 6 0 2.146002 -3.697250 0.026744

6 6 0 0.978294 -3.529356 -0.749486

7 6 0 0.280115 -2.325456 -0.766622

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85 6 0 2.375555 -6.224015 -0.388703

86 6 0 2.880895 -4.964802 0.036063

87 6 0 4.222119 -5.147305 0.471141

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89 6 0 9.803040 -14.565438 0.496188

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91 6 0 12.072144 -15.371973 0.163012

92 6 0 12.508140 -14.643698 1.276737

93 6 0 11.585589 -13.876833 1.999186

94 6 0 10.241065 -13.841901 1.620856

95 6 0 7.776281 -15.745651 -0.286323

96 6 0 7.974067 -16.925277 0.454624

97 6 0 7.347502 -18.112433 0.067022

98 6 0 6.504714 -18.139709 -1.050934

99 6 0 6.301186 -16.965016 -1.785635

100 6 0 6.936696 -15.777158 -1.415202

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103 6 0 7.645697 -10.898346 -0.289972

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105 6 0 5.661275 -12.044057 0.451898

106 6 0 6.358025 -13.250014 0.470697

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111 1 0 2.218023 0.571183 -1.407327

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113 1 0 0.612713 4.347958 1.372010

114 1 0 -0.612570 2.217049 1.383901

115 1 0 -1.602387 -1.624424 1.413136

116 1 0 -4.059387 -1.646955 1.395969

117 1 0 -4.066592 1.629534 -1.397995

118 1 0 -1.609510 1.617533 -1.415482

119 1 0 7.204527 8.618873 -0.880103

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122 1 0 6.527665 6.413347 -1.034146

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124 1 0 4.869824 4.390429 -0.821715

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140 1 0 9.475232 13.297426 -2.187756

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142 1 0 4.577414 12.050524 -0.782254

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147 1 0 -19.503292 3.195571 3.269909

148 1 0 -17.509179 4.041092 2.037129

149 1 0 -16.261134 2.544561 0.507786

150 1 0 -15.188610 0.251137 2.133689

151 1 0 -12.731727 0.279501 2.130210

152 1 0 -12.731258 -0.332783 -2.129780

153 1 0 -15.188234 -0.314324 -2.132382

154 1 0 -18.956474 0.595929 -1.454121

155 1 0 -20.219350 -0.912731 -2.960154

156 1 0 -19.490983 -3.276258 -3.267330

157 1 0 -17.493368 -4.113762 -2.034749

158 1 0 -16.251055 -2.612152 -0.505708

159 1 0 7.239216 -8.589262 0.882648

160 1 0 3.866067 -10.556357 -0.746022

161 1 0 2.296393 -8.868344 -0.927174

162 1 0 6.552999 -6.386664 1.036994

163 1 0 1.373235 -6.418996 -0.745067

164 1 0 4.887129 -4.370555 0.823395

165 1 0 10.400917 -15.884557 -1.102834

166 1 0 12.778278 -15.965726 -0.409027

167 1 0 13.550171 -14.673743 1.577383

168 1 0 11.909086 -13.314142 2.869334

169 1 0 9.526807 -13.259298 2.191664

170 1 0 8.615797 -16.904527 1.328175

171 1 0 7.509084 -19.014748 0.648499

172 1 0 6.014791 -19.061863 -1.345424

173 1 0 5.656724 -16.974577 -2.659135

174 1 0 6.788801 -14.873337 -1.995414

175 1 0 9.383163 -12.122498 -0.607420

176 1 0 8.151110 -9.997290 -0.621645

177 1 0 4.626321 -12.031804 0.777578

178 1 0 5.858596 -14.156865 0.791282

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Method: DFT B3LYP 6-31G\*

Key word: opt freq

E**total** (RB3LYP)= -4148.205875 Hartree

**4.** **Cyclic voltammetry studies**

Electrochemical studies were performed in an acetonitrile solution containing tetrabutylammonium hexafluorophosphate (nBu4NPF6) under an argon atmosphere. Ag/AgCl electrode, glassy carbon electrodes and platinum electrodes were used as reference electrodes, working electrodes and counter electrodes, respectively. 5 μl of a 0.8 mg/ml dichloromethane solution of co-oligomer **6** (or **8**) was pipetted and dropped onto a glass-carbon electrode which was allowed to evaporate under the pressure of a washing flask at room temperature (the circular opening of the electrode had a diameter of 4 mm).

References

1. M. Fujinaga, T. Murafuji, K. Kurotobi, Y. Sugihara, Polyborylation of azulenes. *Tetrahedron* **2009**, *Volume 65*, 7115–7121.
2. T.Tsuchiya, T. Hamano, M. Inoue, T. Nakamura, A. Wakamiya, Y. Mazaki. Intense absorption of azulene realized by molecular orbital inversion. *Chem. Commun*. **2023**, *Volume 59*, 10604–10607.