

**Supporting Information**

**Expanding the Chemical Structure Space of Opto-Electronic  
Molecular Materials: Unprecedented Push–Pull Chromophores by  
Reaction of a Donor-Substituted Tetracyanofulvene with Electron-  
Rich Alkynes**

Govindasamy Jayamurugan,<sup>a</sup> Oliver Dumele,<sup>a</sup> Jean-Paul Gisselbrecht,<sup>b</sup> Corinne Boudon,<sup>b</sup> W. Bernd Schweizer,<sup>a</sup> Bruno Bernet,<sup>a</sup> and François Diederich\*<sup>a</sup>

<sup>a</sup> *Laboratorium für Organische Chemie, ETH Zurich, Hönggerberg, HCI, 8093 Zurich (Switzerland)*

*E-mail: [diederich@org.chem.ethz.ch](mailto:diederich@org.chem.ethz.ch); Fax: +41 44 632 1109, Tel: +41 44 632 2992*

<sup>b</sup> *Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide*

*Institut de Chimie-UMR 7177, C.N.R.S., Université de Strasbourg*

*4, rue Blaise Pascal, CS 90032, 67081 Strasbourg Cedex (France)*

| <b>Section</b> | <b>Table of Contents</b>                                                                                    | <b>Page</b> |
|----------------|-------------------------------------------------------------------------------------------------------------|-------------|
| <b>1SI</b>     | <b>General Experimental Methods .....</b>                                                                   | <b>S3</b>   |
| <b>2SI</b>     | <b>Synthetic Procedures and Characterization<br/>of the Products .....</b>                                  | <b>S5</b>   |
| <b>3SI</b>     | <b>X-ray Data for Compounds 3, 5, (<math>\pm</math>)-6, <i>Z</i>-7, and <i>E</i>-9 .....</b>                | <b>S14</b>  |
| <b>4SI</b>     | <b>Quinoid Character of the DMA Groups and<br/>Torsion Angles of 1, 5, <i>Z</i>-7, and <i>E</i>-9 .....</b> | <b>S23</b>  |
| <b>5SI</b>     | <b><math>^1\text{H}</math> NMR and <math>^{13}\text{C}</math> NMR Spectra of the Products .....</b>         | <b>S24</b>  |
| <b>6SI</b>     | <b><i>E/Z</i> Isomerization of 7 and 9: Full Investigation .....</b>                                        | <b>S30</b>  |
| <b>7SI</b>     | <b>ab initio Calculations for 7 and 9 .....</b>                                                             | <b>S37</b>  |
| <b>8SI</b>     | <b>UV/Vis/NIR Spectroscopic Data .....</b>                                                                  | <b>S63</b>  |
| <b>9SI</b>     | <b>Electrochemistry .....</b>                                                                               | <b>S66</b>  |
| <b>10SI</b>    | <b>References .....</b>                                                                                     | <b>S69</b>  |

## Section 1SI.

### EXPERIMENTAL SECTION

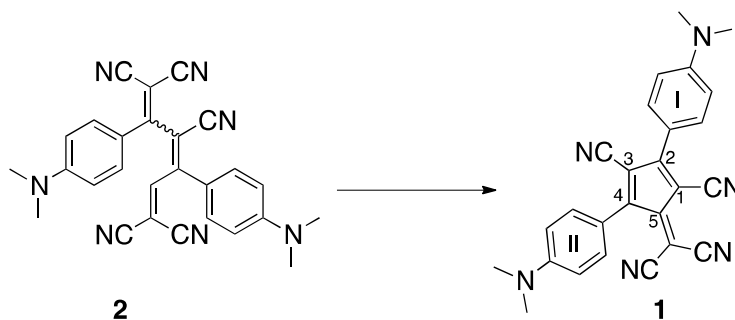
**General Experimental Methods.** Chemicals were purchased from Acros, Aldrich, Fluka and TCI and used as received.  $\text{CH}_2\text{Cl}_2$  was freshly distilled from  $\text{CaH}_2$  under nitrogen atmosphere. Column chromatography (CC) and specified chemical transformations of **1** were carried out with  $\text{SiO}_2$  60 (particle size 0.040–0.063 mm, 230–400 mesh; Aldrich). The synthesis of **2**<sup>1</sup> and **8**<sup>2</sup> was performed according to the literature. An optimized synthesis of **1**<sup>1</sup> is given in the experimental section. Liquid chromatography–mass spectrometry (LC–MS) was performed on an Ultimate 3000 series LC instrument combined with an MSQ Plus mass spectrometer from Dionex, using a Zorbax Eclipse Plus *C18* column (30 × 3 mm; 3.5  $\mu\text{m}$  pore size) from Agilent. The preparative recycling GPC was performed on a Japan Analytical Industries LC-9101 preparative recycling HPLC apparatus equipped with a Jaigel-2H column, using  $\text{CHCl}_3$  (ReagentPlus grade,  $\geq 99.8\%$ ) as the mobile phase, with a flow rate of 4 mL  $\text{min}^{-1}$ . Melting points (m.p.) were measured in open capillaries with a Büchi melting point B540 apparatus and are uncorrected. “Decomp.” refers to decomposition.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured on Varian Mercury VX 300 MHz, Bruker DRX 400 MHz, Bruker DRX 500 MHz or Bruker Avance II 600 MHz instruments. Chemical shifts ( $\delta$ ) are reported in ppm downfield from  $\text{SiMe}_4$ , with the residual solvent signal as an internal reference. The apparent resonance multiplicity is described as s (singlet), d (doublet), dd (doublet of doublet), m (multiplet), and br. stands for broad. Microwave heating was performed using a Biotage Initiator microwave. Infrared spectra (IR) were recorded on a Perkin-Elmer BX FT-IR spectrometer; signal designations: s (strong), m (medium), w (weak), and vw (very

weak). UV/Vis/NIR spectra were recorded on a Varian CARY-500 spectrophotometer. The absorption maxima ( $\lambda_{\text{max}}$ ) are reported in nm with the extinction coefficient ( $\epsilon$ ) in  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  in brackets. Shoulders are indicated as sh. Mass spectrometry was performed by the MS-service at ETH Zürich. Electrospray ionization mass spectrometry (ESI-MS) was performed on a Bruker Daltonics maXis (UHR-TOF). HR-ICR-MALDI spectra were measured on a IonSpec Fourier transform (FT) instrument with 3-hydroxypicolinic acid (3-HPA). The most important signals are reported in  $m/z$  units with  $M^+$  as the molecular ion. Calculations were performed at the Brutus cluster of the Competence Center for Computational Chemistry (C4) at ETH Zürich.

**Electrochemistry:** The electrochemical experiments were carried out at 20 °C in  $\text{CH}_2\text{Cl}_2$  containing 0.1M  $\text{Bu}_4\text{NPF}_6$  in a classical three-electrode cell by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV). The working electrode was a glassy carbon disk electrode (3 mm in a diameter), the auxiliary electrode a Pt wire, and the pseudo-reference electrode a Pt wire. All potentials are referenced to the ferricinium/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) couple, used as an internal standard, and uncorrected from ohmic drop. The cell was connected to an Autolab-PGSTAT30 potentiostat (Eco-Chemie, The Netherlands) driven by a GPSE software running on a personal computer.

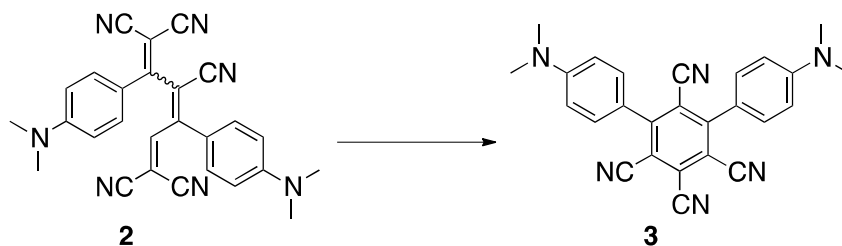
## Section 2SI.

### Synthetic Procedures and Characterization of the Products



**Improved Synthesis of 5-(Dicyanomethylene)-2,4-bis[(4-dimethylamino)phenyl]cyclopenta-1,3-diene-1,3-dicarbonitrile (**1**).** A solution of **2**<sup>1</sup> (250 mg, 0.56 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was treated with wet SiO<sub>2</sub> (25 g, with 10% w/w H<sub>2</sub>O) and stirred at room temperature for 4 h when LC–MS showed complete conversion. The solid was filtered off (washing with CH<sub>2</sub>Cl<sub>2</sub>/Me<sub>2</sub>CO 2:1) using a sintered funnel. The purple filtrate was evaporated in vacuo at 30 °C. The residue was immediately diluted with CH<sub>2</sub>Cl<sub>2</sub> (300 mL), and the solution was left at 20 °C for 5 h until a dark-green solution was formed. Evaporation and column chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/EtOAc 99:1) gave **1**<sup>1</sup> (164 mg, 70%) as a maroon metallic solid. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K; assignment based on DQF-COSY, HSQC, and HMBC spectra): δ = 3.14 (s, 6 H; NMe<sub>2</sub>), 3.25 (s, 6 H; NMe<sub>2</sub>), 6.84 (d, *J* = 9.0 Hz, 2 H; H–C(3<sup>II</sup>,5<sup>II</sup>)), 6.90 (d, *J* = 9.4 Hz, 2 H; H–C(3<sup>I</sup>,5<sup>I</sup>)), 7.45 (d, *J* = 9.1 Hz, 2 H; H–C(2<sup>II</sup>,6<sup>II</sup>)), 8.26 ppm (d, *J* = 9.4 Hz, 2 H; H–C(2<sup>I</sup>,6<sup>I</sup>)); <sup>13</sup>C NMR (150 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K; assignment based on DQF-COSY, HSQC, and HMBC spectra): δ = 40.64 (br., NMe<sub>2</sub>), 40.99 (NMe<sub>2</sub>), 80.01 (C(CαN)<sub>2</sub>), 87.88 (C(1)), 108.48 (C(3)), 112.54 (br., C(3<sup>II</sup>,5<sup>II</sup>)), 113.32/114.05 (C(CαN)<sub>2</sub>), 113.61 (C(3<sup>I</sup>,5<sup>I</sup>)), 116.17 (CαN), 116.72 (CαN), 117.18 (br., C(1<sup>II</sup>)), 119.29 (br., C(1<sup>I</sup>)), 132.97/134.18

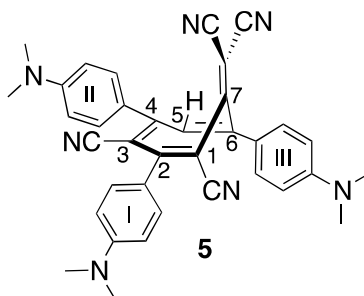
(C(2<sup>I</sup>,6<sup>I</sup>,2<sup>II</sup>,6<sup>II</sup>)), 153.79 (br., C(4<sup>II</sup>)), 155.68 (C(4<sup>I</sup>)), 157.48/159.13 (C(2,4)), 160.70 ppm (C(5)); HR-MALDI-MS (negative mode): *m/z* (%): 418.1857 (17), 417.1824 (79), 416.1754 (100, *M*<sup>-</sup>, calcd for C<sub>26</sub>H<sub>20</sub>N<sub>6</sub><sup>-</sup>: 416.1749).



**4,4''-Bis(dimethylamino)-[1,1':3',1''-terphenyl]-2',4',5',6'-tetracarbonitrile (3).** A solution of **2** (250 mg, 0.56 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was treated with wet silica gel (25 g, with 10% w/w H<sub>2</sub>O) and stirred at room temperature for 4 h when LC–MS showed complete conversion. The solid was filtered off (washing with 300 mL of MeCN) using a sintered funnel, and the filtrate was left at 20 °C for 1 h until a dark red solution was formed. Evaporation and column chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>) gave **3** (206 mg, 88%) as a deep-red metallic solid. *R*<sub>f</sub> = 0.33 (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>); m.p. 215–216 °C; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K; assignment based on a DQF-COSY spectrum): δ = 3.09 (s, 12 H; 2 NMe<sub>2</sub>), 6.86 (d, *J* = 9.0 Hz, 4 H; H–C(3,5,3'',5'')), 7.50 ppm (d, *J* = 9.0 Hz, 4 H; H–C(2,6,2'',6'')); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K; assignment based on DQF-COSY, HSQC, and HMBC spectra): δ = 40.34 (2 NMe<sub>2</sub>), 111.65 (C(3,5,3'',5'')), 113.38 (C≡N), 114.23 (2 C≡N), 114.79 (C(4',6')), 115.71 (C≡N), 117.89 (C(2')), 118.99 (C(1,1'')), 124.01 (C(5')), 130.93 (C(2,6,2'',6'')), 152.37 (C(1',3'')), 154.21 ppm (C(4,4'')); IR (ATR):  $\tilde{\nu}$  = 2904 (w), 2864 (w), 2815 (w), 2204 (m), 1600 (s), 1554 (s), 1520 (s), 1483 (s), 1357 (br. s), 1193 (s), 1166 (s), 1123 (m), 1063 (m), 943 (m), 819 cm<sup>-1</sup> (s); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε) = 510 (5 000, sh), 440 nm (17 000 dm<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>); HR-MALDI/ESI (dual)-MS: *m/z* (%): 417.1778 (27),

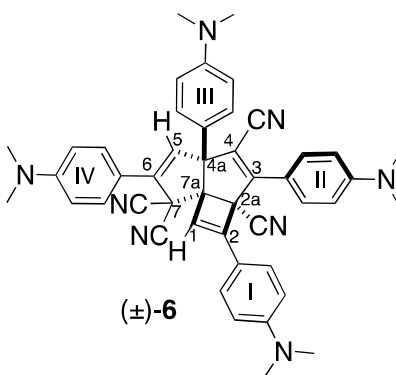
416.1743 ( $M^+$ , calcd for  $C_{26}H_{20}N_6^+$ : 416.1744).

**Cycloaddition of 1 with 4:** A solution of **1** (80 mg, 0.19 mmol) in  $CH_2Cl_2$  (80 mL) under  $N_2$  was treated with 2 eq of **4** (55 mg, 0.38 mmol) and stirred at 20 °C for 24 h. After evaporation, preparative recycling GPC ( $CHCl_3$ ) gave ( $\pm$ )-**6** (48 mg, 36%) and a mixture of **5** and **7**, which was separated by column chromatography on silica gel to afford **5** (25 mg, 23%) and **7** (31 mg, 29%).



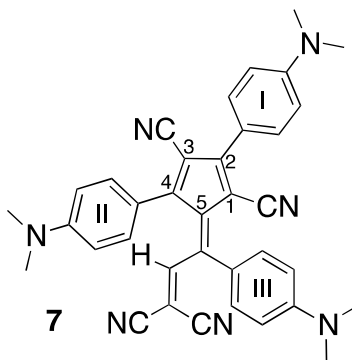
**Data of 7-(Dicyanomethylene)-2,4,6-tris[4-(dimethylamino)phenyl]cyclohepta-1,3,5-triene-1,3-dicarbonitrile (5).** Deep-red metallic solid.  $R_f$  = 0.39 ( $SiO_2$ ,  $CH_2Cl_2/MeCN$  98:2); m.p. 235–237 °C;  $^1H$  NMR (600 MHz,  $CD_2Cl_2$ , 293 K; assignment based on DQF-COSY, HSQC, and HMBC spectra):  $\delta$  = 3.066 (s, 6 H;  $NMe_2$ ), 3.073 (s, 6 H;  $NMe_2$ ), 3.09 (s, 6 H;  $NMe_2$ ), 6.75 (d,  $J$  = 9.0 Hz, 2 H;  $H-C(3^{III}, 5^{III})$ ), 6.80 (d,  $J$  = 9.0 Hz, 2 H;  $H-C(3^{II}, 5^{II})$ ), 6.82 (d,  $J$  = 9.6 Hz, 2 H;  $H-C(3^I, 5^I)$ ), 7.07 (s, 1 H;  $H-C(5)$ ), 7.47 (d,  $J$  = 9.6 Hz, 2 H;  $H-C(2^{III}, 6^{III})$ ), 7.575 (d,  $J$  = 9.0 Hz, 2 H;  $H-C(2^{II}, 6^{II})$ ), 7.583 ppm (d,  $J$  = 9.0 Hz, 2 H;  $H-C(2^I, 6^I)$ );  $^{13}C$  NMR (150 MHz,  $CD_2Cl_2$ , 293 K; assignment based on DQF-COSY, HSQC, and HMBC spectra):  $\delta$  = 40.39 ( $NMe_2$ ), 40.41 ( $NMe_2$ ), 40.48 ( $NMe_2$ ), 92.05 ( $C(CN)_2$ ), 96.83 ( $C(1)$ ), 109.05 ( $C(3)$ ), 110.92 ( $C\equiv N$ ), 111.40 ( $C\equiv N$ ), 111.79 ( $C(3^{II}, 5^{II})$ ), 111.82 ( $C(3^I, 5^I)$ ), 112.85 ( $C(3^{III}, 5^{III})$ ), 115.67 ( $C\equiv N$ ), 119.67 ( $C\equiv N$ ), 121.59 ( $C(1^{III})$ ), 123.19 ( $C(1^I)$ ), 124.96

(C(5)), 126.82 (C(1<sup>II</sup>)), 130.01 (C(2<sup>III</sup>,6<sup>III</sup>)), 131.47 (C(2<sup>II</sup>,6<sup>II</sup>)), 132.62 (C(2<sup>I</sup>,6<sup>I</sup>)), 143.19 (C(6)), 152.64 (C(4<sup>III</sup>)), 153.10 (C(4<sup>I</sup>,4<sup>II</sup>)), 155.75 (C(2)), 159.81 (C(4)), 165.10 ppm (C(7)); IR (ATR):  $\tilde{\nu}$  = 2903 (w), 2855 (w), 2811 (w), 2233 (w), 2200 (m), 1599 (s), 1548 (m), 1516 (s), 1435 (m), 1417 (m), 1364 (s), 1329 (s), 1198 (s), 1163 (s), 1122 (s), 1053 (m), 942 (m), 815 cm<sup>-1</sup> (s); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 490 (29 000), 350 nm (29 000 dm<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>); HR-ESI-MS:  $m/z$  (%): 600.2256 (74, [M + K]<sup>+</sup>, calcd for C<sub>36</sub>H<sub>31</sub>N<sub>7</sub>K<sup>+</sup>: 600.2273), 584.2517 (52, [M + Na]<sup>+</sup>, calcd for C<sub>36</sub>H<sub>31</sub>N<sub>7</sub>Na<sup>+</sup>: 584.2533), 562.2701 (53, [M + H]<sup>+</sup>, calcd for C<sub>36</sub>H<sub>32</sub>N<sub>7</sub><sup>+</sup>: 562.2714), 360.3225 (100).



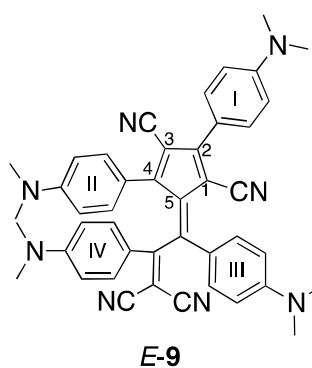
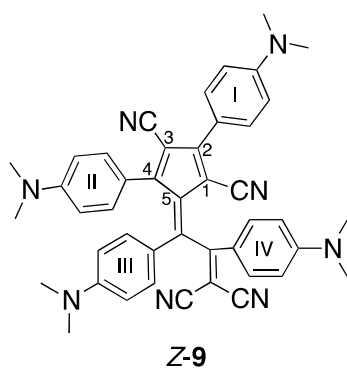
**Data of (2a*R/S*,4a*S/R*,7a*S/R*)-2,3,4a,6-Tetrakis[4-(dimethylamino)phenyl]-2a*H*-cyclobuta[*c*]pentalene-2a,4,7,7(4a*H*)-tetracarbonitrile ((±)-6).** Light-brown solid. m.p. > 278 °C (decomp.); <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K; assignment based on DQF-COSY, HSQC, and HMBC spectra):  $\delta$  = 2.98 (s, 6 H, C(4<sup>I</sup>)-NMe<sub>2</sub>), 2.99 (s, 6 H, C(4<sup>III</sup>)-NMe<sub>2</sub>), 3.02 (s, 6 H, C(4<sup>II</sup>)-NMe<sub>2</sub>), 3.06 (s, 6 H, C(4<sup>IV</sup>)-NMe<sub>2</sub>), 5.92 (s, 1 H; H-C(1)), 6.58 (s, 1 H; H-C(5)), 6.584 (d,  $J$  = 8.5 Hz, 2 H; H-C(3<sup>I</sup>,5<sup>I</sup>)), 6.71 (d,  $J$  = 9.1 Hz, 2 H; H-C(3<sup>II</sup>,5<sup>II</sup>)), 6.77 (d,  $J$  = 7.7 Hz, 2 H; H-C(3<sup>III</sup>,5<sup>III</sup>)), 6.84 (d,  $J$  = 9.0 Hz, 2 H; H-C(3<sup>IV</sup>,5<sup>IV</sup>)), 7.16 (d,  $J$  = 8.6 Hz, 2 H; H-C(2<sup>III</sup>,6<sup>III</sup>)), 7.28 (d,  $J$  = 8.9 Hz, 2 H; H-C(2<sup>I</sup>,6<sup>I</sup>)), 7.64 (d,  $J$  = 9.1 Hz, 2 H; H-C(2<sup>II</sup>,6<sup>II</sup>)), 7.65 ppm (d,  $J$  = 9.0 Hz, 2 H;

H-C(2<sup>IV</sup>,6<sup>IV</sup>)); <sup>13</sup>C NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K; assignment based on DQF-COSY, HSQC, and HMBC spectra):  $\delta$  = 40.42 (2 NMe<sub>2</sub>), 40.58 (2 NMe<sub>2</sub>), 47.33 (C(7)), 58.33 (C(2a)), 65.76 (C(4a)), 70.14 (C(7a)), 111.88 (C(3<sup>I</sup>,5<sup>I</sup>)), 112.03 (C(3<sup>II</sup>,5<sup>II</sup>)), 112.09 (C $\equiv$ N), 112.63 (C(3<sup>IV</sup>,5<sup>IV</sup>)), 112.70 (C $\equiv$ N), 113.61 (C(3<sup>III</sup>,5<sup>III</sup>)), 116.47 (C $\equiv$ N), 116.52 (C $\equiv$ N), 117.29 (C(1<sup>I</sup>)), 117.48 (C(1<sup>IV</sup>)), 117.79 (C(1<sup>III</sup>)), 117.95 (C(4)), 118.54 (C(1<sup>II</sup>)), 119.97 (C(1)), 128.29 (C(2<sup>IV</sup>,6<sup>IV</sup>)), 128.40 (C(2<sup>I</sup>,6<sup>I</sup>)), 128.92 (C(2<sup>III</sup>,6<sup>III</sup>)), 130.12 (C(2<sup>II</sup>,6<sup>II</sup>)), 130.53 (C(5)), 137.47 (C(6)), 151.34 (C(4<sup>III</sup>)), 152.08 (C(4<sup>IV</sup>)), 152.16 (C(4<sup>I</sup>)), 152.49 (C(4<sup>II</sup>)), 153.71 (C(2)), 156.84 ppm (C(3)); IR (ATR):  $\tilde{\nu}$  = 2923 (w), 2855 (w), 2807 (w), 2210 (w), 1607 (s), 1522 (s), 1444 (w), 1365 (m), 1197 (m), 1170 (m), 946 (w), 813 cm<sup>-1</sup> (m); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 460 (3 000), 400 (9 000, sh), 350 nm (29 000 dm<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>); HR-ESI-MS:  $m/z$  (%): 708.3650 (54), 707.3615 (100,  $M^+$ , calcd for C<sub>46</sub>H<sub>43</sub>N<sub>8</sub><sup>+</sup>: 707.3605).



**Data of (Z)-5-{3,3-Dicyano-1-[4-(dimethylamino)phenyl]allylidene}-2,4-bis[4-(dimethylamino)phenyl]cyclopenta-1,3-diene-1,3-dicarbonitrile (7).** Deep-maroon color metallic solid.  $R_f$  = 0.20 (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeCN 98:2); m.p. 255–256 °C; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 253 K):  $\delta$  = 3.06 (s, 6 H; C(4<sup>I</sup>)-NMe<sub>2</sub>), 3.10 (s, 6 H; C(4<sup>III</sup>)-NMe<sub>2</sub>), 3.17 (s, 6 H; C(4<sup>II</sup>)-NMe<sub>2</sub>), 6.76 (d,  $J$  = 8.8 Hz, 2 H; H-C(3<sup>I</sup>,5<sup>I</sup>)), 6.81 (d,  $J$  = 7.7 Hz, 4 H; H-C(3<sup>II</sup>,5<sup>II</sup>,3<sup>III</sup>,5<sup>III</sup>)), 7.23 (s, 1 H; CH=C(CN)<sub>2</sub>), 7.27 (d,  $J$  = 8.7

Hz, 2 H; H-C(2<sup>II</sup>,6<sup>II</sup>)), 7.41 (d,  $J$  = 8.9 Hz, 2 H; H-C(2<sup>III</sup>,6<sup>III</sup>)), 7.82 ppm (d,  $J$  = 8.7 Hz, 2 H; H-C(2<sup>I</sup>,6<sup>I</sup>)); <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K):  $\delta$  = 40.36 (C(4<sup>I</sup>)-NMe<sub>2</sub>), 40.47 (C(4<sup>III</sup>)-NMe<sub>2</sub>), 40.55 (C(4<sup>II</sup>)-NMe<sub>2</sub>), 88.24 (C(C $\equiv$ N)<sub>2</sub>), 94.51 (C(3)), 104.81 (C(1)), 111.65 and 114.44 (CH=C(CN)<sub>2</sub>), 111.85 (C(3<sup>I</sup>,5<sup>I</sup>,3<sup>III</sup>,5<sup>III</sup>)), 112.40 (C(3<sup>II</sup>,5<sup>II</sup>)), 117.97 (CN), 118.16 (CN), 119.24 (C(1<sup>I</sup>)), 120.58 (C(1<sup>II</sup>)), 125.78 (C(1<sup>III</sup>)), 130.82 (C(2<sup>I</sup>,6<sup>I</sup>)), 132.97 (C(2<sup>II</sup>,6<sup>II</sup>)), 135.96 (C(2<sup>III</sup>,6<sup>III</sup>)), 143.64 (C(5)), 145.80 (C=C(5)), 152.12 (C(4<sup>I</sup>)), 152.44 (C(4<sup>II</sup>)), 152.97 (C(4<sup>III</sup>)), 153.46 (C(4)), 156.18 (C(2)), 161.30 ppm (CH=C(CN)<sub>2</sub>); IR (ATR):  $\tilde{\nu}$  = 2909 (w), 2855 (w), 2799 (w), 2224 (w), 2196 (m), 1588 (s), 1532 (m), 1479 (s), 1433 (m), 1346 (s), 1170 (m), 1051 (m), 941 (w), 820 (w), 798 (w), 743 cm<sup>-1</sup> (m); UV/Vis/NIR (CH<sub>2</sub>Cl<sub>2</sub>, 293 K):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 760 (15 200), 680 (15 000), 350 nm (20 000 dm<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>); HR-ESI-MS:  $m/z$  (%): 562.2697 (72, [M + H]<sup>+</sup>, calcd for C<sub>36</sub>H<sub>32</sub>N<sub>7</sub><sup>+</sup>: 562.2714), 584.2516 (72, [M + Na]<sup>+</sup>, calcd for C<sub>36</sub>H<sub>31</sub>N<sub>7</sub>Na<sup>+</sup>: 584.2533), 600.2253 (100, [M + K]<sup>+</sup>, calcd for C<sub>36</sub>H<sub>31</sub>N<sub>7</sub>K<sup>+</sup>: 600.2273), 360.3225 (32).



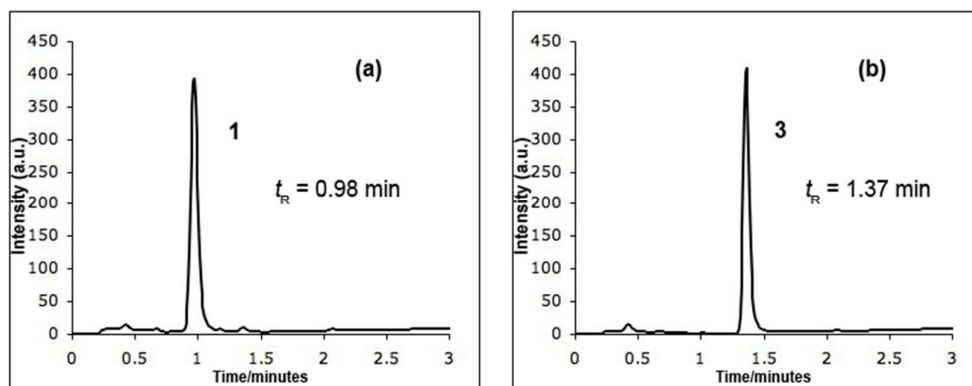
**(*E/Z*)-5-{3,3-Dicyano-1,2-bis[4-(dimethylamino)phenyl]allylidene}-2,4-bis[4-**

**(dimethylamino)phenyl]cyclopenta-1,3-diene-1,3-dicarbonitrile (9).** A solution of

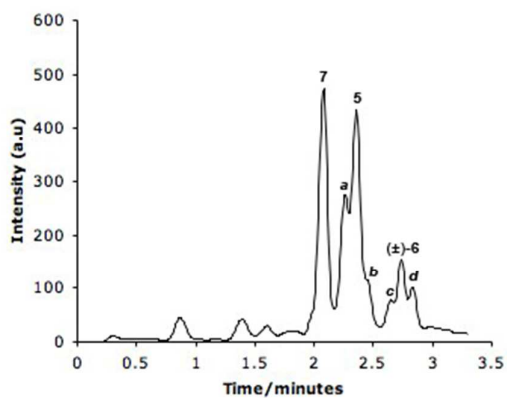
**1** (24 mg, 0.06 mmol) in MeCN/(CH<sub>2</sub>Cl)<sub>2</sub> 1:1 (5 mL) was treated with **8** (16 mg, 0.06 mmol) and heated to 175 °C in a microwave oven for 1 h. Evaporation and CC

(CH<sub>2</sub>Cl<sub>2</sub>) afforded **9** (33 mg, 85%) as a black solid.  $R_f = 0.45$  (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeCN 98:2); m.p. 214–216 °C; <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN, 293 K, with 1.4 equiv. of toluene; *E/Z* ca. 1:1; assignment based on DQF-COSY, HSQC, and HMBC spectra):  $\delta = 2.32$  (s, 4.2 H; Me of toluene), 2.84 (s, 3 H; C(4<sup>II</sup>)-NMe<sub>2</sub> (b)), 2.89 (s, 3 H; C(4<sup>III</sup>)-NMe<sub>2</sub> (Z)), 2.99 (s, 3 H; C(4<sup>II</sup>)-NMe<sub>2</sub> (a)), 3.02 (s, 3 H; C(4<sup>IV</sup>)-NMe<sub>2</sub> (E)), 3.03 (s, 3 H; C(4<sup>I</sup>)-NMe<sub>2</sub> (a)), 3.04 (s, 3 H; C(4<sup>IV</sup>)-NMe<sub>2</sub> (Z)), 3.05 (s, 3 H; C(4<sup>I</sup>)-NMe<sub>2</sub> (b)), 3.16 (s, 3 H; C(4<sup>III</sup>)-NMe<sub>2</sub> (E)), 6.21 (br. d,  $J \approx 9.0$  Hz, 1 H; H-C(3<sup>III</sup>,5<sup>III</sup>) (Z)), 6.46 (d,  $J = 8.9$  Hz, 1 H; H-C(3<sup>II</sup>,5<sup>II</sup>) (b)), 6.54 (d,  $J = 9.3$  Hz, 1 H; H-C(3<sup>IV</sup>,5<sup>IV</sup>) (E)), 6.65 (br. d,  $J = 9.0$  Hz, 1 H; H-C(3<sup>II</sup>,5<sup>II</sup>) (a)), 6.67 (d,  $J = 9.0$  Hz, 1 H; H-C(3<sup>IV</sup>,5<sup>IV</sup>) (Z)), 6.82 (d,  $J = 9.0$  Hz, 1 H; H-C(3<sup>III</sup>,5<sup>III</sup>) (E)), 6.845 (d,  $J = 9.0$  Hz, 1 H; H-C(3<sup>I</sup>,5<sup>I</sup>) (a)), 6.86 (d,  $J = 9.0$  Hz, 1 H; H-C(3<sup>I</sup>,5<sup>I</sup>) (b)), 7.00 (br. d,  $J = 9.0$  Hz, 1 H; H-C(2<sup>II</sup>,6<sup>II</sup>) (a)), 7.07 (d,  $J = 9.0$  Hz, 1 H; H-C(2<sup>IV</sup>,6<sup>IV</sup>) (E)), 7.08 (br. d,  $J = 9.0$  Hz, 1 H; H-C(2<sup>III</sup>,6<sup>III</sup>) (Z)), 7.15 (t,  $J = 7.8$  Hz, 1.4 H; H-C(4) of toluene), 7.17 (d,  $J = 9.0$  Hz, 1 H; H-C(2<sup>II</sup>,6<sup>II</sup>) (b)), 7.19 (d,  $J = 7.8$  Hz, 2.8 H; H-C(2,6) of toluene), 7.25 (t,  $J = 7.8$  Hz, 2.8 H; H-C(3,5) of toluene), 7.49 (d,  $J = 9.0$  Hz, 1 H; H-C(2<sup>III</sup>,6<sup>III</sup>) (E)), 7.66 (d,  $J = 9.3$  Hz, 1 H; H-C(2<sup>IV</sup>,6<sup>IV</sup>) (Z)), 7.73 (d,  $J = 9.1$  Hz, 1 H; H-C(2<sup>I</sup>,6<sup>I</sup>) (a)), 7.76 (d,  $J = 9.1$  Hz, 1 H; H-C(2<sup>I</sup>,6<sup>I</sup>) (b)); <sup>13</sup>C NMR (600 MHz, CD<sub>3</sub>CN, 293 K, with 1.4 equiv. of toluene; *E/Z* ca. 1:1; assignment based on DQF-COSY, HSQC, and HMBC spectra):  $\delta = 21.50$  (Me of toluene), 40.27 (C(4<sup>I</sup>)-NMe<sub>2</sub> (b), C(4<sup>III</sup>)-NMe<sub>2</sub> (Z), C(4<sup>IV</sup>)-NMe<sub>2</sub> (E)), 40.35/40.36 (C(4<sup>I</sup>)-NMe<sub>2</sub> (a), C(4<sup>IV</sup>)-NMe<sub>2</sub> (Z)), 40.44 (C(4<sup>II</sup>)-NMe<sub>2</sub> (b)), 40.53 (C(4<sup>II</sup>)-NMe<sub>2</sub> (a)), 40.60 (C(4<sup>III</sup>)-NMe<sub>2</sub> (E)), 79.62/80.02 (C(C $\equiv$ N)<sub>2</sub>), 96.26/97.70 (C(3)), 107.97/110.97 (C(1)), 111.79 (C(3<sup>IV</sup>,5<sup>IV</sup>) (E)), 112.06 (C(3<sup>IV</sup>,5<sup>IV</sup>) (Z)), 112.47 (C(3<sup>III</sup>,5<sup>III</sup>) (Z)), 112.68 (C(3<sup>I</sup>,5<sup>I</sup>) (b)), 112.74 (C(3<sup>II</sup>,5<sup>II</sup>) (a)), 112.78 (C(3<sup>I</sup>,5<sup>I</sup>) (a)), 113.01 (C(3<sup>III</sup>,5<sup>III</sup>) (E)), 113.14 (C(3<sup>II</sup>,5<sup>II</sup>) (b)), 115.88/116.22/116.69/116.99 (C(C $\equiv$ N)<sub>2</sub>), 118.61/119.20 (C $\equiv$ N), 119.45 (C(1<sup>I</sup>) (b)),

120.04 (C(1<sup>I</sup>) (a)), 121.63 (C(1<sup>II</sup>) (a)), 121.93 (C(1<sup>II</sup>) (b)), 122.82 (C(1<sup>IV</sup>) (Z)), 124.99 (C(1<sup>IV</sup>) (E)), 125.50 (C(1<sup>III</sup>) (Z)), 126.25 (C(4) of toluene), 129.21 (C(3,5) of toluene), 129.44 (C(1<sup>III</sup>) (E)), 129.91 (C(2,6) of toluene), 130.82 (C(2<sup>I</sup>,6<sup>I</sup>) (b)), 130.93 (C(2<sup>I</sup>,6<sup>I</sup>) (a)), 131.43 (C(2<sup>II</sup>,6<sup>II</sup>) (b)), 131.75 (br., C(2<sup>II</sup>,6<sup>II</sup>) (a)), 133.59 (C(2<sup>IV</sup>,6<sup>IV</sup>) (E)), 134.22 (C(2<sup>IV</sup>,6<sup>IV</sup>) (Z)), 136.6/138.35 (very broad, C(2<sup>III</sup>,6<sup>III</sup>) (E/Z)), 138.91 (C(1) of toluene), 139.41/141.84 (C=C(5)), 150.76 (C(4<sup>II</sup>) (b)), 152.46 (C(4<sup>II</sup>) (a)), 152.78 (C(4<sup>I</sup>) (a)), 152.92 (C(4<sup>I</sup>) (b)), 153.63 (C(2) (a)), 153.89 (C(2) (b)), 153.95 (C(4) (a)), 154.17 (C(4<sup>III</sup>) (Z)), 154.60 (C(4<sup>IV</sup>) (E)), 154.70 (C(4<sup>IV</sup>) (Z)), 154.76 (C(4) (b)), 155.06 (C(4<sup>III</sup>) (E)), 155.67 (C=C(5) (Z)), 156.65 (C=C(5) (E)), 170.70 (C=C(C≡N)<sub>2</sub> (Z)), 172.06 ppm, (C=C(C≡N)<sub>2</sub> (E)), two signals for a C≡N group hidden by the solvent signal; IR (ATR):  $\tilde{\nu}$  = 2916 (w), 2855 (w), 2803 (w), 2203 (m), 1594 (s), 1535 (m), 1481 (m), 1432 (m), 1346 (m), 1334 (s), 1228 (w), 1161 (s), 1119 (m), 1046 (m), 1000 (w), 942 (m), 892 (w), 813 (m), 731 (w), 685 cm<sup>-1</sup> (w); UV/Vis/NIR (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 700 (20 000), 600 (20 000), 400 nm (22 000 dm<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>); HR-ESI-MS:  $m/z$  (%): 682.3491 (46), 681.3457 (100, [M + H]<sup>+</sup>, calcd for C<sub>44</sub>H<sub>41</sub>N<sub>8</sub><sup>+</sup>: 681.3449), 360.3242 (79).



**Figure 1SI.** LC–MS profiles of the reaction of **2** with moisturized SiO<sub>2</sub> upon (a) filtration with CH<sub>2</sub>Cl<sub>2</sub>/Me<sub>2</sub>CO 2:1 and dilution with CH<sub>2</sub>Cl<sub>2</sub> and (b) filtration with MeCN.



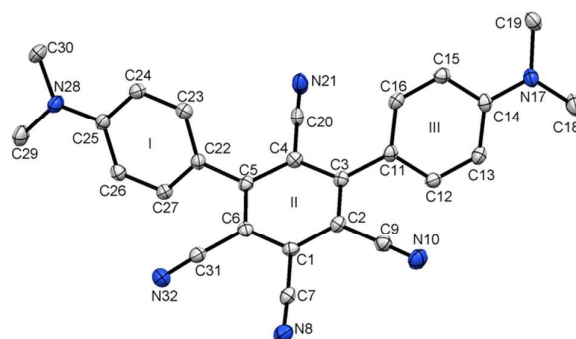
**Figure 2SI.** LC–MS profile of the cycloaddition of **1** with **4** in MeCN at 160 °C under microwave condition. Additionally to **5**, (±)-**6**, and **7**, uncharacterized minor 1:1 adducts (*a* and *b*) and 2:1 adducts (*c* and *d*) were observed after 5 minutes.

### Section 3SI.

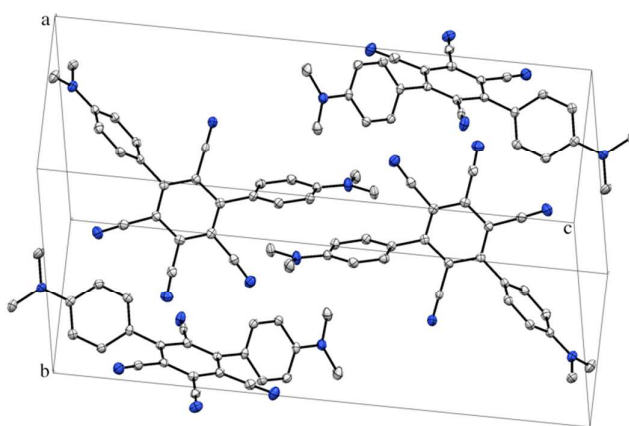
**X-Ray Data for Products 3, 5, (±)-6, Z-7, and E-9.** Crystals of **3**, **5**, (±)-**6**, Z-**7**, and E-**9** were measured on a Bruker Kappa Apex II Duo with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 100 K. The structures were solved by direct methods with SHELXS-97,<sup>3</sup> and refined by full-matrix least-squares analysis (SHELXL-97, OLEX2).<sup>3,4</sup> All non-hydrogen atoms with the exception of split disordered atoms were refined anisotropically; hydrogen atoms were refined isotropically for **5** (with partly fixed positions) and (±)-**6**. Hydrogen positions for compounds Z-**7** and E-**9** are based on stereochemical considerations and included in the final structure factor calculation. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk), or via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

**X-Ray Crystal Structure of 3·CH<sub>2</sub>Cl<sub>2</sub> (CCDC 891529).** A dark red prism-like crystal (cubic dimensions ca. 0.17 × 0.24 × 0.32 mm) was obtained from CH<sub>2</sub>Cl<sub>2</sub>/pentane solution at 20 °C. Crystal data for C<sub>26</sub>H<sub>20</sub>N<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub>,  $M_r = 501.41$ , Monoclinic, space group  $P2(1)/n$ ,  $D_{\text{calcd}} = 1.336$  g cm<sup>-3</sup>,  $Z = 4$ ,  $a = 13.1343(5)$  Å,  $b = 8.4280(11)$  Å,  $c = 22.6288(11)$  Å,  $V = 2492.2(19)$  Å<sup>3</sup>;  $m = 0.289$  mm<sup>-1</sup>. Numbers of measured and unique reflections were 26634 and 5696, respectively ( $R_{\text{int}} = 0.0506$ ). Final  $R(F) = 0.04$ ,  $wR(F2) = 0.093$  for 406 parameters and 5696 reflections with  $I > 2\sigma(I)$  and  $5.2 < 2\theta < 54.77^\circ$  (corresponding R values based on all 5696 reflections are 0.072 and 0.105, respectively).

a)



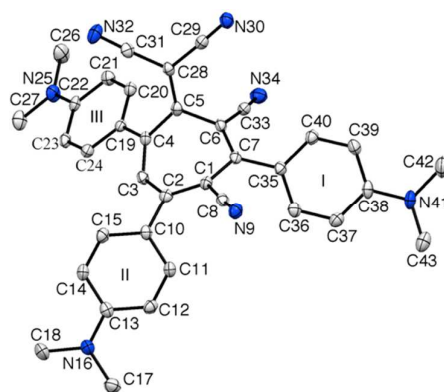
b)



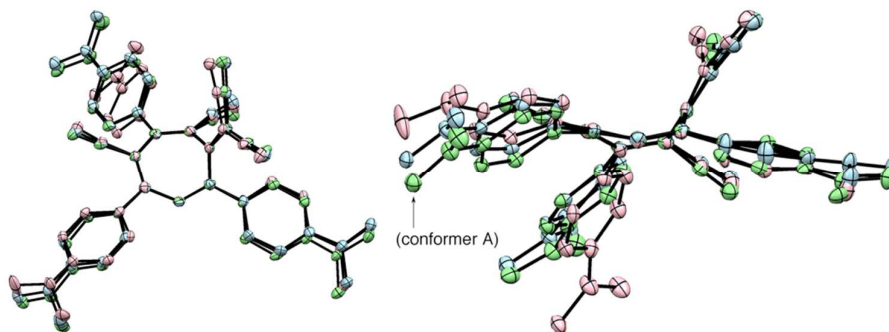
**Figure 3SI.** a) ORTEP plot of **3**·CH<sub>2</sub>Cl<sub>2</sub> (arbitrary numbering, H-atoms, and solvent molecules are omitted for clarity). Atomic displacement parameters are drawn at 50% probability level. Selected bond lengths [Å], angles [°], and torsional angles [°]: C1–C2: 1.401(2), C2–C3: 1.398(2), C3–C4: 1.410(2), C4–C5: 1.409(2), C5–C6: 1.401(2), C1–C6: 1.400(2), C11–C12: 1.394(2), C12–C13: 1.376(2), C13–C14: 1.407(2), C14–C15: 1.412(2), C15–C16: 1.378(2), C11–C16: 1.394(2), C22–C23: 1.397(2), C23–C24: 1.371(2), C24–C25: 1.411(2), C25–C26: 1.406(2), C26–C27: 1.376(2), C22–C27: 1.403(2), C2–C3–C11–C12: –51.20(2), C6–C5–C22–C27: 52.20(2). b) Arrangement of neighboring molecules in the crystal packing of **3**·CH<sub>2</sub>Cl<sub>2</sub> (H-atoms and solvent molecules are omitted for clarity).

**X-Ray Crystal Structure of 5•0.33 CHCl<sub>3</sub> (CCDC 891530).** A black prism-like crystal (cubic dimensions ca. 0.24 × 0.12 × 0.11 mm) was obtained from CHCl<sub>3</sub>/pentane solution at 20 °C. Crystal data for (C<sub>36</sub>H<sub>31</sub>N<sub>7</sub>)<sub>3</sub>•CHCl<sub>3</sub>, *M*<sub>r</sub> = 1804.40, Triclinic, space group *P* $\bar{1}$ , *D*<sub>calcd</sub> = 1.292 g cm<sup>-3</sup>, *Z* = 2, *a* = 16.0228(11) Å, *b* = 16.8314(11) Å, *c* = 17.8423(11) Å,  $\alpha$  = 80.594(2)°,  $\beta$  = 81.100(3)°,  $\gamma$  = 80.250 (2)°, *V* = 4638.5(5) Å<sup>3</sup>; *m* = 0.162 mm<sup>-1</sup>. Numbers of measured and unique reflections were 64273 and 21360, respectively (*R*<sub>int</sub> = 0.0560). Final *R*(*F*) = 0.064, *wR*(*F*<sub>2</sub>) = 0.155 for 1559 parameters and 12681 reflections with *I* > 2σ(*I*) and 1.3 <  $\theta$  < 27.63° (corresponding *R* values based on all 21360 reflections are 0.123 and 0.183, respectively).

a)



b)

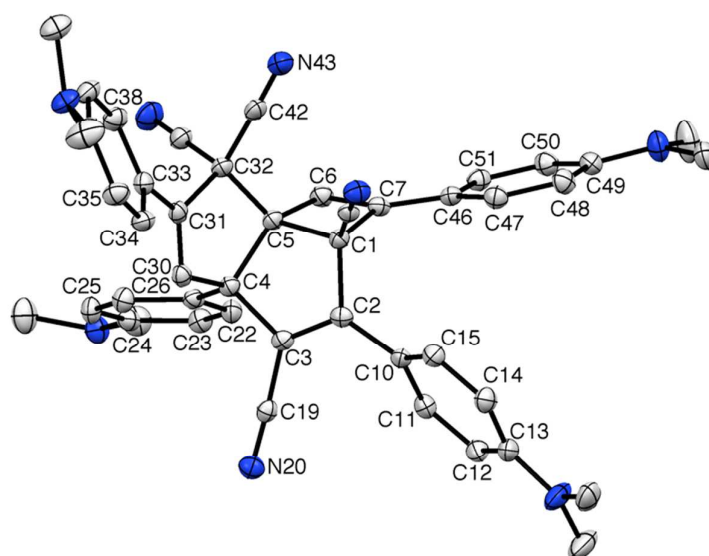


**Figure 4SI.** ORTEP plot of one from the three molecules of 5•0.33 CHCl<sub>3</sub> (arbitrary numbering, H-atoms are omitted for enhanced clarity). Atomic displacement

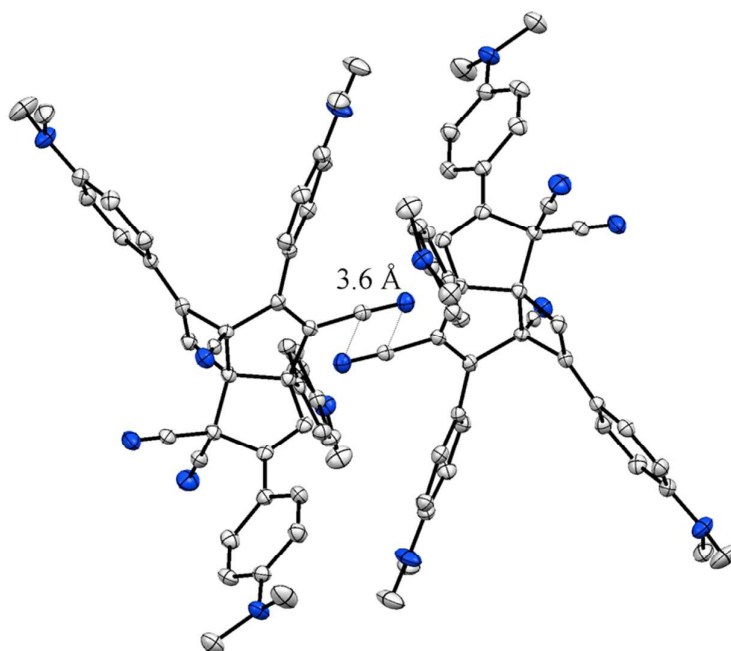
parameters are drawn at 50% probability level. Selected bond lengths [Å] and torsional angles [°] for conformer A: C1–C2: 1.388(4), C3–C4: 1.364(4), C5–C28: 1.342(4), C6–C7: 1.362(4), C10–C11: 1.400(4), C11–C12: 1.370(4), C12–C13: 1.399(4), C13–C14: 1.414(4), C14–C15: 1.369(4), C10–C15: 1.389(4), C19–C20: 1.396(4), C20–C21: 1.375(4), C21–C22: 1.411(4), C22–C23: 1.402(4), C23–C24: 1.376(4), C19–C24: 1.404(4), C35–C36: 1.406(4), C36–C37: 1.367(4), C37–C38: 1.406(4), C38–C39: 1.406(4), C39–C40: 1.378(4), C35–C40: 1.396(4), C28–C5–C4: 126.2(2), C1–C2–C10–C11: –42.4(4), C3–C4–C19–C24: 11.0(4), C6–C7–C35–C40: 34.4(4). b) An overlay of the three symmetry independent molecules of **5**•0.33 CHCl<sub>3</sub> (H-atoms and solvent molecules are omitted for clarity).

**X-Ray Crystal Structure of (±)-6•CH<sub>2</sub>Cl<sub>2</sub> (CCDC 891531).** A clear bronze rod-like crystal (cubic dimensions ca. 0.06 × 0.08 × 0.17 mm) was obtained from CH<sub>2</sub>Cl<sub>2</sub>/pentane solution at 25 °C. Crystal data for C<sub>46</sub>H<sub>42</sub>N<sub>8</sub>•CH<sub>2</sub>Cl<sub>2</sub>, *M<sub>r</sub>* = 791.80, Triclinic, space group *P* $\bar{1}$ , *D*<sub>calcd</sub> = 1.276 g cm<sup>–3</sup>, *Z* = 2, *a* = 10.6434(6) Å, *b* = 13.6284(8) Å, *c* = 14.4880(9) Å, *α* = 79.959(3)°, *β* = 84.754(3)°, *γ* = 88.332 (3)°, *V* = 2060.5(2) Å<sup>3</sup>; *m* = 0.202 mm<sup>–1</sup>. Numbers of measured and unique reflections were 33435 and 9459, respectively (*R*<sub>int</sub> = 0.0311). Final *R*(*F*) = 0.047, *wR*(*F*<sup>2</sup>) = 0.108 for 832 parameters and 6661 reflections with *I* > 2σ(*I*) and 1.9 < *θ* < 27.58° (corresponding *R* values based on all 9459 reflections are 0.0784 and 0.118, respectively).

a)



b)

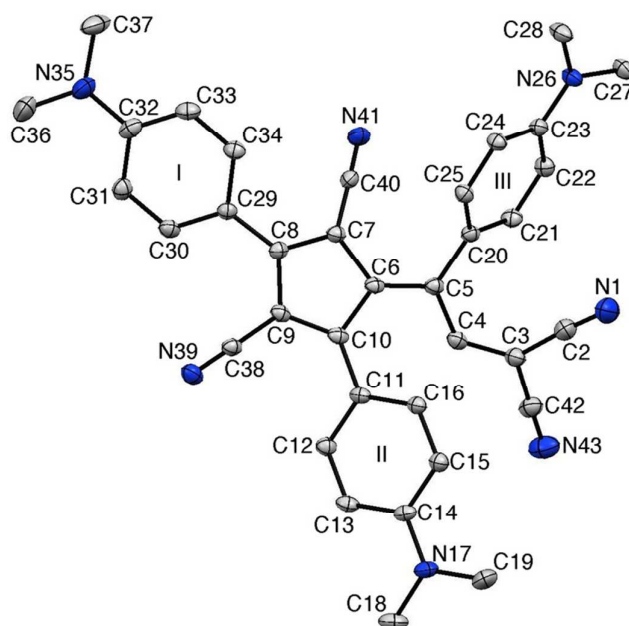


**Figure 5SI.** a) ORTEP plot of (±)-6-CH<sub>2</sub>Cl<sub>2</sub> (arbitrary numbering, H-atoms, and solvent molecules are omitted for clarity). Atomic displacement parameters are drawn at 50% probability level. Selected bond lengths [Å], angles [°], and torsional angles [°]: C1–C5: 1.586(2), C2–C3: 1.342(2), C6–C7: 1.346(2), C30–C31: 1.323(2), C10–C11: 1.395(2), C11–C12: 1.376(2), C12–C13: 1.407(2), C13–C14: 1.408(2),

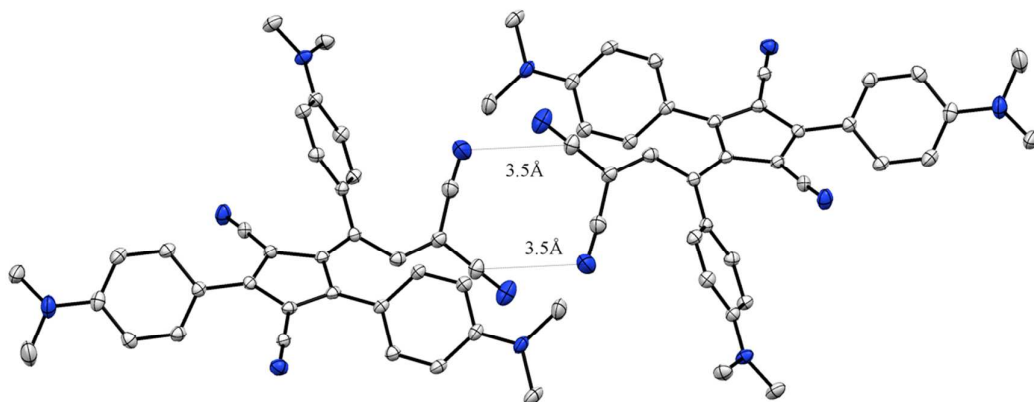
C14–C15: 1.377(2), C10–C15: 1.397(2), C21–C22: 1.391(2), C22–C23: 1.379(2), C23–C24: 1.403(2), C24–C25: 1.396(2), C25–C26: 1.383(2), C21–C26: 1.386(2), C33–C34: 1.397(2), C34–C35: 1.380(2), C35–C36: 1.397(2), C36–C37: 1.408(2), C37–C38: 1.383(2), C33–C38: 1.392(2), C46–C47: 1.395(2), C47–C48: 1.373(2), C48–C49: 1.408(2), C49–C50: 1.401(2), C50–C51: 1.367(2), C46–C51: 1.399(2), C3–C4–C30: 110.82(12), C4–C5–C6: 124.92(13), C1–C5–C32: 119.08(13), C1–C7–C46–C47: –19.10(3), C3–C2–C10–C11: 48.50(2), C3–C4–C21–C22: –50.71(19), C30–C4–C21–C26: 0.40(2), C30–C31–C33–C34: 36.90(3). b) The arrangement of neighboring molecules related by a center of symmetry in the crystal packing of (±)-**6**•CH<sub>2</sub>Cl<sub>2</sub> (H-atoms and solvent molecules are omitted for clarity).

**X-Ray Crystal Structure of 7 (CCDC 891532).** A black needle-like crystal (linear dimensions ca. 0.03 × 0.05 × 0.10 mm) was obtained from CHCl<sub>3</sub>/pentane solution at 25 °C. Crystal data for C<sub>36</sub>H<sub>31</sub>N<sub>7</sub>, *M<sub>r</sub>* = 561.68, monoclinic space group *P*2<sub>1</sub>/*c*, *D*<sub>calcd</sub> = 1.253 Mg m<sup>–3</sup>, *Z* = 4, *a* = 10.8943(4) Å, *b* = 14.1475 (6) Å, *c* = 19.8825(8) Å, *V* = 2977.3(2) Å<sup>3</sup>; *m* = 0.077 mm<sup>–1</sup>. Numbers of measured and unique reflections were 20559 and 6821, respectively (*R*<sub>int</sub> = 0.044). Final *R*(*F*) = 0.049, *wR*(*F*<sup>2</sup>) = 0.121 for 512 parameters and 4329 reflections with *I* > 2σ(*I*) and 1.78 < θ < 24.50° (corresponding *R* values based on all 3818 reflections are 0.095 and 0.147, respectively).

a)



b)

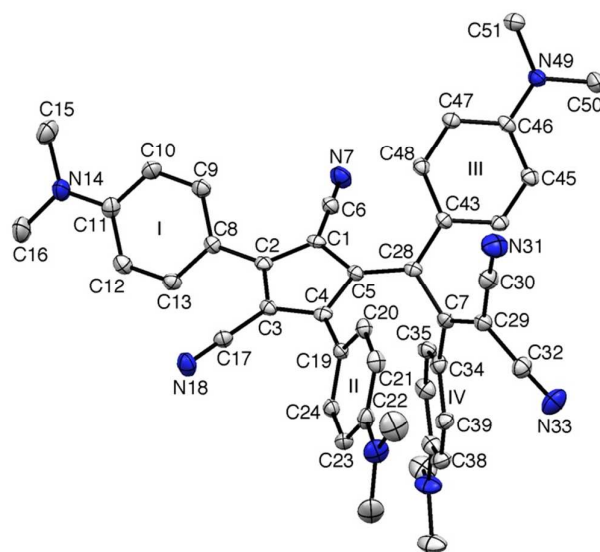


**Figure 6SI.** a) ORTEP plot of **7** (arbitrary numbering, H-atoms are omitted for clarity). Atomic displacement parameters are drawn at 50% probability level. Selected bond lengths [ $\text{\AA}$ ] and torsional angles [ $^\circ$ ]: C3–C4: 1.359(3), C4–C5: 1.451(3), C5–C6: 1.410(3), C6–C7: 1.448(2), C7–C8: 1.389(3), C8–C9: 1.448(2), C9–C10: 1.398(3), C6–C10: 1.454(2), C11–C12: 1.402(2), C12–C13: 1.380(3), C13–C14: 1.411(3), C14–C15: 1.414(3), C15–C16: 1.378(3), C11–C16: 1.402(3),

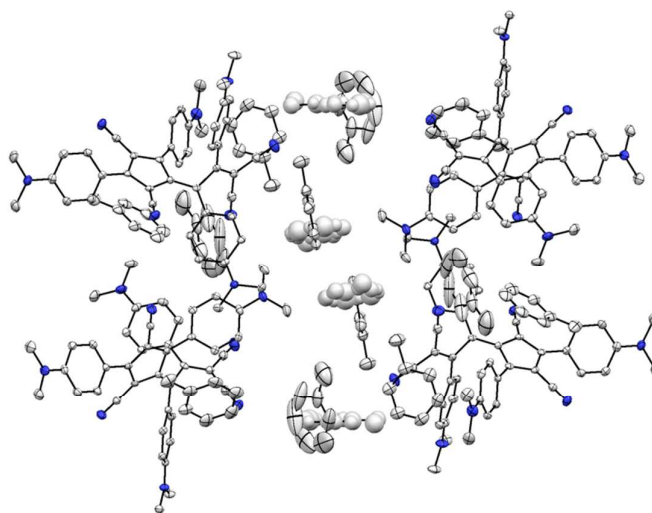
C20–C21: 1.408(3), C21–C22: 1.359(3), C22–C23: 1.415(3), C23–C24: 1.422(3), C24–C25: 1.370(3), C20–C25: 1.414(3), C29–C30: 1.400(3), C30–C31: 1.377(3), C31–C32: 1.412(3), C32–C33: 1.402(3), C33–C34: 1.374(3), C29–C34: 1.408(3), C3–C4–C5–C6:  $-158.0(18)$ , C6–C5–C20–C25:  $36.3(3)$ , C4–C5–C20–C21:  $32.9(3)$ , C9–C10–C11–C12:  $41.1(3)$ , C9–C8–C29–C30:  $-35.7(3)$ . b) The arrangement of neighbouring molecules in the crystal packing of **7** (H-atoms and solvent molecules are omitted for clarity).

**X-Ray Crystal Structure of 9•4 C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (CCDC 891533).** A black plate-like crystal (linear dimensions ca. 0.02 × 0.16 × 0.20 mm) was obtained from toluene/pentane solution at 25 °C. Crystal data for C<sub>44</sub>H<sub>40</sub>N<sub>8</sub>•4 C<sub>7</sub>H<sub>8</sub>,  $M_r = 1049.40$ , monoclinic space group  $P2_1/c$ ,  $D_{\text{calcd}} = 1.172 \text{ Mg m}^{-3}$ ,  $Z = 4$ ,  $a = 15.2956(9) \text{ \AA}$ ,  $b = 19.8622(10) \text{ \AA}$ ,  $c = 19.6049(9) \text{ \AA}$ ,  $V = 5947.3(5) \text{ \AA}^3$ ;  $m = 0.069 \text{ mm}^{-1}$ . Numbers of measured and unique reflections were 52950 and 13655, respectively ( $R_{\text{int}} = 0.0813$ ). One of the toluene molecules is disordered and was refined over two positions. Final  $R(F) = 0.078$ ,  $wR(F2) = 0.183$  for 704 parameters and 7206 reflections with  $I > 2\sigma(I)$  and  $1.68 < \theta < 27.52^\circ$  (corresponding R values based on all 13655 reflections are 0.160 and 0.216, respectively).

a)



b)

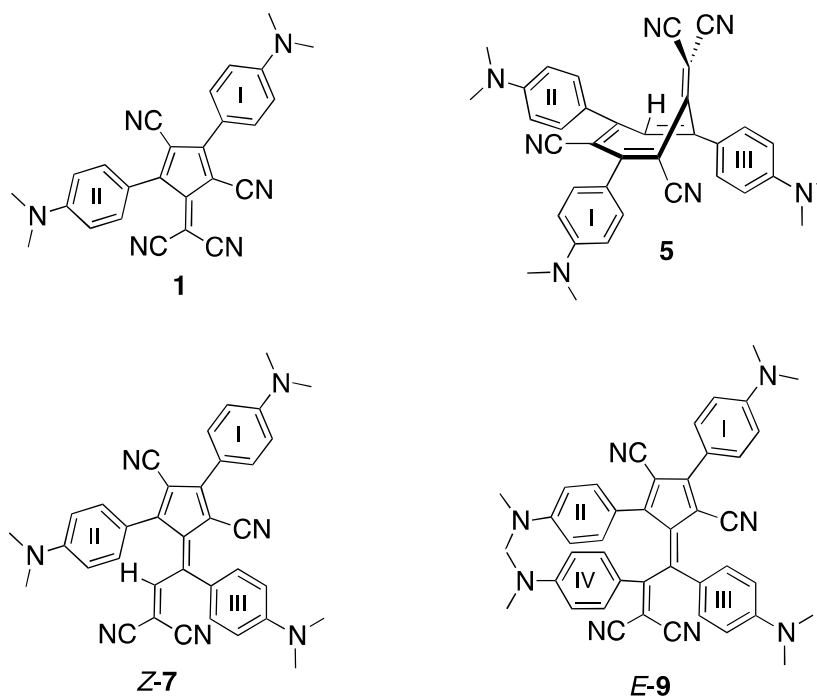


**Figure 7SI.** a) ORTEP plot of *E*-9-4  $C_6H_5CH_3$ , arbitrary numbering, H-atoms are omitted for clarity. Atomic displacement parameters are drawn at 50% probability level. Selected bond lengths [ $\text{\AA}$ ], angles [ $^\circ$ ], and torsional angles [ $^\circ$ ]: C1–C2: 1.393(4), C2–C3: 1.438(4), C3–C4: 1.391(4), C4–C5: 1.443(4), C5–C28: 1.398(4), C7–C28: 1.498(4), C7–C29: 1.371(4), C8–C9: 1.401(4), C9–C10: 1.381(4), C10–C11: 1.402(4), C11–C12: 1.413(4), C12–C13: 1.381(4), C8–C13: 1.397(4), C19–C20:

1.399(4), C20–C21: 1.389(4), C21–C22: 1.400(4), C22–C23: 1.412(4), C23–C24: 1.389(4), C19–C24: 1.397(4), C34–C35: 1.416(4), C35–C36: 1.367(4), C36–C37: 1.418(4), C37–C38: 1.423(4), C38–C39: 1.376(4), C34–C39: 1.406(4), C43–C44: 1.420(4), C44–C45: 1.363(4), C45–C46: 1.421(4), C46–C47: 1.422(4), C47–C48: 1.372(4), C43–C48: 1.419(4), C1–C2–C8–C9:  $-39.0(4)$ , C3–C4–C19–C24:  $59.6(4)$ , C5–C28–C7–C29:  $-125.7(3)$ , C5–C28–C43–C48:  $26.4(4)$ , C29–C7–C34–C39:  $35.0(4)$ , C28–C7–C34–C35:  $30.7(4)$ . b) The arrangement of neighboring molecules related by a  $2_1$  screw axis in the crystal packing of *E*-**9**•4 C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> shows a disordered array of toluene molecules (projection on 1,1,0 plane) (H-atoms and solvent molecules are omitted for clarity).

#### Section 4SI.

#### Quinoid Character of the DMA Groups and Torsion Angles of **1**, **5**, *Z*-**7**, and *E*-**9**

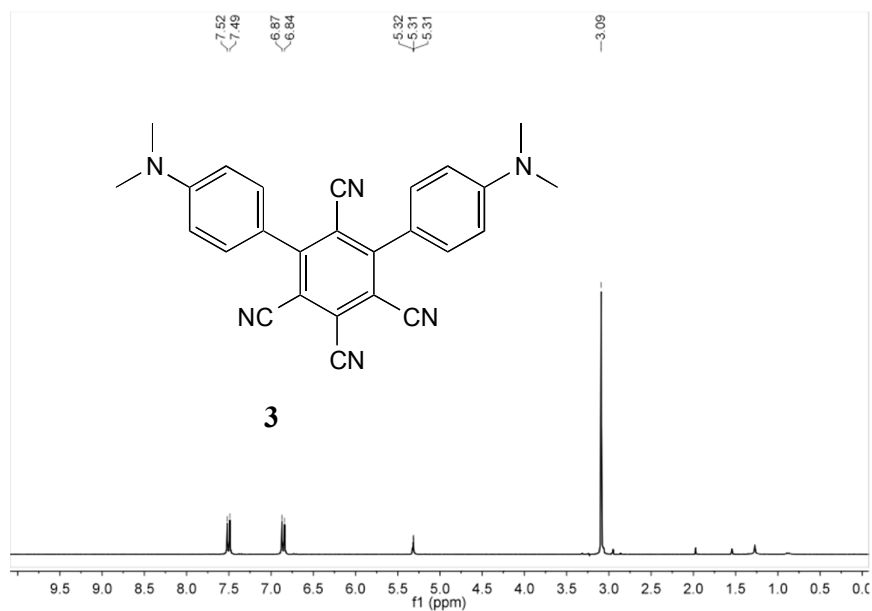


**Table 1SI. Quinoid Character<sup>5</sup>  $\delta r$  of the DMA Groups (Variance  $\leq 0.003$  Å) and Torsion Angles  $\theta$  (Variance  $\leq 0.4^\circ$ ) of the Fulvenes **1**, **5**, **Z-7**, and **E-9**.**

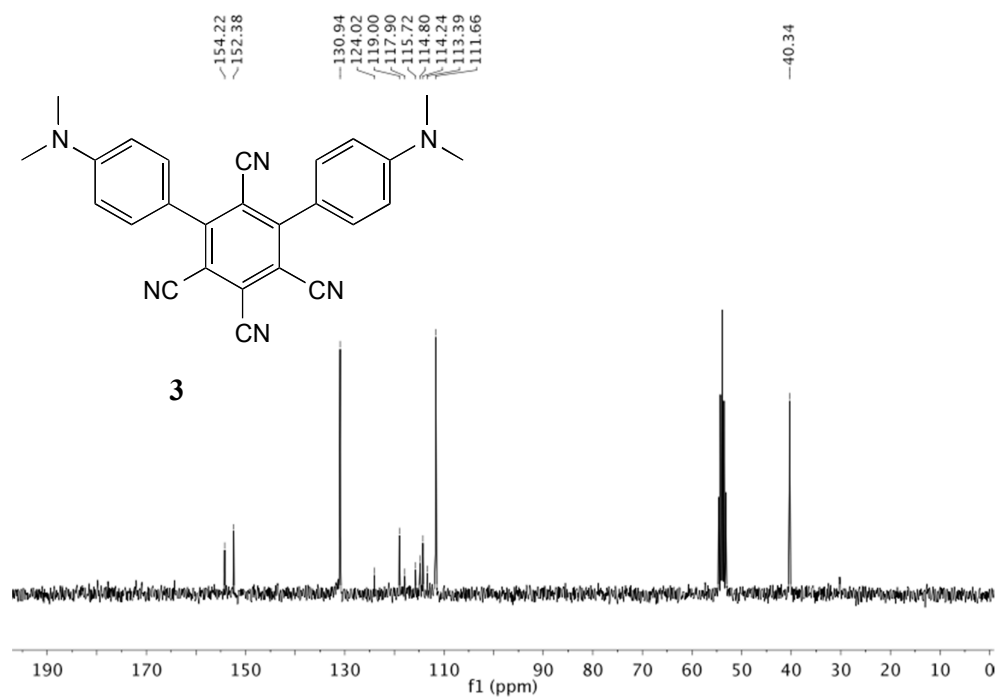
| Compound                  |                | DMA-I | DMA-II | DMA-III | DMA-IV |
|---------------------------|----------------|-------|--------|---------|--------|
| <b>1</b>                  | $\delta r$ [Å] | 0.065 | 0.031  |         |        |
|                           | $\theta$ [°]   | −13.6 | −59.2  |         |        |
| <b>5</b><br>(conformer A) | $\delta r$ [Å] | 0.031 | 0.031  | 0.028   |        |
|                           | $\theta$ [°]   | 34.4  | −42.4  | 11.0    |        |
| <b>Z-7</b>                | $\delta r$ [Å] | 0.030 | 0.028  | 0.05    |        |
|                           | $\theta$ [°]   | −35.7 | 41.1   | 36.3    |        |
| <b>E-9</b>                | $\delta r$ [Å] | 0.022 | 0.013  | 0.053   | 0.044  |
|                           | $\theta$ [°]   | −39.0 | 59.6   | 26.4    | 35.0   |

## Section 5SI

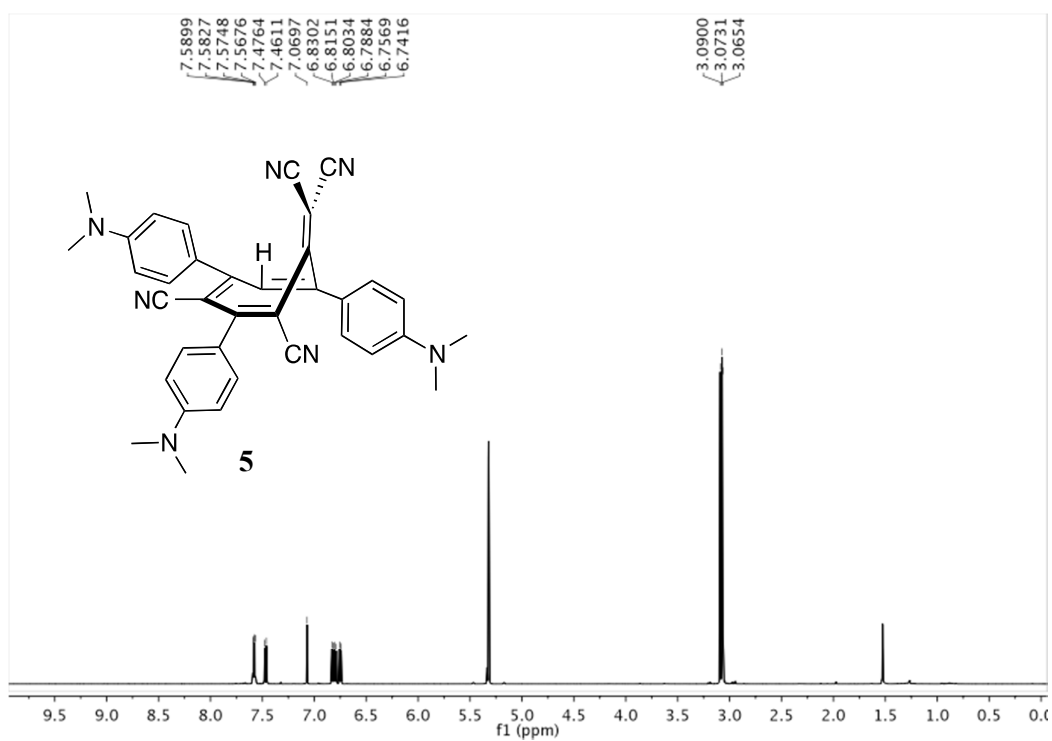
### <sup>1</sup>H and <sup>13</sup>C NMR Spectra of the Products



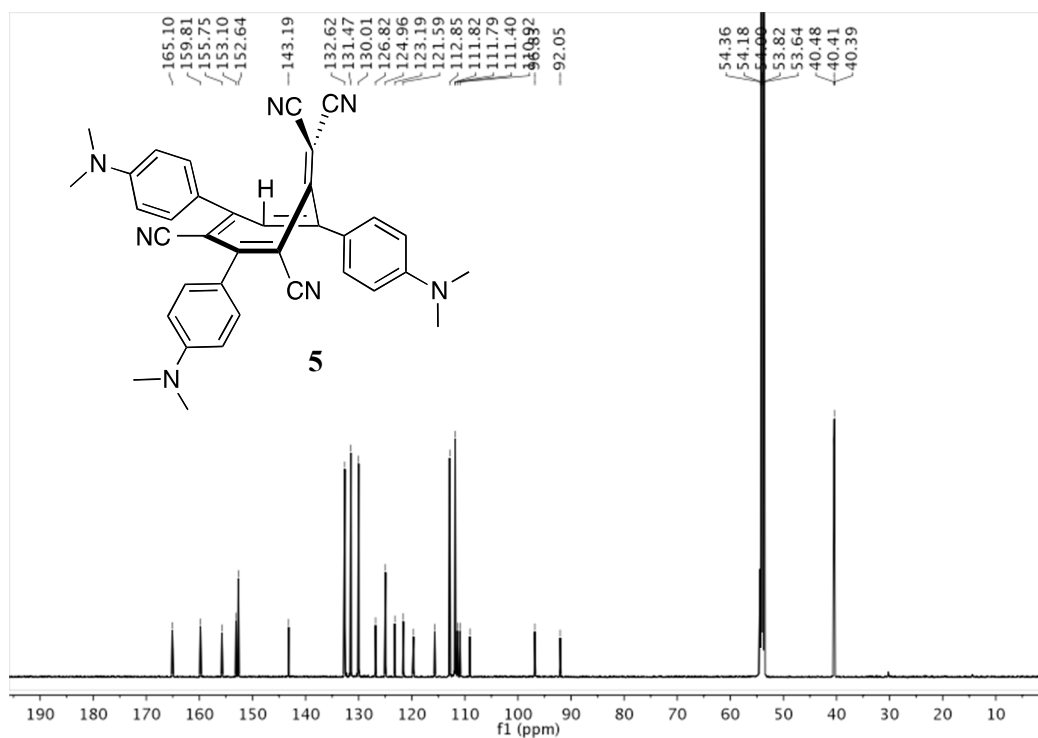
**Figure 8SI.** 300 MHz <sup>1</sup>H NMR spectrum of **3** recorded at 293 K in CD<sub>2</sub>Cl<sub>2</sub>.



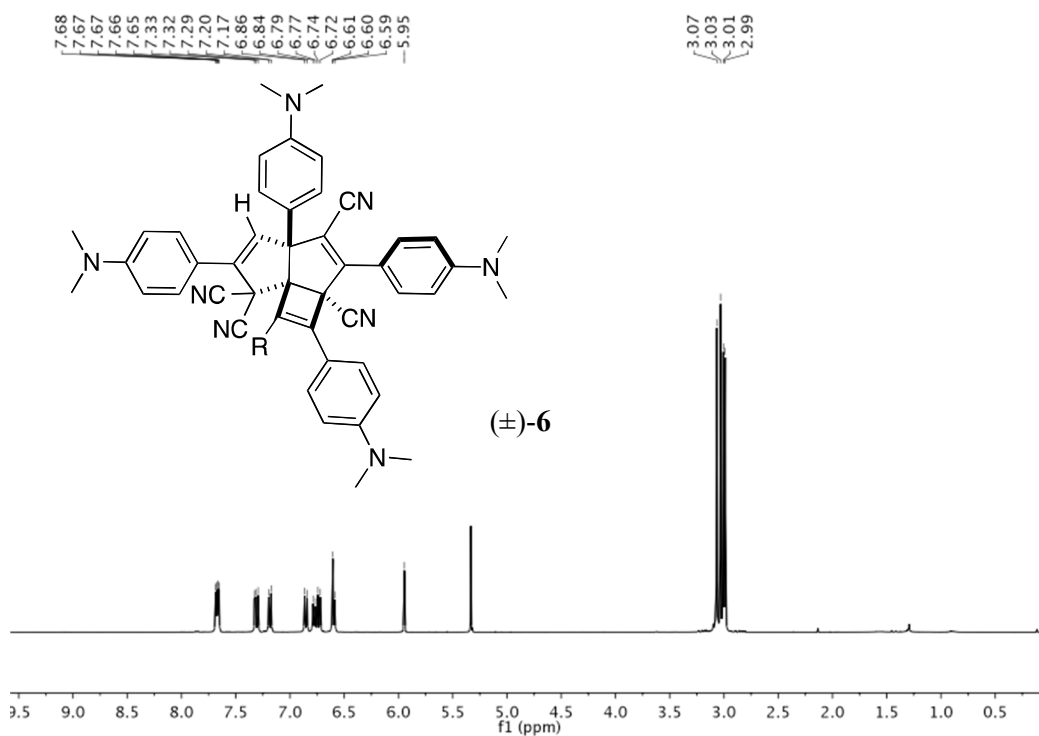
**Figure 9SI.** 75 MHz <sup>13</sup>C NMR spectrum of **3** recorded at 293 K in CD<sub>2</sub>Cl<sub>2</sub>.



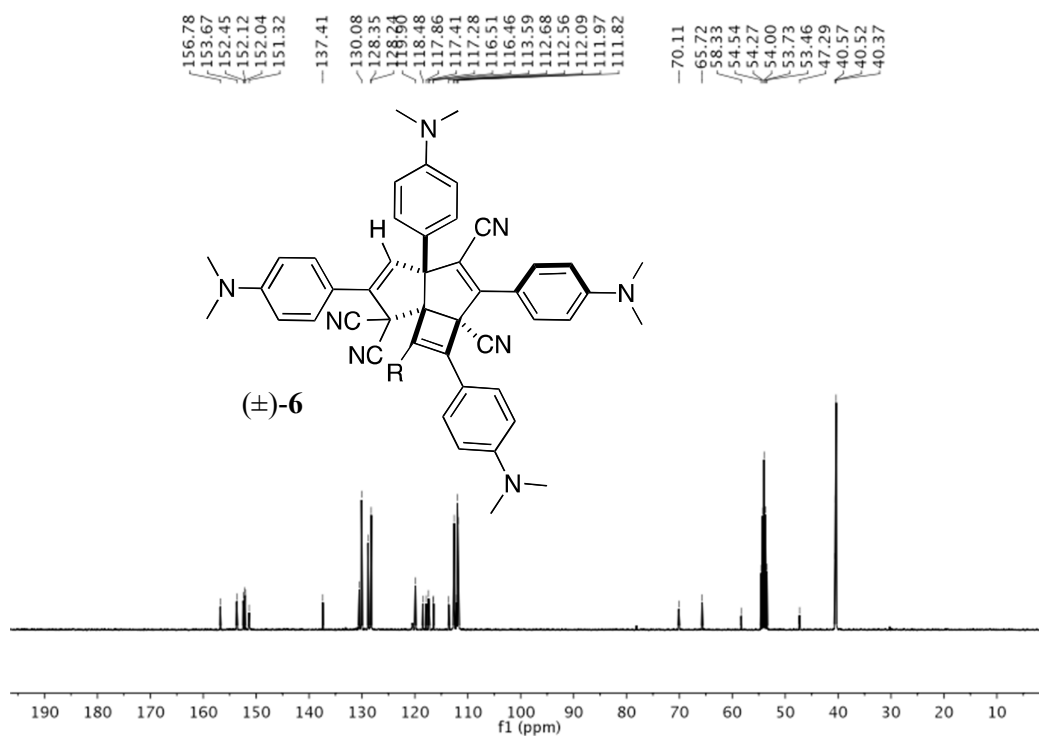
**Figure 10SI.** 600 MHz <sup>1</sup>H NMR spectrum of **5** recorded at 293 K in CDCl<sub>3</sub>.



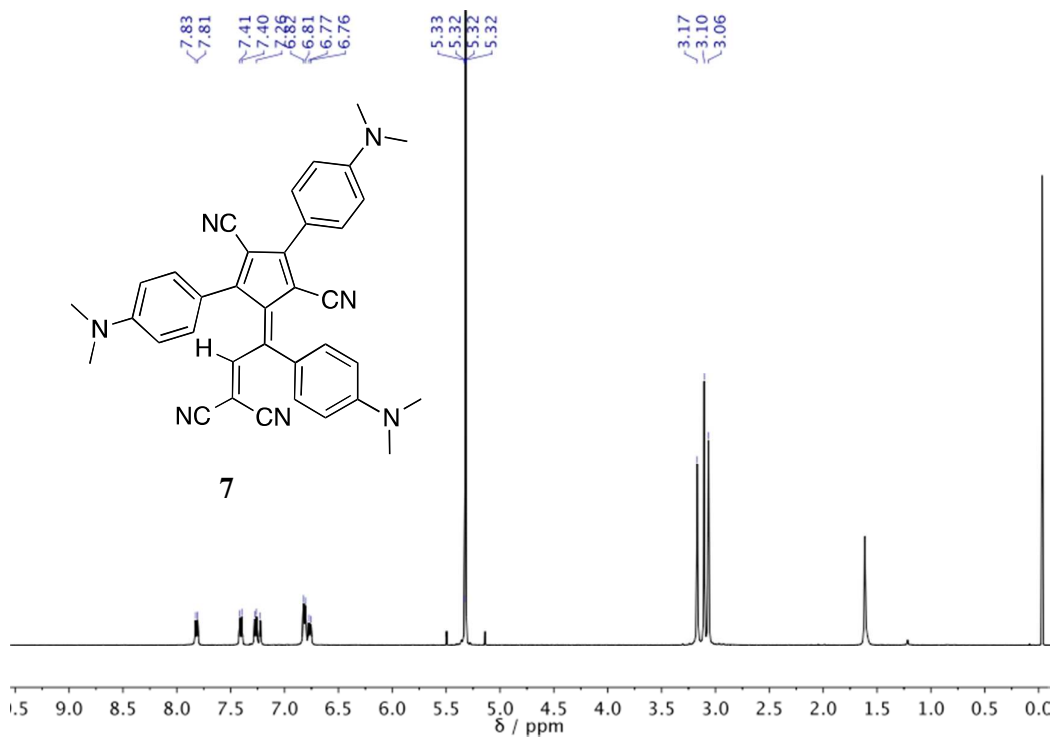
**Figure 11SI.** 150 MHz  $^{13}\text{C}$  NMR spectrum of **5** recorded at 293 K in  $\text{CDCl}_3$ .



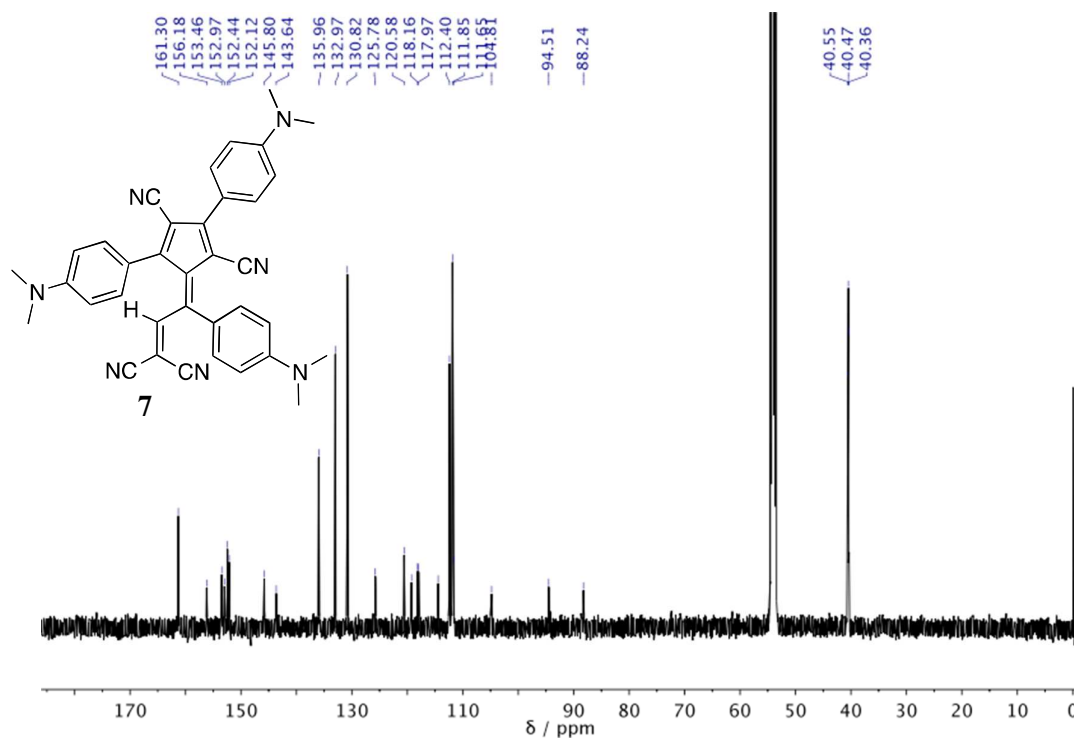
**Figure 12SI.** 400 MHz  $^1\text{H}$  NMR spectrum of **(±)-6** recorded at 293 K in  $\text{CD}_2\text{Cl}_2$ .



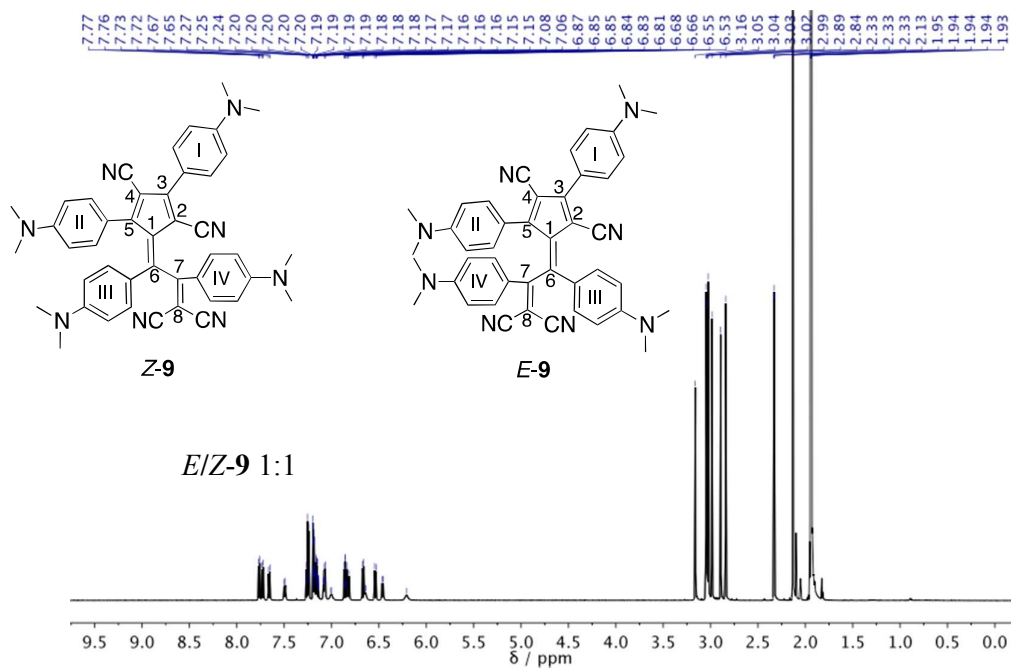
**Figure 13SI.** 75 MHz  $^{13}\text{C}$  NMR spectrum of (±)-**6** recorded at 293 K in  $\text{CD}_2\text{Cl}_2$ .



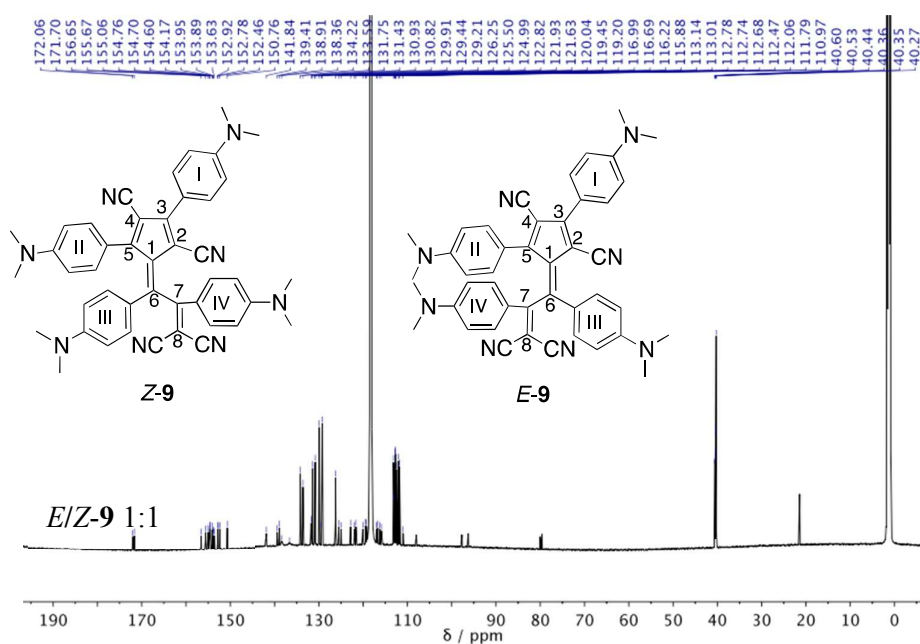
**Figure 14SI.** 500 MHz  $^1\text{H}$  NMR spectrum of **7** recorded at 253 K in  $\text{CD}_2\text{Cl}_2$ .



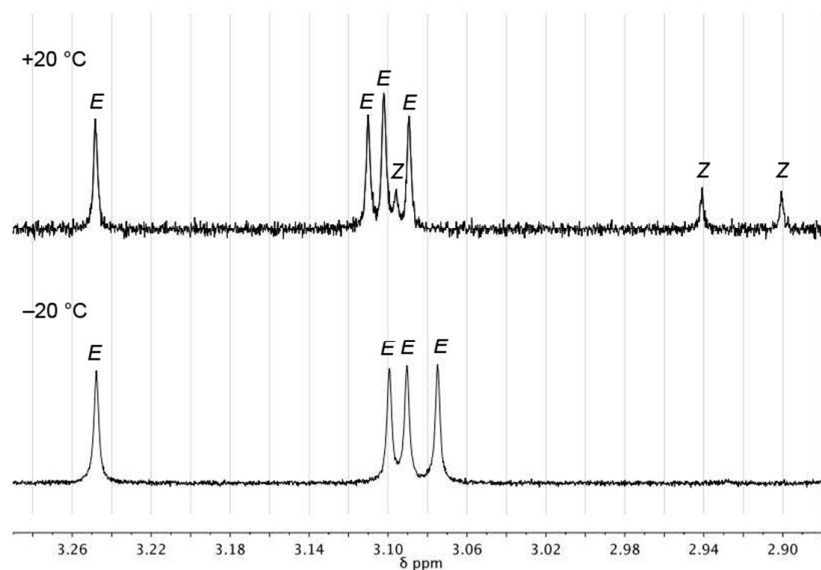
**Figure 15SI.** 125 MHz  $^{13}\text{C}$  NMR spectrum of **7** recorded at 253 K in  $\text{CD}_2\text{Cl}_2$ .



**Figure 16SI.** 600 MHz  $^1\text{H}$  NMR spectrum of *E/Z*-**9** 1:1 (crystals containing four toluene molecules) recorded at 293 K in  $\text{CD}_3\text{CN}$ .



**Figure 17SI.** 150 MHz  $^{13}\text{C}$  NMR spectrum of *E/Z*-**9** 1:1 (crystals containing four toluene molecules) recorded at 293 K in  $\text{CD}_3\text{CN}$ .

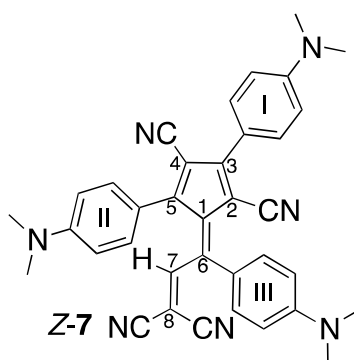


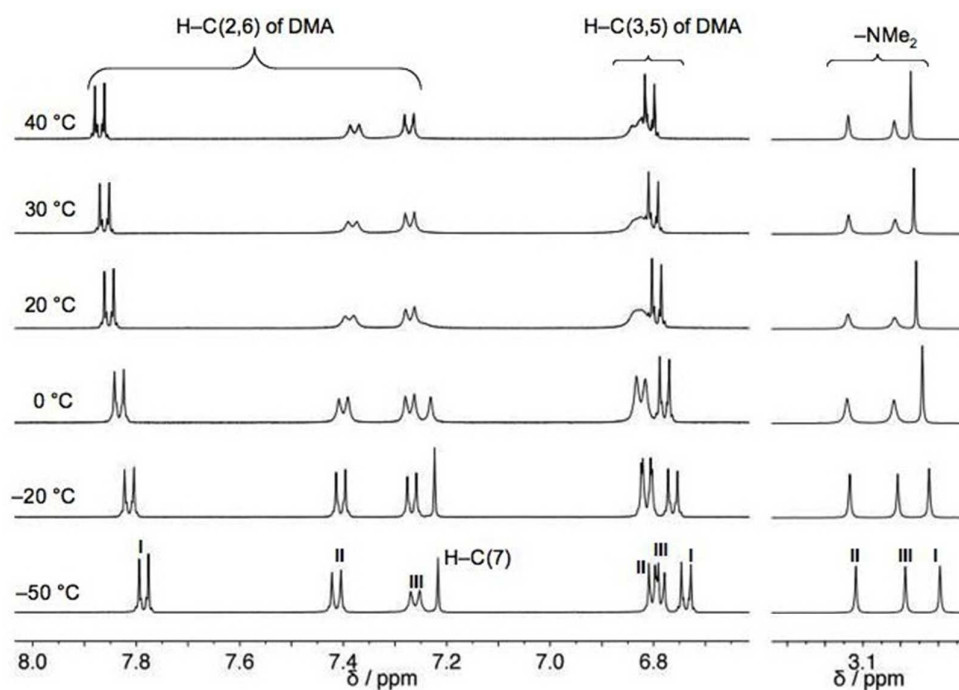
**Figure 18SI.** Temperature dependent partial  $^1\text{H}$  NMR (500 MHz) spectra showing the  $\text{NMe}_2$  signals of plate-like single crystals of **9** in  $\text{CD}_2\text{Cl}_2$  at  $-20$  (bottom) and after warming to  $+20$  °C (*E/Z* 3:1; top). Strong broadening prevented an unambiguous assignment of the aromatic signals to the *E*- and *Z*-isomer.

## Section 6SI.

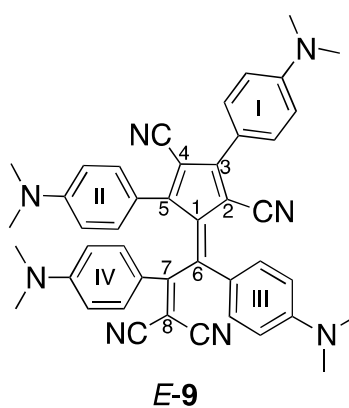
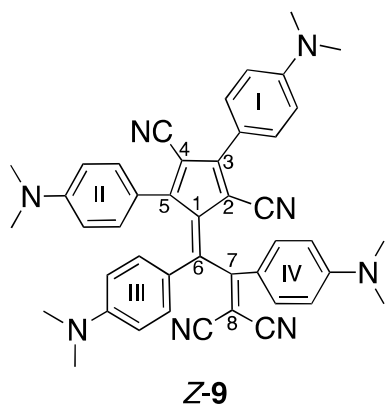
### *E/Z* Isomerization of **7** and **9**: Full Investigation

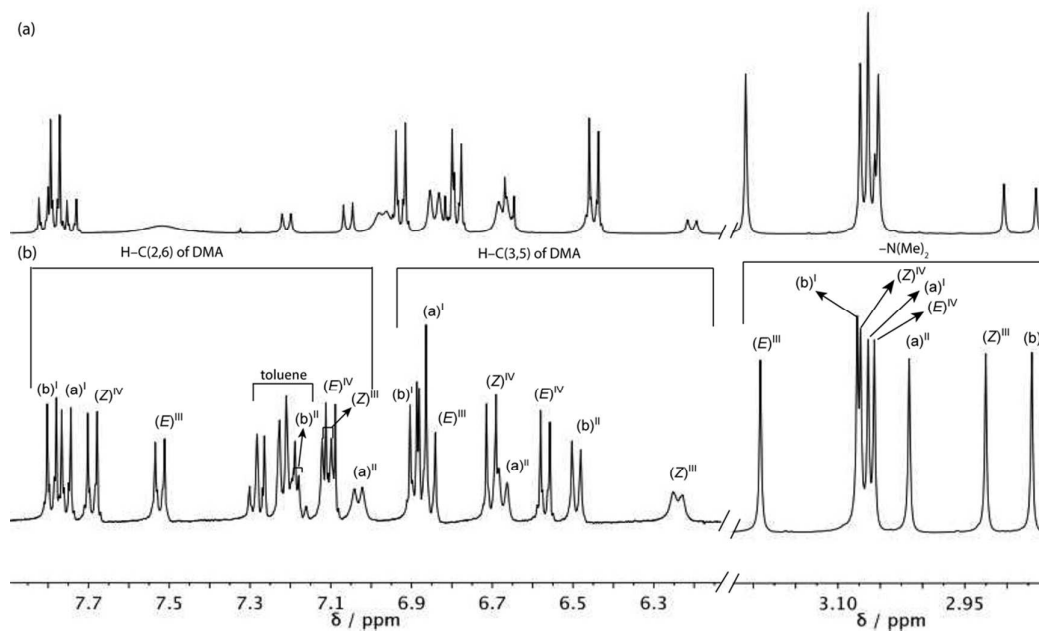
Extended pentafulvene **7** in CD<sub>2</sub>Cl<sub>2</sub> shows at room temperature a set of sharp <sup>1</sup>H NMR signals for one DMA group and two sets of broadened signals for the other two DMA groups, suggesting a relatively fast equilibration on the NMR time scale (Figure 19SI). On the other hand, **9** exists at room temperature in CD<sub>2</sub>Cl<sub>2</sub>, CD<sub>3</sub>CN, and (CDCl<sub>2</sub>)<sub>2</sub> as 3:1, 1:1, and 5:1 *E/Z* mixtures, respectively (Figures 20SI and 21SI). The *E/Z* equilibrium of **7** was further analyzed by measuring low temperature <sup>1</sup>H NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> down to –50 °C and high temperature <sup>1</sup>H NMR spectra in (CDCl<sub>2</sub>)<sub>2</sub> up to 100 °C (see Figures 19SI and 22SI). Both cooling and warming led to sharpening of the broad signals. However, even at –50 °C only signals of the *Z*-isomer could be observed, indicating a *Z/E*-ratio of > 98:2. For **9** in (CDCl<sub>2</sub>)<sub>2</sub>, the *E/Z*-ratio of 5:1 at 20 °C is changed to 3:1 upon heating to 100 °C (Figure 22SI). The sharpening of some signals indicates faster rotation of the corresponding DMA moieties.



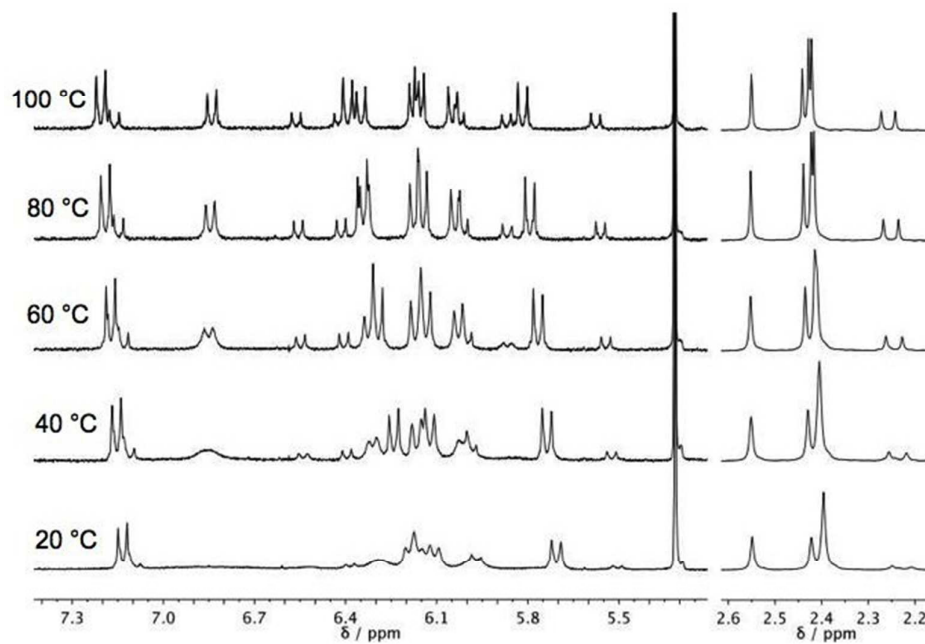


**Figure 19SI.** VT- $^1\text{H}$  NMR spectra (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **7** in the range from  $-50$  to  $40$   $^\circ\text{C}$  (no signal above  $7.9$  ppm). The relative intensity of signals in the two regions is adapted to fit well into the window. The assignment of the signals to DMA moieties at C(3), C(5), and C(6) are denoted with (I), (II), and (III), respectively.

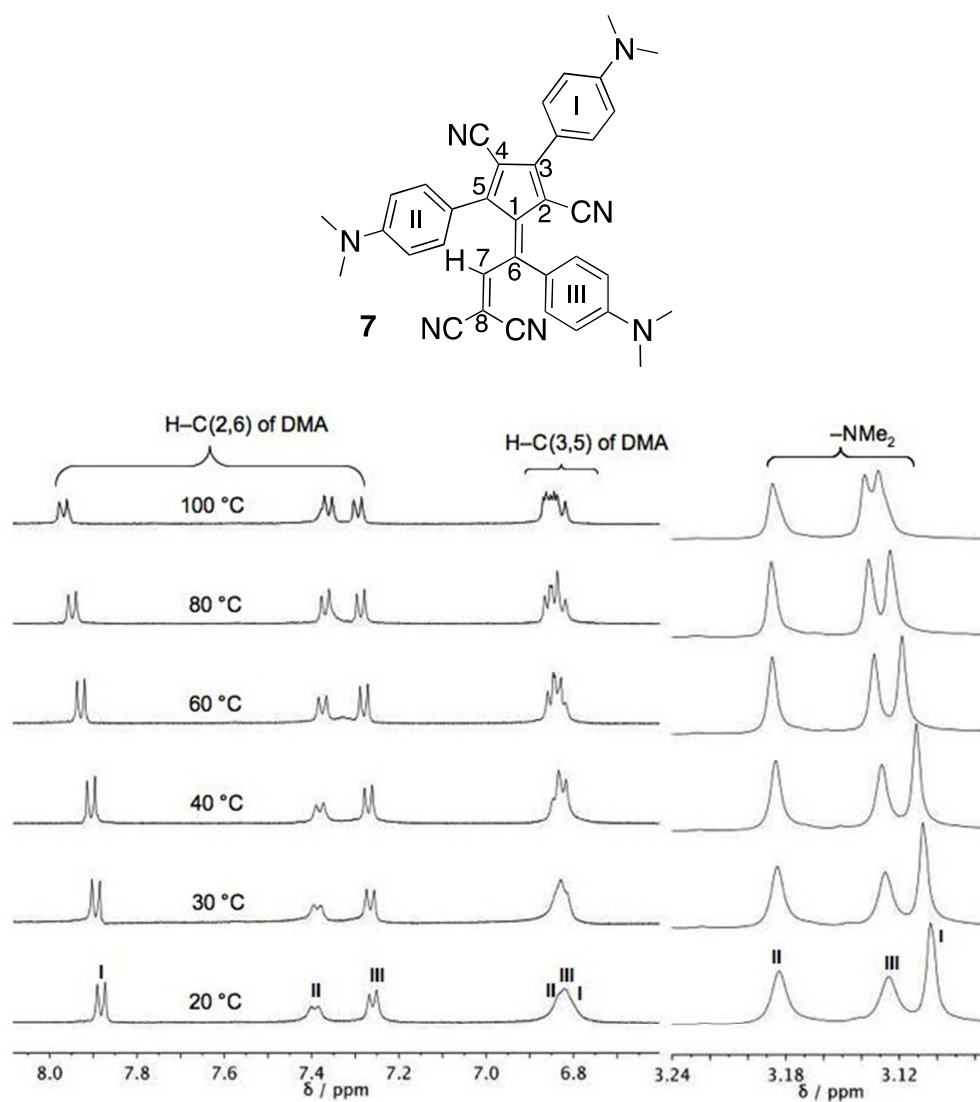




**Figure 20SI.** 400 MHz  $^1\text{H}$  NMR spectra of *E/Z*-**9** a) with an *E:Z* ratio 3:1 in  $\text{CD}_2\text{Cl}_2$  and b) a 1:1 ratio in  $\text{CD}_3\text{CN}$  at 20 °C. The relative intensity of signals in the two regions is adapted to fit the spectral window. The signals corresponding to DMA groups at C(6) and C(7) in the *E*- and *Z*-diastereoisomers are denoted as  $(E)^{\text{III}}$ ,  $(Z)^{\text{III}}$ ,  $(E)^{\text{IV}}$ , and  $(Z)^{\text{IV}}$ , respectively. The signals for the DMA moieties at C(3) and C(5) could not be assigned to the diastereoisomers and are labeled  $(a)^{\text{I}}$ ,  $(b)^{\text{I}}$ ,  $(a)^{\text{II}}$ , and  $(b)^{\text{II}}$ .



**Figure 21SI.** Temperature dependence of  $^1\text{H}$  NMR (300 MHz) spectra of *E/Z*-9 in  $(\text{CDCl}_3)_2$  in the range from 20 to 100 °C. The relative intensity of signals in the two regions is adapted well to fit in to the window.



**Figure 22SI.** Temperature dependence of  $^1\text{H}$  NMR (300 MHz) spectra of **7** in  $(\text{CDCl}_3)_2$  in the range from 20 to 100 °C (no signal above 8.0 ppm). The assignment of the signals is done similarly to the  $\text{CD}_2\text{Cl}_2$  spectrum. The relative intensity of signals in the two regions is adapted well to fit in to the window. The signals of the DMA moieties at C(3), C(5), and C(6) are denoted as (I), (II), and (III), respectively. The signal of H-C(7) is missing due to coalescence at 20 to 40 °C, however a very broad peak appears at 7.32 ppm at 60 °C which moves downfield at higher temperatures.

The assignment of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals of **7** and **9** is hampered by the fact that there are several DMA groups, but only a single additional H-atom in **7**. The spectra of **7** were analyzed in  $\text{CD}_2\text{Cl}_2$  at  $-50\text{ }^\circ\text{C}$ , whereas those of **9** were evaluated in  $\text{CD}_3\text{CN}$  at room temperature, as the  $^1\text{H}$  NMR spectrum of **9** in  $\text{CD}_2\text{Cl}_2$  shows strong line broadening. The combined analysis of DQF-COSY, HSQC, and HMBC spectra allowed an unambiguous assignment of the signals of the three DMA sets of **7** and the eight DMA sets of *E/Z*-**9** and their points of attachment to the extended fulvene skeleton.

HMBC cross peaks between the  $\text{C}(1^{\text{III}})$  signal and both the singlet of  $\text{H}-\text{C}(7)$  and the broad doublet for  $\text{H}-\text{C}(2^{\text{II}}, 6^{\text{II}}, 2^{\text{III}}, 6^{\text{III}})$  evidence that a set of broad signals of **7** belongs to the DMA group III at C(6). The DMA group I at C(3) is in the neighborhood of two cyano groups, whereas the DMA group II at C(5) only has one close cyano neighbor. Hence,  $\text{H}-\text{C}(2^{\text{I}}, 6^{\text{I}})$  should resonate at lower field than  $\text{H}-\text{C}(2^{\text{II}}, 6^{\text{II}})$ , and this is indeed the case (7.82 vs 7.27 ppm). Thus, the expectation that the broad signals of **7** belong to the DMA groups II and III at C(5) and C(6), respectively, is fulfilled. The shielding of the DMA-substituted centers increases in the series from C(3) via C(5) to C(6) (156.2, 153.5, and 143.6 ppm, respectively), whereas C(7) resonates at lowest field (161.30 ppm) due to the two vicinal cyano groups.

In **9**, arylation at C(7) should lead to a further downfield shift of the  $^{13}\text{C}$  resonance. Indeed, C(7) of the *E/Z*-isomers of **9** appears at 170.7 and 172.1 ppm and HMBC cross peaks allow an unambiguous assignment for the signals of DMA IV in both isomers (Figure 20SI). The strong downfield shift for  $\text{H}-\text{C}(2,6)$  of one of these isomers allows an easy assignment to the *Z*-configured (note the different *E/Z* notation of **7** and **9** due to a change of the priority in Cahn-Ingold-Prelog sequence;

7.66 ppm, two cyano neighbors) and the *E*-configured diastereoisomer (7.07 ppm, one cyano and one DMA neighbor). The two sets of signals for the DMA group I at C(3) should be similar and well-resolved, and characterized by a strong downfield shift for their H–C(2,6) signals. Indeed, there is such a pair in the  $^1\text{H}$  NMR spectrum ( $\delta_{\text{H-C(2,6)}}$  = 7.73 and 7.76 ppm); an assignment to the *E*- and *Z*-diastereoisomers, however is not feasible. One of the remaining 4 DMA signal sets (for both isomers of DMA groups II and III) shows weakly broadened signals and a deshielding for its H–C(2,6) signal (7.49 ppm), whereas the signals of the other three sets are broad and show a shielding for their H–C(2,6) signals ( $\leq 7.17$  ppm). The former set may be assigned to DMA group III at C(6) of the *E*-isomer (two cyano neighbors) and the latter to DMA group III at C(6) of the *Z*-isomer and to DMA group II at C(5) of both diastereoisomers. The strong line broadening for the  $^1\text{H}$  NMR signals fits well with the hindered rotation of DMA II at C(5) of both diastereoisomers and DMA III at C(6) of the *Z*-diastereoisomer. Surprisingly, there are two very broad  $^{13}\text{C}$  NMR signals for C(2,6) of DMA groups at 136.6 and 138.35 ppm, probably belonging to DMA III at C(6) of both diastereoisomers and reflecting an anisotropy effect of the dicyanovinyl moiety.

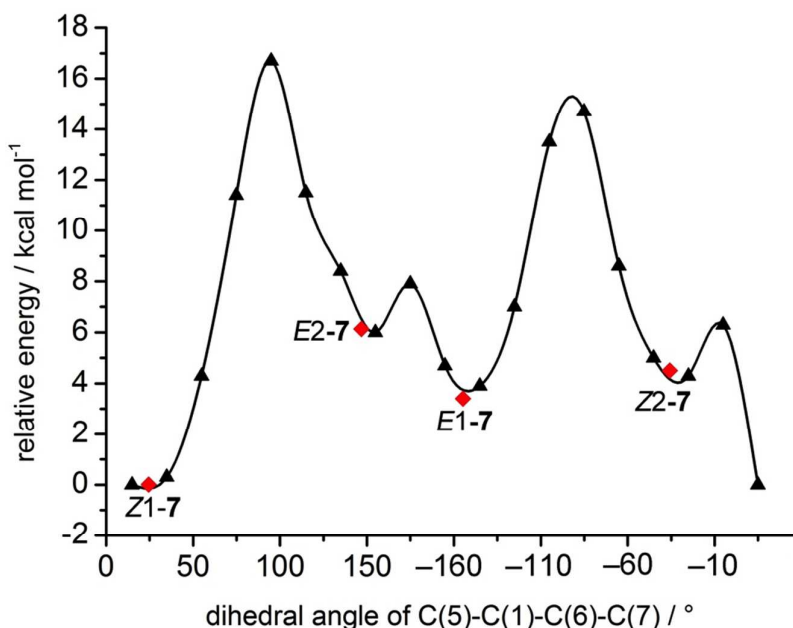
The chemical shift of the olefinic proton of *E/Z*-**7** is influenced by a shielding by DMA group II at C(5) and a deshielding by the cyano group at C(2). This can be concluded from the spectral data for starting material **2** (Scheme 1, main manuscript): In *Z*-**2**, the vinyl proton appears at 7.49 ppm (a cyano and a DMA neighbor) and in *E*-**2**, 8.22 ppm (two cyano neighbors).<sup>1</sup> Thus, the upfield shift of the vinylic H of **7** (7.22 ppm) evidences both a cyano and a DMA neighbor and hence a *Z*-configuration in solution, similar to the X-ray crystal structure. This is corroborated by ab initio calculations (density functional theory at the B3LYP/6-31G(d) level of theory using the polarizable continuum model (PCM) and  $\text{CHCl}_3$  as solvent)<sup>6</sup> of the energy profile

for rotation around the exocyclic C(1)–C(6) double bond (see Section 7SI below). Four minimum energy structures were obtained, two *Z*- and two *E*-rotamers differing essentially by their sign of the rotation (+24.7° vs –35.8° and –154.7° vs +146.9°, see Figure 24SI). Additionally, the chemical shift of the vinylic H-atom of these four minimum structures was calculated (DFT-B3LYP/6-311+G(2d,p) level of theory with PCM solvation in CHCl<sub>3</sub>). The calculated global minimum Z1-7 closely resembles the experimental solid-state structure of **7** (torsional angle: +24.7° vs +28.2°). The energy barriers of 14 and 16 kcal mol<sup>–1</sup> ascertain an easy equilibration at room temperature.<sup>7,8</sup> The  $\delta_{\text{H-7}}$  calculation of the chemical shift for H–C(7) (Z1-7: 7.26, Z2-7: 8.22, E1-7: 8.97, and E2-7: 8.27 ppm) suggests also that **7** in chlorinated solvents adopts the minimum structure Z1-7.

## Section 7SI.

### ab initio Calculations for **7** and **9**

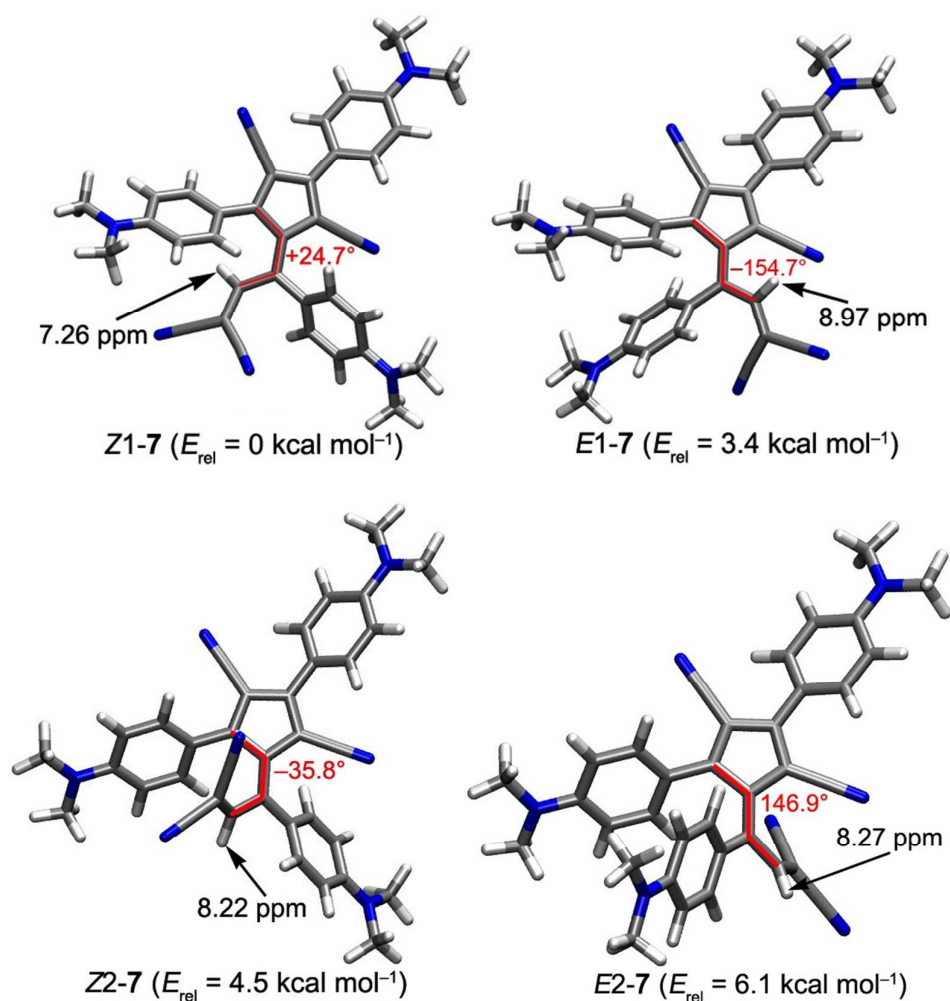
Calculations were performed using the Gaussian 09 program package.<sup>9</sup> Molecular properties in the electronic ground state were computed at the B3LYP/6-31G(d) level of theory. All structures are ground-state minima according to the analysis of their harmonic vibrational analytical frequencies computed at the same level, which show no imaginary frequencies. All energies reported are zero-point corrected electronic energies. The NMR chemical shifts are predicted using the gauge-independent atomic orbital (GIAO) method at the B3LYP/6-311+G(2d,p) level of theory.<sup>6</sup> Unless otherwise stated, the effect of chloroform solvent on geometry optimization and NMR chemical shifts is accounted for using the polarizable continuum solvation model PCM.<sup>10</sup>



**Figure 23SI.** Dihedral angle scan around the exocyclic double bond of **7**. Shown are the calculated relative energies versus the dihedral angle (black triangles). The local minima of the scan were further optimized at the B3LYP/6-31G(d) (RMS < 0.005) level of theory with PCM solvation in chloroform to obtain the four *E/Z* local minima of **7** (red diamonds, see also Figure 24SI).

In order to get minima for *Z*- and *E*-configured **7**, a dihedral angle scan around the exocyclic double bond was carried out. The scan was performed at the B3LYP/G6-31G(d) level of theory in gas phase in 17 steps of 20°. Since steric reasons do not allow a complete conjugation of  $\pi$ -systems, there are two minima for *Z*- and *E*-configured structures, respectively, which differ essentially by the sign of rotation. Further geometry optimizations (including harmonic vibrational frequency analysis) were carried out for the four minimum structures to obtain the most stable rotamers with relative energies for PCM solvation in chloroform: 24.7° (0 kcal mol<sup>-1</sup>, Z1-7, global minimum), 146.9° (6.1 kcal mol<sup>-1</sup>, E2-7, local minimum), -154.7° (3.4 kcal

$\text{mol}^{-1}$ , *E1-7*, local minimum),  $-35.8^\circ$  ( $4.5 \text{ kcal mol}^{-1}$ , *Z2-7*, local minimum) (Figure 24SI). The calculated  $^1\text{H}$  NMR chemical shifts (GIAO, B3LYP/6-311+G(2d,p) with PCM in chloroform) of the dicyanovinyl protons in *Z1-7*, *Z2-7*, *E1-7*, and *E2-7* are 7.26, 8.22, 8.97, and 8.27 ppm, respectively. The experimental value of 7.22 ppm ( $\text{CD}_2\text{Cl}_2$ , 500 MHz, 223 K) closely matches with the calculated value for *Z1-7*. In addition, this global minimum structure *Z1-7* is very similar to the structure in the solid state.



**Figure 24SI.** Optimized minimum energy structures (at the B3LYP/6-31G(d) level of theory with PCM solvation in chloroform) of *Z1-7*, *Z2-7*, *E1-7*, and *E2-7* obtained

from the optimization of the local minima in the dihedral angle scan of **7**. The dihedral angles at the exocyclic C(1)–C(6) double bonds are given in ° (along the red line), and the calculated NMR chemical shifts (GIAO, B3LYP/6-311+G(2d,p) with PCM in chloroform) of the dicyanovinyl protons are given in ppm (experimental value: 7.22 ppm in CD<sub>2</sub>Cl<sub>2</sub> at 500 MHz and 223 K).

**Table 2SI. Cartesian Coordinates of the Calculated Minimum Structures of **7**.**

Z1-7:

| Atomic<br>Type | Coordinates [Å] |           |           |   |           |           |           |
|----------------|-----------------|-----------|-----------|---|-----------|-----------|-----------|
|                | x               | y         | z         |   |           |           |           |
| C              | -0.199676       | -1.458738 | 0.059413  | H | -4.332006 | -2.173565 | -1.907263 |
| C              | 1.116357        | -1.920028 | 0.002939  | N | 1.780211  | -4.351135 | -0.571704 |
| C              | 2.040099        | -0.799571 | 0.098685  | N | 2.251765  | 2.659967  | 0.855319  |
| C              | 1.257081        | 0.364003  | 0.209826  | N | -4.866882 | -4.584374 | -0.834714 |
| C              | -0.144542       | -0.005532 | 0.240718  | N | 7.716531  | -1.157007 | 0.043844  |
| C              | 1.484340        | -3.252815 | -0.311182 | C | -5.948505 | -4.071395 | -1.667040 |
| C              | 1.783421        | 1.633457  | 0.555394  | H | -6.327965 | -3.115642 | -1.285007 |
| C              | -1.243944       | 0.832439  | 0.512905  | H | -5.625999 | -3.924200 | -2.706306 |
| C              | 6.349119        | -1.072221 | 0.056905  | H | -6.770287 | -4.787316 | -1.664345 |
| C              | 5.546886        | -2.103875 | 0.613542  | C | -4.994452 | -5.905867 | -0.231256 |
| C              | 4.166997        | -2.013528 | 0.615219  | H | -5.932847 | -6.355500 | -0.555438 |
| C              | 3.488282        | -0.893868 | 0.081851  | H | -4.175316 | -6.567858 | -0.538571 |
| C              | 4.291203        | 0.132035  | -0.467653 | H | -5.001993 | -5.851397 | 0.865200  |
| C              | 5.670741        | 0.050842  | -0.489414 | C | 8.385097  | -2.328629 | 0.595193  |
| H              | 6.009447        | -2.979137 | 1.052540  | H | 9.462866  | -2.210461 | 0.482382  |
| H              | 3.601114        | -2.820288 | 1.067953  | H | 8.165772  | -2.453528 | 1.663635  |
| H              | 3.818724        | 1.000901  | -0.912323 | H | 8.085696  | -3.247002 | 0.073698  |
| H              | 6.230823        | 0.859740  | -0.942072 | C | 8.513967  | -0.080370 | -0.529814 |
| C              | -3.744657       | -3.831638 | -0.622300 | H | 8.340179  | 0.870856  | -0.010521 |
| C              | -2.690787       | -4.293145 | 0.215320  | H | 9.570856  | -0.330008 | -0.435225 |
| C              | -1.558072       | -3.529918 | 0.424630  | H | 8.291656  | 0.064617  | -1.595243 |
| C              | -1.402728       | -2.250047 | -0.156367 | C | -1.052875 | 5.060266  | -0.364173 |
| C              | -2.446817       | -1.799531 | -0.998300 | C | -1.540661 | 4.590162  | 0.886573  |
| C              | -3.578036       | -2.559199 | -1.232401 | C | -1.615330 | 3.238577  | 1.158368  |
| H              | -2.769562       | -5.252187 | 0.711963  | C | -1.184292 | 2.266820  | 0.227976  |
| H              | -0.785198       | -3.913459 | 1.083031  | C | -0.676616 | 2.737070  | -1.004046 |
| H              | -2.344334       | -0.847760 | -1.509243 | C | -0.628570 | 4.083644  | -1.306550 |
|                |                 |           |           | H | -1.858138 | 5.292211  | 1.647234  |
|                |                 |           |           | H | -1.983799 | 2.922227  | 2.129804  |
|                |                 |           |           | H | -0.348181 | 2.018101  | -1.748884 |
|                |                 |           |           | H | -0.265000 | 4.386439  | -2.280530 |

|   |           |          |           |   |           |           |           |
|---|-----------|----------|-----------|---|-----------|-----------|-----------|
| N | -0.997592 | 6.396581 | -0.649377 | C | -3.696403 | 0.757089  | 1.190855  |
| C | -1.471004 | 7.376996 | 0.320662  | C | -4.672821 | 0.080540  | 1.988987  |
| H | -1.374382 | 8.375235 | -0.106142 | N | -5.469168 | -0.464296 | 2.641800  |
| H | -2.526372 | 7.213933 | 0.572534  | C | -4.210750 | 1.839260  | 0.409728  |
| H | -0.885094 | 7.343583 | 1.248349  | N | -4.718275 | 2.676131  | -0.221920 |
| C | -0.467363 | 6.854303 | -1.928149 | C | -2.409028 | 0.264802  | 1.151154  |
| H | 0.565800  | 6.516757 | -2.076968 | H | -2.258866 | -0.658102 | 1.700576  |
| H | -1.073282 | 6.493340 | -2.769569 |   |           |           |           |
| H | -0.474403 | 7.944054 | -1.947156 |   |           |           |           |

Zero-point correction = 0.590250 (Hartree Particle<sup>-1</sup>)  
 Thermal correction to Energy = 0.631976  
 Thermal correction to Enthalpy = 0.632920  
 Thermal correction to Gibbs Free Energy = 0.511387  
 Sum of electronic and zero-point Energies = -1773.074405  
 Sum of electronic and thermal Energies = -1773.032679  
 Sum of electronic and thermal Enthalpies = -1773.031735  
 Sum of electronic and thermal Free Energies = -1773.153269

Z2-7:

| Atomic<br>Type | Coordinates [Å] |           |           |   |           |           |           |
|----------------|-----------------|-----------|-----------|---|-----------|-----------|-----------|
|                | x               | y         | z         |   |           |           |           |
| C              | 0.351491        | -1.213998 | -0.162310 | C | 2.958763  | -3.951866 | -0.255616 |
| C              | -0.951363       | -1.688474 | -0.326407 | H | 4.584199  | -1.529550 | -2.029248 |
| C              | -1.911718       | -0.621956 | -0.072334 | H | 2.515449  | -0.348765 | -1.579727 |
| C              | -1.158879       | 0.532386  | 0.200518  | H | 1.003797  | -3.758524 | 0.566017  |
| C              | 0.251089        | 0.196271  | 0.202815  | H | 3.059691  | -4.959913 | 0.127565  |
| C              | -1.269090       | -3.014960 | -0.711748 | N | -1.515255 | -4.109967 | -1.031574 |
| C              | -1.696262       | 1.789169  | 0.566287  | N | -2.146571 | 2.824050  | 0.865863  |
| C              | 1.337313        | 1.041631  | 0.513036  | N | 5.192563  | -4.028818 | -1.225338 |
| C              | -6.219881       | -1.023100 | -0.103719 | N | -7.586702 | -1.144994 | -0.119963 |
| C              | -5.397006       | -1.782402 | -0.975550 | C | 5.361210  | -5.397366 | -0.756256 |
| C              | -4.018832       | -1.657154 | -0.950452 | H | 5.299273  | -5.463227 | 0.338289  |
| C              | -3.362385       | -0.761687 | -0.076551 | H | 4.603188  | -6.067221 | -1.182844 |
| C              | -4.186360       | -0.007002 | 0.788919  | H | 6.342977  | -5.760302 | -1.061437 |
| C              | -5.564290       | -0.133323 | 0.787066  | C | 6.277501  | -3.375749 | -1.943067 |
| H              | -5.840366       | -2.472458 | -1.682788 | H | 7.122929  | -4.060539 | -2.013613 |
| H              | -3.441820       | -2.248304 | -1.652010 | H | 5.980343  | -3.095760 | -2.962942 |
| H              | -3.735796       | 0.670684  | 1.504475  | H | 6.616165  | -2.468624 | -1.424973 |
| H              | -6.138237       | 0.454692  | 1.492766  | C | -8.226599 | -2.104927 | -1.009065 |
| C              | 4.023338        | -3.351908 | -0.980097 | H | -9.306497 | -2.058166 | -0.866796 |
| C              | 3.820788        | -2.027263 | -1.443737 | H | -8.013062 | -1.883767 | -2.063081 |
| C              | 2.641260        | -1.349083 | -1.177074 | H | -7.898698 | -3.132405 | -0.801992 |
| C              | 1.588027        | -1.940374 | -0.446355 | C | -8.403307 | -0.358812 | 0.794730  |
| C              | 1.779837        | -3.266931 | -0.011445 | H | -8.244484 | 0.717374  | 0.649791  |
|                |                 |           |           | H | -9.455987 | -0.572605 | 0.607835  |
|                |                 |           |           | H | -8.187044 | -0.598185 | 1.844901  |
|                |                 |           |           | C | 1.499386  | 5.208030  | -0.603914 |
|                |                 |           |           | C | 0.757296  | 4.261647  | -1.365669 |

|   |           |          |           |   |          |           |           |
|---|-----------|----------|-----------|---|----------|-----------|-----------|
| C | 0.689848  | 2.938550 | -0.985784 | C | 2.342358 | 7.469832  | -0.178752 |
| C | 1.363824  | 2.449449 | 0.162114  | H | 1.959998 | 7.551402  | 0.846529  |
| C | 2.118149  | 3.393023 | 0.904545  | H | 3.398430 | 7.177144  | -0.132740 |
| C | 2.183751  | 4.723635 | 0.547495  | H | 2.282870 | 8.453444  | -0.643909 |
| H | 0.243287  | 4.570295 | -2.267146 | C | 2.508994 | -0.324304 | 2.291424  |
| H | 0.135398  | 2.243987 | -1.608403 | C | 3.751108 | -0.670940 | 2.915239  |
| H | 2.633521  | 3.076465 | 1.806840  | N | 4.760052 | -0.944541 | 3.427597  |
| H | 2.757618  | 5.401624 | 1.166603  | C | 1.342128 | -0.908037 | 2.881389  |
| N | 1.562094  | 6.521506 | -0.967605 | N | 0.436144 | -1.390701 | 3.430288  |
| C | 0.823337  | 7.000084 | -2.132162 | C | 2.503465 | 0.541634  | 1.229400  |
| H | 0.978424  | 8.073743 | -2.235109 | H | 3.463054 | 0.987337  | 0.980606  |
| H | 1.168212  | 6.514602 | -3.053844 |   |          |           |           |
| H | -0.252875 | 6.817433 | -2.025988 |   |          |           |           |

Zero-point correction = 0.590080 (Hartree Particle<sup>-1</sup>)  
 Thermal correction to Energy = 0.631896  
 Thermal correction to Enthalpy = 0.632840  
 Thermal correction to Gibbs Free Energy = 0.510747  
 Sum of electronic and zero-point Energies = -1773.067394  
 Sum of electronic and thermal Energies = -1773.025578  
 Sum of electronic and thermal Enthalpies = -1773.024634  
 Sum of electronic and thermal Free Energies = -1773.146727

E1-7:

| Atomic<br>Type | Coordinates [Å] |           |           |   |           |           |           |
|----------------|-----------------|-----------|-----------|---|-----------|-----------|-----------|
|                | x               | y         | z         |   |           |           |           |
| C              | 0.250080        | -0.769521 | -0.233780 | C | -2.900185 | -2.112005 | -1.838932 |
| C              | 1.537127        | -1.271215 | -0.037658 | C | -1.814347 | -1.303212 | -1.548196 |
| C              | 2.516885        | -0.191101 | -0.092483 | C | -0.937940 | -1.587751 | -0.482617 |
| C              | 1.793825        | 0.987947  | -0.341788 | C | -1.214092 | -2.739030 | 0.279361  |
| C              | 0.375293        | 0.687023  | -0.382350 | C | -2.306185 | -3.550918 | 0.012128  |
| C              | 1.868691        | -2.650536 | -0.028837 | H | -3.521475 | -1.858133 | -2.689119 |
| C              | 2.339765        | 2.291794  | -0.261802 | H | -1.619285 | -0.445597 | -2.184273 |
| C              | -0.663607       | 1.636544  | -0.449737 | H | -0.572926 | -2.992393 | 1.117933  |
| C              | 6.779875        | -0.583399 | 0.435049  | H | -2.475036 | -4.415580 | 0.642235  |
| C              | 5.868373        | -1.455256 | 1.091324  | N | 2.147215  | -3.783454 | -0.019306 |
| C              | 4.504949        | -1.332979 | 0.906380  | N | 2.789045  | 3.368053  | -0.195512 |
| C              | 3.947149        | -0.331764 | 0.075623  | N | -4.278629 | -4.058280 | -1.328913 |
| C              | 4.859163        | 0.534315  | -0.574620 | N | 8.131575  | -0.701910 | 0.607196  |
| C              | 6.225083        | 0.415094  | -0.412242 | C | -4.470987 | -5.302073 | -0.596695 |
| H              | 6.234262        | -2.228734 | 1.755031  | H | -3.633727 | -6.000275 | -0.738749 |
| H              | 3.851828        | -2.011536 | 1.443481  | H | -4.582219 | -5.118453 | 0.479356  |
| H              | 4.485300        | 1.298753  | -1.246423 | H | -5.382655 | -5.785935 | -0.948897 |
| H              | 6.872812        | 1.093347  | -0.953561 | C | -5.113565 | -3.781240 | -2.488614 |
| C              | -3.188886       | -3.261612 | -1.058456 | H | -5.937959 | -4.494724 | -2.513632 |
|                |                 |           |           | H | -5.543476 | -2.773472 | -2.436470 |
|                |                 |           |           | H | -4.556919 | -3.866647 | -3.433289 |
|                |                 |           |           | C | 8.675499  | -1.747307 | 1.466104  |
|                |                 |           |           | H | 9.763394  | -1.681023 | 1.462886  |

|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H | 8.329593  | -1.637782 | 2.501945  | C | -5.758407 | 0.110566  | 3.363036  |
| H | 8.392742  | -2.746927 | 1.112295  | H | -6.802939 | -0.010673 | 3.649841  |
| C | 9.042981  | 0.210219  | -0.074146 | H | -5.293218 | -0.882375 | 3.342380  |
| H | 8.852225  | 1.253240  | 0.207799  | H | -5.257808 | 0.710563  | 4.134634  |
| H | 10.067506 | -0.034905 | 0.205364  | C | -6.925279 | 1.223877  | 1.430748  |
| H | 8.956519  | 0.126733  | -1.165231 | H | -6.893228 | 2.305398  | 1.248941  |
| C | -4.487612 | 0.958550  | 1.446083  | H | -7.113807 | 0.718537  | 0.474633  |
| C | -3.267367 | 0.581284  | 2.071605  | H | -7.764006 | 1.015551  | 2.094899  |
| C | -2.053774 | 0.794038  | 1.448164  | C | -0.979089 | 4.110896  | -0.969837 |
| C | -1.963114 | 1.411343  | 0.180372  | C | -0.603360 | 5.183926  | -1.841287 |
| C | -3.176626 | 1.791105  | -0.435541 | N | -0.310434 | 6.056026  | -2.555037 |
| C | -4.400428 | 1.567506  | 0.163412  | C | -1.898305 | 4.479455  | 0.063764  |
| H | -3.274361 | 0.141863  | 3.061275  | N | -2.617704 | 4.873847  | 0.889932  |
| H | -1.140574 | 0.515477  | 1.964764  | C | -0.385428 | 2.880765  | -1.131602 |
| H | -3.156877 | 2.242579  | -1.423381 | H | 0.394255  | 2.850172  | -1.886366 |
| H | -5.299713 | 1.860437  | -0.363826 |   |           |           |           |
| N | -5.694663 | 0.751510  | 2.054772  |   |           |           |           |

Zero-point correction = 0.589899 (Hartree Particle<sup>-1</sup>)

Thermal correction to Energy = 0.631736

Thermal correction to Enthalpy = 0.632680

Thermal correction to Gibbs Free Energy = 0.510395

Sum of electronic and zero-point Energies = -1773.069336

Sum of electronic and thermal Energies = -1773.027498

Sum of electronic and thermal Enthalpies = -1773.026554

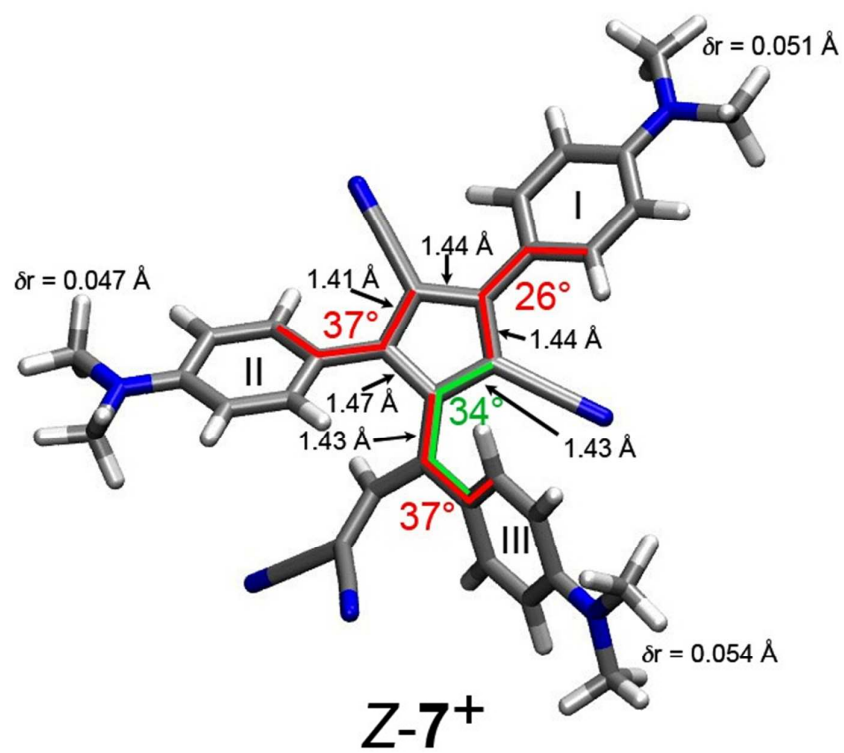
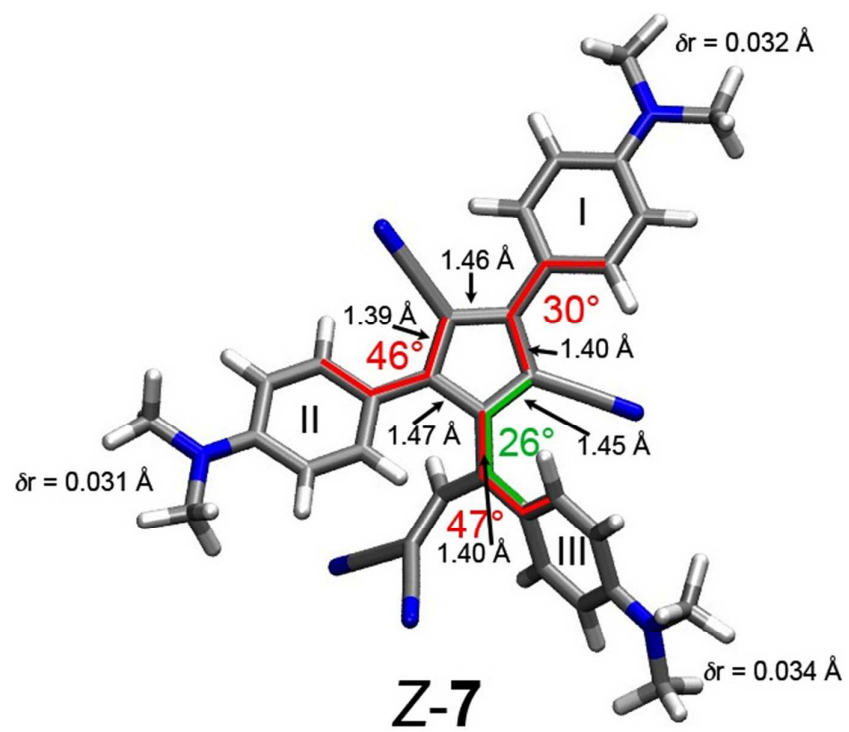
Sum of electronic and thermal Free Energies = -1773.148840

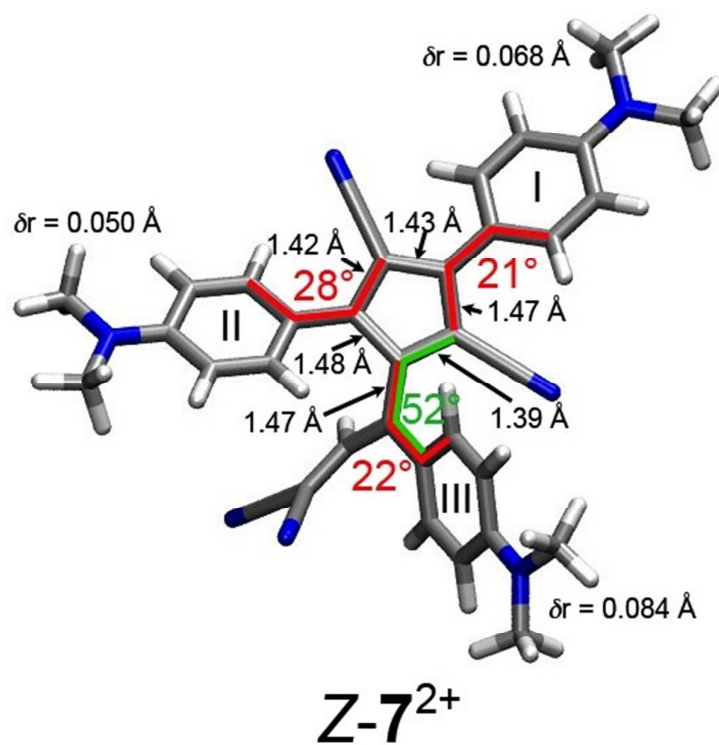
## E2-7:

| Atomic<br>Type | Coordinates [Å] |           |           | H | -3.860400 | -2.252800 | -0.753600 |
|----------------|-----------------|-----------|-----------|---|-----------|-----------|-----------|
|                | x               | y         | z         | H | -4.051700 | 1.419100  | 1.499400  |
| C              | -0.030700       | -0.635800 | -0.180300 | H | -6.409100 | 1.082900  | 1.862900  |
| C              | -1.296100       | -1.207400 | -0.032100 | C | 3.570900  | -2.833600 | -1.154300 |
| C              | -2.311500       | -0.167300 | 0.104600  | C | 2.697300  | -3.263800 | -0.124900 |
| C              | -1.632300       | 1.057800  | -0.012100 | C | 1.549600  | -2.549900 | 0.187400  |
| C              | -0.213900       | 0.816900  | -0.166900 | C | 1.202900  | -1.365400 | -0.489100 |
| C              | -1.540900       | -2.603700 | -0.037700 | C | 2.067700  | -0.942700 | -1.517300 |
| C              | -2.216100       | 2.339000  | 0.115600  | C | 3.210900  | -1.651800 | -1.850800 |
| C              | 0.805900        | 1.799800  | -0.201600 | H | 2.915500  | -4.161800 | 0.440100  |
| C              | -6.539500       | -0.790700 | 0.760200  | H | 0.919900  | -2.911400 | 0.994100  |
| C              | -5.756300       | -1.720800 | 0.026700  | H | 1.818200  | -0.057700 | -2.094000 |
| C              | -4.401500       | -1.522300 | -0.164700 | H | 3.819200  | -1.293400 | -2.672400 |
| C              | -3.729700       | -0.382600 | 0.337200  | N | -1.732100 | -3.754900 | -0.034700 |
| C              | -4.516300       | 0.542300  | 1.064400  | N | -2.674500 | 3.408500  | 0.216000  |
| C              | -5.867700       | 0.348700  | 1.279200  | N | 4.719000  | -3.531500 | -1.462500 |
| H              | -6.215600       | -2.600400 | -0.407100 | N | -7.880700 | -0.983500 | 0.960600  |
|                |                 |           |           | C | 5.531800  | -3.128100 | -2.600500 |
|                |                 |           |           | H | 4.990300  | -3.212500 | -3.554500 |

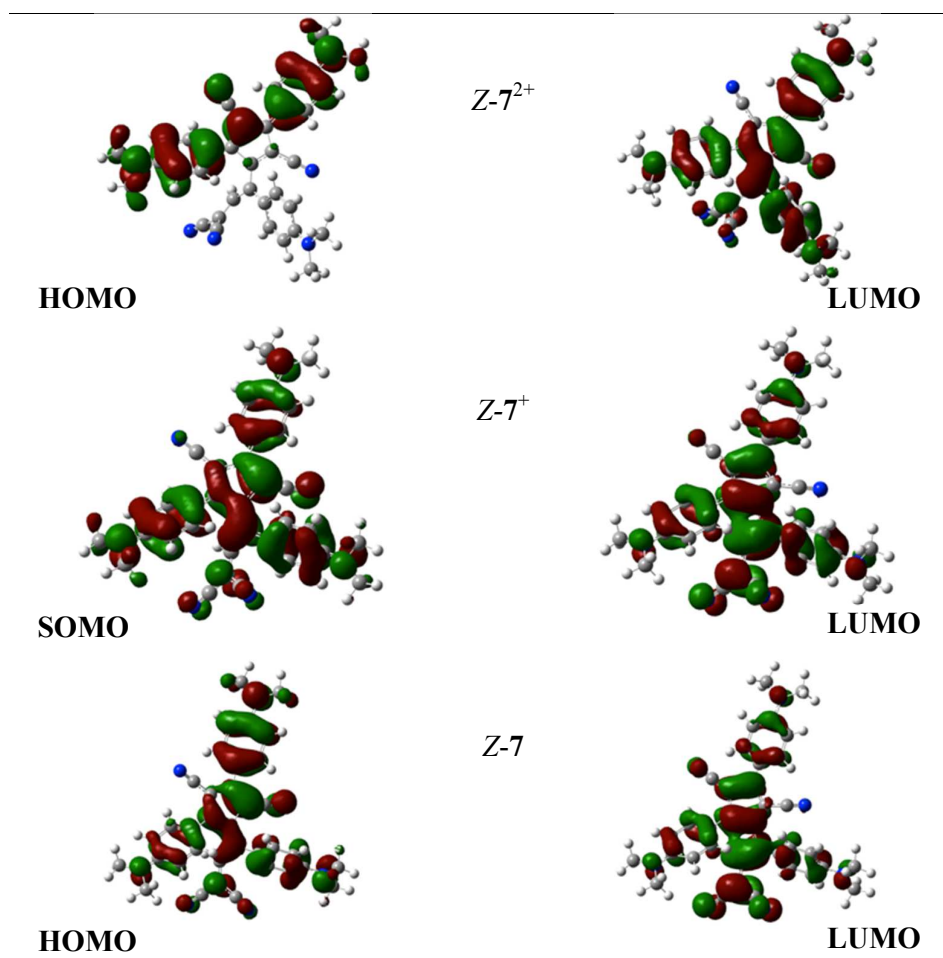
|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H | 5.873900  | -2.091800 | -2.493800 | H | 3.241500  | 2.887600  | -0.819100 |
| H | 6.415000  | -3.766300 | -2.651700 | H | 1.262900  | 0.368500  | 2.062900  |
| C | 4.967500  | -4.825800 | -0.843800 | H | 3.337300  | 0.123500  | 3.289600  |
| H | 5.916200  | -5.219800 | -1.210100 | N | 5.701100  | 1.230900  | 2.635200  |
| H | 5.040700  | -4.737500 | 0.247200  | C | 6.892500  | 1.955000  | 2.204700  |
| H | 4.178700  | -5.556600 | -1.074400 | H | 7.704400  | 1.751100  | 2.902400  |
| C | -8.542100 | -2.163600 | 0.418200  | H | 7.214900  | 1.642100  | 1.203400  |
| H | -9.594800 | -2.143800 | 0.700300  | H | 6.718800  | 3.038100  | 2.189400  |
| H | -8.481900 | -2.195100 | -0.677800 | C | 5.771700  | 0.382200  | 3.819900  |
| H | -8.100900 | -3.087600 | 0.812900  | H | 5.119300  | 0.751400  | 4.621800  |
| C | -8.666600 | 0.010900  | 1.680400  | H | 5.484100  | -0.650300 | 3.588100  |
| H | -8.635400 | 0.988400  | 1.182000  | H | 6.796200  | 0.374100  | 4.191400  |
| H | -9.705400 | -0.317000 | 1.721000  | C | -0.116900 | 3.325600  | -2.000400 |
| H | -8.309400 | 0.139000  | 2.710500  | C | -0.185200 | 4.660800  | -2.512300 |
| C | 4.528300  | 1.359900  | 1.946900  | N | -0.231600 | 5.745100  | -2.933600 |
| C | 4.441600  | 2.162800  | 0.775000  | C | -0.778300 | 2.333000  | -2.790000 |
| C | 3.250600  | 2.291000  | 0.088800  | N | -1.300700 | 1.560500  | -3.486800 |
| C | 2.067400  | 1.632900  | 0.503900  | C | 0.609700  | 3.072000  | -0.862000 |
| C | 2.157600  | 0.847600  | 1.679300  | H | 1.157800  | 3.920700  | -0.462000 |
| C | 3.337500  | 0.711600  | 2.380300  |   |           |           |           |
| H | 5.317600  | 2.676300  | 0.399100  |   |           |           |           |

Zero-point correction = 0.589858 (Hartree Particle<sup>-1</sup>)  
 Thermal correction to Energy = 0.631743  
 Thermal correction to Enthalpy = 0.632687  
 Thermal correction to Gibbs Free Energy = 0.510529  
 Sum of electronic and zero-point Energies = -1773.065026  
 Sum of electronic and thermal Energies = -1773.023140  
 Sum of electronic and thermal Enthalpies = -1773.022196  
 Sum of electronic and thermal Free Energies = -1773.144354





**Figure 25SI.** Calculated geometries of Z-7, Z-7<sup>+</sup>, and Z-7<sup>2+</sup> at the B3LYP/6-31G(d) level of theory in vacuum (for Cartesian coordinates see Table 3SI). The dihedral angles between the DMA groups and the pentafulvene plane are given in red, and the dihedral angle along the exocyclic bond C(1<sup>III</sup>)-C(6)-C(1)-C(2) is given in green. The bond lengths of each bond in the pentafulvene core and the quinoidal character  $\delta r$  of DMA groups I, II, and III are shown.

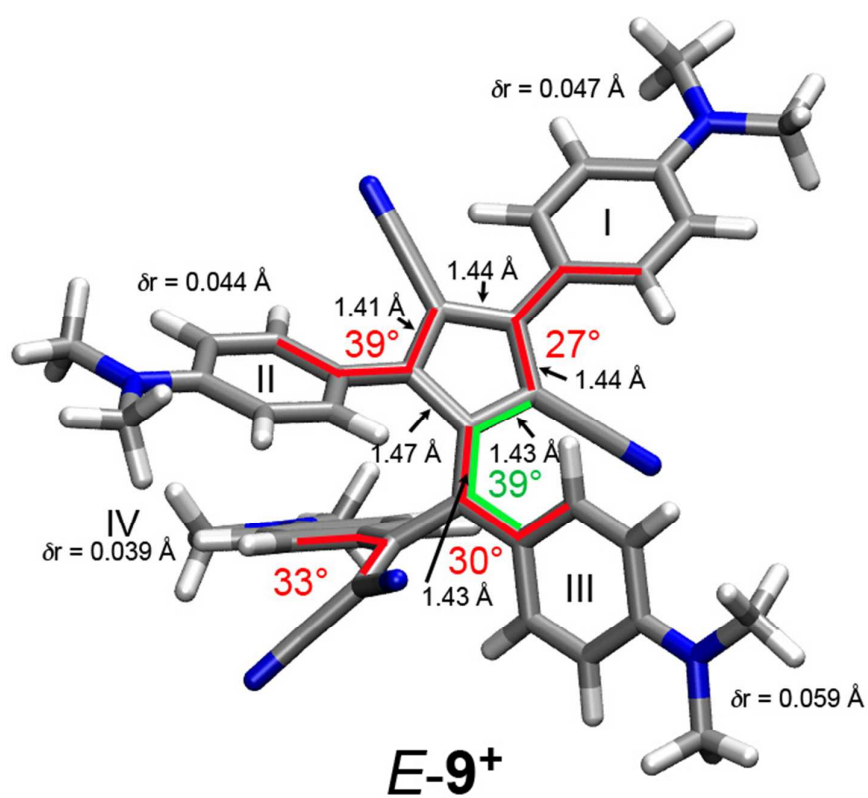
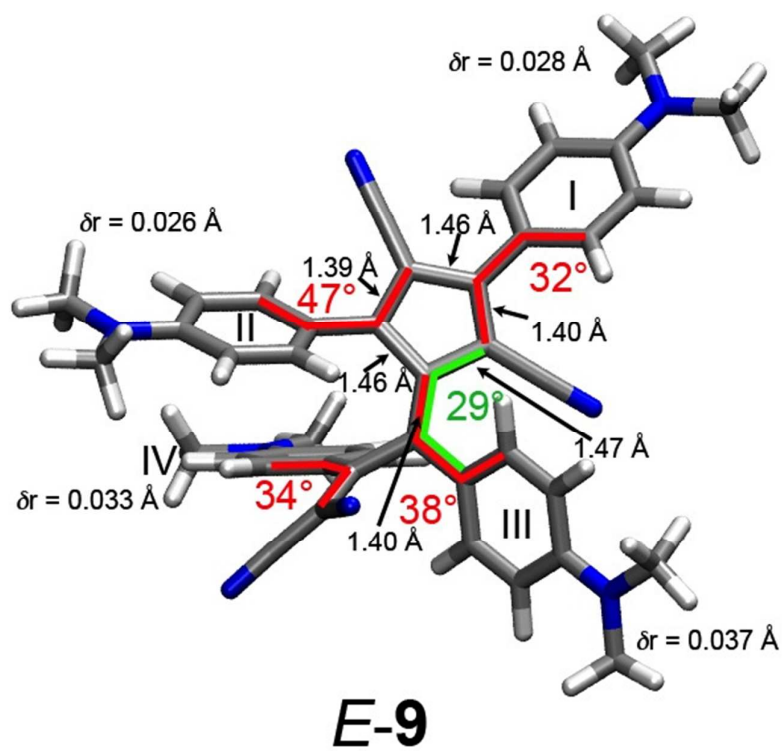


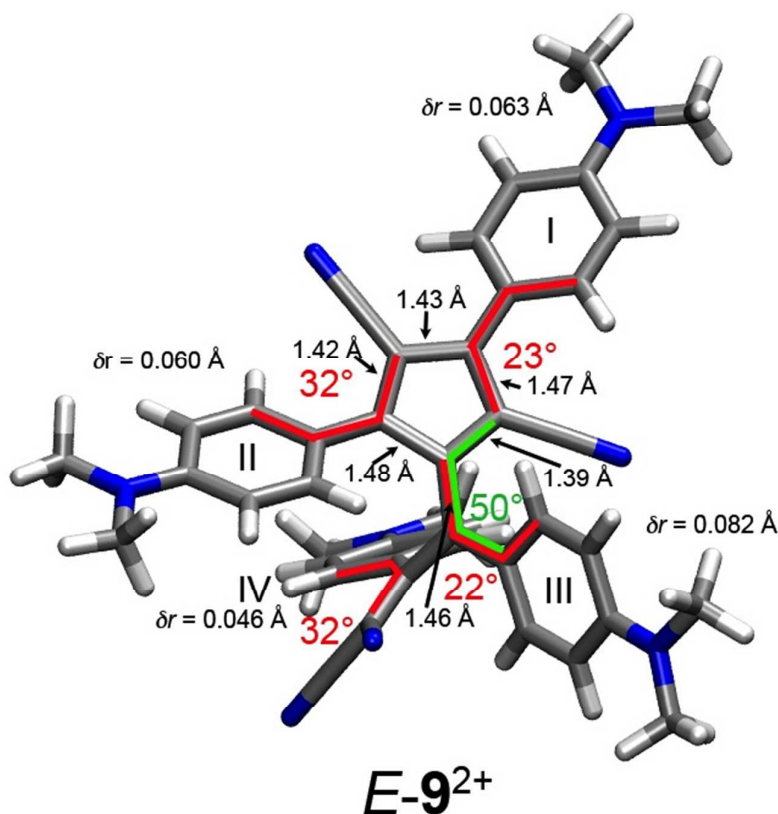
**Figure 26SI.** HOMO and LUMO orbital plots of  $Z-7$  (down),  $Z-7^+$  (middle), and  $Z-7^{2+}$  (top) calculated at the B3LYP/6-31G(d) level of theory (isovalue 0.02 a.u.).

The data obtained based on the computational study of  $Z-7$  and its mono- and dications (Figures 25SI–26SI) revealed the following: i) The torsion angle  $C(1^{III})-C(6)-C(1)-C(2)$  (shown in green in Figure 25SI) increases upon oxidation from  $26^\circ$  ( $Z-7$ ), to  $34^\circ$  ( $Z-7^+$ ), and to  $52^\circ$  ( $Z-7^{2+}$ ). This leads to reduced conjugation between the exocyclic and the intraannular butadiene moieties in the system. ii) The conjugation between the DMA groups I and II and the connecting fragment  $C(3)-C(4)-C(5)$  increases upon oxidation, as evidenced by the decreasing torsional angles between these DMA groups and the pentafulvene core (shown in red in Figure 25SI).

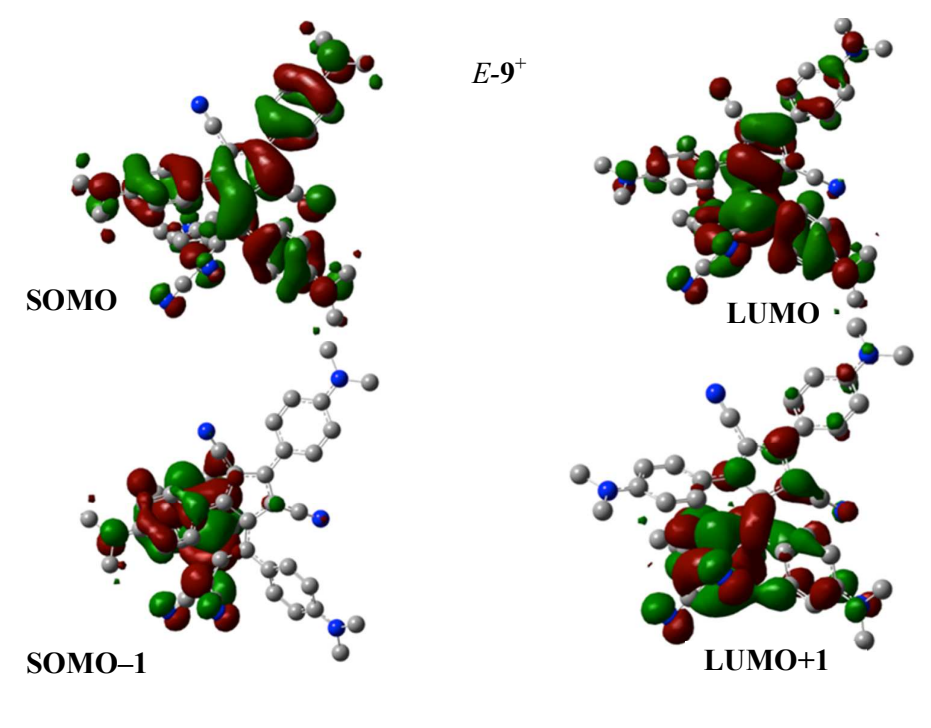
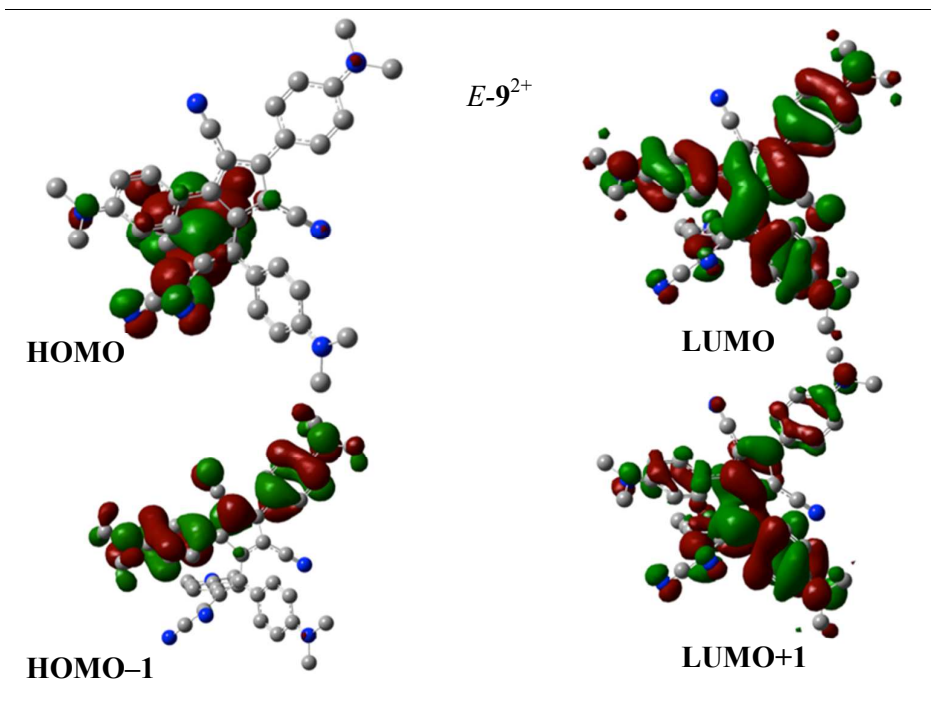
iii) An elongation of the exocyclic bond C(1)–C(6) (Z-**7**: 1.40 Å; Z-**7**<sup>+</sup>: 1.43 Å; and Z-**7**<sup>2+</sup>: 1.47 Å) and the intraannular bond C(2)–C(3) (Z-**7**: 1.40 Å, Z-**7**<sup>+</sup>: 1.44 Å, and Z-**7**<sup>2+</sup>: 1.47 Å) occurs upon oxidation. iv) The HOMO of Z-**7**<sup>2+</sup> (Figure 26SI) shows electron density mainly along the nearly flat array consisting of DMA groups I and II and the connecting C(3)–C(4)–C(5) fragment.

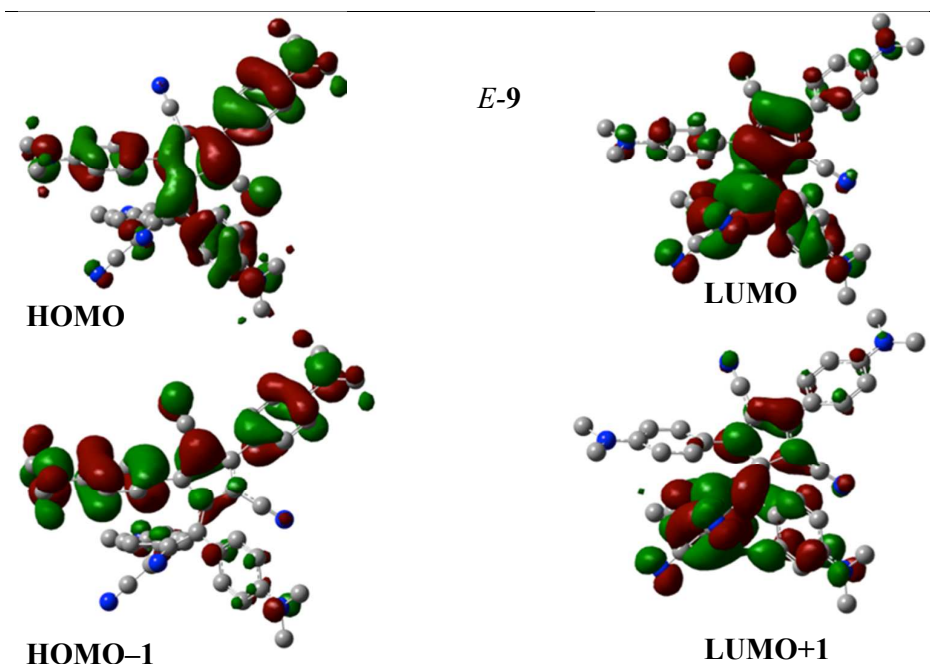
These results clearly suggest for Z-**7**<sup>2+</sup> the possible formation of two separate  $\pi$ -systems in rather orthogonal conformation to each other: the allylic cation C(3)–C(4)–C(5) with the stabilizing DMA groups I and II, and the exocyclic allylidene moiety C(6)–C(7)–C(8) with DMA group III. Accordingly, the first two-electron oxidation steps of **7** might correspond to the one-electron oxidation of DMA group III and additionally the one-electron oxidation of either DMA group II or I, ultimately forming two stabilized cationic  $\pi$ -systems. These findings could explain the driving force of the two-electron transfer (instead of two separately resolved one-electron oxidations) and therefore the remarkably low oxidation potential (0.27 V).





**Figure 27SI.** Calculated geometries of  $E-9$ ,  $E-9^+$ , and  $E-9^{2+}$  at the B3LYP/6-31G(d) level of theory in vacuum (for Cartesian coordinates see Table 4SI). The dihedral angles between the DMA groups I, II, III and the pentafulvene plane, and the dihedral angle between DMA group IV and the adjacent dicyanovinyl moiety are given in red. The dihedral angle along the exocyclic bond  $C(1^{III})-C(6)-C(1)-C(2)$  is given in green. The bond lengths of each bond in the pentafulvene core and the quinoidal character  $\delta r$  of DMA groups I, II, III, and IV are shown.





**Figure 28SI.** Frontier orbital plots of *E-9* (down), *E-9*<sup>+</sup> (middle), and *E-9*<sup>2+</sup> (top) calculated at the B3LYP/6-31G(d) level of theory (isovalue 0.02 a.u.).

Similar to *Z-7*, the computational study of *E-9* and its mono- and dications (Figures 27SI–28SI) revealed the following: i) Upon oxidation, the torsional angle C(1<sup>III</sup>)–C(6)–C(1)–C(2) increases from 29° (*E-9*), to 39° (*E-9*<sup>+</sup>), and to 50° (*E-9*<sup>2+</sup>) again deconjugating the exocyclic and the intraannular butadiene moieties. ii) Enhanced conjugation of DMA groups I and II with the fragment C(3)–C(4)–C(5) upon oxidation is evidenced by the decrease in the torsional angles between DMA groups I, II and the pentafulvene plane. iii) The exocyclic double bond (*E-9*: 1.40 Å, *E-9*<sup>+</sup>: 1.43 Å, and *E-9*<sup>2+</sup>: 1.46 Å) and the intraannular bond C(2)–C(3) (*E-9*: 1.40 Å, *E-9*<sup>+</sup>: 1.44 Å, and *E-9*<sup>2+</sup>: 1.47 Å) elongate upon oxidation. iv) The quinoidal character of the DMA groups I, II, and III increases upon oxidation to values higher than 0.060 Å (for *E-9*<sup>2+</sup>), whereas the extra DMA group IV does not show a significant increase in quinoidal character. v) The HOMO–1 and the HOMO of *E-9*<sup>2+</sup> (Figure 28SI), show

electronic delocalization in two different parts in the molecule. The HOMO–1 of *E*-**9**<sup>2+</sup> shows electron density only along the nearly flat moiety consisting of DMA groups I, II and their linker C(3)–C(4)–C(5) (comparable to the HOMO of *Z*-**7**). In contrast, the HOMO of *E*-**9**<sup>2+</sup> shows electron density on the push–pull system consisting of DMA group IV and its adjacent dicyanovinyl group. Indeed, the extra DMA residue IV (as compared to **7** which lacks this group) seems to have no effect on the electrochemical properties and on the formation of the allylic cation stabilized by DMA groups I and II. Similar to the analysis of *Z*-**7** and its mono- and dication, the data for *E*-**9**<sup>2+</sup> suggest two largely deconjugated moieties to bear the two positive charges: one charge sits on the mentioned allylic cation with DMA groups I and II, and the other charge sits on DMA group III. These computational findings could explain the driving force of the two-electron transfer (instead of two separately resolved one-electron oxidations) and therefore the similarity of the low oxidation potential of **9** (0.28 V) compared to **7** (0.27 V).

**Table 3SI. Cartesian Coordinates for *Z*-**7**, *Z*-**7**<sup>+</sup>, and *Z*-**7**<sup>2+</sup>.**

*Z*-**7**<sup>+</sup>:

| Atomic Type | Coordinates [Å] |           |           |   |           |           |           |
|-------------|-----------------|-----------|-----------|---|-----------|-----------|-----------|
|             | x               | y         | z         |   |           |           |           |
| C           | -0.156509       | -1.454266 | 0.009418  | C | 1.745173  | 1.660414  | 0.574702  |
| C           | 1.173983        | -1.906589 | -0.035509 | C | -1.221089 | 0.835254  | 0.553330  |
| C           | 2.077115        | -0.791676 | 0.076060  | C | 6.375313  | -0.950545 | 0.069606  |
| C           | 1.257179        | 0.383173  | 0.204911  | C | 5.589825  | -2.067008 | 0.485967  |
| C           | -0.117145       | -0.000140 | 0.209511  | C | 4.216907  | -2.010055 | 0.478975  |
| C           | 1.555581        | -3.236450 | -0.353328 | C | 3.512176  | -0.839940 | 0.077413  |
|             |                 |           |           | C | 4.302599  | 0.272415  | -0.328315 |
|             |                 |           |           | C | 5.675870  | 0.223838  | -0.341723 |
|             |                 |           |           | H | 6.069618  | -2.976422 | 0.824355  |
|             |                 |           |           | H | 3.667616  | -2.878831 | 0.819148  |

|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| H | 3.820091  | 1.180632  | -0.667074 | H | 9.580793  | -0.075675 | -0.239512 |
| H | 6.223391  | 1.093717  | -0.681313 | H | 8.325016  | 0.430808  | -1.381983 |
| C | -3.686409 | -3.828444 | -0.666728 | C | -1.203208 | 5.025135  | -0.406987 |
| C | -2.566095 | -4.347092 | 0.048659  | C | -1.747397 | 4.553495  | 0.827500  |
| C | -1.437368 | -3.586640 | 0.251985  | C | -1.766438 | 3.214446  | 1.123703  |
| C | -1.343150 | -2.245982 | -0.208824 | C | -1.216534 | 2.241367  | 0.242322  |
| C | -2.454612 | -1.740474 | -0.935047 | C | -0.648390 | 2.720806  | -0.971620 |
| C | -3.581144 | -2.497347 | -1.167421 | C | -0.656651 | 4.052924  | -1.300389 |
| H | -2.596688 | -5.349480 | 0.456076  | H | -2.137921 | 5.254736  | 1.553379  |
| H | -0.617329 | -4.016928 | 0.815378  | H | -2.164923 | 2.898449  | 2.082006  |
| H | -2.400498 | -0.747019 | -1.367266 | H | -0.246396 | 2.005003  | -1.681473 |
| H | -4.381685 | -2.072337 | -1.759469 | H | -0.261161 | 4.358061  | -2.260541 |
| N | 1.863915  | -4.332281 | -0.603955 | N | -1.209698 | 6.343691  | -0.719533 |
| N | 2.159590  | 2.708417  | 0.876484  | C | -1.844339 | 7.318970  | 0.170053  |
| N | -4.805606 | -4.573944 | -0.866428 | H | -1.833507 | 8.296822  | -0.309782 |
| N | 7.732578  | -1.003671 | 0.065585  | H | -2.886127 | 7.046463  | 0.368222  |
| C | -5.968159 | -4.000791 | -1.543371 | H | -1.308524 | 7.395992  | 1.123793  |
| H | -6.306157 | -3.088255 | -1.039765 | C | -0.584610 | 6.820877  | -1.954333 |
| H | -5.746395 | -3.764512 | -2.591631 | H | 0.463089  | 6.506879  | -2.008969 |
| H | -6.784076 | -4.722326 | -1.521540 | H | -1.115005 | 6.447600  | -2.838765 |
| C | -4.871491 | -5.957776 | -0.397040 | H | -0.615335 | 7.909576  | -1.970126 |
| H | -5.817319 | -6.395571 | -0.714102 | C | -3.630527 | 0.624790  | 1.336546  |
| H | -4.058365 | -6.557251 | -0.821334 | C | -4.543781 | -0.085707 | 2.181683  |
| H | -4.816804 | -6.012492 | 0.697203  | N | -5.282259 | -0.673296 | 2.862578  |
| C | 8.430984  | -2.226274 | 0.466182  | C | -4.223273 | 1.612873  | 0.486078  |
| H | 9.504015  | -2.075549 | 0.355537  | N | -4.754277 | 2.378279  | -0.211547 |
| H | 8.224155  | -2.476122 | 1.513470  | C | -2.313213 | 0.240309  | 1.304554  |
| H | 8.136073  | -3.072750 | -0.163787 | H | -2.071174 | -0.630888 | 1.904988  |
| C | 8.522081  | 0.160729  | -0.337785 |   |           |           |           |
| H | 8.302291  | 1.025607  | 0.298180  |   |           |           |           |

Zero-point correction = 0.591459 (Hartree Particle<sup>-1</sup>)  
 Thermal correction to Energy = 0.633114  
 Thermal correction to Enthalpy = 0.634058  
 Thermal correction to Gibbs Free Energy = 0.512327  
 Sum of electronic and zero-point Energies = -1772.836530  
 Sum of electronic and thermal Energies = -1772.794875  
 Sum of electronic and thermal Enthalpies = -1772.793931  
 Sum of electronic and thermal Free Energies = -1772.915662

Z-7<sup>2+</sup>:

| Atomic<br>Type | Coordinates [Å] |           |           |   |           |           |           |
|----------------|-----------------|-----------|-----------|---|-----------|-----------|-----------|
|                | x               | y         | z         |   |           |           |           |
| C              | 0.026497        | -1.389896 | -0.042221 | C | 1.397380  | -1.740201 | -0.124197 |
|                |                 |           |           | C | 2.217014  | -0.587064 | 0.062062  |
|                |                 |           |           | C | 1.283447  | 0.529524  | 0.279604  |
|                |                 |           |           | C | -0.024130 | 0.057650  | 0.244996  |
|                |                 |           |           | C | 1.870600  | -3.007267 | -0.556287 |

|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | 1.638208  | 1.840986  | 0.692391  | H | 9.703490  | -1.284593 | 0.002945  |
| C | -1.180491 | 0.814348  | 0.730182  | H | 8.584540  | -1.927131 | 1.220723  |
| C | 6.504713  | -0.374661 | 0.054407  | H | 8.347751  | -2.297815 | -0.510868 |
| C | 5.813085  | -1.609511 | 0.298613  | C | 8.550226  | 0.966627  | -0.111578 |
| C | 4.447575  | -1.666399 | 0.296424  | H | 8.179171  | 1.702636  | 0.606793  |
| C | 3.636226  | -0.505880 | 0.066848  | H | 9.611677  | 0.812468  | 0.074320  |
| C | 4.335098  | 0.724118  | -0.164104 | H | 8.426662  | 1.355723  | -1.128646 |
| C | 5.701083  | 0.792900  | -0.177810 | C | -2.005017 | 4.792045  | -0.594737 |
| H | 6.370602  | -2.511423 | 0.515097  | C | -2.504236 | 4.306822  | 0.669653  |
| H | 3.977375  | -2.616410 | 0.513438  | C | -2.242243 | 3.039511  | 1.086522  |
| H | 3.781608  | 1.629957  | -0.374002 | C | -1.446853 | 2.122657  | 0.305385  |
| H | 6.173005  | 1.743190  | -0.391091 | C | -0.923602 | 2.630906  | -0.940299 |
| C | -3.334911 | -3.950874 | -0.822806 | C | -1.194241 | 3.889799  | -1.378894 |
| C | -2.109820 | -4.467786 | -0.285263 | H | -3.048815 | 4.972543  | 1.326341  |
| C | -1.042907 | -3.646252 | -0.035694 | H | -2.584234 | 2.735959  | 2.069134  |
| C | -1.101072 | -2.236141 | -0.268235 | H | -0.353546 | 1.964036  | -1.577998 |
| C | -2.331063 | -1.726279 | -0.788363 | H | -0.838559 | 4.194439  | -2.354515 |
| C | -3.398661 | -2.537981 | -1.068822 | N | -2.279877 | 6.026539  | -1.020524 |
| H | -2.018753 | -5.521529 | -0.056313 | C | -3.250599 | 6.897533  | -0.334547 |
| H | -0.146547 | -4.083335 | 0.385996  | H | -3.645449 | 7.609046  | -1.060585 |
| H | -2.414234 | -0.672719 | -1.032609 | H | -4.084090 | 6.315380  | 0.058216  |
| H | -4.289306 | -2.099679 | -1.500308 | H | -2.765758 | 7.452613  | 0.476697  |
| N | 2.254030  | -4.050383 | -0.905961 | C | -1.633220 | 6.609774  | -2.208662 |
| N | 1.901063  | 2.929659  | 1.013234  | H | -0.587499 | 6.307274  | -2.268153 |
| N | -4.382781 | -4.756137 | -1.081702 | H | -2.161810 | 6.313213  | -3.121886 |
| N | 7.847440  | -0.315116 | 0.048535  | H | -1.668394 | 7.695923  | -2.119957 |
| C | -5.648002 | -4.208811 | -1.590830 | C | -3.323615 | 0.132839  | 1.898512  |
| H | -6.037181 | -3.439101 | -0.917248 | C | -3.939208 | -0.601771 | 2.963729  |
| H | -5.514925 | -3.781219 | -2.590857 | N | -4.438195 | -1.209497 | 3.820536  |
| H | -6.381072 | -5.010795 | -1.653446 | C | -4.215465 | 0.722485  | 0.941811  |
| C | -4.289644 | -6.207521 | -0.864657 | N | -4.939222 | 1.165025  | 0.146206  |
| H | -5.211833 | -6.675896 | -1.203366 | C | -1.964155 | 0.144714  | 1.769744  |
| H | -3.457309 | -6.631965 | -1.434274 | H | -1.409216 | -0.466682 | 2.476939  |
| H | -4.154495 | -6.435458 | 0.198350  |   |           |           |           |
| C | 8.661989  | -1.530823 | 0.201937  |   |           |           |           |

Zero-point correction = 0.592648 (Hartree Particle<sup>-1</sup>)  
 Thermal correction to Energy = 0.634450  
 Thermal correction to Enthalpy = 0.635394  
 Thermal correction to Gibbs Free Energy = 0.513845  
 Sum of electronic and zero-point Energies = -1772.522027  
 Sum of electronic and thermal Energies = -1772.480224  
 Sum of electronic and thermal Enthalpies = -1772.479280  
 Sum of electronic and thermal Free Energies = -1772.600829

**Table 4SI. Cartesian Coordinates for  $E-9$ ,  $E-9^+$ , and  $E-9^{2+}$ .**

| <i>E-9:</i> |                 |           |           | H | -6.276477 | -4.360439 | -3.412476 |
|-------------|-----------------|-----------|-----------|---|-----------|-----------|-----------|
|             |                 |           |           | H | -4.590374 | -4.903468 | -3.338346 |
|             |                 |           |           | H | -5.442933 | -4.426924 | -1.852906 |
| Atomic Type | Coordinates [Å] |           |           | C | 8.185673  | -3.639135 | -0.037137 |
|             | x               | y         | z         | H | 9.273617  | -3.721977 | -0.020387 |
| C           | 0.019571        | -0.942581 | -0.948667 | H | 7.803005  | -4.036177 | 0.913157  |
| C           | 1.232571        | -1.619489 | -1.031090 | H | 7.807570  | -4.278264 | -0.847906 |
| C           | 2.319036        | -0.767287 | -0.560517 | C | 8.851102  | -1.251694 | -0.444951 |
| C           | 1.747976        | 0.460028  | -0.214283 | H | 8.766326  | -0.419493 | 0.266285  |
| C           | 0.297026        | 0.385105  | -0.398882 | H | 9.829031  | -1.714675 | -0.303225 |
| C           | 1.401531        | -2.894563 | -1.632993 | H | 8.815710  | -0.833548 | -1.461895 |
| C           | 2.428106        | 1.469488  | 0.513870  | C | 0.355531  | 5.549858  | 0.114172  |
| C           | -0.641383       | 1.351605  | -0.023279 | C | 0.867749  | 4.698454  | -0.899320 |
| C           | 6.485307        | -1.890706 | -0.306621 | C | 0.556803  | 3.354795  | -0.922493 |
| C           | 5.452955        | -2.843322 | -0.128559 | C | -0.300119 | 2.767485  | 0.036586  |
| C           | 4.119082        | -2.478364 | -0.213995 | C | -0.831358 | 3.627007  | 1.026664  |
| C           | 3.723670        | -1.149863 | -0.473739 | C | -0.507216 | 4.967529  | 1.080454  |
| C           | 4.755852        | -0.205082 | -0.651172 | H | 1.504242  | 5.097427  | -1.679264 |
| C           | 6.092844        | -0.556274 | -0.575467 | H | 0.950087  | 2.737831  | -1.723782 |
| H           | 5.692650        | -3.879063 | 0.079794  | H | -1.490389 | 3.221594  | 1.788264  |
| H           | 3.367329        | -3.244735 | -0.062163 | H | -0.921951 | 5.571212  | 1.878299  |
| H           | 4.505156        | 0.826244  | -0.873074 | N | 0.671045  | 6.884252  | 0.151911  |
| H           | 6.838712        | 0.212441  | -0.737690 | C | 1.589037  | 7.447532  | -0.827414 |
| C           | -3.717339       | -2.360812 | -2.599148 | H | 1.733738  | 8.507334  | -0.613859 |
| C           | -2.901194       | -3.193714 | -1.793042 | H | 2.569412  | 6.954695  | -0.790850 |
| C           | -1.707178       | -2.730123 | -1.264587 | H | 1.196791  | 7.357507  | -1.849317 |
| C           | -1.257132       | -1.414354 | -1.488191 | C | 0.117354  | 7.740145  | 1.190532  |
| C           | -2.058918       | -0.596117 | -2.306217 | H | -0.980128 | 7.745613  | 1.164879  |
| C           | -3.253223       | -1.046148 | -2.848090 | H | 0.436092  | 7.422719  | 2.192832  |
| H           | -3.202742       | -4.211397 | -1.576021 | H | 0.463182  | 8.762578  | 1.033402  |
| H           | -1.118523       | -3.396280 | -0.642133 | C | -3.111796 | 1.654432  | -0.045446 |
| H           | -1.727840       | 0.408551  | -2.549084 | C | -4.422373 | 1.564503  | 0.519527  |
| H           | -3.818246       | -0.373390 | -3.481701 | N | -5.504097 | 1.547510  | 0.953211  |
| N           | 1.537589        | -3.948166 | -2.114242 | C | -3.040723 | 2.506043  | -1.193459 |
| N           | 3.002223        | 2.280863  | 1.125746  | N | -3.035724 | 3.171193  | -2.150262 |
| N           | -4.910916       | -2.813551 | -3.121502 | C | -2.008542 | 0.958895  | 0.431707  |
| N           | 7.815553        | -2.246698 | -0.224382 | C | -2.321744 | -2.030386 | 3.540548  |
| C           | -5.717056       | -1.940223 | -3.958354 | C | -3.330406 | -1.892378 | 2.552103  |
| H           | -6.000854       | -1.023607 | -3.424865 | C | -3.230875 | -0.938704 | 1.556684  |
| H           | -5.191580       | -1.648576 | -4.879372 | C | -2.119575 | -0.073705 | 1.463075  |
| H           | -6.633142       | -2.460917 | -4.241776 | C | -1.101084 | -0.236854 | 2.428375  |
| C           | -5.317603       | -4.193195 | -2.919355 | C | -1.197066 | -1.172402 | 3.442831  |

|   |           |           |          |
|---|-----------|-----------|----------|
| H | -4.191733 | -2.548867 | 2.553088 |
| H | -4.010149 | -0.89676  | 0.805217 |
| H | -0.224146 | 0.401331  | 2.395079 |
| H | -0.39279  | -1.237837 | 4.1652   |
| N | -2.426338 | -2.964172 | 4.543478 |
| C | -3.583141 | -3.844118 | 4.606548 |
| H | -4.517334 | -3.27284  | 4.679529 |
| H | -3.65093  | -4.499975 | 3.726876 |
| H | -3.505185 | -4.474656 | 5.493285 |
| C | -1.343866 | -3.132859 | 5.501129 |
| H | -1.608725 | -3.923177 | 6.204787 |
| H | -0.403039 | -3.415484 | 5.009075 |

|                                                  |           |          |          |
|--------------------------------------------------|-----------|----------|----------|
| H                                                | -1.165994 | -2.21387 | 6.075305 |
| Zero-point correction=0.744225 (Ha/Particle)     |           |          |          |
| Thermal correction to Energy=0.795611            |           |          |          |
| Thermal correction to                            |           |          |          |
| Enthalpy=0.796555                                |           |          |          |
| Thermal correction to Gibbs Free Energy=0.649955 |           |          |          |
| Sum of electronic and zero-point                 |           |          |          |
| Energies=-2137.919515                            |           |          |          |
| Sum of electronic and thermal Energies=-         |           |          |          |
| 2137.868129                                      |           |          |          |
| Sum of electronic and thermal Enthalpies=-       |           |          |          |
| 2137.867185                                      |           |          |          |
| Sum of electronic and thermal Free Energies=-    |           |          |          |
| 2138.013785                                      |           |          |          |

$E-9^+$ :

| Atomic<br>Type | Coordinates [Å] |           |           |
|----------------|-----------------|-----------|-----------|
|                | x               | y         | z         |
| C              | 0.025016        | -0.906656 | -1.040041 |
| C              | 1.315645        | -1.461791 | -1.152022 |
| C              | 2.298895        | -0.528248 | -0.679014 |
| C              | 1.574721        | 0.634943  | -0.252279 |
| C              | 0.171891        | 0.415187  | -0.4265   |
| C              | 1.608544        | -2.67748  | -1.824449 |
| C              | 2.134093        | 1.679068  | 0.525203  |
| C              | -0.86204        | 1.249614  | 0.092271  |
| C              | 6.567741        | -1.082024 | -0.593237 |
| C              | 5.674           | -2.190239 | -0.529922 |
| C              | 4.310198        | -2.006542 | -0.558963 |
| C              | 3.726264        | -0.713571 | -0.637231 |
| C              | 4.623224        | 0.387204  | -0.689988 |
| C              | 5.988803        | 0.21774   | -0.674979 |
| H              | 6.059544        | -3.198861 | -0.452273 |
| H              | 3.674452        | -2.881106 | -0.496506 |
| H              | 4.234428        | 1.394738  | -0.774429 |
| H              | 6.621059        | 1.094176  | -0.738533 |
| C              | -3.552191       | -2.559371 | -2.775575 |
| C              | -2.582063       | -3.392571 | -2.145256 |
| C              | -1.439434       | -2.860339 | -1.58903  |
| C              | -1.188395       | -1.464134 | -1.589822 |
| C              | -2.155429       | -0.640948 | -2.21896  |
| C              | -3.29272        | -1.159346 | -2.799236 |
| H              | -2.733963       | -4.463275 | -2.093345 |
| H              | -0.734848       | -3.530603 | -1.110324 |
| H              | -1.980941       | 0.42606   | -2.298722 |
| H              | -3.978998       | -0.479638 | -3.288191 |
| N              | 1.845739        | -3.683841 | -2.362834 |
| N              | 2.59407         | 2.532725  | 1.174315  |
| N              | -4.680172       | -3.081328 | -3.335929 |
| N              | 7.918359        | -1.257318 | -0.576792 |
| C              | -5.669341       | -2.204849 | -3.959849 |
| H              | -6.061644       | -1.474801 | -3.242172 |
| H              | -5.241749       | -1.662555 | -4.812128 |
| H              | -6.501586       | -2.807484 | -4.322357 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -4.908821 | -4.523979 | -3.334989 |
| H | -5.848403 | -4.736514 | -3.84406  |
| H | -4.106259 | -5.055009 | -3.860667 |
| H | -4.977487 | -4.916693 | -2.312939 |
| C | 8.491452  | -2.600993 | -0.522389 |
| H | 9.578236  | -2.525883 | -0.539884 |
| H | 8.19869   | -3.122163 | 0.39709   |
| H | 8.175215  | -3.20304  | -1.382309 |
| C | 8.815864  | -0.104938 | -0.628504 |
| H | 8.643136  | 0.570573  | 0.217458  |
| H | 9.846959  | -0.4536   | -0.580822 |
| H | 8.686998  | 0.45954   | -1.56009  |
| C | -0.510112 | 5.527203  | 0.112748  |
| C | 0.130578  | 4.731533  | -0.887787 |
| C | 0.030026  | 3.365241  | -0.872382 |
| C | -0.734325 | 2.672268  | 0.114013  |
| C | -1.387777 | 3.477336  | 1.096392  |
| C | -1.270389 | 4.842672  | 1.111569  |
| H | 0.679568  | 5.206931  | -1.690277 |
| H | 0.495979  | 2.79534   | -1.669001 |
| H | -1.958553 | 2.995215  | 1.882238  |
| H | -1.754539 | 5.399723  | 1.90314   |
| N | -0.410631 | 6.877419  | 0.107746  |
| C | 0.415346  | 7.560935  | -0.889683 |
| H | 0.434143  | 8.626601  | -0.664832 |
| H | 1.444725  | 7.188101  | -0.866927 |
| H | 0.011196  | 7.428188  | -1.900518 |
| C | -1.138479 | 7.683907  | 1.09023   |
| H | -2.212501 | 7.472995  | 1.052471  |
| H | -0.774754 | 7.496035  | 2.107404  |
| H | -0.990543 | 8.738923  | 0.863049  |
| C | -3.324725 | 1.101942  | 0.375242  |
| C | -4.527707 | 0.738929  | 1.056966  |
| N | -5.535207 | 0.492783  | 1.587701  |
| C | -3.539497 | 1.975087  | -0.738129 |
| N | -3.751077 | 2.655729  | -1.660018 |
| C | -2.064269 | 0.622217  | 0.717631  |
| C | -1.44161  | -2.393576 | 3.749413  |
| C | -2.570025 | -2.442335 | 2.884706  |

|   |           |           |          |   |           |           |          |
|---|-----------|-----------|----------|---|-----------|-----------|----------|
| C | -2.767674 | -1.484597 | 1.911425 | C | -2.249192 | -4.371887 | 4.950302 |
| C | -1.851518 | -0.42646  | 1.707439 | H | -3.237381 | -3.95029  | 5.172058 |
| C | -0.708766 | -0.404047 | 2.54332  | H | -2.339938 | -5.028772 | 4.075556 |
| C | -0.509973 | -1.340569 | 3.537904 | H | -1.943273 | -4.982225 | 5.800014 |
| H | -3.293656 | -3.242661 | 2.97521  | C | -0.08762  | -3.256142 | 5.601005 |
| H | -3.633984 | -1.580639 | 1.267748 | H | -0.119793 | -4.084304 | 6.308989 |
| H | 0.021195  | 0.392425  | 2.435907 | H | 0.843381  | -3.337009 | 5.025803 |
| H | 0.368803  | -1.25299  | 4.16448  | H | -0.061762 | -2.319581 | 6.172931 |
| N | -1.258278 | -3.32306  | 4.733581 |   |           |           |          |

Zero-point correction=0.746050 (Ha/Particle)  
Thermal correction to Energy=0.796975  
Thermal correction to Enthalpy=0.797919  
Thermal correction to Gibbs Free Energy=0.655326  
Sum of electronic and zero-point Energies=-2137.714383  
Sum of electronic and thermal Energies=-2137.663458  
Sum of electronic and thermal Enthalpies=-2137.662514  
Sum of electronic and thermal Free Energies=-2137.805107

*E-9*<sup>2+</sup>:

| Atomic<br>Type | Coordinates [Å] |           |           |   |           |           |           |
|----------------|-----------------|-----------|-----------|---|-----------|-----------|-----------|
|                | x               | y         | z         |   |           |           |           |
| C              | 0.025016        | -0.906656 | -1.040041 | H | -5.241749 | -1.662555 | -4.812128 |
| C              | 1.315645        | -1.461791 | -1.152022 | H | -6.501586 | -2.807484 | -4.322357 |
| C              | 2.298895        | -0.528248 | -0.679014 | C | -4.908821 | -4.523979 | -3.334989 |
| C              | 1.574721        | 0.634943  | -0.252279 | H | -5.848403 | -4.736514 | -3.84406  |
| C              | 0.171891        | 0.415187  | -0.4265   | H | -4.106259 | -5.055009 | -3.860667 |
| C              | 1.608544        | -2.67748  | -1.824449 | H | -4.977487 | -4.916693 | -2.312939 |
| C              | 2.134093        | 1.679068  | 0.525203  | C | 8.491452  | -2.600993 | -0.522389 |
| C              | -0.86204        | 1.249614  | 0.092271  | H | 9.578236  | -2.525883 | -0.539884 |
| C              | 6.567741        | -1.082024 | -0.593237 | H | 8.19869   | -3.122163 | 0.39709   |
| C              | 5.674           | -2.190239 | -0.529922 | H | 8.175215  | -3.20304  | -1.382309 |
| C              | 4.310198        | -2.006542 | -0.558963 | C | 8.815864  | -0.104938 | -0.628504 |
| C              | 3.726264        | -0.713571 | -0.637231 | H | 8.643136  | 0.570573  | 0.217458  |
| C              | 4.623224        | 0.387204  | -0.689988 | H | 9.846959  | -0.4536   | -0.580822 |
| C              | 5.988803        | 0.21774   | -0.674979 | H | 8.686998  | 0.45954   | -1.56009  |
| H              | 6.059544        | -3.198861 | -0.452273 | C | -0.510112 | 5.527203  | 0.112748  |
| H              | 3.674452        | -2.881106 | -0.496506 | C | 0.130578  | 4.731533  | -0.887787 |
| H              | 4.234428        | 1.394738  | -0.774429 | C | 0.030026  | 3.365241  | -0.872382 |
| H              | 6.621059        | 1.094176  | -0.738533 | C | -0.734325 | 2.672268  | 0.114013  |
| C              | -3.552191       | -2.559371 | -2.775575 | C | -1.387777 | 3.477336  | 1.096392  |
| C              | -2.582063       | -3.392571 | -2.145256 | C | -1.270389 | 4.842672  | 1.111569  |
| C              | -1.439434       | -2.860339 | -1.58903  | H | 0.679568  | 5.206931  | -1.690277 |
| C              | -1.188395       | -1.464134 | -1.589822 | H | 0.495979  | 2.79534   | -1.669001 |
| C              | -2.155429       | -0.640948 | -2.21896  | H | -1.958553 | 2.995215  | 1.882238  |
| C              | -3.29272        | -1.159346 | -2.799236 | H | -1.754539 | 5.399723  | 1.90314   |
| H              | -2.733963       | -4.463275 | -2.093345 | N | -0.410631 | 6.877419  | 0.107746  |
| H              | -0.734848       | -3.530603 | -1.110324 | C | 0.415346  | 7.560935  | -0.889683 |
| H              | -1.980941       | 0.42606   | -2.298722 | H | 0.434143  | 8.626601  | -0.664832 |
| H              | -3.978998       | -0.479638 | -3.288191 | H | 1.444725  | 7.188101  | -0.866927 |
| N              | 1.845739        | -3.683841 | -2.362834 | H | 0.011196  | 7.428188  | -1.900518 |
| N              | 2.59407         | 2.532725  | 1.174315  | C | -1.138479 | 7.683907  | 1.09023   |
| N              | -4.680172       | -3.081328 | -3.335929 | H | -2.212501 | 7.472995  | 1.052471  |
| N              | 7.918359        | -1.257318 | -0.576792 | H | -0.774754 | 7.496035  | 2.107404  |
| C              | -5.669341       | -2.204849 | -3.959849 | H | -0.990543 | 8.738923  | 0.863049  |
| H              | -6.061644       | -1.474801 | -3.242172 | C | -3.324725 | 1.101942  | 0.375242  |
|                |                 |           |           | C | -4.527707 | 0.738929  | 1.056966  |
|                |                 |           |           | N | -5.535207 | 0.492783  | 1.587701  |

|   |           |           |           |   |           |           |          |
|---|-----------|-----------|-----------|---|-----------|-----------|----------|
| C | -3.539497 | 1.975087  | -0.738129 | H | 0.368803  | -1.25299  | 4.16448  |
| N | -3.751077 | 2.655729  | -1.660018 | N | -1.258278 | -3.32306  | 4.733581 |
| C | -2.064269 | 0.622217  | 0.717631  | C | -2.249192 | -4.371887 | 4.950302 |
| C | -1.44161  | -2.393576 | 3.749413  | H | -3.237381 | -3.95029  | 5.172058 |
| C | -2.570025 | -2.442335 | 2.884706  | H | -2.339938 | -5.028772 | 4.075556 |
| C | -2.767674 | -1.484597 | 1.911425  | H | -1.943273 | -4.982225 | 5.800014 |
| C | -1.851518 | -0.42646  | 1.707439  | C | -0.08762  | -3.256142 | 5.601005 |
| C | -0.708766 | -0.404047 | 2.54332   | H | -0.119793 | -4.084304 | 6.308989 |
| C | -0.509973 | -1.340569 | 3.537904  | H | 0.843381  | -3.337009 | 5.025803 |
| H | -3.293656 | -3.242661 | 2.97521   | H | -0.061762 | -2.319581 | 6.172931 |
| H | -3.633984 | -1.580639 | 1.267748  |   |           |           |          |
| H | 0.021195  | 0.392425  | 2.435907  |   |           |           |          |

Zero-point correction=0.747004 (Ha/Particle)

Thermal correction to Energy=0.798113

Thermal correction to Enthalpy=0.799057

Thermal correction to Gibbs Free Energy=0.656035

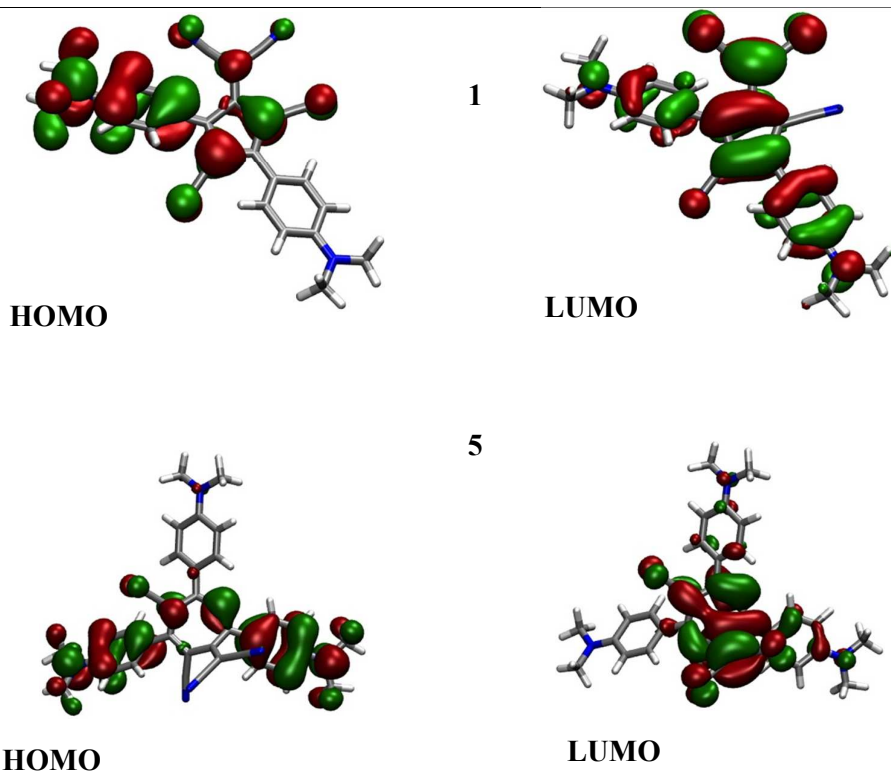
Sum of electronic and zero-point Energies = -2137.414222

Sum of electronic and thermal Energies=-2137.363112

Sum of electronic and thermal Enthalpies=-2137.362168

Sum of electronic and thermal Free Energies=-

2137.505191



**Figure 29SI.** HOMO and LUMO orbital plots of **1** (top) and **5** (down) calculated at the B3LYP/6-31G(d) level of theory (for Cartesian coordinates, see Tables 5SI and 6SI, respectively).

**Table 5SI. Cartesian Coordinates of the Calculated Structure of 1.**

| Atomic Type | Coordinates [Å] |           |           |   |           |           |           |
|-------------|-----------------|-----------|-----------|---|-----------|-----------|-----------|
|             | x               | y         | z         |   |           |           |           |
| N           | 3.836798        | 2.694757  | -1.235668 | C | -1.339809 | 0.365748  | -0.017238 |
| N           | 0.711646        | 5.239253  | -0.153115 | C | -0.862153 | 1.680477  | 0.056639  |
| N           | -0.223143       | -3.096027 | -0.011195 | C | 1.4039    | 2.747003  | -0.340278 |
| N           | -2.395958       | 3.757305  | 0.112779  | C | 2.754122  | 2.655108  | -0.807264 |
| N           | 6.265158        | -1.837213 | 0.353591  | C | 0.966085  | 4.106397  | -0.24092  |
| N           | -6.739393       | -1.384772 | 0.106498  | C | -0.198621 | -1.931565 | -0.063053 |
| C           | 0.578788        | 1.66325   | -0.093099 | C | -1.681677 | 2.836393  | 0.078631  |
| C           | 0.997271        | 0.235071  | -0.121079 | C | 2.35556   | -0.272825 | -0.02759  |
| C           | -0.164034       | -0.514449 | -0.139089 | C | 2.777989  | -1.387674 | -0.782947 |
|             |                 |           |           | C | 4.056956  | -1.899048 | -0.670117 |
|             |                 |           |           | C | 4.992783  | -1.336358 | 0.237009  |
|             |                 |           |           | C | 4.558537  | -0.236053 | 1.02133   |
|             |                 |           |           | C | 3.284335  | 0.278217  | 0.880982  |

|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| C | 7.226745  | -1.194479 | 1.237915  | C | -0.10059  | 1.360194  | 0.146772  |
| C | 6.682676  | -2.973731 | -0.454243 | C | 1.126586  | 0.668613  | -0.170346 |
| C | -2.711438 | -0.085601 | 0.028576  | H | 1.801528  | 1.282717  | -0.767135 |
| C | -3.714881 | 0.644015  | 0.713062  | C | 1.583696  | -0.559483 | 0.191342  |
| C | -5.026723 | 0.219351  | 0.750801  | C | 0.737376  | 1.413732  | 1.036843  |
| C | -5.435357 | -0.966287 | 0.082342  | C | -0.617838 | 1.700441  | 0.494064  |
| C | -4.434923 | -1.699427 | -0.609232 | C | -1.579067 | 0.734033  | 0.28213   |
| C | -3.121638 | -1.274515 | -0.622809 | C | -2.415342 | 1.453451  | 0.902102  |
| C | -7.129458 | -2.613203 | -0.572644 | C | -0.049628 | 2.831181  | 0.090057  |
| C | -7.750629 | -0.599564 | 0.80253   | C | -1.009823 | 3.629905  | -0.518216 |
| H | 2.097361  | -1.837789 | -1.497887 | H | -1.870205 | 3.165856  | -0.978687 |
| H | 4.337464  | -2.735107 | -1.29862  | C | -0.897098 | 5.006274  | -0.574333 |
| H | 5.223338  | 0.216649  | 1.746251  | H | -1.673674 | 5.5715    | -1.075344 |
| H | 2.987316  | 1.110043  | 1.512261  | C | 0.218056  | 5.677425  | -0.000305 |
| H | 8.187114  | -1.704307 | 1.152835  | C | 1.218087  | 4.869574  | 0.593025  |
| H | 6.90871   | -1.243811 | 2.288116  | H | 2.099006  | 5.323841  | 1.041477  |
| H | 7.375784  | -0.139511 | 0.973137  | C | 1.095398  | 3.485423  | 0.624085  |
| H | 7.708571  | -3.238465 | -0.195538 | H | 1.880312  | 2.914114  | 1.102853  |
| H | 6.649358  | -2.745886 | -1.528658 | C | -0.697505 | 7.848648  | -0.680851 |
| H | 6.049795  | -3.851282 | -0.269782 | H | -0.747347 | 7.654203  | -1.76127  |
| H | -3.452781 | 1.549848  | 1.245572  | H | -1.687897 | 7.654682  | -0.255226 |
| H | -5.744804 | 0.80843   | 1.307469  | H | -0.463465 | 8.913226  | -0.537418 |
| H | -4.690818 | -2.606259 | -1.142757 | C | 1.526723  | 7.687671  | 0.488834  |
| H | -2.400773 | -1.864245 | -1.175977 | H | 2.431108  | 7.393577  | -0.070731 |
| H | -8.195158 | -2.784337 | -0.417526 | H | 1.418791  | 8.77079   | 0.382425  |
| H | -6.584647 | -3.481063 | -0.179372 | H | 1.681009  | 7.471951  | 1.5461    |
| H | -6.947482 | -2.553928 | -1.653987 | C | 2.894621  | -1.052466 | -0.223674 |
| H | -8.721747 | -1.080809 | 0.682351  | C | 3.164067  | -2.436355 | -0.377403 |
| H | -7.821255 | 0.417141  | 0.395414  | H | 2.385473  | -3.156418 | -0.152161 |
| H | -7.537549 | -0.52593  | 1.877166  | C | 4.371218  | -2.915711 | -0.841886 |
|   |           |           |           | H | 4.502628  | -3.982391 | -0.940784 |
|   |           |           |           | C | 5.425527  | -2.020269 | -1.172313 |
|   |           |           |           | C | 5.183594  | -0.63394  | -1.003959 |
|   |           |           |           | H | 5.962465  | 0.089702  | -1.209148 |
|   |           |           |           | C | 3.957735  | -0.174366 | -0.555611 |
|   |           |           |           | H | 3.836014  | 0.895884  | -0.41731  |
|   |           |           |           | C | 6.881812  | -3.916269 | -1.738692 |
|   |           |           |           | H | 7.887797  | -4.075359 | -2.128482 |
|   |           |           |           | H | 6.809123  | -4.412712 | -0.761077 |
|   |           |           |           | H | 6.170939  | -4.396958 | -2.423359 |
|   |           |           |           | C | 7.702803  | -1.544589 | -1.960922 |
|   |           |           |           | H | 8.023162  | -0.967345 | -1.083146 |
|   |           |           |           | H | 7.389233  | -0.839119 | -2.741864 |
|   |           |           |           | H | 8.562888  | -2.100442 | -2.333972 |
|   |           |           |           | C | 1.165383  | -2.000462 | 2.200957  |
|   |           |           |           | C | 0.293998  | -2.813991 | 2.996762  |
|   |           |           |           | C | 2.468081  | -1.782997 | 2.754486  |
|   |           |           |           | C | -0.832441 | -3.078104 | 0.168504  |

**Table 6SI. Cartesian Coordinates of the Calculated Structure of 5.**

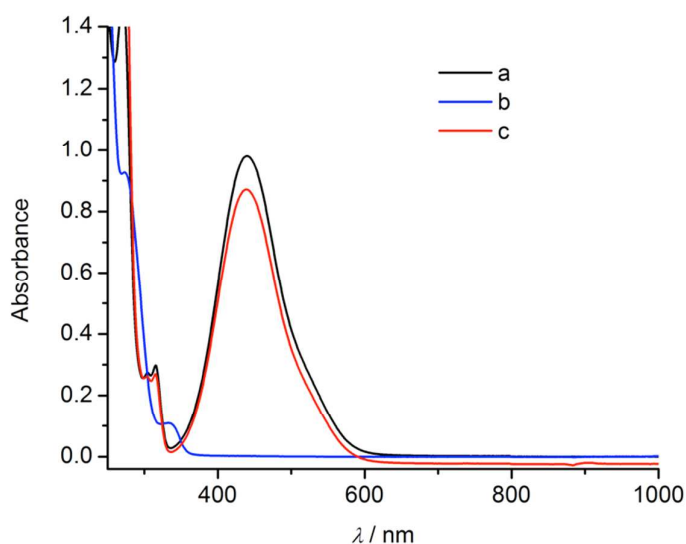
| Atomic Type | Coordinates [Å] |           |           |
|-------------|-----------------|-----------|-----------|
|             | x               | y         | z         |
| N           | -3.321593       | 2.057276  | 1.354064  |
| N           | 0.326381        | 7.042637  | -0.028939 |
| N           | 6.634604        | -2.478776 | -1.631057 |
| N           | -0.410655       | -3.470618 | 3.661056  |
| N           | 3.497293        | -1.599523 | 3.266486  |
| N           | -0.890666       | -4.213885 | -0.105982 |
| N           | -6.851102       | -2.336045 | -1.212657 |
| C           | -1.311193       | 0.681904  | 0.41625   |

|   |           |           |           |
|---|-----------|-----------|-----------|
| C | -2.956214 | -1.141715 | -0.082478 |
| C | -3.663354 | -0.474502 | -1.105496 |
| H | -3.190212 | 0.346824  | -1.637162 |
| C | -4.93743  | -0.861118 | -1.483278 |
| H | -5.424489 | -0.322366 | -2.287512 |
| C | -5.595765 | -1.94459  | -0.840503 |
| C | -4.897072 | -2.59314  | 0.211768  |
| H | -5.362708 | -3.399206 | 0.764016  |
| C | -3.617796 | -2.200776 | 0.569383  |

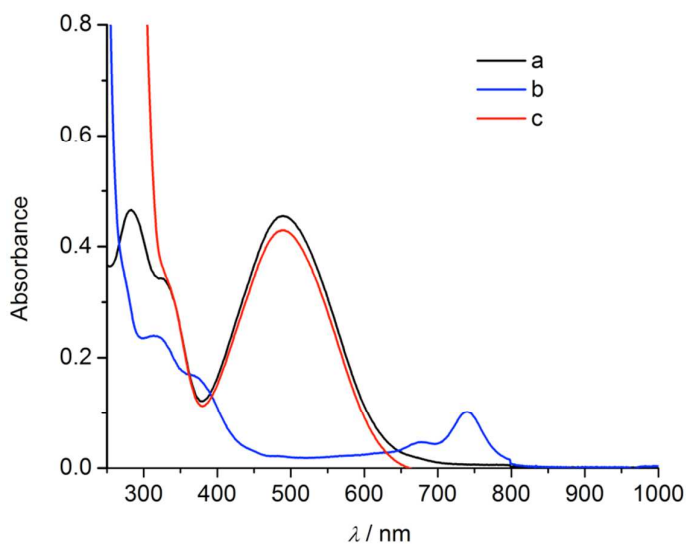
|   |           |           |           |
|---|-----------|-----------|-----------|
| H | -3.133531 | -2.709389 | 1.398643  |
| C | -7.524568 | -3.424665 | -0.508871 |
| H | -7.702492 | -3.18058  | 0.548201  |
| H | -8.488571 | -3.617328 | -0.980229 |
| H | -6.937928 | -4.351764 | -0.551926 |
| C | -7.590322 | -1.580463 | -2.219675 |
| H | -7.050063 | -1.545122 | -3.174499 |
| H | -7.777004 | -0.549081 | -1.891011 |
| H | -8.552026 | -2.063293 | -2.396368 |

## Section 8SI.

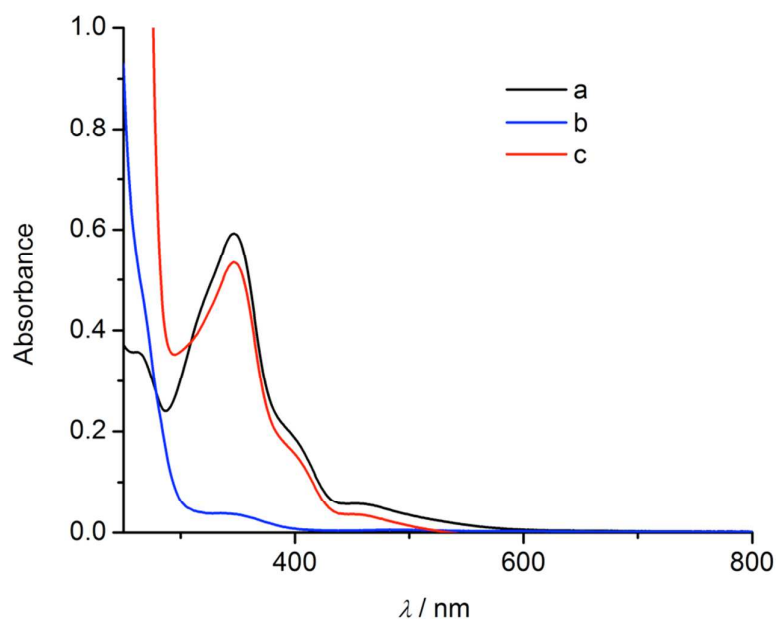
### UV/Vis/NIR Spectroscopic Data



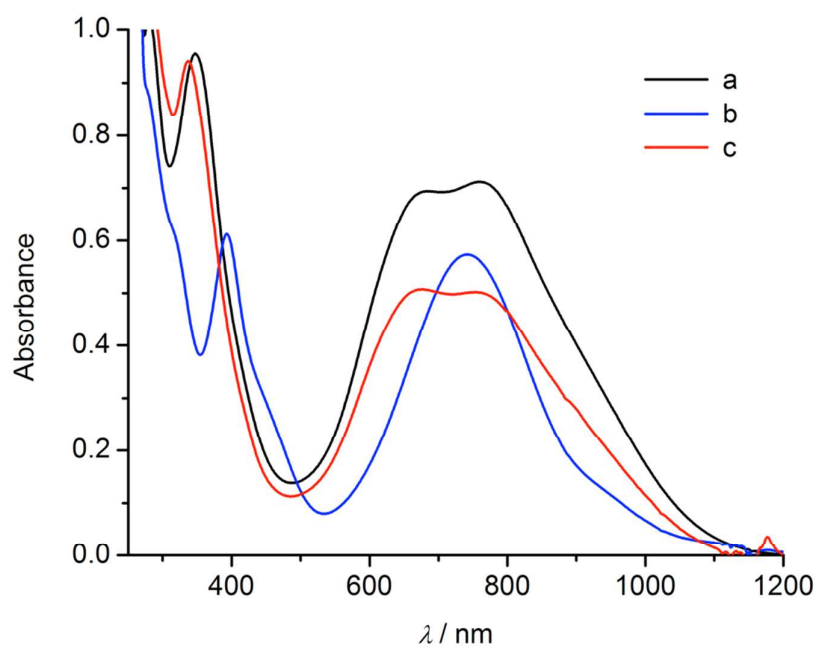
**Figure 30SI.** UV/Vis/NIR absorption of **3** in  $\text{CH}_2\text{Cl}_2$  at 293 K recorded a) neat, b) after acidification with trifluoroacetic acid (TFA), and c) after neutralization with  $\text{Et}_3\text{N}$ .



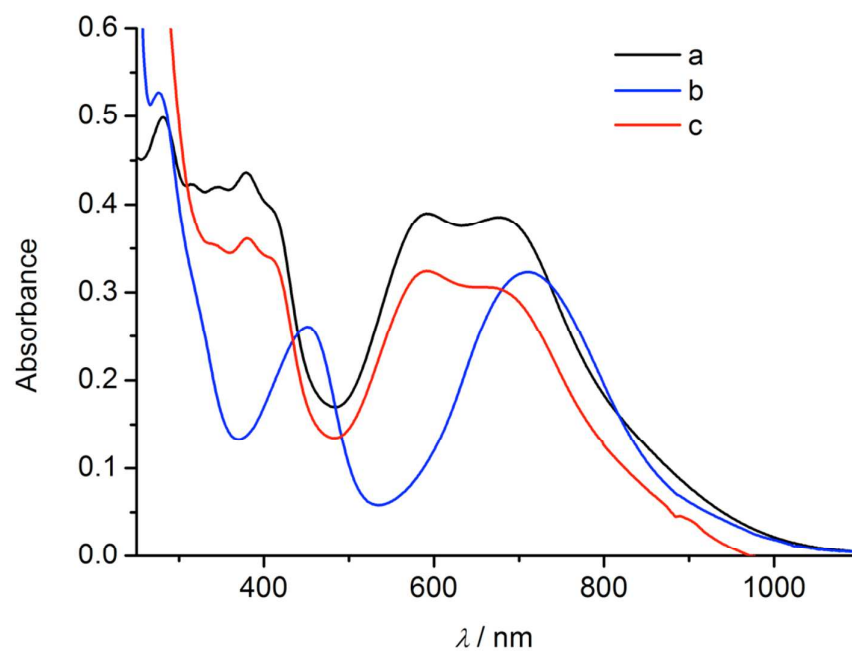
**Figure 31SI.** UV/Vis/NIR absorption of **5** in  $\text{CH}_2\text{Cl}_2$  at 293 K recorded a) neat, b) after acidification with TFA, and c) after neutralization with  $\text{Et}_3\text{N}$ . We have no explanation for the weak bands around 700–800 nm, which form reproducibly upon acidification and completely disappear upon neutralization.



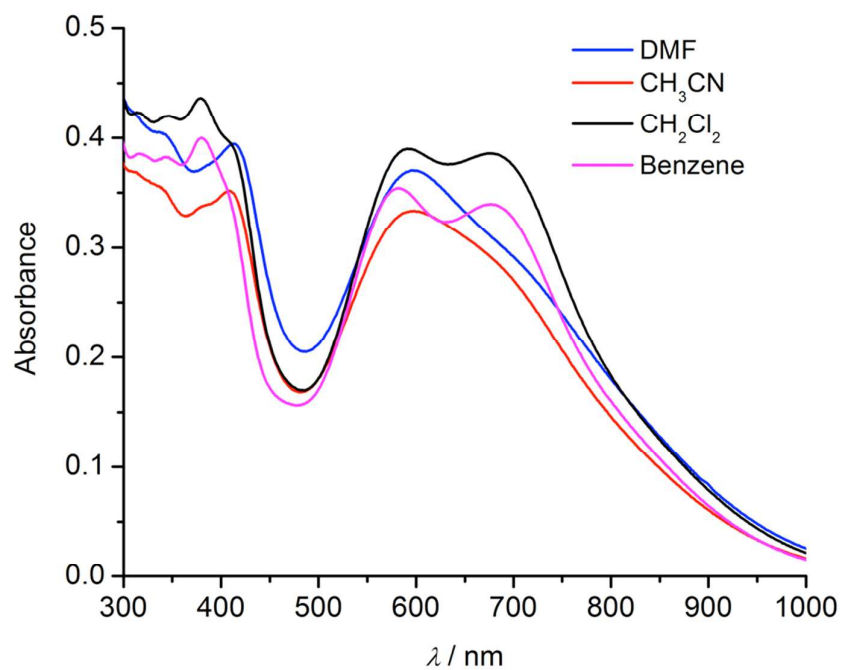
**Figure 32SI.** UV/Vis/NIR absorption of ( $\pm$ )-**6** in  $\text{CH}_2\text{Cl}_2$  at 293 K recorded a) neat, b) after acidification with TFA, and c) after neutralization with  $\text{Et}_3\text{N}$ .



**Figure 33SI.** UV/Vis/NIR absorption of **7** in  $\text{CH}_2\text{Cl}_2$  at 293 K recorded a) neat, b) after acidification with TFA, and c) after neutralization with  $\text{Et}_3\text{N}$ .



**Figure 34SI.** UV/Vis/NIR absorption of *E/Z*-9 in  $\text{CH}_2\text{Cl}_2$  at 298 K recorded a) neat, b) after acidification with TFA, and c) after neutralization with  $\text{Et}_3\text{N}$ .



**Figure 35SI.** UV/Vis/NIR absorption of *E/Z*-9 in different solvents at 298 K.

## Section 9SI.

### Electrochemistry

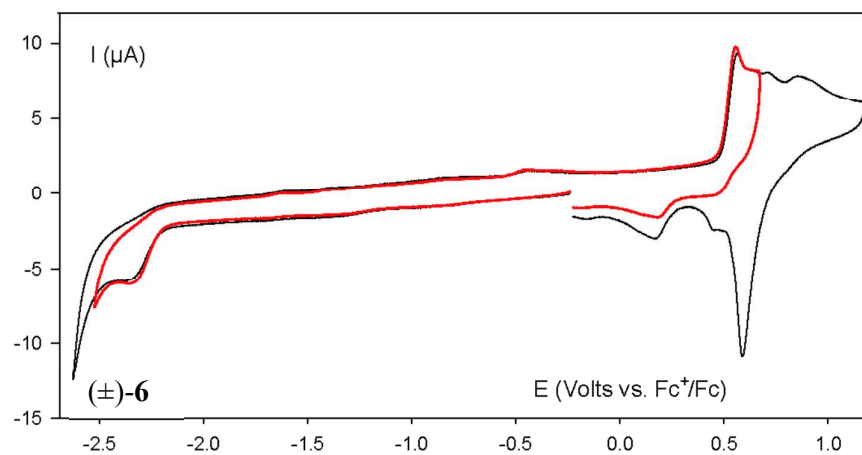
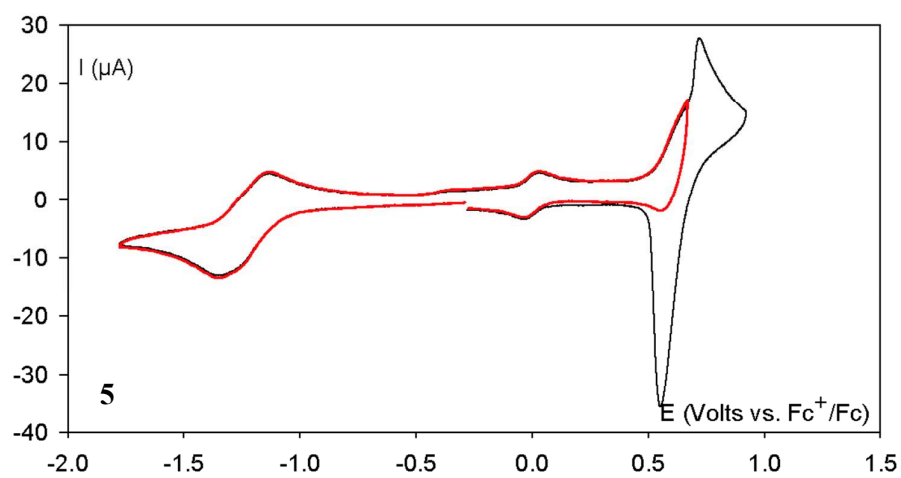
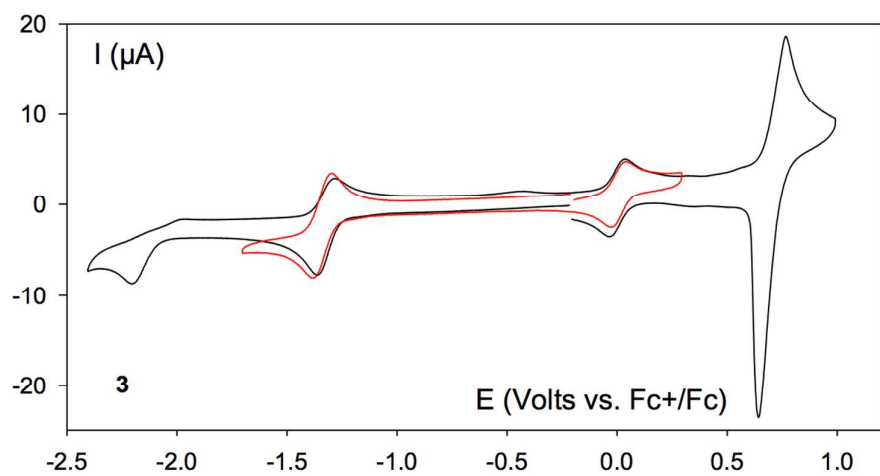
**Table 7SI. Electrochemical Data of 1,<sup>1</sup> 3, 5, (±)-6, 7, and E/Z-9 Observed by Cyclic Voltammetry (CV) (Scan Rate  $\nu = 0.1 \text{ V s}^{-1}$ ) and Rotating-Disk Voltammetry (RDV) in  $\text{CH}_2\text{Cl}_2$  (in the Presence of 0.1M  $\text{Bu}_4\text{NPF}_6$ ).**

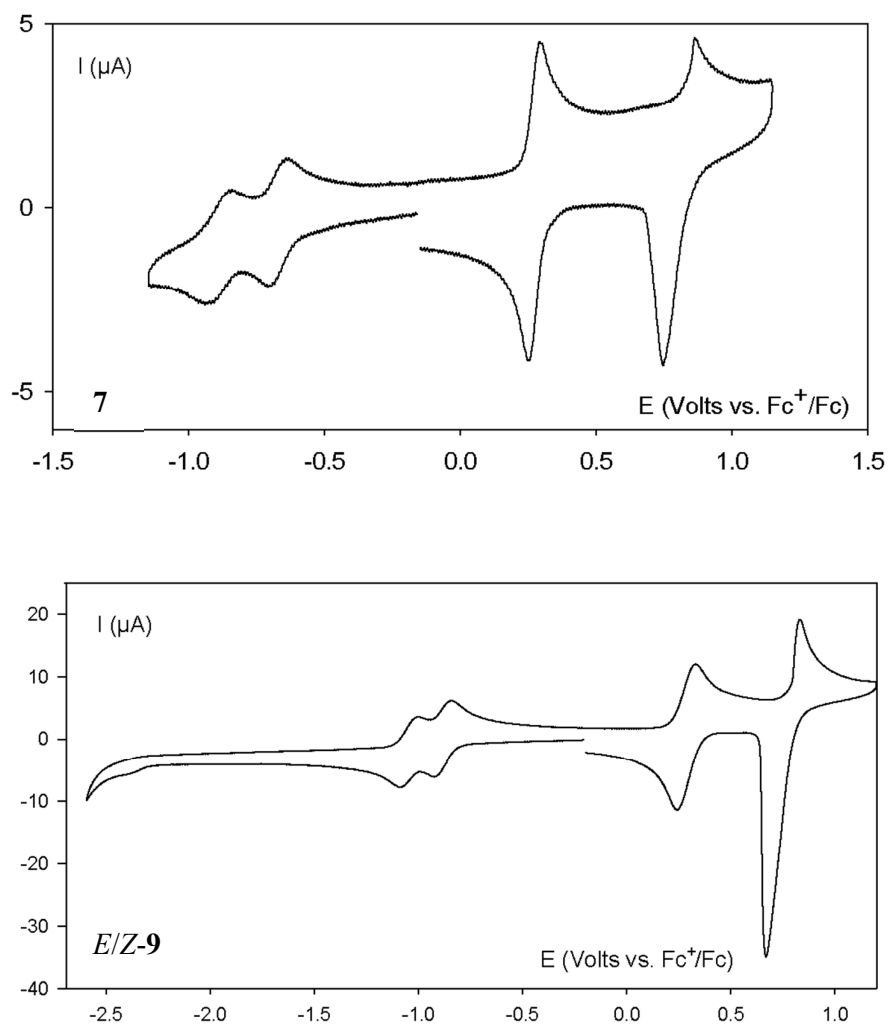
| Compound             | Cyclic Voltammetry            |                                   | Rotating-Disk Voltammetry             |                            |
|----------------------|-------------------------------|-----------------------------------|---------------------------------------|----------------------------|
|                      | $E^\circ$<br>[V] <sup>a</sup> | $\Delta E_p$<br>[mV] <sup>b</sup> | $E_{1/2}$<br>[V] <sup>c</sup>         | Slope<br>[mV] <sup>d</sup> |
| <b>1<sup>e</sup></b> | +0.90 <sup>f</sup>            |                                   | <sup>g</sup>                          |                            |
|                      | +0.67                         | 60                                | +0.67 (1e <sup>-</sup> )              | 60                         |
|                      | -0.45                         | 60                                | -0.47 (1e <sup>-</sup> )              | 60                         |
|                      | -0.96 <sup>f</sup>            |                                   | -0.97 (1e <sup>-</sup> )              | 80                         |
| <b>3</b>             | +0.76 <sup>f</sup>            |                                   | <sup>g</sup>                          |                            |
|                      | -1.32                         | 70                                | -1.37 (1e <sup>-</sup> )              | 80                         |
|                      | -2.21 <sup>f</sup>            |                                   | -2.24 (1e <sup>-</sup> )              | 60                         |
| <b>5</b>             | +0.72 <sup>f,h</sup>          |                                   |                                       | 75                         |
|                      | +0.60                         | 60                                | +0.62 (1e <sup>-</sup> )              |                            |
|                      | -1.18                         | 80                                | -1.33 (2e <sup>-</sup> ) <sup>i</sup> | 200                        |
|                      | -1.30                         | 80                                |                                       |                            |
| <b>(±)-6</b>         | +0.82 <sup>f</sup>            |                                   |                                       |                            |
|                      | +0.64 <sup>f</sup>            |                                   |                                       |                            |
|                      | +0.54 <sup>f</sup>            |                                   | +0.49                                 | <sup>j</sup>               |
|                      | -2.34 <sup>f</sup>            |                                   | -2.33                                 | 90                         |
| <b>7</b>             | +0.85 <sup>f</sup>            |                                   | +0.83 (1e <sup>-</sup> )              | 60                         |
|                      | +0.27                         | 45                                | +0.27 (2e <sup>-</sup> )              | 60                         |
|                      | -0.67                         | 75                                | -0.69 (1e <sup>-</sup> )              | 80                         |
|                      | -0.89                         | 100                               | -0.94 (1e <sup>-</sup> )              | 90                         |

|                  |                    |    |                          |    |
|------------------|--------------------|----|--------------------------|----|
| $E/Z$ - <b>9</b> | +0.81 <sup>f</sup> |    | <sup>j</sup>             |    |
|                  | +0.28              | 70 | +0.29 (2e <sup>-</sup> ) | 70 |
|                  | -0.88              | 60 | -0.93 (1e <sup>-</sup> ) | 75 |
|                  | -1.05              | 80 | -1.13 (1e <sup>-</sup> ) | 85 |

---

<sup>a</sup> $E^0 = (E_{pc} + E_{pa})/2$ , where  $E_{pc}$  and  $E_{pa}$  correspond to the cathodic and anodic peak potentials, respectively. Values reported versus Fc/Fc<sup>+</sup>. <sup>b</sup> $\Delta E_p = E_{pa} - E_{pc}$ . <sup>c</sup> $E_{1/2}$  = Half-wave potential. <sup>d</sup>Logarithmic analysis of the wave obtained by plotting  $E$  versus  $\text{Log}[I/(I_{lim}-I)]$ . <sup>e</sup>Taken from reference 1. <sup>f</sup> $E_p$  = Irreversible peak potential. <sup>g</sup>Poorly resolved oxidation due to strong electrode inhibition. <sup>h</sup>A redissolution peak was observed on the reverse scan at +0.55 V. <sup>i</sup>Unresolved two electron step. <sup>j</sup>No data could be obtained due to electrode inhibition during oxidation.





**Figure 36SI.** Cyclic voltammograms of **3** (in the presence of ferrocene), **5**, ( $\pm$ )-**6**, **7**, and *E/Z*-**9** in  $\text{CH}_2\text{Cl}_2$  and in the presence of 0.1M  $\text{Bu}_4\text{NPF}_6$  and at a scan rate of 0.1 V/s.

## Section 10SI.

### References

- (1) Jayamurugan, G.; Gisselbrecht, J.-P.; Boudon, C.; Schoenebeck, F.; Schweizer, W. B.; Bernet, B.; Diederich, F. *Chem. Commun.* **2011**, 47, 4520–4522.
- (2) Rudenko, A. P.; Vasil'ev, A. V. *Zh. Org. Khim.* **1995**, 31, 1502–1522.
- (3) Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112–122.
- (4) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, 42, 339–341.
- (5) (a) Dehu, C.; Meyers, F.; Brédas, J. L. *J. Am. Chem. Soc.* **1993**, 115, 6198–6206. (b) Beckmann, J.; Dakternieks, D.; Duthie, A.; Mitchell, C.; Schürmann, M. *Aust. J. Chem.* **2005**, 58, 119–127.
- (6) (a) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, 112, 8251–8260. (b) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, 104, 5497–5509.
- (7) These values correspond well with the experimental observed barriers in 2-(cyclopenta-2,4-dien-1-ylidene)-3-methyloxazolidine, see reference 8.
- (8) Olsson, T.; Sandström, J. *Acta Chem. Scand. B* **1982**, 36, 23–30.
- (9) Frisch, G. W. T. M. J.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, Jr., J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J.

M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

(10) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999–3093.