Electronic Supplementary Information for:

# Quinoidal Diindenothienoacenes: Synthesis and Properties of New Functional Organic Materials

Gabriel E. Rudebusch, Aaron G. Fix, Hillary A. Henthorn, Chris L. Vonnegut, Lev N. Zakharov, and Michael M. Haley\*

Department of Chemistry and Biochemistry and the Materials Science Institute University of Oregon, Eugene, OR 97403-1253 USA

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#### **Experimental details**

**General information.** Air sensitive manipulations were performed by standard Schlenk line technique. THF and toluene were refluxed with sodium benzophenone ketyl for 24 h prior to distillation and use. CH<sub>2</sub>Cl<sub>2</sub> was distilled from calcium hydride. All other reagents were used without prior purification. 2-Ethoxycarbonylbenzeneboronic acid was purchased from Synthonix, Inc. (Trialkylsilyl)acetylenes were purchased from GFS Chemicals. Chromatography was performed on 230-400 mesh silica gel purchased from Aldrich. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> using a Varian Inova 500 (<sup>1</sup>H: 500.11 MHz, <sup>13</sup>C: 125.75 MHz) or Bruker Avance-III-HD 600 (<sup>1</sup>H: 599.98 MHz, <sup>13</sup>C: 150.87 MHz) NMR spectrometer. Chemical shifts (δ) are expressed in ppm relative to the residual chloroform (<sup>1</sup>H: 7.26 ppm, <sup>13</sup>C: 77.16 ppm) reference. UV-Vis spectra were recorded on a HP 8453 UV-Vis spectrometer. High resolution mass spectra were recorded on a JEOL MS-Route mass spectrometer.



**Diethyl 2,2'-(thiophene-3,4-diyl)dibenzoate (8)** In a dry glass pressure vessel, 2ethoxycarbonyl-benzeneboronic acid (6.0 g, 31 mmol), Pd<sub>2</sub>dba<sub>3</sub> (120 mg, 0.124 mmol), SPhos (100 mg, 0.248 mmol), anhydrous K<sub>3</sub>PO<sub>4</sub> (10.5 g, 49.6 mmol) and toluene (35 mL) were combined. The mixture was sparged with nitrogen (10 min) then 3,4-dibromothiophene (3.0 g, 12.4 mmol) was added via syringe. The vessel was sealed and heated at 100 °C for 16 h. Upon cooling to rt, the reaction was diluted with CH<sub>2</sub>Cl<sub>2</sub> then filtered. The organics were washed with brine then dried over MgSO<sub>4</sub>. Volatiles were removed under reduced pressure to give an orange oil in quantitative yield. This material can be used directly or purified by silica gel chromatography (20% EtOAc/hexanes) (v/v). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.35 (td, *J* = 7.5, 1.5 Hz, 2H), 7.30 (td, *J* = 7.6, 1.5 Hz, 2H), 7.26 (dd, *J* = 7.5, 1.4 Hz, 2H), 7.20 (s, 2H), 4.08 (q, *J* = 7.2 Hz, 4H), 1.12 (t, *J* = 7.1 Hz, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.92, 141.38, 136.60, 131.98, 131.74, 130.87, 129.40, 127.11, 122.62, 60.84, 13.84. HRMS (ES+) calcd for C<sub>22</sub>H<sub>21</sub>O<sub>4</sub>S (M+H)<sup>+</sup> 381.1161, found 381.1168.



**Diindeno[2,1-***b***:1',2'-***d***]thiophene-5,7-dione (9). To a solution of the crude diester 8 (4.4 g) in ethanol (100 mL) was added aqueous KOH (115 mmol, 5 M). The reaction was heated at reflux for 16 h then cooled to rt. The volume was reduced** *in vacuo* **(30 mL) and acidified with conc. HCl. The diacid was collected, washed with water and dried. To a suspension of the diacid in CH<sub>2</sub>Cl<sub>2</sub>(100 mL) was added 5 drops DMF. Oxalyl chloride (4.0 mL, 46 mmol) was added dropwise via syringe. The reaction was stirred at rt for 3 h then the volatiles were removed** *in vacuo***. CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added and the flask was cooled to 0 °C. AlCl<sub>3</sub> (9.25 g, 69 mmol) was added and the reaction was stirred at 0 °C for 16 h. The dark solution was poured onto ice and the precipitate was collected by filtration then washed with water. Recrystallization from CHCl<sub>3</sub> (1.5 L) provided the title compound as orange needles (1.71 g, 46% from 3,4-dibromothiophene). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) \delta 7.64 (d,** *J* **= 7.2 Hz, 2H), 7.54 (t,** *J* **= 7.5 Hz, 2H), 7.46 (d,** *J* **= 7.3 Hz, 2H), 7.34 (t,** *J* **= 7.5 Hz, 2H); limited solubility of the title compound hindered acquisition of <sup>13</sup>C NMR spectra; UV-Vis (CHCl<sub>3</sub>) \lambda\_{max}: 313, 440 (br) nm; HRMS (EI+) calcd for C<sub>18</sub>H<sub>8</sub>O<sub>2</sub>S (M<sup>+</sup>) 289.0245, found 288.0240.** 



**DI1T-TIPSE.** In a dry two-neck flask, (triisopropylsilyl)acetylene (0.8 mL, 3.45 mmol) was added to THF (5 mL) and cooled to 0  $^{\circ}$ C. A solution of *n*-butyllithium (3.1 mmol, 1.6 M) was added dropwise then stirred for 5 min. In a second flask, dione **9** (200 mg, 0.69 mmol) was suspended in THF (25 mL) at 0  $^{\circ}$ C. The (triisopropylsilyl)ethynyllithium solution was transferred via syringe to the dione suspension and stirred for 30 min. The reaction was quenched with

saturated NH<sub>4</sub>Cl soln (50 mL). The organics were extracted with EtOAc (2 x 50 mL), washed with brine and dried over MgSO<sub>4</sub>. The volatiles were removed under reduced pressure, then the crude material was passed through a short plug of silica, eluting first with hexanes then EtOAc. The polar fractions were combined and reduced *in vacuo*. Toluene (15 mL) was added and the solution was degassed thoroughly under dynamic vacuum. Finely ground SnCl<sub>2</sub> (400 mg, 10.4 mmol) was added then further degassed under dynamic vacuum. The slurry was stirred for 3 h at rt, then poured onto a plug of silica and eluted with 1:1 CH<sub>2</sub>Cl<sub>2</sub>/hexanes. Removal of the volatiles under reduced pressure provided the title compound (270 mg, 63%) as a green solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.51 (d, *J* = 7.3 Hz, 2H), 7.20 (td, *J* = 7.5, 1.0 Hz, 2H), 7.13 (d, *J* = 7.3 Hz, 2H), 7.07 (td, *J* = 7.5, 1.2 Hz, 2H), 1.17 (s, 42H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  153.77, 148.89, 144.03, 130.77, 130.19, 125.78, 124.37, 120.68, 116.32, 105.90, 99.70, 18.73, 11.28; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  ( $\epsilon$ ): 266 (36000), 303 (30000), 311 (30300), 416 (31600), 443 (38400), 655 (br, 6400), 765 (sh, 6000) nm; HRMS (ES+) calcd for C<sub>40</sub>H<sub>51</sub>SSi<sub>2</sub> (M+H)<sup>+</sup> 619.3250, found 619.3243.



**DI1T-TESE**. The procedure for **DI1T-TIPSE** was adapted with (triethylsilyl)acetylene (521 mg, 3.71 mmol), n-butyllithium (3.34 mmol, 1.6 M) and **9** (214 mg, 0.74 mmol) to provide the title compound (147 mg, 37%) as a green solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 (d, *J* = 7.3 Hz, 2H), 7.19 (td, *J* = 7.5, 1.0 Hz, 2H), 7.11 (d, *J* = 7.4 Hz, 2H), 7.06 (td, *J* = 7.5, 1.1 Hz, 2H), 1.14 (t, *J* = 7.9 Hz, 18H), 0.77 (q, *J* = 7.9 Hz, 12H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  153.79, 148.73, 144.01, 130.66, 130.11, 125.80, 124.35, 120.62, 116.17, 106.53, 99.06, 7.63, 4.48; HRMS (ES+) calcd for C<sub>34</sub>H<sub>38</sub>SSi<sub>2</sub> (M<sup>+</sup>) 534.2233, found 534.2208.



**2-Benzoyl-3,4-dibromothiophene** (**10**). AlCl<sub>3</sub> (15 g, 125 mmol) was added in three portions to a stirred solution of 3,4-dibromothiophene (10.0 g, 41.3 mmol) and benzoyl chloride (8.7 g, 62 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) at 0 °C. The cooling bath was removed and the reaction was stirred for 16 h. The dark solution was poured onto ice, diluted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and washed successively with aqueous NaOH (1 M) and brine. The organic phases were combined and dried over MgSO<sub>4</sub>. Removal of volatiles by reduced pressure provided the title compound (13.13 g, 92%) as a yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.88–7.84 (m, 2H), 7.67 (s, 1H), 7.67–7.63 (m, 1H), 7.52 (dd, J = 8.5, 7.1 Hz, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  187.38, 136.87, 136.82, 133.42, 129.86, 128.56, 128.08, 118.19, 116.67; HRMS (ES+) calcd for C<sub>11</sub>H<sub>6</sub>SBr<sub>2</sub> (M<sup>+</sup>), 343.8506 found 343.8521.



Ethyl 6-bromo-3-phenylthieno[3,2-*b*]thiophene-2-carboxylate (11). To a solution of 10 (13.13 g, 37.9 mmol) in DMF (50 mL) was added K<sub>2</sub>CO<sub>3</sub> (15.7 g, 113.8 mmol) and the reaction was rigorously degassed under dynamic vacuum. With stirring, ethyl thioglycolate (4.79 g, 39.8 mmol) was added dropwise via syringe and then the reaction was heated at 60 °C for 1 d. After cooling, the mixture was poured into water (100 mL). The solids were collected and washed with water. Recrystallization from ethanol (500 mL) provided 11 (11.2 g, 80%) as tan needles. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.60–7.55 (m, 2H), 7.53–7.45 (m, 4H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  162.08, 141.75, 141.14, 140.77, 133.72, 129.21, 129.05, 128.82, 128.30, 128.17, 103.14, 61.36, 14.08; HRMS (ES+) calcd for C<sub>15</sub>H<sub>12</sub>S<sub>2</sub>O<sub>2</sub>Br (M+H)<sup>+</sup> 366.9462, found 366.9454.



**Diester 12.** In a dry glass pressure vessel, 2-ethoxycarbonylbenzeneboronic acid (581 mg, 2.99 mmol), Pd<sub>2</sub>dba<sub>3</sub> (25 mg, 0.027 mmol), SPhos (22 mg, 0.054 mmol), anhydrous K<sub>3</sub>PO<sub>4</sub> (1.15 g, 5.44 mmol), **11** (1.00 g, 2.72 mmol) and toluene (10 mL) were combined. The mixture was sparged with nitrogen (10 min). The vessel was sealed and brought to 100 °C for 16 h. Upon cooling to rt the reaction was diluted with CH<sub>2</sub>Cl<sub>2</sub> then filtered. The organics were washed with brine and dried over MgSO<sub>4</sub>. Removal of volatiles under reduced pressure provides the title compound in quantitative yield. This material can be used directly or purified by silica gel chromatography (20% EtOAc/hexanes) (v/v) to give a yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.66–7.63 (m, 2H), 7.61 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.55–7.47 (m, 4H), 7.45 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.58, 162.35, 141.73, 141.01, 140.94, 134.82, 134.78, 134.28, 131.91, 131.07, 130.61, 130.55, 129.17, 128.61, 128.44, 128.21, 127.88, 127.84, 61.23, 61.09, 14.10, 13.71; HRMS (ES+) calcd for C<sub>24</sub>H<sub>21</sub>S<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> 437.0881, found 437.0875.



Indeno[2,1-*b*]indeno[1',2':4,5]thieno[2,3-*d*]thiophene-6,12-dione (13). To a solution of 12 (0.98 g, 2.25 mmol) in ethanol (100 mL) was added aqueous KOH (12 mmol, 1.5 M). The reaction was heated at reflux for 16 h then cooled to rt. The volume was reduced *in vacuo* (to 20 mL) and acidified with conc. HCl. The diacid was collected, washed with water and dried. To a suspension of the diacid in CH<sub>2</sub>Cl<sub>2</sub>(100 mL) was added DMF (5 drops). Oxalyl chloride (1.0

mL, 11.2 mmol) was added dropwise via syringe. The reaction was stirred at rt for 3 h then the volatiles were removed *in vacuo*. CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added and the flask was cooled to 0 °C. AlCl<sub>3</sub> (3.0 g, 22.3 mmol) was added as a solid. The reaction was allowed to warm to rt and stir for 16 h. The dark solution was poured onto ice and the precipitate was collected by filtration. Successive washes with water and acetone gave the title compound (630 mg, 79%) as a magenta solid. Limited solubility hindered acquisition of NMR spectra; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{max}$ : 370, 490, 522 (sh) nm; HRMS (EI+) calcd for C<sub>20</sub>H<sub>8</sub>O<sub>2</sub>S<sub>2</sub> (M<sup>+</sup>) 343.9966, found 343.9959.



DI2T-TIPSE. To a solution of (triisopropylsilyl)acetylene (527 mg, 2.9 mmol) in THF (5 mL) at 0 °C was added *n*-butyllithium (2.6 mmol, 1.6 M in hexanes) dropwise. In a separate flask, 13 (200 mg, 0.58 mmol) was suspended in THF (25 mL) at 0 °C. The (triisopropylsilyl)ethynyllithium solution was transferred to the dione suspension via syringe then sonicated for 10 min. After quenching with a saturated NH<sub>4</sub>Cl solution, the organics were extracted with Et<sub>2</sub>O and dried over MgSO<sub>4</sub>. The volume was reduced in vacuo and passed through a short plug of silica, eluting with EtOAc. Volatiles were removed under reduced pressure. Toluene (15 mL) was added and the flask was rigorously degassed under dynamic vacuum. Finely ground SnCl<sub>2</sub> (250 mg, 1.25 mmol) was added and the reaction was stirred for 3 h. The mixture was passed through a plug of silica (CH<sub>2</sub>Cl<sub>2</sub>/hexanes). Evaporation of the volatiles provided the title compound (260 mg, 66%) as a dark blue solid. <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.36 (d, J = 7.3 Hz, 2H), 7.28–7.24 (m, 2H), 7.22 (dd, J = 7.5, 1.1 Hz, 2H), 7.12 (td, J= 7.3, 1.4 Hz, 2H), 1.21 (s, 42H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  150.07, 147.30, 146.98, 139.43, 129.62, 128.82, 125.51, 122.65, 120.76, 114.77, 105.47, 99.95, 18.76, 11.30; UV-Vis  $(CH_2Cl_2) \lambda_{max}$  ( $\epsilon$ ): 267 (22100), 444 (13100), 477 (11800), 652 (br, 15100) nm; HRMS (ES+) calcd for  $C_{42}H_{50}S_2Si_2$  (M<sup>+</sup>) 674.2893, found 674.2892.



**3,5-Dibromodithieno**[**3,2-***b***:2',<b>3'**-*d*]**thiophene**. In a 3-neck flask, tetrabromodithieno[3,2-*b*:2',3'-*d*]thiophene<sup>1</sup> (2.7 g, 5.3 mmol) in glacial AcOH (150 mL) was brought to reflux. Zn powder (3.44 g, 53 mmol) was added to the suspension. The reaction was refluxed for a further 30 min and then hot filtered through a fritted funnel. The solution was allowed to cool to rt, then the crude product was precipitated by the addition of water. The solids were collected by filtration. Recrystallization from chloroform provided the title compound as colorless needles (450 mg, 24%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>)  $\delta$  7.31 (s); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>)  $\delta$  142.74, 130.84, 123.16, 103.90. These spectroscopic data correspond to previously reported data.<sup>2</sup>



**Diester 14.** In a dry glass pressure vessel, 3,5-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene (450 mg, 1.27 mmol), 2-ethoxycarbonylbenzeneboronic acid (754 mg, 3.18 mmol), Pd<sub>2</sub>dba<sub>3</sub> (12 mg, 0.013 mmol), SPhos (24 mg, 0.05 mmol), anhydrous K<sub>3</sub>PO<sub>4</sub> (1.0 g, 5.1 mmol) and toluene (15 mL) were combined and sparged with nitrogen (10 min). The vessel was sealed and brought to 100 °C for 24 h. Upon cooling to rt the reaction was diluted with CH<sub>2</sub>Cl<sub>2</sub> then filtered. The organics were washed with brine and dried over MgSO<sub>4</sub>. Removal of volatiles under reduced pressure provided the title compound in quantitative yield. This material can be used directly or purified by silica gel chromatography (20% EtOAc/hexanes) (v/v) to give a yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 (d, *J* = 7.8 Hz, 2H), 7.58-7.54 (m, 4H), 7.50-7.42 (m, 2H), 7.23 (s, 2H), 4.12 (q, *J* = 7.2 Hz, 4H), 1.01 (t, *J* = 7.2 Hz, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.76, 142.24, 135.53, 135.00, 131.73, 131.27, 130.42, 130.40, 130.18, 128.25, 122.45, 61.13, 13.75; HRMS (ES+) calcd for C<sub>26</sub>H<sub>21</sub>S<sub>3</sub>O<sub>4</sub> (M+H)<sup>+</sup> 493.0602, found 493.0601.



**Diindenodithieno**[3,2-*b*:2',3'-*d*]**thiophene-3,13-dione (15)**. To a solution of **14** (0.50 g, 2.25 mmol) in ethanol (100 mL) was added aqueous KOH (14.3 mmol, 1.4 M). The reaction was heated at reflux for 16 h then cooled to rt. The volume was reduced *in vacuo* (to 15 mL) and acidified with conc. HCl. The diacid was collected, washed with water and dried. To a suspension of the diacid in CH<sub>2</sub>Cl<sub>2</sub>(100 mL) was added DMF (5 drops). Oxalyl chloride (0.35 mL, 11.2 mmol) was added dropwise via syringe. The reaction was stirred at rt for 3 h then the volatiles were removed *in vacuo*. CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added and the flask was cooled to 0 °C. AlCl<sub>3</sub> (1.0 g, 22.3 mmol) was added as a solid and the reaction was stirred for 1 h. The dark solution was poured onto ice and the precipitate was collected by filtration. Successive washes with water and acetone gave the title compound (328 mg, 81%) as a red solid. Limited solubility hindered acquisition of NMR spectra; UV-Vis (CHCl<sub>3</sub>)  $\lambda_{max}$ : 296, 481, 514 nm; HRMS (EI+) calcd for C<sub>22</sub>H<sub>8</sub>O<sub>2</sub>S<sub>3</sub> (M<sup>+</sup>) 399.9686, found 399.9700.



**DI3T-TIPSE.** To a solution of (triisopropylsilyl)acetylene (227 mg, 1.25 mmol) in THF (5 mL) at 0 °C was added *n*-butyllithium (1.12 mmol, 1.5 M in hexanes) dropwise. In a separate flask, **15** (100 mg, 0.25 mmol) was suspended in THF (25 mL) and cooled to 0 °C. The (triisopropylsilyl)ethynyllithium solution was transferred to the dione suspension via syringe then sonicated for 10 min. After quenching with a saturated NH<sub>4</sub>Cl solution, the organics were extracted with  $Et_2O$  and dried over MgSO<sub>4</sub>. The volume was reduced *in vacuo* and passed through a short plug of silica, eluting with EtOAc. Volatiles were removed under reduced pressure. Toluene (15 mL) was added and the flask was rigorously degassed under dynamic vacuum. Finely ground SnCl<sub>2</sub> (250 mg, 1.25 mmol) was added and the reaction was stirred for 10

min. The mixture was passed through a plug of silica (CH<sub>2</sub>Cl<sub>2</sub>/hexanes). Evaporation of the volatiles provided the title compound (131 mg, 72%) as a deep purple solid.<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (d, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 2H), 1.21 (s, 42H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  148.91, 146.56, 143.92, 142.96, 138.51, 129.20, 128.52, 125.08, 122.04, 120.72, 113.17, 105.36, 100.45, 18.78, 11.34; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  ( $\epsilon$ ): 256 (32300), 320 (8000), 513 (27600), 553 (39400), 683 (19600), 740 (sh, 16600) nm; HRMS (ES+) calcd for C<sub>44</sub>H<sub>51</sub>S<sub>3</sub>Si<sub>2</sub> (M+H)<sup>+</sup> 731.2691, found 731.2711.



**Fig. S1** Comparison of the electronic absorption spectra of **DI1T-TIPSE** and **DI2T-TIPSE** with the analogous indeno[2,1-*c*]fluorene and fluoreno[3,4-*c*]fluorene cores.

#### X-ray Crystallography

General. Diffraction intensities for DI1T-TIPSE, DI2T, DI1T-TESE, 9 and 13 were collected at 100(2) K and for DI3T at 150(2) K on a Bruker Apex2 CCD diffractometer with a micro-focus  $I\mu S$  source using CuK $\alpha$  radiation  $\lambda$ = 1.54178 Å or a sealed X-ray tube with a triumph monochromator, MoK $\alpha$  radiation  $\lambda$ = 0.71073 Å (9 only). Absorption corrections were applied by SADABS.<sup>3</sup> Structures were solved by direct methods and Fourier techniques and refined on  $F^2$  using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. All H atoms were refined in calculated positions in a rigid group model. The Flack parameter for non-centrosymmetrical structure of 9 is 0.00(15). The structures of DI2T and DI1T-TESE have two symmetrically independent molecules. One of terminal -i-Pr groups in DI3T is disordered over two positions in ratio 42/58. X-ray diffraction from crystals of DI2T, DI1T-TESE and 13 at high angles were very weak; even with a strong Incoatec  $I\mu S$  Cu source we could collected data only up to  $2\theta_{max} = 114.98^{\circ}$ , 120.0° and 132.0°, respectively. All calculations were performed by the Bruker SHELXTL (v. 6.10) package.<sup>4</sup>



Fig. S2 Additional views of the pairwise arrangement for DI1T-TIPSE.



Fig. S3 Pairwise slipped stack of DI1T-TESE.



Fig. S4 Expanded packing view of dione 9.



Fig. S5 Expanded packing view of dione 13.

#### **Cyclic Voltammetry**

All electrochemical experiments were conducted in a traditional 3-electrode geometry using a Solartron 1287 potentiostat. Electrolyte solutions (0.1 M) were prepared from HPLC-grade CH<sub>2</sub>Cl<sub>2</sub> and anhydrous Bu<sub>4</sub>NBF<sub>4</sub>, and the solutions were freeze-pump-thaw degassed (3x) prior to analysis. Cyclic voltammetry was conducted under a nitrogen atmosphere. The working electrode was a glassy carbon electrode (3-mm diameter), with a Pt-coil counter electrode and Ag wire pseudo reference. The ferrocene/ ferrocenium (Fc/Fc<sup>+</sup>) couple was used as an internal standard following each experiment. Potential values were re-referenced to SCE using a value of 0.46 (V vs. SCE) for the Fc/Fc<sup>+</sup> couple in CH<sub>2</sub>Cl<sub>2</sub>. When necessary, potentials were re-referenced to NHE using SCE = -0.24 (V vs. NHE). LUMO and HOMO levels were approximated using SCE = -4.68 eV vs. vacuum.<sup>5</sup> Cyclic voltammetry experiments were conducted at sweep rates of 50 (reported), 75, 100 and 125 mV s<sup>-1</sup>. All scan rates show quasi-reversible kinetics with no alteration of peak splitting with scan rate.  $E_{1/2}$  values were calculated assuming  $E_{1/2} \approx E^{\circ} = (E_{anodic})^{\circ}$ +  $E_{cathodic}$ /2 based on these observations for reversible couples; for irreversible couples the E<sup>o</sup> value is estimated as the potential at peak current. The  $E_{ac}$  peak splitting of the Fc/Fc<sup>+</sup> couple was similar to that of the analyte (~100 mV). The anodic peak current increases linearly with the square root of the scan rate in the range 50 to 125 mV s<sup>-1</sup>, indicating a diffusion-controlled process. Analyte concentrations were ca. 1-5 mM.

#### **Electronic Paramagnetic Resonance**

**Experimental details**. An apparatus (Fig. S6) was constructed from borosilicate glass and dried in a 100 °C oven. The apparatus was then cooled to rt under nitrogen and approximately 0.05 mg of **DI**[n]T was collected on a melting point capillary that was open on both ends and deposited at point A. Potassium metal was added at point B and then opening C was sealed with an oxygen/natural gas torch. Vacuum was pulled (ca. 10<sup>-6</sup> torr) and K metal was sublimed with a Bunsen burner, resulting in a metal mirror inside D. The apparatus was then sealed at point E. Dry THF (approx. 1 mL) from a NaK still was directly distilled through the vacuum system to A and the apparatus was sealed at point F. Controlled exposure to the potassium mirror resulted in formation of DI[n]T radical anion, from which the EPR spectra in Figs. S5-S7 were obtained. The EPR spectra were collected on a Bruker EMX-080 spectrometer.



Fig. S6 Apparatus used for generation of anion radical.

**EPR Computational Details**. To determine the hyperfine coupling constants for the hydrogen and silicon nuclei coupled with the anion radical, the EPR spectra were simulated with the EasySpin<sup>6</sup> package utilizing MATLAB code.<sup>7</sup> DFT calculations were performed for the gas phase molecules using Gaussian09 Revision C.01<sup>8</sup> and the results were used to assign the HFCC and carbon spin density locations (Table S1). These computations were carried out at the UB3W91/6-311++G(2df,2pd)//UCAM-B3LYP/6-31++G(d,p) level of theory.







Fig. S8 EPR spectrum of DI2T<sup>--</sup>.



Fig. S9 EPR spectrum of DI3T<sup>--</sup>.



**Table S1** Hyperfine Coupling Constants and Carbon spin densities ( $\rho_c$ ).

	DI1T	DI2T	DI3T
C(A)	0.034	0.022	0.024
C(B)	0.012	0.016	0.014
C(C)	0.044	0.029	0.028
C(D)	0.004	0.010	0.010
C(E)	0.112	0.103	0.094
H(A)	0.95	0.63	0.63
H(B)	0.35	0.46	0.38
H(C)	1.25	0.82	0.77
H(D)	0.11	0.28	0.27
Si	2.00	1.92	1.88
$Q_{\rm H}$	28.1	28.2	26.6
$Q_{Si}$	17.9	18.6	20

# **Geometry Calculations**

DFT calculations were performed for gas phase molecules using the Gaussian09 Revision C.01.<sup>8</sup> Harmonic frequency analyses, performed at the same level of theory as the minimization, were used to confirm minimized structures.

# **Cartesian Coordinates**

# **DI1T Neutral**

UCAM-B3LYP/6-31G(d,p)	
Zero-point correction=	0.448804 (Hartree/Particle)
Thermal correction to Energy=	0.481967
Thermal correction to Enthalpy=	0.482911
Thermal correction to Gibbs Free Energy=	0.379259
Sum of electronic and zero-point Energies=	-2058.703728
Sum of electronic and thermal Energies=	-2058.670565
Sum of electronic and thermal Enthalpies=	-2058.669621
Sum of electronic and thermal Free Energies=	-2058.773273
NIMAG = 0	

С	1.93558	4.11556	-0.00060
С	1.82260	2.73673	0.00025
С	3.21007	4.68787	-0.00134
С	2.98224	1.92787	0.00039
С	4.24123	2.49387	-0.00043
С	4.34546	3.88761	-0.00129
Η	5.12629	1.86635	-0.00056
Η	5.32724	4.34978	-0.00197
Η	1.05689	4.74990	-0.00074
Η	3.31141	5.76782	-0.00203
С	2.58279	0.49782	0.00128
С	0.67455	1.82696	0.00094
С	1.22605	0.46961	0.00151
С	3.48230	-0.59110	0.00156
S	-0.00314	-0.78434	0.00212
С	-1.23106	0.47082	0.00153
С	-0.67827	1.82761	0.00099
С	-1.82548	2.73845	0.00041
С	-2.58779	0.50027	0.00113
С	-2.98589	1.93067	0.00049

С	-1.93713	4.11738	-0.00020
С	-4.24428	2.49795	-0.00002
С	-3.21106	4.69094	-0.00073
С	-4.34721	3.89178	-0.00064
Η	-1.05782	4.75087	-0.00025
Η	-3.31135	5.77098	-0.00121
Η	-5.12994	1.87126	0.00010
Η	-5.32855	4.35489	-0.00105
С	-3.48759	-0.5882	0.00093
С	4.26800	1.51855	0.00153
Si	5.44268	2.93551	-0.00042
С	-4.27192	-1.51704	0.00060
Si	-5.43894	-2.94056	-0.00053
С	-6.63740	-2.73204	1.43019
С	-4.44445	-4.51988	0.20022
С	-6.36728	-2.95221	-1.63294
С	4.87476	-4.17921	-1.28695
С	5.44532	-3.71522	1.70780
С	7.15304	-2.28615	-0.42501
Η	-3.88452	-4.51898	1.13918
Η	-3.72743	-4.64272	-0.61587
Η	-5.10247	-5.39445	0.20288
Η	-6.11060	-2.70409	2.38770
Η	-7.34853	-3.56343	1.46294
Η	-7.21065	-1.80570	1.33711
Η	3.86916	-4.54664	-1.06559
Η	5.54809	-5.04165	-1.31499
Η	4.85564	-3.73611	-2.28617
Η	4.45105	-4.08030	1.97859
Η	5.75677	-2.99762	2.47150
Η	6.13549	-4.56399	1.74364
Η	7.16412	-1.81134	-1.40976
Η	7.88358	-3.10100	-0.43824
Η	7.49054	-1.54744	0.30704
Η	-6.93524	-2.02873	-1.77418
Η	-7.07292	-3.78810	-1.67030
Η	-5.68142	-3.05482	-2.47804

## **DI1T Radical Anion**

UCAM-B3LYP/6-31++G(d,p) Zero-point correction= Thermal correction to Energy= Thermal correction to Enthalpy= Thermal correction to Gibbs Free Energy= Sum of electronic and zero-point Energies= Sum of electronic and thermal Energies= Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies= NIMAG = 0

С	1.94799	4.11942	0.00310
С	1.83308	2.73021	0.00100
С	3.21242	4.70462	0.00361
С	3.01300	1.92490	-0.00045
С	4.27089	2.52068	-0.00017
С	4.36507	3.91079	0.00198
Η	5.16532	1.90406	-0.00199
Η	5.34346	4.38340	0.00221
Η	1.06232	4.74584	0.00427
Η	3.30306	5.78712	0.00523
С	2.62682	0.51601	-0.00248
С	0.70015	1.82703	-0.00023
С	1.23578	0.50367	-0.00224
С	3.50917	-0.57731	-0.00251
S	0.00000	-0.74381	-0.00407
С	-1.23578	0.50367	-0.00223
С	-0.70015	1.82703	-0.00023
С	-1.83308	2.73021	0.00101
С	-2.62682	0.51601	-0.00246
С	-3.01300	1.92490	-0.00043
С	-1.94799	4.11942	0.00311
С	-4.27088	2.52067	-0.00015
С	-3.21241	4.70462	0.00363
С	-4.36507	3.91079	0.00201
Η	-1.06232	4.74584	0.00428
Η	-3.30306	5.78711	0.00525
Η	-5.16532	1.90406	-0.00196
Η	-5.34345	4.38340	0.00224

0.444806 (Hartree/Particle) 0.478102 0.479046 0.375054 -2058.828161 -2058.794866 -2058.793921 -2058.897913

С	-3.50917	-0.57731	-0.00250
С	4.28847	-1.52013	-0.00336
Si	5.42442	-2.93673	0.00093
С	-4.28847	-1.52012	-0.00335
Si	-5.42442	-2.93673	0.00093
С	-5.70944	-3.54927	1.76173
С	-4.69630	-4.34160	-1.02205
С	-7.08060	-2.42031	-0.73782
С	4.69622	-4.34167	-1.02191
С	5.70953	-3.54918	1.76176
С	7.08056	-2.42037	-0.73794
Η	-3.72561	-4.65081	-0.62244
Η	-4.54105	-4.02936	-2.05921
Η	-5.35811	-5.21507	-1.02284
Η	-4.76626	-3.85770	2.22313
Η	-6.39345	-4.40553	1.77888
Η	-6.13788	-2.75819	2.38493
Η	3.72557	-4.65085	-0.62221
Η	5.35804	-5.21514	-1.02270
Η	4.54089	-4.02948	-2.05908
Η	4.76637	-3.85757	2.22323
Η	6.13802	-2.75806	2.38489
Η	6.39354	-4.40544	1.77892
Η	6.95664	-2.07507	-1.76888
Η	7.78968	-3.25584	-0.74047
Η	7.52492	-1.60041	-0.16514
Η	-7.52495	-1.60041	-0.16493
Η	-7.78971	-3.25579	-0.74040
Η	-6.95674	-2.07492	-1.76874

## **DI1T Dianion**

UCAM-B3LYP/6-31++G(d,p)Zero-point correction= 0.442213 (Hartree/Particle) Thermal correction to Energy= 0.475713 Thermal correction to Enthalpy= 0.476657 Thermal correction to Gibbs Free Energy= 0.372411 Sum of electronic and zero-point Energies= -2058.797119 Sum of electronic and thermal Energies= -2058.763620 Sum of electronic and thermal Enthalpies= -2058.762676 Sum of electronic and thermal Free Energies= -2058.866921 NIMAG = 0

С	-1.96138	4.10054	0.01211
С	-1.84371	2.70439	0.00652
С	-3.21726	4.69851	0.01847
С	-3.04402	1.90052	0.00746
С	-4.29859	2.52313	0.01394
С	-4.38387	3.91054	0.01938
Η	-5.20058	1.91486	0.01461
Η	-5.36013	4.39176	0.02441
Η	-1.06942	4.72052	0.01145
Η	-3.29776	5.78361	0.02274
С	-2.67242	0.50957	0.00102
С	-0.72161	1.80756	-0.00055
С	-1.24168	0.51219	-0.00370
С	-3.54520	-0.57112	-0.00026
S	0.00252	-0.72847	-0.01276
С	1.24609	0.51285	-0.01205
С	0.72540	1.80793	-0.00535
С	1.84709	2.70530	-0.00535
С	2.67682	0.51087	-0.01663
С	3.04781	1.90205	-0.01225
С	1.96399	4.10152	-0.00014
С	4.30196	2.52549	-0.01386
С	3.21951	4.70024	-0.00180
С	4.38655	3.91291	-0.00865
Η	1.07167	4.72096	0.00517
Н	3.29943	5.78537	0.00220
Н	5.20432	1.91777	-0.01967
Н	5.36254	4.39469	-0.01005

С	3.54968	-0.56971	-0.02105
С	-4.33915	-1.51613	-0.00131
Si	-5.47090	-2.89818	-0.00313
С	4.34126	-1.51671	-0.02839
Si	5.46945	-2.90140	0.00762
С	6.97412	-2.59983	-1.10675
С	4.61708	-4.48486	-0.58232
С	6.15385	-3.25367	1.74296
С	-5.25356	-4.01577	1.51347
С	-5.25297	-4.01171	-1.52255
С	-7.26553	-2.28942	-0.00239
Η	4.26668	-4.37379	-1.61323
Η	3.74198	-4.70303	0.03801
Η	5.29410	-5.34677	-0.53729
Η	6.66070	-2.46141	-2.14636
Η	7.68083	-3.43812	-1.06633
Η	7.50346	-1.69155	-0.80001
Η	-4.22906	-4.39879	1.56319
Η	-5.93945	-4.87200	1.48701
Η	-5.43698	-3.45376	2.43487
Η	-4.22832	-4.39419	-1.57322
Η	-5.43653	-3.44738	-2.44250
Η	-5.93853	-4.86825	-1.49835
Η	-7.46419	-1.67427	0.88113
Η	-7.97161	-3.12884	-0.00306
Η	-7.46436	-1.67267	-0.88475
Η	6.68105	-2.37674	2.13321
Η	6.85063	-4.10176	1.74123
Η	5.33797	-3.47963	2.43715

## **DI2T Neutral**

UCAM-B3LYP/6-31G(d,p) Zero-point correction= Thermal correction to Energy= 0.498623 Thermal correction to Enthalpy= 0.499567 Thermal correction to Gibbs Free Energy= 0.389852 Sum of electronic and zero-point Energies= -2533.040684 Sum of electronic and thermal Energies= -2533.005123 Sum of electronic and thermal Enthalpies= -2533.004179 Sum of electronic and thermal Free Energies= -2533.113894 NIMAG = 0

С	4.07561	3.49564	-0.11229
С	3.20184	2.42553	-0.07788
С	1.80398	2.63860	-0.08716
С	1.28393	3.92068	-0.13100
С	1.18186	1.32102	-0.04381
С	2.17037	4.99840	-0.16571
Η	0.21176	4.08979	-0.13835
С	3.54523	4.78691	-0.15638
Η	1.78196	6.01058	-0.20021
Η	4.21720	5.63849	-0.18375
Н	5.14807	3.33146	-0.10499
С	3.47382	0.96806	-0.02864
С	2.26383	0.34784	-0.00955
С	4.75780	0.38065	-0.00730
S	1.69141	-1.31324	0.04584
С	0.03465	-0.72812	0.02395
С	-0.03348	0.73074	-0.02549
S	-1.69023	1.31584	-0.04716
С	-2.26267	-0.34524	0.00830
С	-1.18069	-1.31841	0.04249
С	-1.80276	-2.63600	0.08627
С	-3.20062	-2.42295	0.07732
С	-1.28270	-3.91807	0.13045
С	-3.47262	-0.96550	0.02768
С	-4.07444	-3.49300	0.11253
С	-4.75682	-0.37858	0.00620
С	-2.16916	-4.99576	0.16585
Η	-0.21054	-4.08720	0.13761

0.463062 (Hartree/Particle)

С	-3.54403	-4.78425	0.15694
Η	-5.14691	-3.32878	0.10588
Η	-1.78075	-6.00792	0.20066
Η	-4.21599	-5.63582	0.18502
С	5.86787	-0.11460	0.01072
Si	7.54086	-0.88138	0.03869
С	7.35853	-2.68171	0.53848
С	8.59984	0.04180	1.28481
С	8.28952	-0.75030	-1.67858
Η	7.67699	-1.27178	-2.41887
Н	9.29024	-1.19324	-1.69931
Н	8.37893	0.29253	-1.99449
Н	8.16859	-0.01122	2.28800
Η	8.69798	1.09772	1.01872
Н	9.60609	-0.38647	1.32941
Н	6.90672	-2.77443	1.52967
Η	8.33457	-3.17600	0.56758
Η	6.72821	-3.22759	-0.16863
С	-5.86751	0.11525	-0.01154
Si	-7.54251	0.87760	-0.03825
С	-7.47622	2.49142	0.91892
С	-8.75046	-0.31375	0.76682
С	-8.02979	1.19393	-1.82393
Η	-7.17916	2.32397	1.95761
Η	-8.45629	2.97862	0.92488
Η	-6.75957	3.18732	0.47460
Н	-7.32683	1.87389	-2.31248
Η	-9.02566	1.64477	-1.87897
Η	-8.05049	0.26505	-2.40012
Η	-8.46854	-0.52677	1.80141
Η	-8.78962	-1.26437	0.22808
Η	-9.76070	0.10721	0.77492

## **DI2T Radical Anion**

UCAM-B3LYP/6-31++G(d,p)Zero-point correction= Thermal correction to Energy= Thermal correction to Enthalpy= Thermal correction to Gibbs Free Energy= Sum of electronic and zero-point Energies= Sum of electronic and thermal Energies= Sum of electronic and thermal Enthalpies= Sum of electronic and thermal Free Energies= -2533.248975 NIMAG = 0

С	-4.21159	-3.38926	-0.00394
С	-3.31638	-2.32209	-0.00479
С	-1.91111	-2.57068	-0.00592
С	-1.42996	-3.87850	-0.00620
С	-1.25784	-1.28240	-0.00644
С	-2.33681	-4.93529	-0.00538
Η	-0.36109	-4.07301	-0.00706
С	-3.71594	-4.69068	-0.00424
Η	-1.97135	-5.95801	-0.00561
Η	-4.40836	-5.52791	-0.00363
Η	-5.28185	-3.20355	-0.00314
С	-3.54674	-0.87917	-0.00471
С	-2.28392	-0.29342	-0.00581
С	-4.80016	-0.24338	-0.00226
S	-1.64880	1.34103	-0.00591
С	-0.00921	0.70770	-0.00633
С	0.00920	-0.70771	-0.00660
S	1.64880	-1.34104	-0.00635
С	2.28391	0.29341	-0.00559
С	1.25784	1.28239	-0.00590
С	1.91111	2.57067	-0.00485
С	3.31637	2.32209	-0.00376
С	1.42996	3.87849	-0.00465
С	3.54674	0.87917	-0.00422
С	4.21158	3.38925	-0.00246
С	4.80016	0.24338	-0.00195
С	2.33681	4.93528	-0.00339
Н	0.36108	4.07300	-0.00549

0.459072 (Hartree/Particle)
0.494818
0.495763
0.385295
-2533.175198
-2533.139451
-2533.138507

С	3.71593	4.69067	-0.00229
Η	5.28184	3.20354	-0.00169
Η	1.97134	5.95800	-0.00325
Η	4.40835	5.52790	-0.00132
С	-5.89532	0.30046	0.00009
Si	-7.51188	1.13178	0.00846
С	-7.25687	2.99101	-0.14876
С	-8.42389	0.76311	1.61691
С	-8.55965	0.52167	-1.43529
Η	-8.06651	0.73011	-2.38961
Η	-9.54154	1.00827	-1.44483
Η	-8.71772	-0.55963	-1.37436
Η	-7.84865	1.11356	2.47929
Η	-8.57984	-0.31324	1.73958
Η	-9.40395	1.25313	1.63854
Η	-6.65148	3.37340	0.67866
Η	-8.21506	3.52251	-0.14385
Η	-6.73625	3.23630	-1.07939
С	5.89532	-0.30046	0.00024
Si	7.51189	-1.13177	0.00841
С	7.25690	-2.99096	-0.14934
С	8.42385	-0.76353	1.61699
С	8.55969	-0.52124	-1.43514
Η	6.65151	-3.37359	0.67796
Η	8.21510	-3.52244	-0.14457
Η	6.73630	-3.23599	-1.08004
Η	8.06659	-0.72942	-2.38953
Η	9.54159	-1.00782	-1.44479
Η	8.71774	0.56005	-1.37391
Η	7.84860	-1.11425	2.47925
Η	8.57977	0.31278	1.73998
Η	9.40393	-1.25353	1.63850

# **DI2T** Dianion

UCAM-B3LYP/ $6-31++G(d,p)$	
Zero-point correction=	0.456790 (Hartree/Particle)
Thermal correction to Energy=	0.492717
Thermal correction to Enthalpy=	0.493661
Thermal correction to Gibbs Free Energy=	0.383872
Sum of electronic and zero-point Energies=	-2533.159282
Sum of electronic and thermal Energies=	-2533.123355
Sum of electronic and thermal Enthalpies=	-2533.122411
Sum of electronic and thermal Free Energies=	-2533.232201
NIMAG = 0	

С	4.26785	3.38184	-0.01673
С	3.37813	2.29933	-0.01833
С	1.95863	2.55021	-0.02045
С	1.48655	3.86803	-0.02107
С	1.30352	1.27556	-0.02133
С	2.38848	4.92602	-0.01961
Н	0.41642	4.06204	-0.02268
С	3.77505	4.68087	-0.01742
Н	2.02113	5.94968	-0.02012
Н	4.46863	5.51933	-0.01630
Η	5.33993	3.19867	-0.01518
С	3.60419	0.87589	-0.01804
С	2.29996	0.29414	-0.02008
С	4.84110	0.23817	-0.01184
S	1.64345	-1.33004	-0.02079
С	0.00295	-0.68926	-0.02210
С	-0.00294	0.68926	-0.02217
S	-1.64345	1.33004	-0.02095
С	-2.29996	-0.29414	-0.02011
С	-1.30351	-1.27556	-0.02123
С	-1.95863	-2.55021	-0.02025
С	-3.37813	-2.29933	-0.01817
С	-1.48654	-3.86802	-0.02073
С	-3.60418	-0.87588	-0.01803
С	-4.26785	-3.38184	-0.01648
С	-4.84110	-0.23817	-0.01190
С	-2.38847	-4.92601	-0.01917
Н	-0.41641	-4.06203	-0.02230

С	-3.77505	-4.68087	-0.01703
Η	-5.33993	-3.19866	-0.01496
Η	-2.02113	-5.94967	-0.01958
Η	-4.46863	-5.51933	-0.01583
С	5.94404	-0.31148	-0.00690
Si	7.53776	-1.12707	0.03143
С	7.33030	-2.99939	-0.12974
С	8.47601	-0.78915	1.64397
С	8.66210	-0.54360	-1.37868
Н	8.20645	-0.76314	-2.34944
Н	9.64427	-1.03093	-1.33945
Η	8.81583	0.53934	-1.32618
Η	7.90266	-1.14967	2.50394
Н	8.63034	0.28624	1.78130
Η	9.45725	-1.28012	1.65278
Η	6.70855	-3.39030	0.68175
Η	8.29894	-3.51276	-0.09911
Н	6.83564	-3.25378	-1.07230
С	-5.94404	0.31148	-0.00703
Si	-7.53776	1.12706	0.03139
С	-7.33050	2.99918	-0.13247
С	-8.47485	0.79134	1.64505
С	-8.66307	0.54160	-1.37712
Н	-6.70809	3.39120	0.67798
Η	-8.29912	3.51256	-0.10172
Η	-6.83662	3.25232	-1.07578
Н	-8.20817	0.75989	-2.34851
Н	-9.64526	1.02889	-1.33780
Η	-8.81666	-0.54128	-1.32306
Η	-7.90087	1.15302	2.50412
Η	-8.62909	-0.28386	1.78395
Η	-9.45608	1.28234	1.65392

## **DI3T Neutral**

UCAM-B3LYP/6-31G(d,p) Zero-point correction= 0.476970 (Hartree/Particle) Thermal correction to Energy= 0.515018 Thermal correction to Enthalpy= 0.515962 Thermal correction to Gibbs Free Energy= 0.400435 Sum of electronic and zero-point Energies= -3007.373585 Sum of electronic and thermal Energies= -3007.335538 Sum of electronic and thermal Enthalpies= -3007.334594 Sum of electronic and thermal Free Energies= -3007.450121 NIMAG = 0

С	-6.14426	-2.29908	0.00174
С	-4.89363	-1.70945	0.00162
С	-6.22368	-3.69286	0.00177
С	-5.07472	-4.47804	0.00164
С	-3.72473	-2.50607	0.00140
С	-3.81027	-3.88826	0.00143
С	-4.51073	-0.27776	0.00156
С	-2.59609	-1.58565	0.00107
С	-3.15007	-0.24067	0.00119
С	-5.41514	0.80620	0.00162
S	-1.91719	1.01190	0.00067
С	-1.24379	-1.57253	0.00053
С	-0.67621	-0.23443	0.00028
С	0.67622	-0.23443	-0.00029
С	1.24379	-1.57254	-0.00054
S	0.00000	-2.81411	-0.00001
С	2.59609	-1.58565	-0.00107
С	3.15007	-0.24068	-0.00120
S	1.91720	1.01190	-0.00068
С	3.72473	-2.50607	-0.00140
С	4.89364	-1.70946	-0.00161
С	4.51073	-0.27776	-0.00155
С	5.41514	0.80619	-0.00161
Н	-2.91685	-4.50493	0.00128
Н	-5.16182	-5.55922	0.00167
Н	-7.04067	-1.68783	0.00168
Н	-7.19764	-4.17128	0.00184
С	3.81027	-3.88826	-0.00143

С	5.07472	-4.47804	-0.00164
С	6.22368	-3.69287	-0.00175
С	6.14426	-2.29909	-0.00172
Η	2.91685	-4.50494	-0.00128
Η	5.16182	-5.55922	-0.00166
Η	7.19764	-4.17128	-0.00182
Η	7.04067	-1.68784	-0.00166
С	6.20350	1.73175	-0.00134
Si	7.38808	3.13985	0.00115
С	-6.20350	1.73175	0.00136
Si	-7.38810	3.13984	-0.00115
С	6.82671	4.39115	1.28349
С	7.40236	3.91793	-1.70792
С	9.09226	2.47852	0.43185
С	-7.40305	3.91739	1.70815
С	-9.09209	2.47863	-0.43275
С	-6.82621	4.39155	-1.28286
Η	9.09687	2.00532	1.41742
Η	9.82886	3.28788	0.44578
Η	9.42627	1.73598	-0.29790
Н	5.82513	4.76729	1.05846
Η	7.50744	5.24775	1.31167
Η	6.80089	3.95047	2.28363
Н	8.09990	4.76071	-1.74261
Н	6.41219	4.29148	-1.98226
Н	7.70993	3.19690	-2.46996
Η	-5.82470	4.76758	-1.05732
Н	-7.50689	5.24820	-1.31099
Н	-6.80003	3.95123	-2.28315
Η	-7.71084	3.19612	2.46988
Η	-8.10064	4.76013	1.74286
Н	-6.41299	4.29091	1.98296
Η	-9.42642	1.73590	0.29667
Η	-9.09626	2.00567	-1.41844
Η	-9.82868	3.28799	-0.44680

## **DI3T Radical Anion**

UCAM-B3LYP/6-31++G(d,p)Zero-point correction=0.4Thermal correction to Energy=0.5Thermal correction to Enthalpy=0.5Thermal correction to Gibbs Free Energy=0.3Sum of electronic and zero-point Energies=-30Sum of electronic and thermal Free Energies=-30NIMAG = 0-30

С	6.18998	-2.32068	0.00125
С	4.93936	-1.70687	0.00111
С	6.26311	-3.71100	0.00113
С	5.10098	-4.49305	0.00088
С	3.75533	-2.50307	0.00084
С	3.84434	-3.89396	0.00074
С	4.56729	-0.29403	0.00106
С	2.63834	-1.58870	0.00071
С	3.17681	-0.26837	0.00089
С	5.45642	0.79531	0.00115
S	1.93882	0.97404	0.00072
С	1.24775	-1.57160	0.00044
С	0.69588	-0.26928	0.00049
С	-0.69229	-0.26898	0.00021
С	-1.24477	-1.57104	-0.00018
S	0.00121	-2.80299	-0.00006
С	-2.63538	-1.58750	-0.00052
С	-3.17328	-0.26694	-0.00026
S	-1.93469	0.97487	0.00027
С	-3.75276	-2.50143	-0.00104
С	-4.93643	-1.70473	-0.00104
С	-4.56377	-0.29204	-0.00052
С	-5.45289	0.79728	-0.00016
Η	2.94626	-4.50545	0.00053
Н	5.18084	-5.57607	0.00078
Η	7.09342	-1.71772	0.00131
Η	7.23494	-4.19651	0.00120
С	-3.84241	-3.89226	-0.00154

0.473045 (Hartree/Particle)
0.511285
0.512229
0.396153
-3007.518003
-3007.479764
-3007.478820
-3007.594896

С	-5.09936	-4.49073	-0.00204
С	-6.26113	-3.70815	-0.00203
С	-6.18740	-2.31784	-0.00153
Η	-2.94463	-4.50419	-0.00156
Η	-5.17972	-5.57372	-0.00244
Η	-7.23318	-4.19321	-0.00243
Η	-7.09058	-1.71446	-0.00153
С	-6.23505	1.73653	0.00022
Si	-7.38483	3.14656	0.00125
С	6.23663	1.73618	0.00086
Si	7.38182	3.15018	-0.00096
С	-7.10643	4.20854	-1.52998
С	-7.11081	4.20277	1.53725
С	-9.15536	2.50131	-0.00245
С	8.59216	2.99190	-1.43703
С	8.35441	3.19731	1.61291
С	6.39797	4.74511	-0.18300
Η	-9.34573	1.88620	-0.88730
Η	-9.87491	3.32761	-0.00199
Η	-9.34825	1.88303	0.87963
Η	-6.07977	4.58606	-1.56149
Η	-7.78528	5.06869	-1.54290
Η	-7.27297	3.62882	-2.44297
Н	-6.08427	4.58025	1.57305
Н	-7.27980	3.61954	2.44756
Η	-7.78979	5.06278	1.55160
Н	5.82900	4.74885	-1.11761
Н	7.05952	5.61851	-0.18338
Н	5.68434	4.85983	0.63850
Η	9.17031	2.06575	-1.36058
Η	9.29665	3.83109	-1.45523
Η	8.06123	2.97196	-2.39359
Η	8.92847	2.27570	1.75039
Η	7.68187	3.29827	2.47015
Η	9.05536	4.03957	1.62828

## **DI3T Dianion**

UCAM-B3LYP/6-31++G(d,p)Zero-point correction= Thermal correction to Energy= 0.509493 Thermal correction to Enthalpy= 0.510437 Thermal correction to Gibbs Free Energy= 0.394727 Sum of electronic and zero-point Energies= -3007.516246 -3007.477803 Sum of electronic and thermal Energies= Sum of electronic and thermal Enthalpies= -3007.476858 Sum of electronic and thermal Free Energies= -3007.592569 NIMAG = 0

С	6.23630	2.32246	-0.00002
С	4.98782	1.68616	-0.00002
С	6.30279	3.70966	-0.00001
С	5.12980	4.48844	-0.00001
С	3.78808	2.48293	-0.00002
С	3.88060	3.87977	-0.00001
С	4.62741	0.29019	-0.00003
С	2.68036	1.57474	-0.00002
С	3.20379	0.27583	-0.00003
С	5.50715	-0.79130	-0.00002
S	1.95893	-0.95867	-0.00003
С	1.25122	1.55585	-0.00002
С	0.71212	0.28281	-0.00003
С	-0.71215	0.28281	-0.00002
С	-1.25125	1.55585	-0.00001
S	-0.00001	2.78121	-0.00001
С	-2.68039	1.57475	-0.00001
С	-3.20383	0.27585	-0.00002
S	-1.95897	-0.95866	-0.00003
С	-3.78810	2.48295	0.00002
С	-4.98785	1.68618	0.00002
С	-4.62745	0.29021	-0.00000
С	-5.50719	-0.79127	-0.00001
Η	2.97771	4.48603	-0.00001
Η	5.20237	5.57337	-0.00001
Η	7.14565	1.72614	-0.00002
Η	7.27315	4.20151	-0.00001
С	-3.88062	3.87979	0.00003

0.471050 (Hartree/Particle)

С	-5.12982	4.48847	0.00005
С	-6.30281	3.70969	0.00005
С	-6.23632	2.32249	0.00004
Η	-2.97773	4.48604	0.00003
Η	-5.20238	5.57339	0.00006
Η	-7.27316	4.20154	0.00007
Η	-7.14568	1.72617	0.00004
С	-6.29781	-1.73430	-0.00001
Si	-7.43862	-3.11928	-0.00000
С	6.29778	-1.73432	-0.00002
Si	7.43866	-3.11923	0.00003
С	-7.21031	-4.22179	1.52162
С	-7.21154	-4.22085	-1.52249
С	-9.22451	-2.49378	0.00088
С	7.21083	-4.22142	1.52195
С	9.22451	-2.49359	0.00035
С	7.21131	-4.22115	-1.52216
Η	-9.41826	-1.87689	0.88414
Н	-9.93767	-3.32673	0.00097
Н	-9.41899	-1.87645	-0.88191
Η	-6.18709	-4.60834	1.56708
Η	-7.89854	-5.07579	1.50656
Н	-7.38621	-3.65321	2.44028
Η	-7.89976	-5.07487	-1.50742
Н	-6.18836	-4.60736	-1.56903
Н	-7.38819	-3.65170	-2.44065
Η	6.18813	-4.60771	-1.56841
Η	7.89956	-5.07514	-1.50703
Η	7.38775	-3.65221	-2.44050
Η	7.38699	-3.65264	2.44044
Η	7.89908	-5.07541	1.50688
Η	6.18764	-4.60799	1.56781
Η	9.41844	-1.87654	0.88345
Η	9.41871	-1.87640	-0.88259
Η	9.93774	-3.32649	0.00040



Table S2 Bond distances (Å) for DI1T-TMSE

Fig. S10 Calculated bond distances upon reduction of DI1T, R = TMSE.

bond #	neutral	radical anion	dianion
1	1.382	1.393	1.401
2	1.397	1.393	1.389
3	1.391	1.401	1.408
4	1.396	1.393	1.390
5	1.384	1.394	1.400
6	1.414	1.427	1.442
7	1.483	1.461	1.441
8	1.360	1.392	1.428
9	1.456	1.425	1.399
10	1.458	1.444	1.433
11	1.351	1.391	1.432
12	1.461	1.416	1.379



 Table S3 Bond distances (Å) for DI2T-TMSE

Fig. S11 Calculated bond distances upon reduction of DI2T, R = TMSE.





Fig. S12 Calculated bond distances upon reduction of DI3T, R = TMSE.

#### References

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 $\mathsf{GER}\text{-}1\text{-}281\text{-}3\text{-}\mathsf{H}$ 



GER-1-281-3_C	—167.92	$\int_{122.62}^{141.38} 141.38$ $\int_{131.98}^{131.98} 131.74$ $\int_{122.62}^{122.62} 122.62$	60.84	—13.84
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230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 f1 (ppm) 30 20 80 70 60 50 40 10 0 -10 S40

GER-1-131-2/H















DI1T-TESE









87	82	42	86	56	08	19	67
36.	36.	33.	29.	28.	28.	18.	16.
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 $\mathsf{GER}\text{-}2\text{-}181\text{-}2\text{-}\mathsf{H}$ 













![](_page_55_Figure_0.jpeg)

![](_page_56_Figure_1.jpeg)

GER-2-119-3_C 92. 192. 	$\int_{122.45}^{142.24} 135.53 \\ \int_{131.73}^{131.73} 131.27 \\ 130.40 \\ 130.40 \\ 122.45$	-61.13	-13.75
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100 90 f1 (ppm) S58 (

![](_page_58_Picture_1.jpeg)

![](_page_58_Figure_2.jpeg)

![](_page_58_Figure_3.jpeg)

GER-2-125-3\_H

![](_page_59_Figure_1.jpeg)

![](_page_60_Figure_0.jpeg)

![](_page_61_Figure_0.jpeg)