## **Supporting Information**

## Anthroxyl-Based Biradical: Toward the Construction of Highly Stable Multi-Spin Systems

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**4,4'-di**(*tert*-butylphenyl)methane (5a). To a solution of diphenylmethane (20.0 g, 119 mmol) and *tert*-butyl chloride (33 ml, 303 mmol) in a 500-mL round-bottomed flask at 0 °C, anhydrous aluminium chloride (0.14 g, 1.02 mmol) was added. After stirring for 5 minutes, a second portion of anhydrous aluminium chloride (0.16 g, 1.23 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. The resulting viscous yellowish brown solid was recrystallized from hot isopropanol. After cooling in a refrigerator, **5a** (24.0 g, 72%) was obtained as a colorless solid: <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  /ppm 1.31 (s, 18H), 3.93 (s, 2H), 7.14 (AA'XX', 4H), 7.31 (AA'XX', 4H).

(2,2'-dibromo-4,4'-di-*tert*-butylphenyl)methane (6a). A solution of 5a (20.0 g, 72 mmol) and iron powder (0.36 g, 6.4 mmol) in dichloromethane (72 mL) was prepared in 200-mL round-bottomed flask and cooled on the ice-bath. To the solution was added bromine (7.7 mL, 150 mmol) dissolved in dichloromethane (36 mL) over 30 minutes, and the reaction mixture was allowed to warm to room temperature. After stirring for 1 h, aqueous NaHSO<sub>3</sub> was added, and the aqueous layer was extracted twice with dichloromethane. The combined organic layer was washed with water and brine dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. After column chromatography on alumina, **6a** (30.9 g, 99%) was obtained as a vivid yellow solid: <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  /ppm 1.30 (s, 18H), 4.13 (s, 2H), 6.92 (d, *J* = 8.1 Hz, 2H), 7.23 (dd, *J* = 8.1, 2.2 Hz, 2H), 7.59 (d, *J* = 2.2 Hz, 2H).

**2,7-di-***tert*-**butyl-9,10-dihydro-9-oxoanthracene (7a).** *n*-Butyl lithium (1.6 M in hexane, 27.5 mL, 44.0 mmol) was added slowly to a solution of **6a** in THF (150 mL) at -78 °C in a 300-mL round-bottomed flask under argon atmosphere. After stirring for 2 h at -78 °C, dimethyl calbamyl chloride (1.9 mL, 21 mmol) was added, and the mixture was stirred for 30 minutes. After addition of aqueous NH<sub>4</sub>Cl, the aqueous mixture was extracted with a mixture of hexane and ethyl acetate. The combined organic layer was washed with water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed in vacuo, and column chromatography on silica gel (hexane/dichloromethane = 2:1  $\nu/\nu$ ) afforded the colorless solid **7a** (4.74 g, 77%): mp 117.8 –118.8 °C. *R*<sub>f</sub> = 0.45 (CH<sub>2</sub>Cl<sub>2</sub>/Hex 1:2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  /ppm 1.40 (s, 18H), 4.29 (s 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.65 (dd, *J* = 8.6, 2.4 Hz, 2H), 8.40 (d, *J* = 2.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  /ppm 31.37, 31.69, 34.86, 123.83 128.20, 130.05, 131.74, 137.74, 149.95, 184.69. IR (KBr,  $\nu$ /cm<sup>-1</sup>) 2961 (s), 1658 (s), 1604 (s), 1497 (m), 1472 (w), 1408 (w), 1361 (m), 1308 (m), 1249 (s), 1171 (w), 1138 (w), 926 (w), 825 (w), 772 (m). MS (EI) m/z (rel intensity) 306 [M]+ (39), 291 (56), 250 (100), 235 (39). Anal. Calcd for C<sub>22</sub>H<sub>26</sub>O: C, 86.20; H, 8.55; O, 5.22. Found: C, 85.83; H, 8.55.

**2,7-di-***tert***-butyl-9-methoxyanthracene (8a).** To a solution of **7a** (2.53 g, 8.3 mmol) and potassium carbonate (4.84 g, 35 mmol) in acetone (100 mL) at argon atmosphere, dimethyl sulfate (2 mL, 21 mmol) was added and the reaction mixture was refluxed for 6 h. After cooling to room temperature, water was added to the mixture. The aqueous mixture was extracted with a mixture of hexane and dichloromethane. The combined organic layer was washed with water and brine, dried over anhydrous  $Na_2SO_4$ , and filtered. The solvent was removed in vacuo, and

the resulting crude product was recrystallized from hexane to give **8a** (2.11 g, 80%) as a pale yellow solid: mp 136.8–137.2 °C.  $R_f = 0.51$  (CH<sub>2</sub>Cl<sub>2</sub>/Hex 1:3). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  /ppm 1.48 (s, 18H), 4.16 (s, 3H), 7.55 (dd, J = 8.6, 1.6 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 8.12 (s, 1H), 8.18 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm 31.12, 35.22, 62.65, 116.09, 120.98, 124.36, 124.60, 128.10, 130.70, 147.42, 151.70. IR (KBr, v /cm<sup>-1</sup>) 3060 (w), 3004 (w), 2956 (s), 2867 (s), 1765 (w), 1676 (w), 1628 (m), 1446 (s), 1362 (s), 1334 (s), 1282 (m), 1111 (s), 1073 (s), 1024 (w), 976 (s), 934 (w), 887 (s), 802 (s), 748 (w). MS (EI) m/z (rel intensity) 320 [M]<sup>+</sup> (82), 305 (100), 290 (31). Anal. Calcd for C<sub>23</sub>H<sub>28</sub>O<sub>2</sub>: C, 86.20; H 8.81; O, 4.99. Found: C, 86.31; H, 8.76.

**10-bromo-2,7-di***-tert*-**butyl-9-methoxyanthracene (2a).** A solution of **8a** (2.11 g, 6.6 mmol) in DMF (50 mL) was prepared in 200-mL round-bottomed flask under argon atmosphere, and cooled on ice-bath. After addition of NBS (1.35 g, 7.6 mmol) in DMF (30 mL), the reaction mixture was stirred for 3 h. A mixture of hexane and dichloromethane was added to the solution, and the organic layer was washed with water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed in vacuo, and column chromatography on silica gel (hexane/dichloromethane = 2:1 *v/v*) afforded the pale yellow solid **2a** (1.08 g, 41%): mp 129.8–130.7 °C. *R*<sub>f</sub> = 0.64 (CH<sub>2</sub>Cl<sub>2</sub>/Hex 1:4). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  /ppm 1.48 (s, 18H), 4.15 (s, 3H), 7.68 (dd, *J* = 9.3, 2.0 Hz, 2H), 8.19 (d, *J* = 2.0 Hz, 2H), 8.43 (d, *J* = 9.3 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  /ppm 31.04, 35.11, 62.93, 116.33, 116.47, 125.28, 126.41, 127.65, 129.31, 147.89, 151.93. IR (KBr, v /cm<sup>-1</sup>) 3076 (w), 2959 (s), 2903 (m), 2868 (m), 1622 (w), 1480 (m), 1450 (s), 1363 (s), 1325 (s), 1265 (m), 1115 (s), 1074 (s), 1025 (w), 987 (w), 969 (s), 916 (s), 892 (s), 862 (w), 818 (s). MS (EI) m/*z* (rel intensity) 400 [M+2<sup>+</sup>, 86], 398 [M]<sup>+</sup> (87), 385 (99), 383 (100). Anal. Calcd for C<sub>23</sub>H<sub>27</sub>BrO: C, 69.17; H, 6.81; Br, 20.01; O 4.01. Found: C, 69.05; H, 6.71.

**9-methoxyanthracene (8b).** A solution of 9,10-dihydro-9-oxoanthracene (anthrone) (2.89 g, 20 mmol) and potassium carbonate (11.1 g, 81 mmol) in acetone (100 mL) was prepared in 300-mL round-bottomed flask under argon atmosphere. Dimethyl sulfate (4 mL, 42 mmol) was added to the solution, and the reaction mixture was refluxed for 6 h. After cooling, water was added to the mixture and the product was extracted with a mixture of hexane and dichloromethane. The combined organic layer was washed with water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtrated. The solvent was removed in vacuo to give **8b** (4.46 g, quant) as a pale yellow solid: <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  /ppm 4.16 (s, 3H), 7.44-7.52 (m, 4H), 8.00 (m, 2H), 8.23 (s, 1H), 7.28 (m, 2H).

**10-bromo -9-methoxyanthracene (2b).** A solution of **8b** (5.00 g, 24 mmol) in DMF (60 mL) was prepared in 200-mL round-bottomed flask under argon atmosphere, and cooled on ice-bath. After addition of NBS (4.72 g, 27 mmol) in DMF (40 mL), the reaction mixture was stirred over night. A mixture of hexane and dichloromethane was added to the solution, and the organic layer was washed with water and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and filtered. The solvent was removed in vacuo, and column chromatography on silica gel (hexane/dichloromethane = 2:1 *v/v*) afforded the pale yellow solid **2b** (3.37 g, 67%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  /ppm 4.15 (s, 3H), 7.53 (m, 2H), 7.61 (m, 2H), 8.33 (d, *J* = 8.8 Hz, 2H), 8.54 (d, *J* = 8.8 Hz, 2H). MS (EI) m/z (rel intensity) 288 [M+2]<sup>+</sup> (29), 286 (30), 273 (50), 271 (54), 163 (100).



*Figure S1* Temporal change in the optical absorption spectrum of **1b** after exposing it to the refluxed ethanol in air. The blue solid line represents the spectrum obtained after 1 h. The red solid line represents the spectrum obtained after 1 week.



*Figure S2* Crystal packing of **1a** at 120 K. Ethyl acetate solvates were disordered. Hydrogen atoms and <sup>*t*</sup>Bu groups were omitted for clarity.



*Figure S3* (a) Molecular structure of **1b** at 240 K (50% probability). Hydrogen atoms are omitted for clarity. (b) Crystal packing of **1b** at 240 K. Dioxane solvates were disordered. Hydrogen atoms were omitted for clarity.



*Figure S4* UV-Vis spectra of the electrochemical oxidation and reduction of **1a** in  $CH_2Cl_2$  with 0.1 M ( $^nBu$ )<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte at room temperature. A constant voltage of a) +1.4 V, b) +0.2 V, and c) -1.4 V was applied during spectral measurements.



*Figure S5* The ESR spectra at 123 K for (a) the as-prepared **1b** in toluene and for (b) the redissolved **1b** in toluene after exposing it to the refluxed ethanol in air for 1 week.