## **Supporting Information**

## **Radical-Site-Dependent Exchange Interactions**

## in Acridane-Based Bisnitroxides

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## **Materials and methods**

Compounds 2,5-dibromoaniline, 1,4-dibromo-2-iodobenzene,  $Pd_2(dba)_3$ ·CHCl<sub>3</sub> (dba = *trans,trans*dibenzylideneacetone) and 10-methyl-9(10*H*)acridone were prepared according to the reported procedure.<sup>S1–S4</sup> Solvents toluene and *N,N*-dimethylformamide (DMF) were purchased and dried over a molecular sieve (4A). Dehydrated diethyl ether was purchased. The other materials and organic solvents were purchased and used without further purification. Melting point measurement was performed using ATM-02 (ASONE). Electronic spectra (ultraviolet-visible, UV-Vis) were obtained on a JASCO V-650 spectrometer. Infrared (IR) spectra were obtained on an FT/IR-4600 spectrometer (JASCO) using a diamond attenuated total reflectance (ATR) method. The spectral data are obtained by recording the major peaks in wavenumbers (cm<sup>-1</sup>) and are recorded in a spectral window of 4000– 400 cm<sup>-1</sup>. NMR experiments (<sup>1</sup>H and <sup>13</sup>C for 400 and 100 MHz, respectively) were performed on JNM-ECZ400S (JEOL) at room temperature (RT). The chemical shift (given in ppm) was measured against a reference peak of tetramethylsilane (TMS). The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet) and dd (doublet of doublets). High-resolution mass spectra (HRMS) were recorded in electrospray ionization (ESI) mode using an AccuTOF-JMS-T100LP spectrometer (JEOL). Elemental analyses were performed on a Perkin Elmer Series II CHNS/O 2400 analyzer.

#### Synthesis of 2,4-dibromo-N-(2,5-dibromophenyl)aniline (2-mp)



Compounds 2,4-dibromoaniline (7.47 g, 30 mmol), 1,4-dibromo-2-iodobenzene (10.83 g, 30 mmol), sodium *tert*-butoxide (4.09 g, 36 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (1.55 g, 1.5 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (dppf, 1.46 g, 2.6 mmol) were dissolved in degassed toluene (80 mL) under an Ar gas. The solution

was refluxed for 3 days and then cooled to RT. The mixture was extracted with CHCl<sub>3</sub> and washed with brine. The organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered and condensed under the reduced pressure. The residue was purified by silica-gel column chromatography (9/1 *n*-hexane/THF). Recrystallization from THF/*n*-hexane gave a colorless solid **2-mp** (8.14 g, 17 mol, 56%) from the initial brown residue. Mp. 153–155 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>; Fig. S14a):  $\delta$  7.89 (d, *J* = 2.3 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.53–7.50 (m, 2H), 7.09 (dd, *J* = 8.7 Hz, *J*' = 2.3 Hz, 1H) and 7.00–6.96 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>; Fig. S14b):  $\delta$  141.22, 138.47, 135.68, 134.37, 131.52, 125.46, 121.99, 120.25, 119.74, 115.78, 114.88 and 112.34. HRMS (ESI+): *m/z* calcd. for C<sub>12</sub>H<sub>7</sub>Br<sub>4</sub>N, 482.72917 [M]<sup>+</sup>; found, 482.72995. IR (ATR): 1578, 1507, 1465, 1021, 870, 803, 785, 457, 429 and 420 cm<sup>-1</sup>. UV-vis (ethanol)  $\lambda_{max}$ /nm (log  $\varepsilon$ ) 289 (4.07).

## Synthesis of bis(2,5-dibromophenyl)aniline (2-mm)



Compounds 2,5-dibromoaniline (12.55 g, 50 mmol), 1,4-dibromo-2-iodobenzene (18.09 g, 50 mmol), sodium *tert*-butoxide (9.54 g, 85.0 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (1.55 g, 1.5 mmol) and dppf (0.83 g, 1.5 mmol) were dissolved in degassed toluene (80 mL) under an Ar gas. The solution was refluxed for 3 days and then cooled to RT. The

mixture was extracted with CHCl<sub>3</sub> and washed with brine. The organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered and condensed under the reduced pressure. The residue was purified by silica-gel column chromatography (9/1 *n*-hexane/THF) to give a colorless solid **2-mm** (17.7 g, 37 mol, 73%). Mp. 128–129 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>; Fig. S15a):  $\delta$  7.44 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 2.3 Hz, 2H), 7.01 (dd, *J* = 8.2, *J*' = 2.3 Hz, 2H) and 6.39 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>; Fig. S15b):  $\delta$  140.60, 134.30, 126.10, 121.90, 120.82 and 113.03. HRMS (ESI+): *m/z* calcd. for C<sub>12</sub>H<sub>7</sub>Br<sub>4</sub>N, 482.72917 [M]<sup>+</sup>; found, 482.73085. IR (ATR): 1576, 1506, 1464, 1394, 1023, 833, 786, 565, 430 and 423 cm<sup>-1</sup>. UV-vis (ethanol)  $\lambda_{max}$ /nm (log  $\varepsilon$ ) 220 (4.42).

### Synthesis of N-benzyl-2,4-dibromo-N-(2,5-dibromophenyl)aniline (3-mp)



Compound **2-mp** (5.34 g, 11 mmol) was dissolved in dry DMF (25 mL) and added to a suspension of 55% dispersion NaH in paraffin liquid (768 mg, 18 mmol) in dry DMF (10 mL). The reaction mixture was stirred at RT for 6.5 h, followed by the addition of benzyl bromide (2.2 mL, 18 mmol). After stirring for 21 h, the solution

was quenched with water. The organic layer was extracted with *n*-hexane/CHCl<sub>3</sub> and washed with water. The filtrate was concentrated under reduced pressure and the crude product was purified by silica-gel column chromatography (2/1 *n*-hexane/CHCl<sub>3</sub>) to give a colorless solid **3-mp** (5.86 g, 10 mmol, 93%). Mp. 130–134 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>; Fig. S16a):  $\delta$  7.71 (d, *J* = 2.3 Hz, 1H), 7.46–7.41 (m, 3H), 7.29–7.18 (m, 4H), 7.07–7.02 (m, 2H), 6.84 (d, *J* = 8.7 Hz, 1H) and 4.76 (s, 2H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>; Fig. S16b): δ 148.09, 146.12, 137.63, 136.39, 136.15, 131.89, 129.00, 128.91, 128.85, 128.16, 127.95, 127.69, 122.14, 121.42, 120.07, 117.49 and 56.21. HRMS (ESI+): *m/z* calcd. for C<sub>19</sub>H<sub>13</sub>Br<sub>4</sub>N, 574.77406 [M]<sup>+</sup>; found, 574.77509. IR (ATR): 1464, 1455, 1022, 869, 808, 728, 711, 692, 566 and 444 cm<sup>-1</sup>. UV-vis (ethanol) λ<sub>max</sub>/nm (log ε) 288 (3.97).

## Synthesis of N-benzyl-bis(2,5-dibromophenyl)aniline (3-mm)



Compound **2-mm** (9.70 g, 20 mmol) was dissolved in dry DMF (40 mL) and added to a suspension of 55% dispersion NaH in paraffin liquid (1.40 mg, 32 mmol) in dry DMF (100 mL). The reaction mixture was stirred at RT for 4 h, followed by the addition of benzyl bromide (3.7 mL, 30 mmol). After stirring overnight, the solution was quenched

with water. The organic layer was extracted with ethyl acetate and washed with water. The organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude

product was purified by recrystallization (THF/*n*-hexane) to give a light brown solid **3-mm** (8.92 g, 16 mmol, 78%). Mp. 155–156 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>; Fig. S17a):  $\delta$  7.59 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 7.3 Hz, 2H), 7.30–7.17 (m, 7H) and 4.83 (s, 2H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>; Fig. S17b):  $\delta$  147.40, 137.04, 135.64, 128.71, 128.65, 128.35, 127.40, 127.20, 120.89, 119.66 and 55.72. HRMS (ESI+): *m/z* calcd. for C<sub>19</sub>H<sub>14</sub>Br<sub>4</sub>N, 573.78398 [M+H]<sup>+</sup>; found, 573.78151. IR (ATR): 1560, 1459, 1452, 1019, 804, 727, 709, 693, 450 and 444 cm<sup>-1</sup>. UV-vis (ethanol)  $\lambda_{max}/nm$  (log  $\varepsilon$ ) 229 (4.42).

#### Synthesis of 10-benzyl-3,7-dibromo-10'-methyl-9,9'(10H,10'H)-spirobiacridine (4-mp)



Under an Ar atmosphere, **3-mp** (5.75 g, 10 mmol) was dissolved in dry diethyl ether (100 mL) and cooled to -80 °C. Solution 1.58 M *n*-BuLi in *n*-hexane (13.9 mL, 22 mmol) was added to the solution. After stirring for 3 h at -80 °C, *N*-methyl-9(10*H*)acridone (2.30 g, 11 mmol) was added to the reaction mixture, and the mixture was stirred for an additional 4.5 h. The solution was warmed to

0 °C over 4 h and stirred overnight. After reaching RT and stirring for 8 h, the reaction was quenched with the aqueous NH<sub>4</sub>Cl. The organic layer was extracted with CHCl<sub>3</sub> and dried over anhydrous MgSO<sub>4</sub>. After evaporation of the solvent, the residue was dissolved in CHCl<sub>3</sub> (20 mL), acetic acid (40 mL) and 37% HCl (6 mL). The mixture was refluxed for 23 h and then neutralized with aqueous NaOH in an ice bath. The organic layer was extracted with CHCl<sub>3</sub> and dried over anhydrous MgSO<sub>4</sub>. After concentration of the filtrate, the crude product was purified by silica-gel column chromatography (3/2 *n*-hexane/CHCl<sub>3</sub>) to give a colorless powder **4-mp** (2.53 g, 4.2 mmol, 42%). Mp. 265–269 °C (decomp.). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>; Fig. S18a):  $\delta$  7.43 (t, *J* = 7.5 Hz, 2H), 7.34–7.30 (m, 3H), 7.22–7.14 (m, 5H), 6.96 (d, *J* = 1.4 Hz, 1H), 6.90 (dd, *J* = 8.7 Hz, *J*<sup>2</sup> = 1.8 Hz, 1H), 6.83–6.77 (m, 6H), 6.69 (d, *J* = 8.2 Hz, 1H), 5.33 (s, 2H) and 3.51 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>; Fig. S18b):  $\delta$  139.40, 139.20, 137.31, 136.03, 134.51, 134.35, 133.57, 132.33, 131.95. 131.52, 130.54, 129.38, 127.76, 127.68, 126.02, 124.28, 121.31, 120.78, 115.53, 114.95, 113.76, 112.25, 51.79, 47.26 and 33.78. HRMS (ESI+): *m/z* calcd. for C<sub>33</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>2</sub>: 606.03062 [M]<sup>+</sup>; found: 606.02975. IR (ATR): 1471, 1450, 1425, 1353, 1255, 796, 744, 720, 693 and 471 cm<sup>-1</sup>. UV-vis (ethanol)  $\lambda_{max}$ /nm (log  $\varepsilon$ ) 300 (4.19).

### Synthesis of 10-benzyl-3,6-dibromo-10'-methyl-9,9'(10H,10'H)-spirobiacridine (4-mm)



Under the Ar atmosphere, *N*-benzyl-bis(2,5-dibromophenyl)amine (5.75 g, 10.0 mmol) was dissolved in dry diethyl ether (100 mL) and cooled to -80 °C. Solution 1.59 M *n*-BuLi in *n*-hexane (13.8 mL, 22 mmol) was added dropwise to the solution, and the mixture was stirred for 3 h. Compound *N*-methyl-9(10*H*)acridone (2.30 g, 11.0 mmol) as a solid was then added to the reaction

mixture which was stirred for an additional 2 h and allowed to warm to 0 °C overnight. After stirring at RT for 4 h, the reaction was quenched with aqueous NH<sub>4</sub>Cl. The organic layer was extracted with CHCl<sub>3</sub>, washed with brine, dried over anhydrous MgSO<sub>4</sub> and filtered. After removing the solvent under reduced pressure, the residue was dissolved in CHCl<sub>3</sub> (20 mL), acetic acid (40 mL) and 37% HCl (6 mL), and the mixture was refluxed overnight. After cooling to RT, the reaction mixture was neutralized with aqueous NaOH. The organic layer was extracted with CHCl<sub>3</sub>, dried over anhydrous MgSO<sub>4</sub> and condensed under reduced pressure. The crude product was purified by silica-gel column chromatography (2/1 *n*-hexane/CHCl<sub>3</sub>) to give **4-mm** as colorless solid (3.15 g, 5.2 mmol, 51%). Mp. 291 °C (decomp.). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>; Fig. S19a):  $\delta$  7.46 (t, *J* = 7.3 Hz, 2H), 7.36–7.32 (m, 3H), 7.19–7.12 (m, 4H), 6.97 (d, *J* = 1.8 Hz, 2H), 6.91 (dd, *J* = 8.2 Hz, *J*' = 1.8 Hz, 2H), 6.82–6.75 (m, 4H), 6.71 (d, *J* = 8.4 Hz, 2H), 5.35 (s, 2H) and 3.50 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>; Fig. S19b):  $\delta$  139.19, 139.03, 135.69, 133.46, 132.49, 131.86, 131.48, 129.30, 127.60, 127.53, 125.89, 124.37, 121.13, 120.60, 115.63, 112.27, 51.68, 46.88 and 33.62. HRMS (ESI+): *m/z* calcd. for C<sub>33</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>2</sub>: 608.02886 [M]<sup>+</sup>; found: 608.02661. IR (ATR): 1577, 1471, 1429, 1354, 920, 790, 749, 742, 724 and 695 cm<sup>-1</sup>. UV-vis (ethanol)  $\lambda_{max}/nm$  (log  $\varepsilon$ ) 238 (3.91).

## <u>Synthesis of 10-benzyl-10'-methyl-3,7-bis(*N-tert*-butyl hydroxylamino)-9,9'(10H,10'H)spirobiacridine (5-mp)</u>



Under an Ar atmosphere, TMEDA (1.5 mL, 10 mmol) was added to a dry THF solution (10 mL) of **4-mp** (1.22 g, 2.00 mmol). After cooling to -80 °C, 1.60 M *t*-BuLi in *n*-pentane (5.5 mL, 8.8 mmol) was added dropwise to the mixture, which was then stirred at -80 °C for 1 h. The mixture was heated to 0 °C and stirred for 1 h, then cooled to -80 °C and stirred for an

additional 1 h. A dry THF (3.5 mL) solution of 2-methyl-2-nitrosopropane (1.05 g, 12 mmol) was then added into the reaction mixture, and the mixture was stirred at -80 °C for 4.5 h. The solution was warmed to 0 °C over several hours and stirred overnight at 0 °C. After stirring for 9 h at RT, the reaction was quenched with aqueous NH<sub>4</sub>Cl and extracted with CHCl<sub>3</sub>. The organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was recrystallized from *n*-hexane/THF to give **5-mp** as a pale orange powder (526 mg, 0.84 mmol, 42%). Mp. 180–185 °C (decomp.). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>; Fig. S20a):  $\delta$  8.06 (s, 1H), 7.91 (s, 1H), 7.42–7.26 (m, 5H), 7.15–7.07 (m, 4H), 6.90 (dd, J = 8.7 Hz, J' = 2.3 Hz, 1H), 6.82–6.67 (m, 6H), 6.59-6.56 (m, 3H), 5.22 (s, 2H), 3.49 (s, 3H), 0.88 (s, 9H) and 0.75 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>; Fig. S20b):  $\delta$  148.60, 142.34, 139.65, 137.84, 136.21, 133.31, 131.80, 131.05, 128.99, 127.03, 126.28, 123.27, 120.31, 117.02, 112.14, 111.94, 109.27, 60.68, 60.53, 51.61, 47.36, 33.84, 25.99 and 25.69. HRMS (ESI+): m/z calcd. for C<sub>41</sub>H<sub>44</sub>N<sub>4</sub>O<sub>2</sub> [M]<sup>+</sup>: 624.34643, found: 624.34510. IR (ATR): 1592, 1476, 1456, 1435, 1356, 1298, 1265 1202, 745 and 728 cm<sup>-1</sup>. UV-vis (ethanol)  $\lambda_{max}/nm$  (log  $\varepsilon$ ) 299 (4.39).

## <u>Synthesis of 10-benzyl-10'-methyl-3,6-bis(*N-tert*-butyl hydroxylamino)-9,9'(10*H*,10'*H*)spirobiacridine (5-mm)</u>



Compounds 4-mm (1.22 g, 2.0 mmol) and TMEDA (1.5 mL, 10 mmol) were dissolved in dry THF (10 mL) under an Ar atmosphere. After cooling to -80 °C, 1.60 M *t*-BuLi in *n*-pentane (5.5 mL, 8.8 mmol) was added dropwise, and the mixture was stirred for 1 h. The reaction mixture was warmed to 0 °C and stirred for an additional 1 h. The solution was cooled

again to -80 °C, and a dry THF solution (3.5 mL) of 2-methyl-2-nitrosopropane (1.05 g, 12 mmol) was added dropwise. The reaction mixture was stirred at -80 °C overnight and then stirred at 0 °C for 7 h. After stirring for 24 h at RT, the mixture was quenched with aqueous NH<sub>4</sub>Cl. The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhydrous MgSO<sub>4</sub>, filtrated and concentrated under the reduced pressure. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane to give **5-mm** as a colorless powder (0.48 g, 0.77 mmol, 38%). Mp. 160–164 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>; Fig. S21a):  $\delta$  8.06 (s, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.32-7.26 (m, 3H), 7.15-7.07 (m, 4H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 7.4 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.61 (s, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 5.18 (s, 2H), 3.50 (s, 3H) and 0.88 (s, 18H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>; Fig. S21b):  $\delta$  150.12, 139.39, 138.04, 137.73, 133.48, 131.70, 130.72, 129.29, 128.60, 127.55, 127.42, 126.48, 120.61, 117.22, 113.00, 109.37, 59.77, 50.74, 46.74, 34.06 and 26.49. HRMS (ESI+): *m/z* calcd. for C<sub>41</sub>H<sub>45</sub>N<sub>4</sub>O<sub>2</sub>, 626.35744 [M+H]<sup>+</sup>; found, 626.35548. IR (ATR): 1592, 1472, 1456, 1440, 1356, 1266, 1199, 867, 746 and 728 cm<sup>-1</sup>. UV-vis (ethanol)  $\lambda_{mas}/nm$  (log  $\varepsilon$ ) 244 (3.65).

# Synthesis of 10-benzyl-10'-methyl-9,9'(10H,10'H)spirobiacridine-3,7-diyl bis(*tert*-butyl nitroxide) (1-mp)



Compound **5-mp** (64.0 mg, 0.10 mmol) was dissolved in  $CH_2Cl_2$  (10 mL) followed by the addition of  $Ag_2O$  (327 mg). The mixture was stirred for 1 h and then filtered through Celite. The filtrate was concentrated under reduced pressure, and the crude product was recrystallized from  $CH_2Cl_2/n$ -hexane to give a dark red block crystal **1-mp**. The yield was 26.6 mg

(0.0427 mmol, 42%). Mp. 134–137 °C. HRMS (ESI+): *m/z* calcd. for C<sub>41</sub>H<sub>42</sub>N<sub>4</sub>O<sub>2</sub>, 622.33078 [M]<sup>+</sup>; found: 622.32796. IR (ATR): 1471, 1434, 1354, 1339, 1265, 1187, 748, 731, 702 and 471 cm<sup>-1</sup>. UV-vis (ethanol)  $\lambda_{max}$ /nm (log  $\varepsilon$ ) 296 (4.37).

# Synthesis of 10-benzyl-10'-methyl-9,9'(10H,10'H)spirobiacridine-3,6-diyl bis(*tert*-butyl nitroxide) (1-mm)



Compound **5-mm** (63.0 mg, 0.10 mmol) was dissolved in  $CH_2Cl_2$  (10 mL), and then  $Ag_2O$  (357 mg) was added to the solution. After stirring for 1 h at RT, the mixture was filtered through Celite. The solvent was evaporated, and then the residue was purified by silica-gel column chromatography (2% methanol in  $CH_2Cl_2$ ) to give **1-mm**. Recrystallization from  $CH_2Cl_2/n$ -

hexane gave dark-red needle crystals. The yield was 22.9 mg (0.037 mmol, 36%). Mp. 191–193 °C. HRMS (ESI+): m/z calcd. for C<sub>41</sub>H<sub>42</sub>N<sub>4</sub>O<sub>2</sub>, 622.33078 [M]<sup>+</sup>; found, 622.32897. IR (ATR): 1474, 1442, 1353, 1262, 1191, 745, 729, 504, 499 and 411 cm<sup>-1</sup>. UV-vis (ethanol)  $\lambda_{max}$ /nm (log  $\varepsilon$ ) 295 (4.66).

# Synthesis of 10-benzyl-10'-methyl-9,9'(10H,10'H)spirobiacridine-2,7-diyl bis(*tert*-butyl nitroxide) (1-pp)



Compound 10-benzyl-10'-methyl-3,6-bis(*N-tert*-butyl hydroxylamino)-9,9'(10*H*,10'*H*)-spirobiacridine (63.0 mg, 0.101 mmol) was dissolved in  $CH_2Cl_2$  (10 mL), followed by the addition of  $Ag_2O$  (357 mg) to the solution. The mixture was stirred at RT for 2 h and then filtered through Celite. The filtrate was concentrated under reduced pressure, and the

residue was purified by silica-gel column chromatography (1% MeOH in CH<sub>2</sub>Cl<sub>2</sub>). A dark-red block crystal **1-pp** were obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane solution. The yield was 22.5 mg (0.038 mmol, 37%). Mp. 172–176 °C. HRMS (ESI+): *m/z* calcd. for C<sub>41</sub>H<sub>42</sub>N<sub>4</sub>O<sub>2</sub> [M]+, 622.3308; found, 622.3291. IR (ATR): 1472, 1453, 1430, 1354, 1264, 1222, 1190, 745, 728 and 505 cm<sup>-1</sup>. UV-vis (EtOH)  $\lambda_{max}$ /nm (log  $\varepsilon$ ) 290 (4.34). Calcd.for (C<sub>41</sub>H<sub>42</sub>N<sub>4</sub>O<sub>2</sub>)<sub>0.97</sub>(C<sub>40</sub>H<sub>33</sub>N<sub>3</sub>OBr)<sub>0.03</sub>: C, 78.90; H, 6.74; N, 8.92%. Found: C, 78.80; H, 6.80; N, 8.95%. As reference, calcd. for C<sub>41</sub>H<sub>42</sub>N<sub>4</sub>O<sub>2</sub>: C, 79.07; H, 6.80; N, 9.00%.

## Electron spin resonance (ESR) spectroscopy

ESR spectra were recorded on a Bruker EMXnano X-band (9.6 GHz) spectrometer at RT after the sample solution in toluene was thoroughly purged with the Ar gas. Frozen solution ESR spectrum for **1-mp** was also recorded on the same spectrometer at 77 K.



**Fig. S1.** X-Band ESR spectrum for **1-pp** in a degassed toluene solution at RT. The ref and black lines represent the experimental and simulated curves, respectively. For these parameters in the simulation, see the text.



**Fig. S2.** X-Band ESR spectrum for **1-mp** in a degassed toluene solution at RT. The green and black lines represent the experimental and simulated curves, respectively. For these parameters in the simulation, see the text.



Fig. S3. X-Band ESR spectrum for 1-mm in a degassed toluene solution at RT. The blue and black lines represent the experimental and simulated curves, respectively. For these parameters in the simulation, see the text.



**Fig. S4.** Frozen-solution ESR spectrum of **1-mp** at 77 K. The green and black lines represent the experimental and simulated curves, respectively. For these parameters in the simulation, see the text. A central signal denoted with a purple asterisk is assigned to monoradicals.

## Single Crystal X-ray Diffractions

The X-ray diffraction data of **1-pp**, **1-mp** and **1-mm** at 93 K were collected on a Rigaku VariMax Dual (Mo K $\alpha$  radiation:  $\lambda = 0.71073$  Å). The selected crystallographic data are given in Table S1. X-ray data analyses were carried out using the SHELXT<sup>S5</sup> and SHELXL<sup>S6</sup> programs operated with the Olex2 interface.<sup>S7</sup> All the hydrogen atoms were refined as "riding". The thermal displacement parameters of the non-hydrogen atoms were refined anisotropically. The contribution of the disordered solvent was removed using the SQUEEZE option from PLATON operated with the Olex2 interface.<sup>S7</sup> The estimated total solvent-accessible void spaces (1.2 Å probe) were 324 Å<sup>3</sup> (17.7%), 531 Å<sup>3</sup> (14.7%) and 281 Å<sup>3</sup> (8.2%) per unit cell, respectively. In addition, the squeeze electron count per formula unit were 42, 42 and 21 electrons, respectively, which correlates with the electron density CH<sub>2</sub>Cl<sub>2</sub> (40 electrons) for **1-pp** and **1-mp** and 0.5CH<sub>2</sub>Cl<sub>2</sub> (20 electrons) for **1-mm**. The CCDC numbers of **1-pp**, **1-mp** and **1-mm** are 2394806–2394808, respectively.

	1-рр	1-mp	1-mm
Formula	$C_{40.88}H_{41.73}Br_{0.03}N_{3.97}O_{1.97}$	$C_{41}H_{42}N_4O_2$	$C_{41}H_{42}N_4O_2$
Fw	622.55	622.78	622.78
T/K	93	93	93
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	PÌ	$P2_{1}/c$	$P2_{1}/c$
a/Å	12.3776(5)	17.4124(8)	21.4155(5)
b/Å	13.0243(4)	10.2091(4)	13.3956(3)
$c/\text{\AA}$	130653(3)	20.8163(9)	11.9815(3)
$\alpha/^{o}$	96.956(2)	90	90
β/°	103.047(3)	102.887(4)	97.165(2)
$\gamma^{\prime o}$	113.442(3)	90	90
$V/Å^3$	1829.35(11)	3607.2(3)	3410.33(14)
Ζ	2	4	4
$d_{\rm calcd}/{\rm g~cm^{-3}}$	1.130	1.147	1.213
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	0.103	0.071	0.075
$R(F)^a (I \ge 2\sigma(I))$	0.0580	0.0470	0.0439
$R_w(F^2)^b$ (all data)	0.1282	0.1078	0.1098
Goodness of fit	1.081	1.031	1.043
No. unique reflns	7722	7370	7459

Table S1. Selected crystallographic data for 1-pp, 1-mp and 1-mm.

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. \ {}^{b}R_{w} = [\Sigma w (|F_{o}| - |F_{c}|)^{2} / \Sigma w |F_{o}|^{2}]^{1/2}.$ 

## **Theoretical calculations**

The DFT calculations of **1-pp**, **1-mp** and **1-mm** were performed on the Gaussian09 program.<sup>S8</sup> The theoretical results were generated using GaussView 5 software. The energies of the triplet (T) and broken-symmetry singlet (BS) states were calculated at the UB3LYP/6-311G+(2d,p) level. The structural parameters were given from crystallographic data. In the calculation of the intramolecular exchange coupling, the *N*-methyl acridine moiety was replaced by methyl groups to reduce the computational costs. The calculated spin densities of the T and BS states for **1-pp**, **1-mp** and **1-mm** have been mapped onto the molecular skeleton shown in Figs. S5–S7, respectively. The triplet and singlet energy states for **1-pp**, **1-mp** and **1-mm** are summarized in Tables S2. The exchange coupling constant (*J*) was estimated by using Yamaguchi's equation.<sup>S9</sup> On the other hand, in the calculation of the nearest intermolecular exchange coupling, the molecule was replaced with *tert*-butyl phenyl nitroxide to reduce the computational costs. The calculated spin densities of the T and BS states of the T and BS states for the nearest intermolecular exchange coupling, the molecule was replaced with *tert*-butyl phenyl nitroxide to reduce the computational costs. The calculated spin densities of the T and BS states for the nearest intermolecular contacts of **1-pp**, **1-mp** and **1-mm** have been mapped onto the molecular skeleton shown in Figs. S8–S10, respectively. The triplet and single energy states are summarized in Table S4.



**Fig. S5.** Spin density maps drawn from the DFT MO calculations for **1-pp** with the (a) triplet and (b) singlet states. Blue and red lobes stand for positive and negative spin densities, respectively, with the isocontour of 0.001 e Å<sup>-3</sup>.



**Fig. S6.** Spin density maps drawn from the DFT MO calculations for **1-mp** with the (a) triplet and (b) singlet states. Blue and red lobes stand for positive and negative spin densities, respectively, with the isocontour of 0.001 e  $Å^{-3}$ .



**Fig. S7.** Spin density maps drawn from the DFT MO calculations for **1-mm** with the (a) triplet and (b) singlet states. Blue and red lobes stand for positive and negative spin densities, respectively, with the isocontour of 0.001 Å<sup>-3</sup>.

Compounds	Spin states	E / au	<Ŝ2>	$2J/k_{\rm B}$
1-рр	Т	-1244.35553993	2.0002	
	BS	-1244.35604848	0.1769	-176.05
1-mp	Т	-1244.35770394	2.0004	
	BS	-1244.35753910	0.1716	+56.89
1-mm	Т	-1244.36058402	2.0003	
	BS	-1244.36061701	0.1815	-11.45

**Table S2.** The energy levels *E* and  $\langle S^2 \rangle$  in the triplet and singlet spin states for 1-pp, 1-mp and 1-mm.

	1-pp (singlet)	1-mm (singlet)	1-mp (triplet)
01	-0.4786	+0.4923	+0.4951
N1	-0.3940	+0.3823	+0.3873
C1	+0.1127	+0.1260	+0.1103
C2	-0.0954	-0.0557	-0.0597
C3	+0.0526	+0.1285	+0.1386
C4	-0.0961	-0.0472	-0.0529
C5	+0.0419	+0.1117	+0.1213
C6	-0.0982	-0.1247	-0.1178
N3	-0.0049	+0.0009	+0.0230
C13	+0.0035	+0.0041	-0.0083
C12	+0.0868	+0.0862	+0.1102
C11	-0.0405	-0.1057	-0.0455
C10	+0.0888	+0.0396	+0.0965
C9	-0.0544	-0.1042	-0.0539
C8	+0.0876	+0.0499	+0.1018
C7	-0.1002	-0.0872	-0.1175
N2	+0.3972	-0.3979	+0.3937
02	+0.4906	-0.4983	+0.4777

 Table S3. Spin densities for the benzyl acridane side for 1-pp (singlet state), 1-mp (triplet state) and

 1-mm (singlet state).





**1-pp** :  $R^1 = NO1$ ,  $R^2 = H$ ,  $R^3 = NO2$ ,  $R^4 = H$  **1-mp** :  $R^1 = H$ ,  $R^2 = NO1$ ,  $R^3 = NO2$ ,  $R^4 = H$ **1-mm** :  $R^1 = H$ ,  $R^2 = NO1$ ,  $R^3 = H$ ,  $R^4 = NO2$ 

Compounds	Spin states	E / au	<\$2>	$2J/k_{\rm B}$
1-рр	Т	-1038.87144708	2.0002	
	BS	-1038.87145128	0.1530	-1.44
1-mp	Т	-1038.87017616	2.0003	
	BS	-1038.87018155	0.1800	-1.87
1-mm	Т	-1038.87160574	2.0002	
	BS	-1038.87160678	0.1545	-0.36

**Table S4.** The energy levels E and  $\langle S^2 \rangle$  in the triplet and singlet spin states for the nearest intermolecular contacts of 1-pp, 1-mp and 1-mm.



**Fig. S8.** Spin density maps drawn from the DFT MO calculations for the nearest intermolecular contact of **1-pp** with the (a) triplet and (b) singlet states. Blue and red lobes stand for positive and negative spin densities, respectively, with the isocontour of 0.001 e Å<sup>-3</sup>.



**Fig. S9.** Spin density maps drawn from the DFT MO calculations for the nearest intermolecular contact of **1-mp** with the (a) triplet and (b) singlet states. Blue and red lobes stand for positive and negative spin densities, respectively, with the isocontour of 0.001 e  $Å^{-3}$ .



**Fig. S10.** Spin density maps drawn from the DFT MO calculations for the nearest intermolecular contact of **1-pp** with the (a) triplet and (b) singlet states. Blue and red lobes stand for positive and negative spin densities, respectively, with the isocontour of 0.001 e Å<sup>-3</sup>.

## **Magnetic measurements**

The direct current magnetic susceptibilities of **1-pp**, **1-mp** and **1-mm** were measured on a Quantum Design MPMS-XL7AC SQUID magnetometer equipped with a 7 T coil in a temperature range of 2–300 K under the static field of 0.5 T. The magnetic data were corrected using diamagnetic blank data of the sample holder measured. The diamagnetic contribution of the sample itself was estimated from Pascal's constants.<sup>S10</sup>



**Fig. S11.** Temperature dependence of the product  $\chi_m T$  for **1-pp** (black circles). The red solid line represents the fitting curve.



**Fig. S12.** Temperature dependence of the product  $\chi_m T$  for **1-mp** (black circles). The red solid line represents the fitting curve.



**Fig. S13.** Temperature dependence of the product  $\chi_m T$  for **1-mm** (black circles). The red solid line represents the fitting curve.





Fig. S14. (a)  $^{1}$ H- and (b)  $^{13}$ C-NMR spectra for 2-mp.





Fig. S15. (a)  $^{1}$ H- and (b)  $^{13}$ C-NMR spectra for 2-mm.







**Fig. S16.** (a) <sup>1</sup>H- and (b) <sup>13</sup>C-NMR spectra for **3-mp**.







Fig. S17. (a)  $^{1}$ H- and (b)  $^{13}$ C-NMR spectra for 3-mm.





Fig. S18. (a)  $^{1}$ H- and (b)  $^{13}$ C-NMR spectra for 4-mp.





Fig. S19. (a)  $^{1}$ H- and (b)  $^{13}$ C-NMR spectra for 4-mm.





Fig. S20. (a)  $^{1}$ H- and (b)  $^{13}$ C-NMR spectra for 5-mp.





**Fig. S21.** (a) <sup>1</sup>H- and (b) <sup>13</sup>C-NMR spectra for **5-mm**.

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