Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Synthesis and Characterization of Spin-Labelled [2]Rotaxanes Containing Tetrathiafulvalene and 1,5-Dioxynaphthalene Molecular Stations

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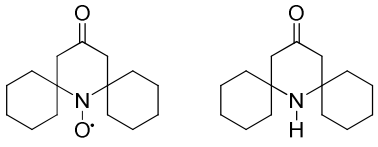
General procedure

ESR spectra has been recorded by using the following instrument settings: microwave power 0.79 mW, modulation amplitude 0.04 mT, modulation frequency 100 kHz, scan time 180 s, 2K data points.

^{1}H NMR spectra were recorded at 298 K on a Varian Inova spectrometer operating at 600 MHz in DMSO-d^6 and CD_3CN solutions using the solvent peak as internal standard (2.50 e 1.94 ppm, respectively). Chemical shifts are reported in parts per million (δ scale).

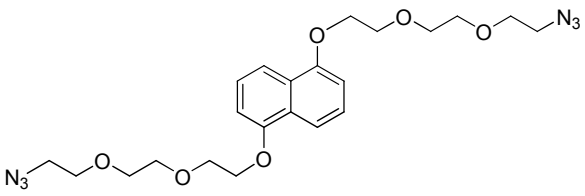
ESI-MS spectra were recorded with Micromass ZMD spectrometer by using the following instrumental settings: positive ions; desolvation gas (N2) 230 L/h; cone gas (skimmer): 50 L/h; desolvation temp. 120° C; capillary voltage: 3.2 kV; cone voltage: 40 and 100 V; hexapole extractor: 3 V.

All reagents were commercially available and were used without further purification. Compounds **5a**,[S1] **5b**,[S2] **1**,[S3] **17**,[S4] **18**,[S5] **9**,[S6] **10**,[S7] **11**,[S7] **13**,[S8] were synthesized according to literature procedures.



5a

5b



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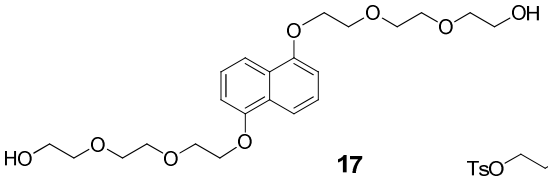

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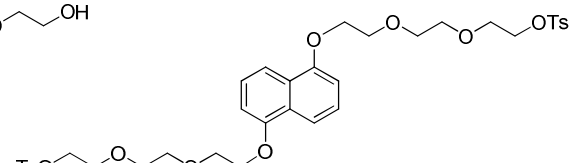

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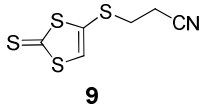

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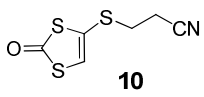

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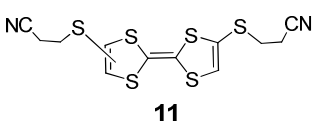

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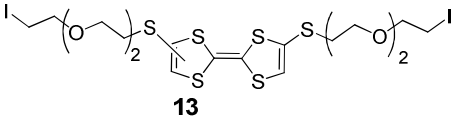
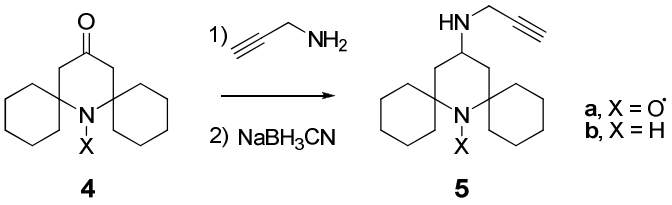


13

Additional NMR data for 2b: ^{1}H NMR (600 MHz, d_7-DMF): δ 0.95-1.05 (m, 4H), 1.06 (s, 12H), 1.13 (s, 12H), 1.90 (dd, *J* = 12.0 and 3.0 Hz, 4H), 3.64-3.67 (m, 4H), 3.49-3.73 (m, 4H), 3.84-3.89 (m, 1H), 3.91-3.95 (m, 8H), 4.28-4.33 (m, 4H), 4.58-4.61 (m, 4H), 4.60 (s, 4H), 7.04 (d, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.7 Hz), 7.81 (d, *J* = 7.7 Hz, 2H), 8.08 (s, 2H).

NMR data for 2a-OH: The ^{1}H NMR spectrum of bis-*N*-hydroxy amine of **2a** (**2a-OH**) was recorded after *in situ* reduction of the sample containing the dinitroxide **2a** by using phenylhydrazine. ^{1}H NMR (600 MHz, d_6-DMSO): δ 1.00 (s, 12H), 1.04 (m, 12H), 1.23 (t, *J* = 11.0 Hz, 4H), 1.85 (d, *J* = 11.0 Hz, 4H), 3.55-3.68 (m, 8H), 3.78-3.88 (m, 10H), 4.20-4.26 (m, 4H), 4.46 (s, 4H), 4.50 (t, *J* = 5Hz, 4H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.98 (s, 2H), 7.37 (t, *J* = 8.0 Hz), 7.71 (d, *J* = 8.0 Hz, 2H), 8.00 (s, 2H).

Preparation of 5a and 5b



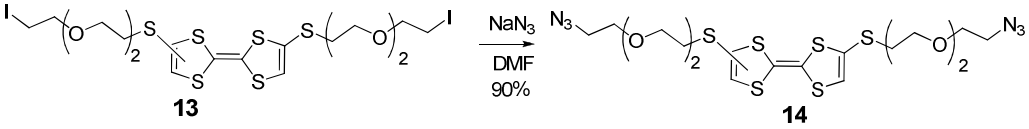
4 **5**

Ketone **4a** (0.2 g, 0.8 mmol) was treated with propargylamine (1.02 mL, 16 mmol) under inert N_2 atmosphere at room temperature and the mixture kept under magnetic stirring until disappearance of the ketone. After ca. 8 h methanol (5 mL), tetrahydrofurane (THF, 5 mL) and sodium cyanoborohydride (0.11 g, 1.76 mmoli) in two portions were added and the mixture was stirred for 3 h at room temperature. After aqueous work-up with 5 M HCl and then with 5M NaOH until pH = 10, the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL), the combined organic extracts were dried (Na_2SO_4), and the solvent evaporated. The crude product was chromatographed (SiO_2, ethyl acetate and then cyclohexane/ethyl acetate 8:2) to give 162 mg (70% yield) of **5a** as an orange solid. **5a**: ESI-MS *m/z* 312.23 $(M+Na)^+$. EPR: (a_N = 16.64 G, g = 2.0057). ^{1}H NMR (600 MHz, CD_3CN): δ 2.40 (s, 1H), 3.20 (br s, 2H).

The ^{1}H NMR spectrum of *N*-hydroxy amine of **5a** (**5a-OH**) was also recorded after *in situ* reduction of the sample containing the nitroxide **5a** by using phenylhydrazine.[S9] ^{1}H NMR (600 MHz, CD_3CN): δ 0.74 (t, *J* = 12.3 Hz, 2H), 1.00-1.20 (m, 2H), 1.19 (d, *J* = 12.9 Hz, 2H), 1.33-1.45 (m, 6H), 1.50-1.70 (m, 12H), 2.35 (d, *J* = 12.3 Hz, 2H), 2.40 (s, 1H), 2.80-2.88 (m, 1H), 3.42 (s, 2H).

The above procedure was followed using **4b** (0.4 g, 1.7 mmol) as the starting ketone. The crude product was chromatographed (SiO_2, ethyl acetate/methanol 9:1, then methanol: 30% NH_3 99:1) to give 335 mg (72% yield) of **5b** as a white solid. **5b**: ESI-MS *m/z* 275.44 $(M+H)^+$. ^1H NMR (600 MHz, d_6-DMSO): δ 0.60 (t, *J* = 12.0 Hz, 2H). 1.22-1.29 (m, 4H), 1.30-1.35 (m, 8H), 1.50-1.59 (m, 8H), 1.89 (d, *J* = 12.0 Hz, 2H), 2.94 (tt, *J* = 12.0 and 3.3 Hz, 1H), 2.99 (t, *J* = 2.2 Hz, 1H), 3.34 (d, *J* = 2.2 Hz, 2H).

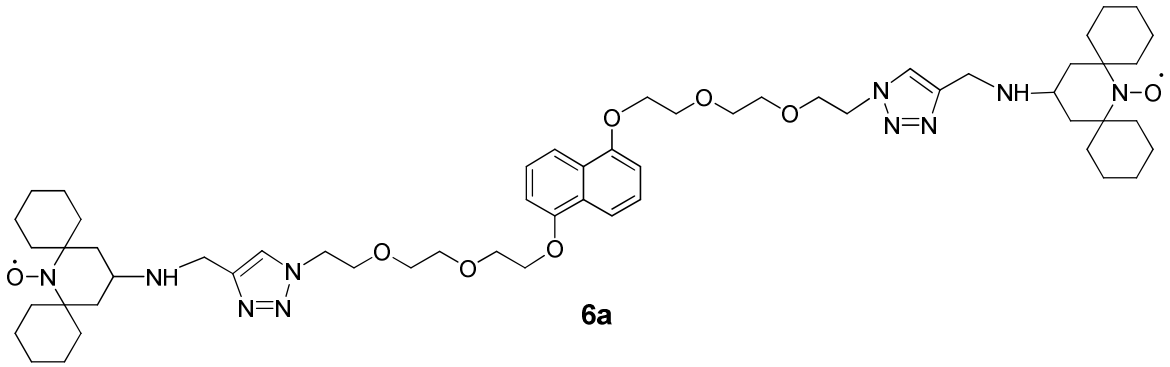
Preparation of 4,4'-bis((2-(2-(2-azidoethoxy)ethoxy)ethyl)thio)-2,2'-bi(1,3-dithiolylidene) (14)



13 **14**

4,4'-Bis((2-(2-(2-iodoethoxy)ethoxy)ethyl)thio)-2,2'-bi(1,3-dithiolylidene) (**13**, 0.200 g, 0.294 mmol) and sodium azide (0.382 g, 5.88 mmol) were dissolved in DMF (3 mL) and heated to 80° C for 24 h. The crude reaction mixture was partitioned between 50 mL of water and CH_2Cl_2, and the aqueous phase was washed with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and the solvent evaporated. The crude product was chromatographed (SiO_2, CH_2Cl_2 eluent) to give 135 mg (90% yield) of **14** as a pale yellow solid. ^1H NMR (600 MHz, d_6-DMSO): δ 2.98 (t, *J* = 6.3 Hz, 4H), 3.39 (t, *J* = 4.8 Hz, 4H), 3.55 (br s, 8H), 3.55-3.65 (m, 8H), 6.88 (s, 2H). ESI-MS: *m/z* 581.9 $(M+H)^+$, 604.9 $(M+Na)^+$.

Additional NMR data for biradical dumbbell 6a



6a

^1H NMR (600 MHz, d_6-DMSO): 3.58 (br s, 4H), 3.64 (br s, 4H), 3.84 (br s, 8H), 4.24 (br s, 4H), 4.51 (br s, 4H), 6.99 (br s, 2H), 7.37 (br s, 2H), 7.71 (br s, 2H), 7.95 (br s)

The ^1H NMR spectrum of bis-*N*-hydroxy amine of **6a** (**6a-OH**) was also recorded after *in situ* reduction of the sample containing the dinitroxide **6a** by using phenylhydrazine.

^{1}H NMR (600 MHz, d_6-DMSO): δ 0.75-0-85 (m, 4H), 0.90-1.00 (m, 4H), 1.10-1.16 (m, 4H), 1.20-1.35 (m, 12H), 1.40-1.60 (m, 16H), 1.75-1.84 (m, 4H), 1.85-1.95 (m, 4H), 2.36 (d, *J* = 11.0 Hz, 4H), 2.75-2.82 (m, 2H), 3.58 (br s, 4H), 3.64 (br s, 4H), 3.82 (br s, 6H), 3.85 (br s, 6H), 4.24 (br s, 4H), 4.51 (br s, 4H), 6.97 (s, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.97 (s, 2H).

Additional NMR data for [2]rotaxane 7a

The ^{1}H NMR spectrum of bis-*N*-hydroxy amine of **7a** (**7a-OH**) was recorded after *in situ* reduction of the sample containing the dinitroxide **7a** by using phenylhydrazine.

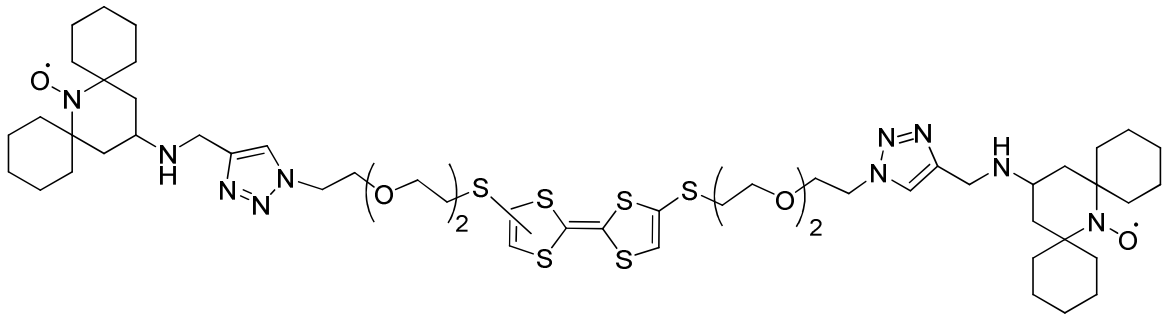
7a-OH: ^{1}H NMR (600 MHz, CD_3CN): δ 1.06-1.12 (m, 8H), 1.22-1.40 (m, 16H), 1.50-1.70 (m, 20H), 1.85-1.90 (m, 4H), 2.41 (d, *J* = 8.4 Hz, 2H), 2.48-2.53 (m, 4H), 3.90 (br s, 8H), 3.98-4.06 (m, 8H), 4.21 (br s, 4H), 4.30 (br s, 4H), 4.55 (t, *J* = 5.4 Hz, 4H), 5.67 (br s, 8H), 5.98 (t, *J* = 7.8 Hz, 2H), 6.27 (d, J 7.2 Hz, 2H), 7.21 (br s, 4H), 7.38 (br s, 4H), 7.98 (bs, 10H), 8.65 (bs. 4H), 8.92 (bs, 4H).

The spectra of **7a** and **7a-OH** were also measured in d_6-DMSO.

7a: δ 2.26-2.32 (m, 2H), 3.80-3.90 (m, 8H), 3.96-4.06 (m, 4H), 4.15-4.35 (m, 8H), 4.54-4.68 (m, 4H), 5.63-5.86 (m, 10H), 6.09-6.15 (m, 2H), 7.63-7.78 (m, 8H), 8.09 (br s, 8H), 8.12-8.22 (m, 2H), 9.12 (br s, 8H).

7a-OH: δ 0.94-1.08 (m, 4H), 1.12-1.19 (m, 4H), 1.21-1.37 (m, 28H), 1.45-1.61 (m, 4H), 1.77-1.83 (m, 8H), 1.88-1.95 (m, 4H), 2.28 (d, *J* = 8.4 Hz, 2H), 2.81-2.83 (m, 2H), 3.83-3.90 (m, 8H), 3.96-4.03 (m, 8H), 4.17-4.31 (m, 8H), 4.56-4.66 (m, 4H), 5.70-5.86 (m, 10H), 6.14 (d, *J* = 7.2 Hz, 2H), 7.09 (s, 2H), 7.70-7.77 (m, 8H), 8.05-8.16 (m, 10H), 9.13 (br s, 8H).

Additional NMR data for diradical dumbell 15a

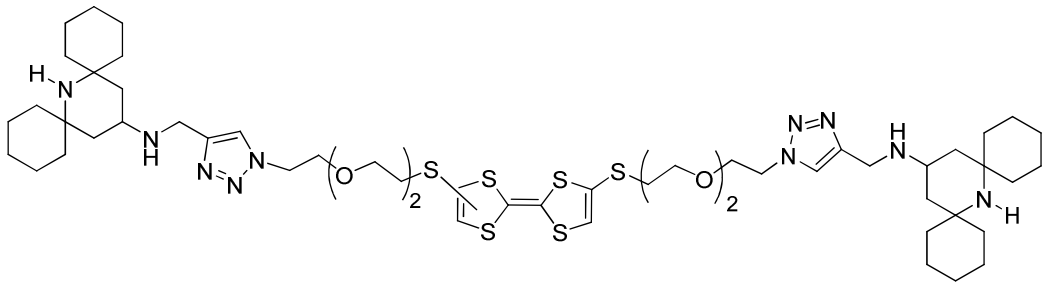


15a

The ^{1}H NMR spectrum of bis-*N*-hydroxy amine of **15a** (**15a-OH**) was recorded after *in situ* reduction of the sample containing the dinitroxide **15a** by using phenylhydrazine.

15a-OH: ^{1}H NMR (600 MHz, CD_3CN): 0.78-0-90 (m, 4H), 1.00-1.11 (m, 4H), 1.22-1.32 (m, 12H), 1.33-1.46 (m, 8H), 1.50-1.68 (m, 16H), 1.84-1.92 (m, overlapped with CHD_2CN signal), 2.72-2.79 (m, 2H), 2.91-2.98 (m, 4H), 3.50-3.73 (m, 12H), 3.83 (br s, 4H), 3.89 (br s, 4H), 4.48 (br s, 4H), 6.54 (br s, 2H), 7.74 (br s, 2H).

Additional NMR data for dumbell 15b



15b

^{1}H NMR (600 MHz, d_6-DMSO): δ 0.70 (t, *J* = 12.0 Hz, 4H), 1.23-1.40 (m, 20H), 1.45-1.62 (m, 20H), 1.99 (t, *J* = 12.0 Hz, 4H), 2.74-2.83 (m, 2H), 2.95 (t, *J* = 6.2 Hz, 4H), 3.51 (s, 8H), 3.55 (t, *J* = 6.2 Hz, 4H), 3.78 (t, *J* = 5.0 Hz, 4H), 3.80 (s, 4H), 4.48 (t, *J* = 5.0 Hz, 4H), 6.87 (s, 2H), 7.87 (s, 2H).

Additional NMR data for [2]rotaxane 16a

The ^{1}H NMR spectrum of bis-*N*-hydroxy amine of **16a** (**16a-OH**) was also recorded after *in situ* reduction of the sample containing the dinitroxide **16a** by using phenylhydrazine.

^{1}H NMR (600 MHz, CD_3CN): δ: 0.78-0-90 (m, 4H), 1.20-1.77 (m, 40H), 1.90-2.00 (m, overlapped with water signal), 2.78-2.81 (m, 2H), 3.03-3.10 (m, 4H), 3.68-3.76 (m, 12H), 3.76-3.82 (m, 4H), 3.90-3.96 (m, 4H), 4.50-4.56 (m, 4H), 5.75 (s, 8H), 5.96 (s, 1H), 6.00 (s, 1H), 7.00(s, 2H), 7.74 (s, 8H), 8.04-8.10 (m, 10H), 9.07-9.15 (m, 8H).

References

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S9) The spectra of **5a** and **5a-OH** (recorded after *in situ* reduction of the sample containing **5a** with phenylhydrazine) were also measured in d_6-DMSO. **5a**: δ 1.20-1.80 (m). **5a-OH**: δ 0.67 (t, J = 12.0 Hz, 2H). 0.90-1.00 (m, 2H), 1.21 (d, J = 13.0 Hz, 2H), 1.40-2.00 (m, 16H), 2.26 (d, J = 12.0 Hz, 2H), 2.72-2.82 (m, 1H), 3.02 (s, 1H), 3.36 (s, 2H), 7.00 (s, 1H).