Electronic Supporting Information for

Evidence of electrochemical transduction of cation recognition by TEMPO derivatives

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ESI 1:Details about organic synthesis of compounds 1, 2 and 3

ESI 2:Details about binding constants calculation

ESI 1. Details about organic synthesis of compounds 1, 2 and 3

_N_-(2,2,6,6-tetramethylpiperidin-4-yloxyl)-2,3,5,6,8,9,11,12,14,15-decahydrobenzo[b][1,4,7,10,13,16]hexaoxacyclooctadecine-18-carboxamide (1)

To a stirred, nitrogen flushed solution of 4-carboxybenzo-18-crown-6 (300 mg, 0.842 mmol) in CH_2Cl_2 (5 mL) at 0°C were added 4-aminoTEMPO (173 mg, 1.010 mmol, 1.2 eq.) in CH_2Cl_2 (2 mL), 1-hydroxybenzotriazole (HOBt) (171 mg, 1.263 mmol, 1.5 eq.) and finally dicyclohexylcarbodiimide (DCC, 261 mg, 1.263 mmol, 1.5 eq.). After 1h stirring at 0-5°C and 3 days at room temperature under N_2, CH_2Cl_2 (30 mL) was added and the solution was filtered. The filtrate was washed three times with water (30 mL), dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography (silica gel, eluent CH_2Cl_2/MeOH 9/1) giving 1 as an orange powder (300 mg, 82 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.60-7.30 (m, 2H, H_{ar}), 6.90 (br s, 1H, H_{ar}), 4.22 (br s, 4H, CH_2-O-C_{ar}), 3.96 (br s, 4H, CH_2-O), 3.80-3.60 (m, 13H, CH_2-O and CH-NH), 1.64 (br s, 4H), 1.27 (br s, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 162.6, 147.7, 144.5, 125.7, 118.2, 109.6, 108.7, 66.6, 65.3, 65.0, 25.5. HR-MS: *m/z* 509.2876 $[M]^{\bullet+}$ (calc. for $C_{26}H_{41}N_2O_8^{\bullet}$: 509.2863). m.p. = 116°C

(1,4,7,10,13,16-hexaoxacyclooctadecan-2-yl)methyl (2,2,6,6-tetramethylpiperidin-4-yloxyl)carboxylate (2)

To a stirred solution of 4-carboxy-TEMPO (50 mg, 0.250 mmol) in CH_2Cl_2 (4 mL) were added 4-dimethylaminopyridine (DMAP, 3mg, 0.025 mmol, 0.1 eq.) and 2-hydroxymethyl-18-crown-6 (160 mg, 0.544 mmol, 2.2 eq.) in CH_2Cl_2 (1 mL). The mixture was cooled in an ice bath and dicyclohexylcarbodiimide (DCC, 81 mg, 0.393 mmol, 1.6 eq.) was added. After 5 min stirring at 0-5°C and 3 days at room temperature, the white precipitate was filtered. The filtrate was washed three times with water (30 mL), dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography (silica gel, eluent CH_2Cl_2/MeOH 92/8) giving 2 as an orange oil (60 mg, 50 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 4.48-4.35 (m, CH_2OCO), 3.82 (m, CH_2O), 1.20-1.10 (m, TEMPO). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 180, 73.94, 67.82, 67.77, 67.72, 67.63, 67.56, 66.61, 61.21, 26.54. HR-MS: *m/z* 476.2850 $[M]^{\bullet+}$ (calc. for $C_{23}H_{42}NO_9^{\bullet}$: 476.2859).

(1,4,7,10,13-pentaoxa-16-azacyclooctadecan-16-yl)(2,2,6,6-tetramethylpiperidin-4-yloxyl)methanone (3)

To a stirred, nitrogen flushed solution of 4-carboxy-TEMPO (125 mg, 0.624 mmol) in CH_2Cl_2 (5 mL) at 0°C were added 1-aza-18-crown-6 (190 mg, 0.722 mmol, 1.15 eq.) in CH_2Cl_2 (5 mL), 1-hydroxybenzotriazole (HOBt) (126 mg, 0.936 mmol, 1.5 eq.) and finally dicyclohexylcarbodiimide (DCC, 193 mg, 0.936 mmol, 1.5 eq.). After 1h stirring at 0-5°C and 7 days at room temperature under N_2, CH_2Cl_2 (30 mL) was added and the solution was filtered. The filtrate was washed three times with water (30 mL), dried over $MgSO_4$ and

filtered. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography (silica gel, eluent CH_2Cl_2/MeOH 94/6) giving 3 as a red oil (128 mg, 46 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 4.00-3.50 (m, 24H, CH_2-N and CH_2-O), 1.55 (br s, 5H), 1.27 (br s, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 70.4, 69.9, 69.7, 69.6, 69.5, 69.4, 69.2, 68.9, 68.5, 47.9, 47.1, 28.4. HR-MS: *m/z* 445.2901 $[M]^{\bullet+}$ (calc. for $C_{22}H_{41}N_2O_7^{\bullet}$: 445.2914).

ESI 2.Details about binding constants calculation

The usual method described by Pistolis and Malliaris in reference 23 (G. Pistolis and A. Malliaris, *Chemical Physics Letters*, 1999, **310**, 501-507) was used to determine binding constants. Experimental data (at λ=263nm, T=293K) were fitted with sigmaplot software using the following equations:

H + G →HG

$$ABS(\lambda,x)=\varepsilon(H).\ell.[H]+\varepsilon(HG).\ell.[HG]$$

$$\text{with}\begin{cases}[G_0]=x.[H_0]\ (x=nb\ of\ equivalent)\ and\ \varepsilon,\lambda,\ell,K\ \text{have their usual meanings}\\ \varepsilon(H)=\dfrac{ABS(\lambda,x=0)}{\ell.[H_0]}\\ [H]=\dfrac{\sqrt{\left([H_0]+x.[H_0]-\dfrac{1}{K}\right)^2+\dfrac{4[H_0]}{K}}}{2}+\dfrac{[H_0]}{2}-\dfrac{x.[H_0]}{2}-\dfrac{1}{2K}\\ [HG]=-\dfrac{\sqrt{\left([H_0]+x.[H_0]-\dfrac{1}{K}\right)^2+\dfrac{4[H_0]}{K}}}{2}+\dfrac{[H_0]}{2}+\dfrac{x.[H_0]}{2}+\dfrac{1}{2K}\end{cases}$$