Supporting Information

Synthesis of Functional *meso*-Aryl Porphomono- and Porphodimethenes: Application to the Preparation of a Chiral Calix[4]phyrin Dimer.

Markéta Bernátková, Bruno Andrioletti, Vladimír Král, Eric Rose, and Jacqueline Vaissermann

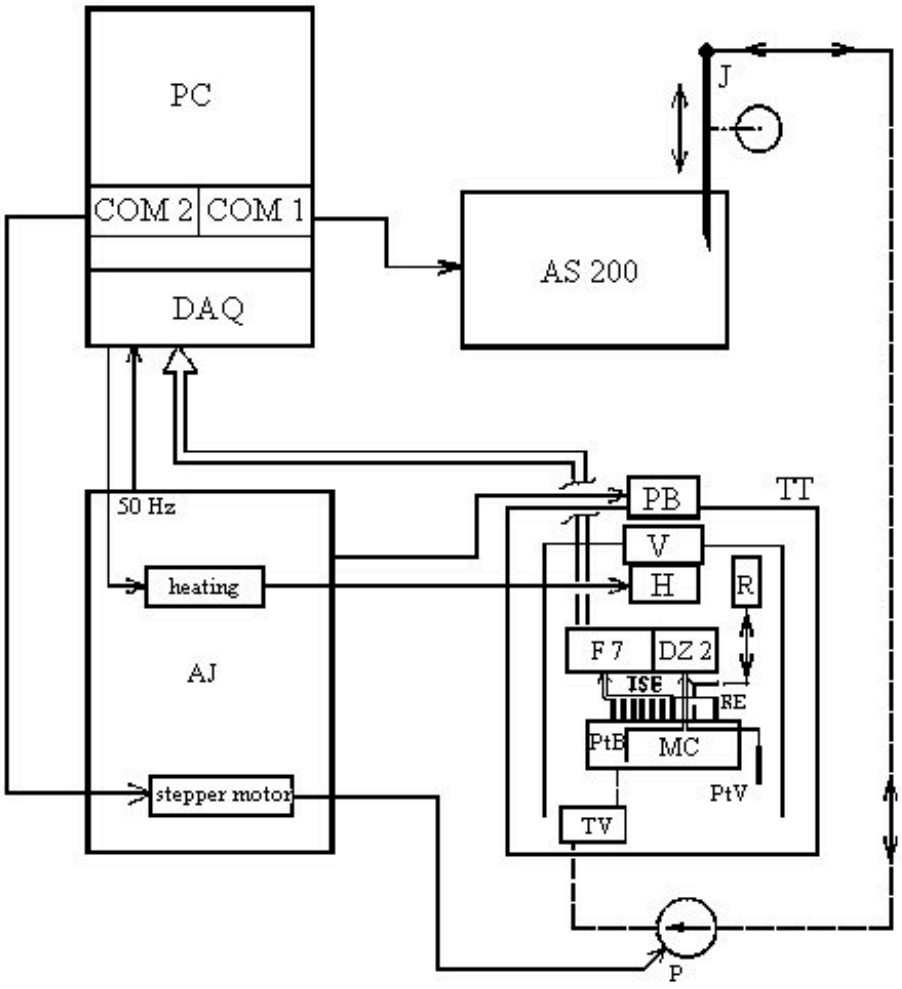
Table of Contents:

1°) **Instrumentation**

The potentiometric response of the various experimental electrodes prepared for the course of study was monitored at a temperature of 25.00 ± 0.01 °C using a custom five-channel flow-through cell that was built in house (cf. Figure S1)

The pH was monitored using a glass electrode Type SEUJ 212 (Electrochemical Detectors, Turnov, Czech Republic) in conjuction with a Type OP-201/2 pH-meter (Radelkis, Hungary).

Figure S1 : Schematic representation of the flow-through cell[a]



[a]AS*200*, autosampler; *P*, peristaltic pump; *AJ*, analog unit box; *TT*, hot-air thermostat, *COM 1* and *COM 2*, computer serial ports; *DAQ*, data-aquisition card PC 516; *J*, sampling needle; *MC*, measuring cell; *V*, ventilator; *H*, heating; *PB*, cooler; *R*, solution reservoir; *PtB* and *PtV*, platinum thermometers; *DZ 2*, two differencial amplifiers; *ISE*, tested electrodes; *RE*, reference electrode (Ag/AgCl electrode, (3 mol.L^{-1} KCl)); *F7*, amplifiers

2°) Electrode preparation

PVC-membrane electrodes were prepared according to a procedure described in the literature.[1] In the present study, 0.7 mL THF was used to dissolve about 100 mg of a mixture containing 3 wt% of the ionophore considered in the study, 50 mol% (relative to the ionophore) of an anionic lipophilic additive (TDDMACl), of PVC and plasticizer (o-NPOE) in a 1: 2 (w/w) ratio. The resulting membranes obtained after evaporation of the solvent were mounted in the flow-through cell.

3°) Potentiometric measurements

The working solutions were prepared by diluting freshly prepared stock solutions (10^{-1} mol.L^{-1}) of the anionic species with water. Linear concentration working range was measured in accord with the IUPAC recommendation.[2] The potentiometric selectivity coefficients were determined using the fixed interference method[3] where the concentrations of primary and interfering anions were 10^{-2} M.

Table S1. Potentiometric properties of PVC-membranes based on selected calixphyrins[a]

Entry			bpFPC **4**	mpFPC **5**	mmNPC **7**
1	Nitrite	Working range, M	10^{-5} – 10^{-1}	10^{-3} – 10^{-1}	10^{-2} – 10^{-1}
		Sensitivity mV/dec	-40.5	-29	-40
2	Nitrate	Working range, M	10^{-5} – 10^{-1}	10^{-4} – 10^{-1}	10^{-5} – 10^{-1}
		Sensitivity mV/dec	-51.0	-41.5	-45.9
3	Acetate	Working range, M	10^{-2} – 10^{-1}	10^{-3} – 10^{-1}	10^{-2} – 10^{-1}
		Sensitivity mV/dec	-66.7	-34.3	-48.0
4	Lactate	Working range, M	10^{-3} – 10^{-1}	10^{-3} – 10^{-1}	10^{-3} – 10^{-1}

		Sensitivity mV/dec	-53.0	-30.8	-47.5
5	Benzoate	Working range, M	10^{-5} – 10^{-1}	10^{-4} – 10^{-1}	10^{-5} – 10^{-1}
		Sensitivity mV/dec	-54.7	-50.2	-61.3
6	Salicylate	Working range, M	10^{-5} – 10^{-1}	10^{-4} – 10^{-1}	10^{-5} – 10^{-1}
		Sensitivity mV/dec	-54.3	-49.1	-61.1

[a] PVC-membrane consisted of 3 wt % of receptor, 50 mol % relative to receptor of cationic lipophilic additive TDDMACl (tridodecylmethyl ammonium chloride), poly(vinyl chloride) and plasticizer *o*-NPOE (*o*-nitrophenyl octyl ether) in the ratio 1:2 wt %.

Table S2. Potentiometric properties of a PVC-membrane incorporating calix[4]phyrin **11**[a]

Entry	Working range, M	Sensitivity mV/dec
D-malic acid	10^{-3} – 10^{-2}	-28.5
L-malic acid	10^{-4} – 10^{-1}	-27

[a] PVC-membrane consisted of 3 wt % of receptor, poly(vinyl chloride) and plasticizer *o*-NPOE (*o*-nitrophenyl octyl ether) in the ratio 1:2 wt %.

4°) References

1) Král, V.; Sessler, J. L.; Shishkanova T. V.; Gale, P. A.; Volf, R. *J. Am. Chem. Soc.* **1999**, *121*, 8771-8775.
2) Guilbault, G. G.; Durst R. A.; Frant M. S.; Freiser, H.; Hansen, E. H.; Light, T. S.; Pungor, E.; Rechnitz, G.; Rice, N. M.; Rohm, T. J.; Simon, W.; Thomas, J. D. R. *Pure Appl. Chem.* **1976**, 48, 127.
3) Umezawa, Y.; Buhlmann, P.; Umezawa, K.; Tohda, K.; Amemiya, S.; *Pure Appl. Chem.* **2000**, 72, 1851-2082.