Supporting Information

Apparatus

The absorbance spectra of dissolved dyes and of sensor layers were recorded on an *Perkin Elmer Lambda 16 spectrometer*. The sensor layers were fixed in a flow-through-cell. Absorption measurements were performed by placing the flow-cell into the spectrometer and pumping amine solutions through the cell using a peristaltic pump (flow rate: 1,7 ml/min). Fluorescence measurements were performed on a Spex Fluorolog 3 spectrometer (Jobin Yvon).

Reagents

All amines were of analytical reagent grade. For membrane preparation, poly(vinyl chloride) (PVC, high molecular weight, Fluka order number: 81392), bis(2-ethylhexyl)sebacate (DOS), and tetrahydrofuran (THF) were obtained from Fluka.

Amine solutions were prepared by dissolving the appropiate amount of each amine in 0.1 M sodium hydroxide solution. Due to the high pH of 13.0, the amines were mainly present in their electrically neutral form.

Syntheses

*Synthesis of 1-{4-[2-(2,7-Di-tert-butyl-9,9-dimethyl-5-{2-[4-(2,2,2-trifluoro-acetyl)-phenyl]-vinyl}-9H-xanthen-4-yl)-vinyl]-phenyl}-2,2,2-trifluoro-ethanone (**1**) and 1-{4-[2-(5-Bromo-2,7-di-tert-butyl-9,9-dimethyl-9H-xanthen-4-yl)-vinyl]-phenyl}-2,2,2-trifluoro-ethanone (**1a**):* 4,5-Dibromo-2,7-di-tert.-butyl-9,9-dimethylxanthene (0.73 g, 1.52 mmol), 2,2,2-trifluoro-1-(4-vinyl-phenyl)-ethanone (0.74 g, 3.7 mmol), dry THF (10 ml), triethylamine (10 ml) and $Pd(PPh_3)_2Cl_2$ (Dichlorobis(triphenylphosphine)palladium(II)) (40 mg, 0.057 mmol) were added to a heavy walled reaction chamber and tightly closed. The mixture was heated up to 115°C for 40 h. After cooling, water was added and the reaction mixture was extracted three times with dichloromethane. The combined organic phase was dried over magnesium sulfate, filtered and concentrated. The resulting crude product was adsorbed on silica gel and two products were isolated *via* column chromatography (hexane-dichloromethane 2:1) to give 130 mg (0.18 mmol) (12%) of (**1**) and 0.49 g (0.82 mmol) (54%) of (**1a**).

Compound 1:

Elemental analysis: Found: C, 71.82; H, 5.45 %; M^+, 718. Calc. for $C_{43}H_{40}F_6O_3$: C, 71.85; H, 5.61 %; M^+, 718.

^{1}H-NMR [ppm]: 1.32 (s, 18 H), 1.6 (s, 6 H), 7.18 (d, 2 H), 7.38 (d, 2 H), 7.45 (d, 2 H), 7.54 (d, 4 H), 7.79 (d, 2 H), 7.84 (d, 4 H)

Compound 1a:

Elemental analysis: Found: C, 66.33; H, 5.86 %; M$^+$, 598. Calc. for $C_{33}H_{34}BrF_3O_2$: C, 66.11; H, 5.72 %; M$^+$, 598.

^{1}H-NMR [ppm]: 1.34 (s, 9 H), 1.38 (s, 9 H), 1.65 (s, 6 H), 7.33 (d, 1 H), 7.38 (s, 1 H), 7,45 (d, 1 H), 7.48 (d, 1 H), 7.50 (d, 1 H), 7.77 (d, 2 H), 8.06 (d, 1 H), 8.11 (d, 2 H)

Synthesis of 1-[4-(2-{2,7-Di-tert-butyl-9,9-dimethyl-5-[2-(4-nitro-phenyl)-vinyl]-9H-xanthen-4-yl}-vinyl)-phenyl]-2,2,2-trifluoro-ethanone (2): **1a** (260 mg, 0.6 mmol), 4-nitrostyrene (0.11 g, 0.73 mmol), dry THF (5 ml), triethylamine (5 ml) and $Pd(PPh_3)_2Cl_2$ (30 mg, 0.042 mmol) were added to a heavy walled reaction chamber and tightly closed. The reaction mixture was heated up to 105-110°C for 63 h. After cooling, water was added and the reaction mixture was extracted three times with dichloromethane. The combined organic phase was dried over magnesium sulfate, filtered and concentrated. The resulting crude product was purified *via* column chromatography (hexane-dichloromethane 1:1) to give 40 mg (10%) of **2**.

Compound 2:

Elemental analysis: Found: C, 73.78; H, 6.06; N, 1.99 %; M$^+$, 667. Calc. for $C_{41}H_{40}F_3NO_4$: C, 73.75; H, 6.04; N, 2.10 %; M$^+$, 667.

^{1}H-NMR [ppm]: 1.33 (s, 18 H), 1.61 (s, 6 H), 7.16 (d, 2 H), 7.38 (d, 2 H), 7.45 (d, 2 H), 7.50 (d, 4 H), 7.80 (d, 2 H), 7.97 (d, 4 H)

Preparation of Sensor Layers. Sensor membrane **S1** was obtained by dissolving 40 mg of PVC, 80 mg of DOS, and 1 mg of compound **1** in 0.8 mL of THF. **S2** was obtained by dissolving 40 mg of PVC, 80 mg of DOS, and 1 mg of compound **2** in 0.8 mL of THF.

The mixtures were spread on a dust-free quarz plate which was placed in a spin-coating device. A 0.2 mL aliquot of the solution was transferred onto the rotating glass support. The resulting membranes were placed in ambient air for drying. Final layer thickness is 3-5 µm.

Procedure for isolating the hemiaminal: To a solution of 0.1 g of compound **1** in 3 ml of dichloromethane and 1 ml 1,3-diaminopropane 1 ml of 1-(trimethylsilyl)imidazole were added. After 5 days water was added and the mixture was extracted 3 times with dichloromethane. The organic phase was dried over $MgSO_4$ and concentrated to give 45 mg of a yellow oil.

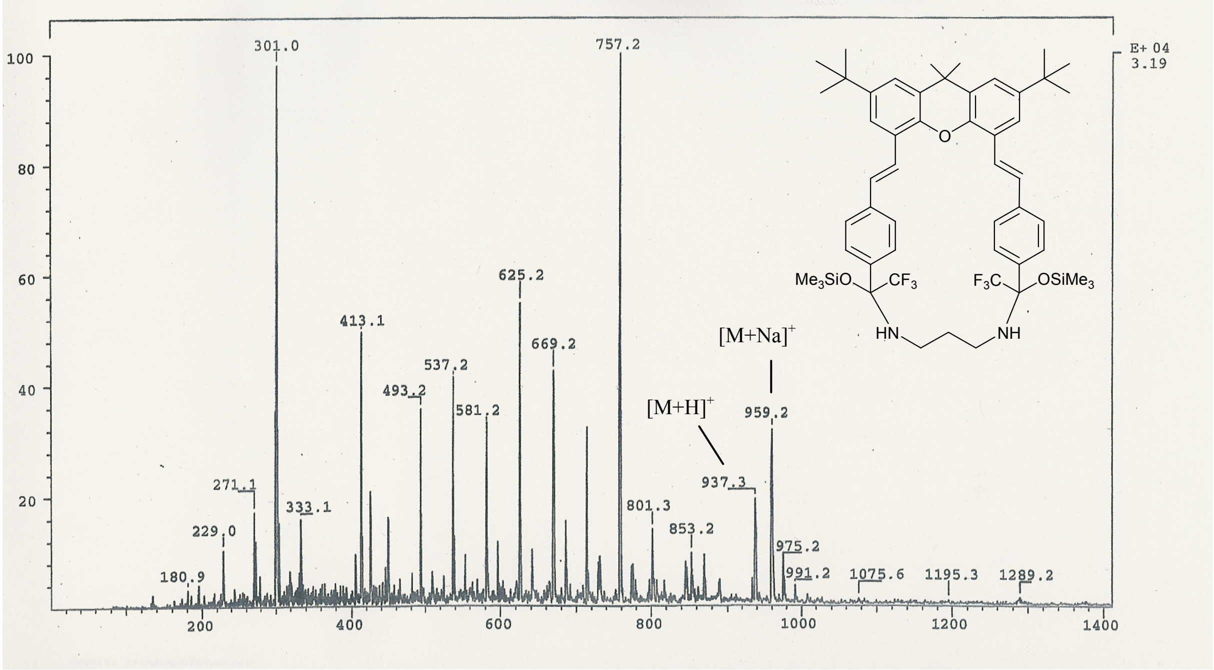
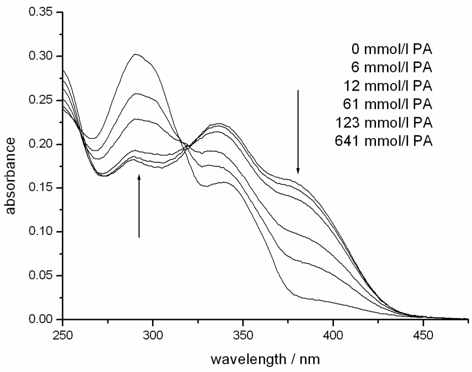
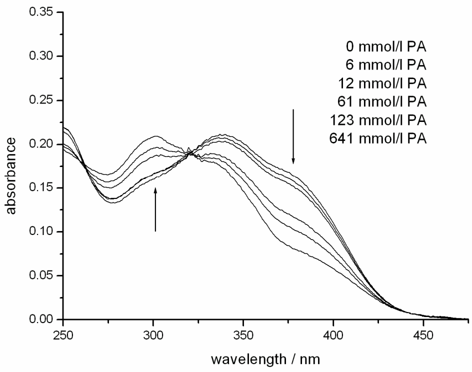
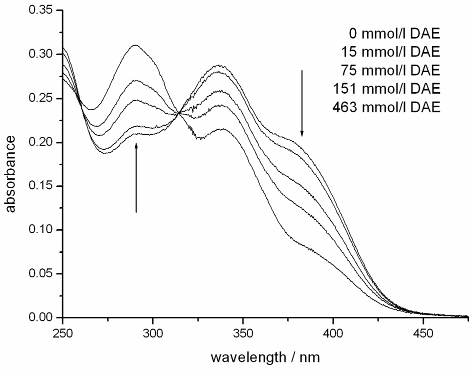
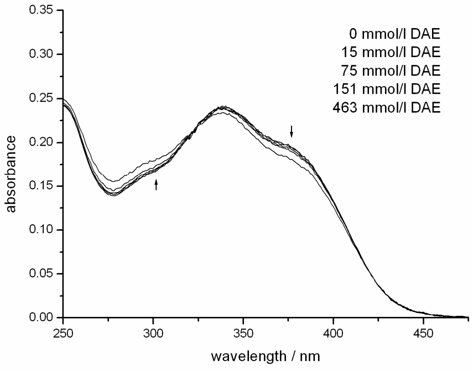


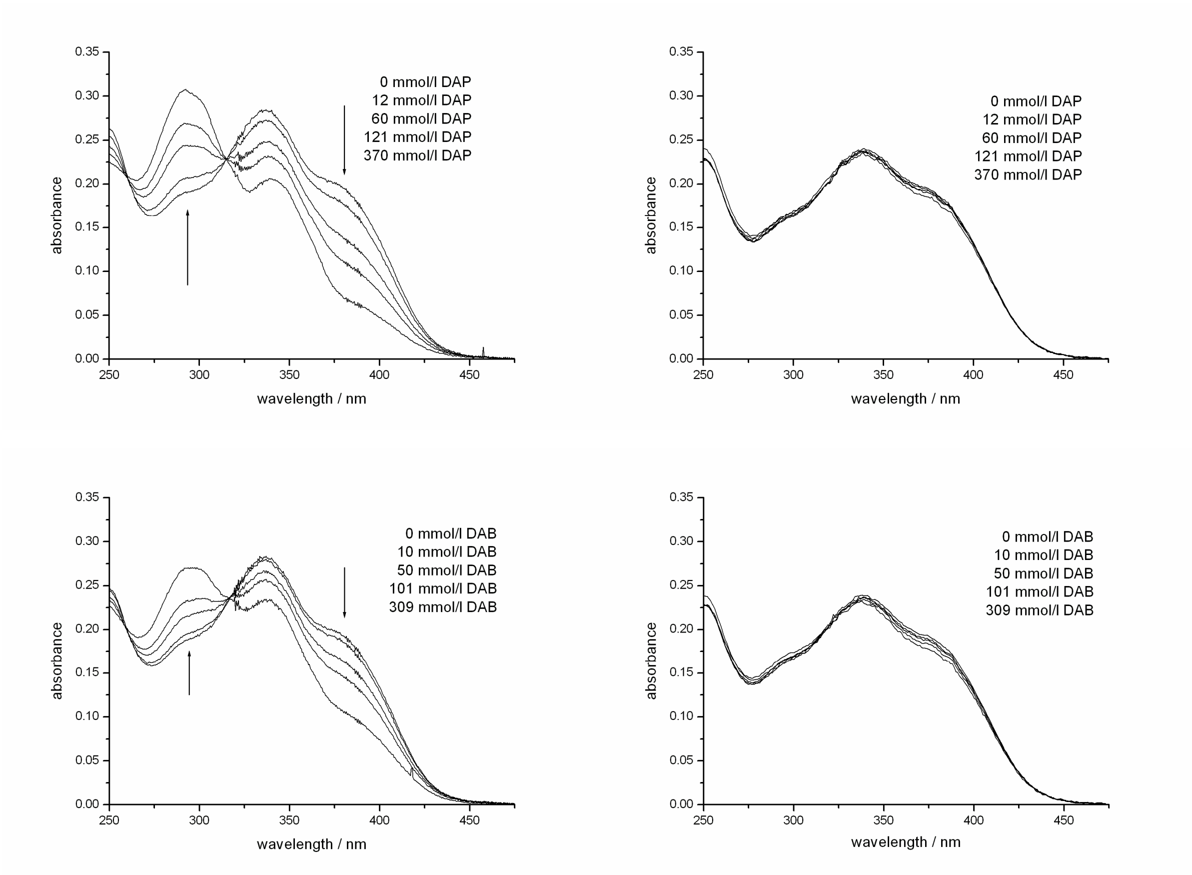
Figure: Micro-ESI spectra of the isolated hemiaminal of **1**, 1,3-diaminopropane and TSIM (in CH_2Cl_2 und MeOH)











Figures: Absorption spectra of **S1** (left side) and **S2** (right side) upon addition of increasing concentrations of different amines (PA, 1-propylamine; DAE, 1,2-diaminoethane; DAP, 1,3-diaminopropane; DAB, 1,4-diaminobutane).