Electronic Supporting information (ESI):

Experimental section

Chemicals and membrane materials

Chemical reagents and solvents for the synthesis were commercially purchased and purified according to the standard methods, if necessary. All inorganic salts, 1-morpholino-ethanesulfonic acid (MES) were of analytical grade and were purchased from Fluka. The solutions of inorganic salts (0.01 M) and MES buffer (0.01 M) were prepared with deionised water. High-molecular-weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS), o-nitrophenyl octyl ether (o-NPOE), potassium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (KTFPB) were obtained from Fluka (Selectophore). Freshly distilled tetrahydrofuran (Fluka) was used as a solvent for membrane components.

Characterization of the obtained compounds

The NMR experiments were carried out using a Varian VNMRS 500 MHz spectrometer (^{1}H NMR at 500 MHz, ^{13}C{^{1}H} NMR at 125 MHz) equipped with a multinuclear z-gradient inverse probe head. The spectra were recorded at 25 °C and standard 5 mm NMR tubes were used. ^{1}H chemical shifts (δ) were reported in parts per million (ppm) relative to the solvent signal, *i.e.*, $CDCl_3$, δ_H (residual $CHCl_3$) 7.26 ppm, δ_C (residual $CHCl_3$) 77.2 ppm. NMR spectra were analyzed with the MestReNova v12.0 software (Mestrelab Research S.L). ESI-HRMS (TOF) measurements were performed with a Q-Exactive ThermoScientific spectrometer.

Synthesis of sumanene 1

Sumanene **1** was synthesized following a literature procedure.[1]

Synthesis of octyloxybenzene sumanene receptor 3

Sumanene (**1**; 0.038 mmol) was placed in a test tube. The content of the tube was evacuated and filled with argon. Tetrabutylammonium bromide (0.019 mmol) was added, followed by the addition of dry THF (0.5 mL) and $NaOH_{aq}$ (30%; 2 mL). The reaction mixture was stirred for 3 min at 27°C under argon atmosphere. 4-Octyloxybenzaldehyde (**2**; 0.19 mmol) was added in one portion, and the reaction mixture was stirred for 48 hours at 27°C under argon atmosphere. Distilled water (6 mL) was added, and the crude product was extracted with CH_2Cl_2 (3x20 mL). Organic layers were combined, washed with saturated NH_4Cl, water, and brine. After drying with $MgSO_4$ followed by filtration, volatiles were distilled off on a rotary evaporator. Finally, the product was purified using a preparative thin layer chromatography (PTLC; SiO_2, 40% CH_2Cl_2/hex) to provide the octyloxybenzene sumanene derivative **3** as a yellow-orange solid (22.1 mg, 65%).

Mp: >300 °C; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm), δ_H 7.88-7.77 (m, 6H), 7.50-7.48 (m, 2H), 7.37-7.35 (m, 3H), 7.32-7.30 (m, 2H), 7.16-7.13 (m, 2H), 7.01-6.93 (m, 6H), 4.07-3.99 (m, 6H), 1.86-1.79 (m, 6H), 1.51-1.45 (m, 6H), 1.36-1.28 (m, 24H), 0.92-0.89 (m, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, ppm), δ_C 159.9x3, 159.8, 147.9, 147.5x2, 147.4, 147.2, 147.1, 146.0, 145.6, 145.4, 145.1, 143.3, 143.0, 141.4, 141.1, 138.9x2, 138.8x2, 131.4x2, 131.3, 131.3, 128.8x2, 128.7, 128.6, 128.4, 128.2, 128.1, 127.9, 123.4, 123.3, 123.2, 123.0, 120.7, 120.6, 120.5, 120.4, 114.8, 114.7, 68.3x2, 32.0x2, 29.54x3, 29.4, 29.4, 26.2x2, 22.8x2, 14.3; ESI-HRMS (TOF): calcd. for $C_{66}H_{72}O_3$ $[M]^+$ = 912.5476, found: m/z 912.5467; R_f (40% CH_2Cl_2/hex) = 0.40.

For the spectra, see Figures S1-S4, ESI.

UV–Vis and fluorescence spectra measurements

The measurements were carried out in methanol-chloroform mixture (1:1 *v*/*v*). Appropriate volumes of 1 mM CsCl solution were mixed with 1 mM solution of octyloxybenzene sumanene derivative **3** to reach 1:10 sumanene-to-metal cation molar ratio. UV-Vis absorption spectra of the obtained samples were recorded on a Varian Cary® 60 Spectrophotometer (Agilent), over the spectral range 200–900 nm with 1 cm path quartz cuvette (Helma). Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer with the spectral resolution of 1 nm. The excitation wavelength was 475 nm. The apparent binding constant (K_{app}) was estimated with the Benesi-Hildebrand method[2],[3] , using the following equation:

$$\frac{1}{I - I_0} = \frac{1}{a} + \frac{1}{a \cdot K_{app} \cdot C(Cs^+)}$$

where I_0 and I are the fluorescence intensities of octyloxybenzene sumanene in the absence and presence of caesium cations, respectively, a is a constant, and $C(\mathrm{Cs}^+)$ is the concentration of caesium cations in solution. The association constant was determined as a ratio of intercept-to-slope of $1/(I - I_0)$ vs. $1/C(\mathrm{Cs}^+)$ linear plot (Figure S7; $R^2 = 0.895$).

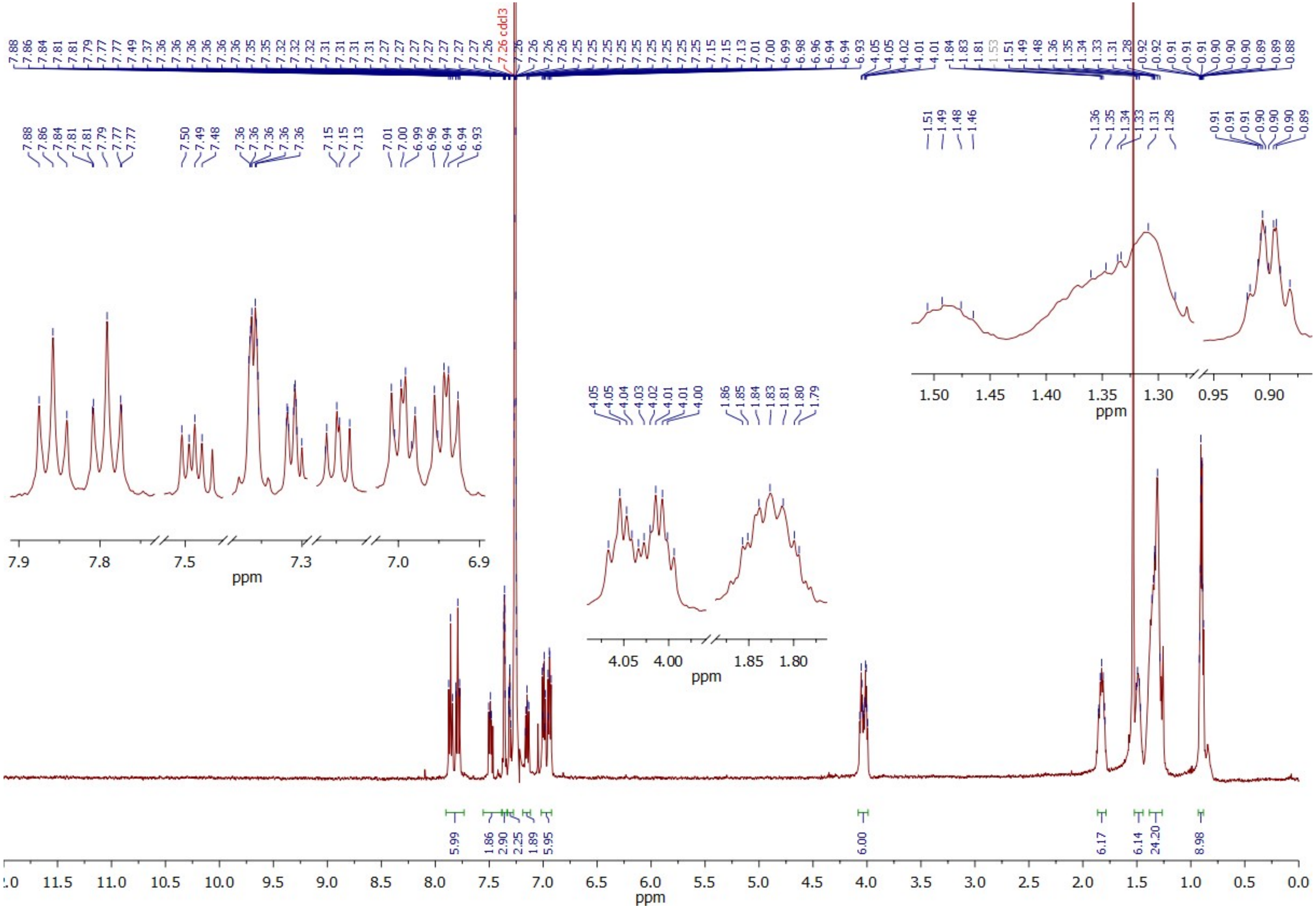

Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of octyloxybenzene sumanene **3**.

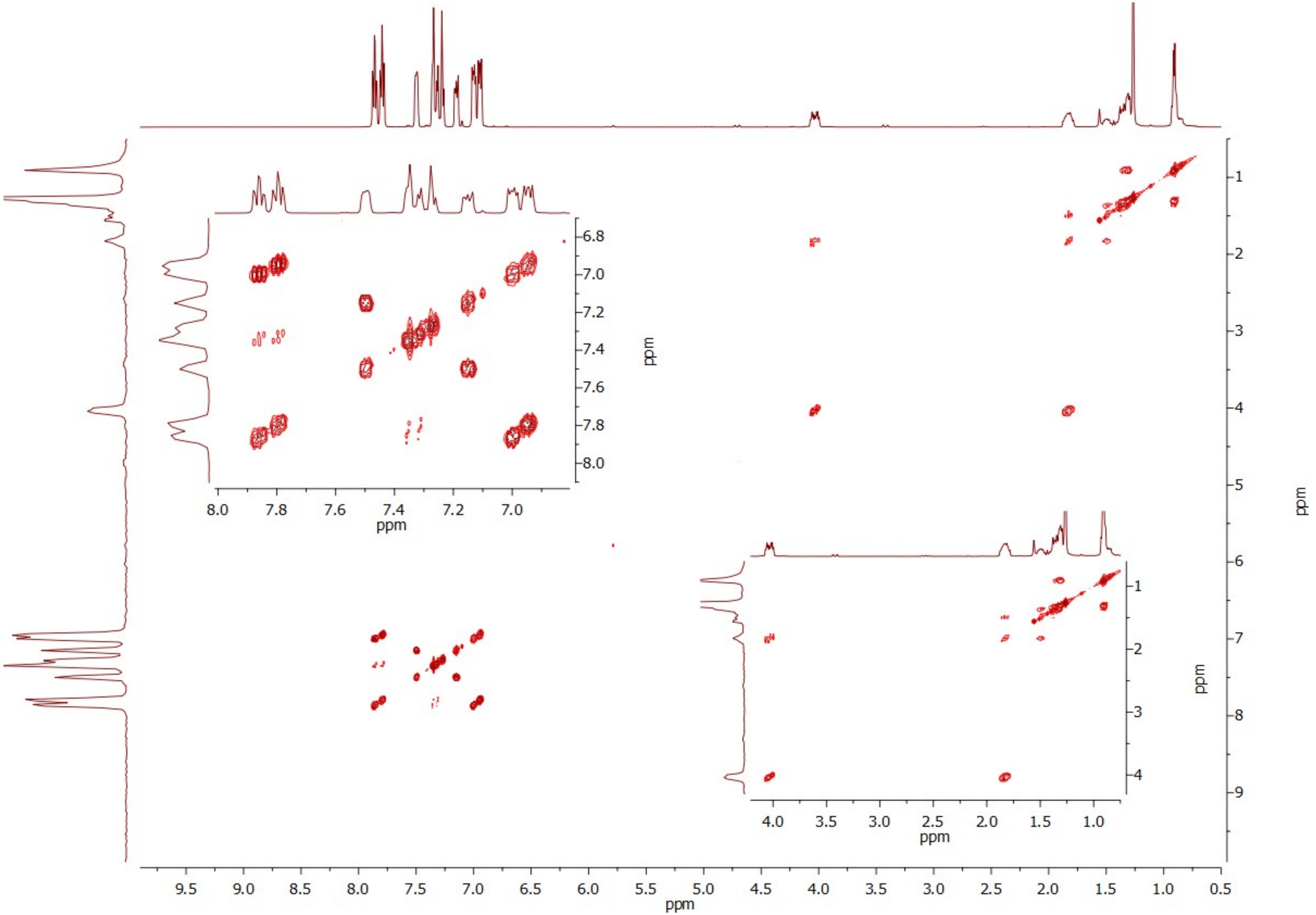

Figure S2. ^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$) spectrum of octyloxybenzene sumanene **3**.

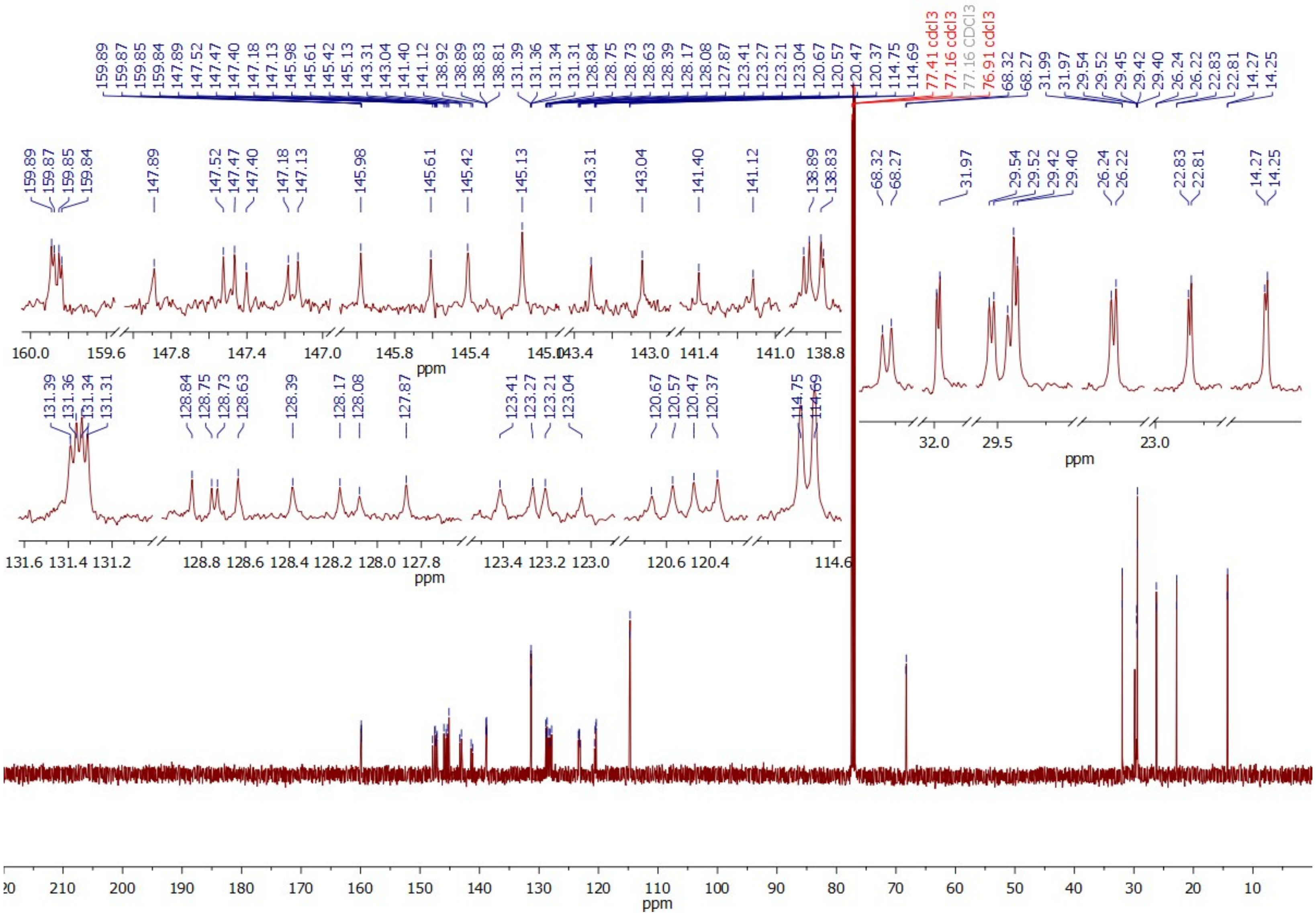

Figure S3. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of octyloxybenzene sumanene **3**.

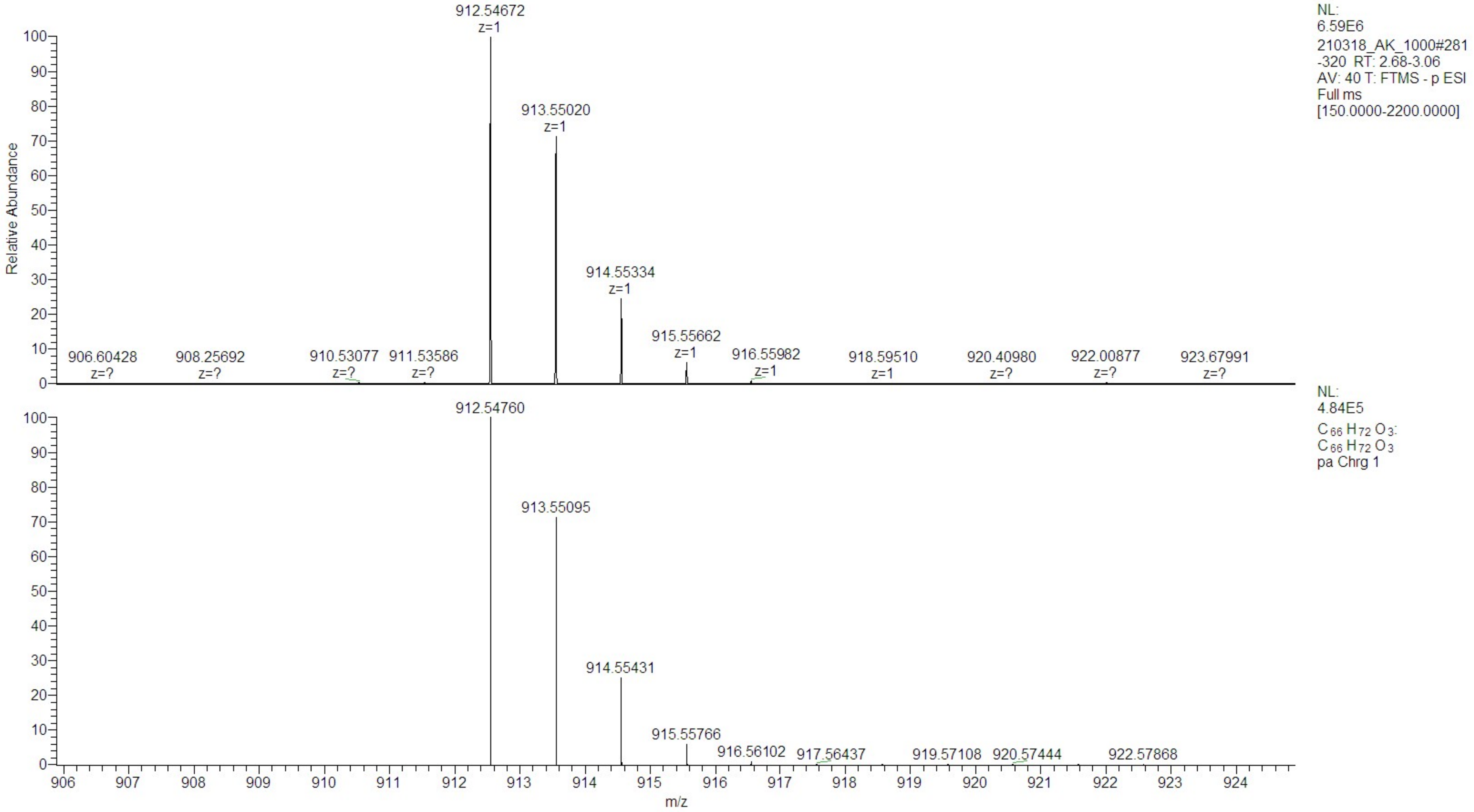

Figure S4. ESI-HRMS (TOF) spectrum of octyloxybenzene sumanene **3**.

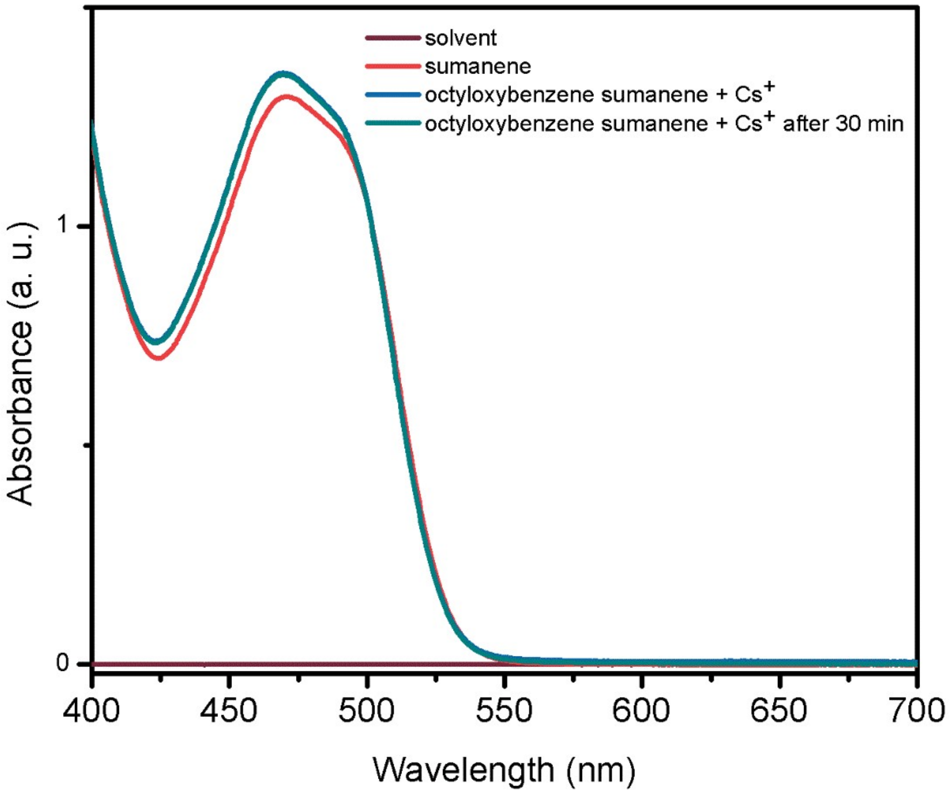

Figure S5. UV-Vis spectra of octyloxybenzene sumanene **3** in the absence and in the presence of caesium cations (10 eq).

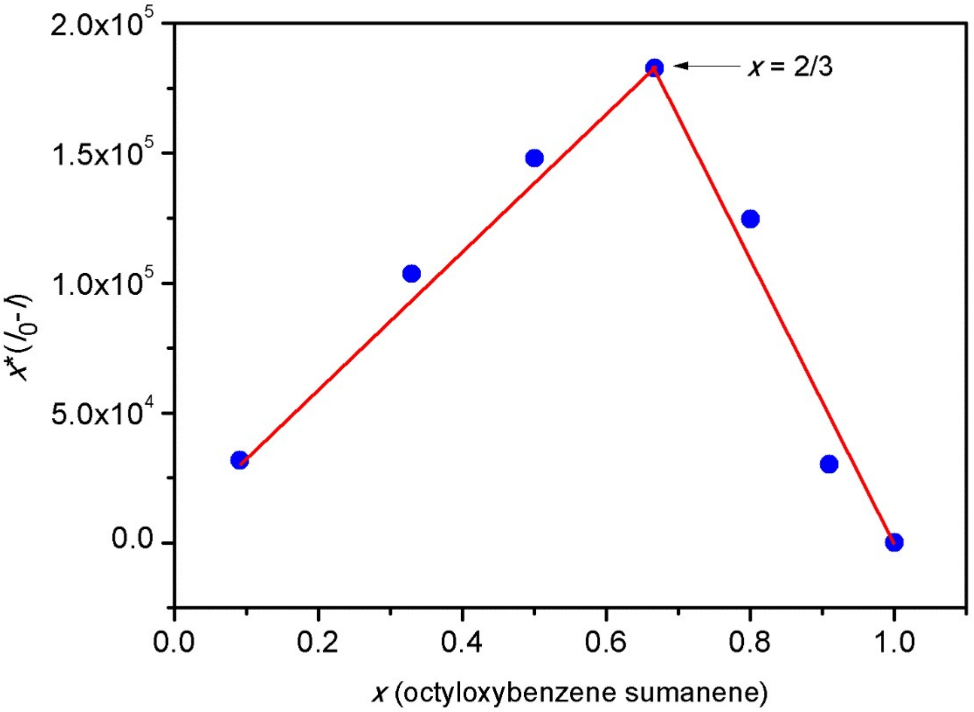

Figure S6. Job's plot regarding the interactions between octyloxybenzene sumanene **3** and caesium cations (*x* stands for the molar fraction of octyloxybenzene sumanene; I_0 and I are the fluorescence intensities of octyloxybenzene sumanene **3** in the absence and in the presence of caesium cations).

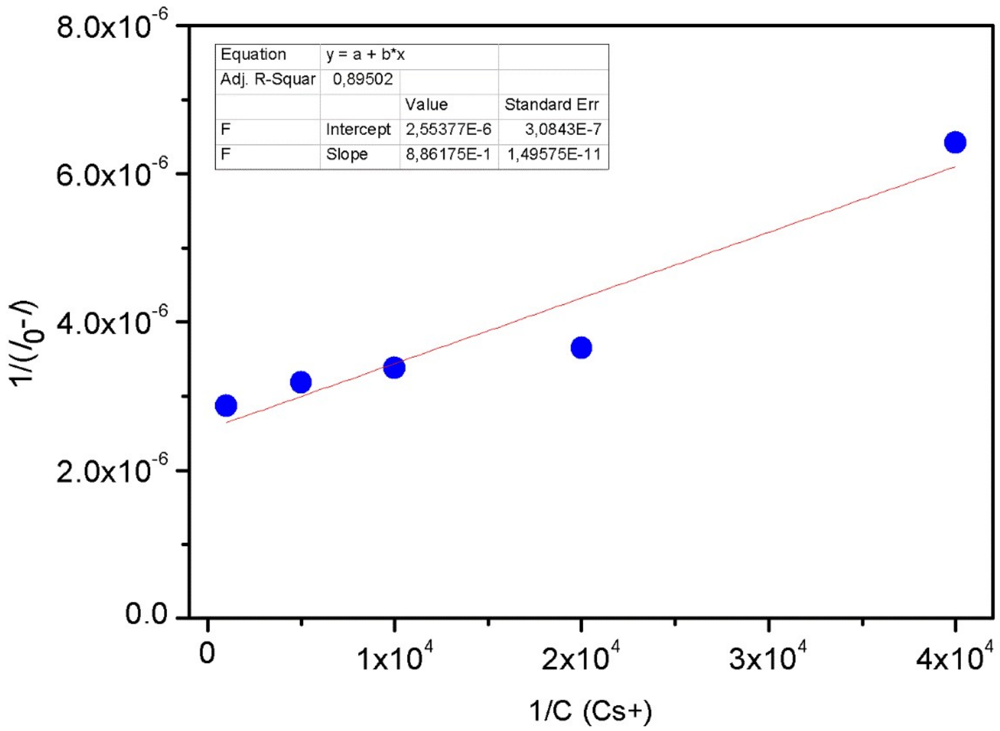

Figure S7. Benesi-Hildebrand plot regarding the interactions between octyloxybenzene sumanene **3** and caesium cations (*C* stands for the molar concentration of caesium cations in the sample; I_0 and I are the fluorescence intensities of octyloxybenzene sumanene **3** in the absence and in the presence of caesium cations). The linear fit data are also presented.

Table S1. Comparison of K_{app} values for the studied complex and other sumanene-based caesium cation complexes.

Entry	Sumanene derivative	K_{app} [M^{-2}]	Method of estimation	Ref.
1	octyloxybenzene sumanene **3**	$2.88 \cdot 10^4$ M^{-2}	emission spectra	This work
2	various ferrocenylsumanenes	$1.7\text{-}45.0 \cdot 10^4$ M^{-2}	emission spectra	[1]
3	Triphenylbenzene sumanene	$9.0 \cdot 10^5$ M^{-2}	emission spectra	[5]

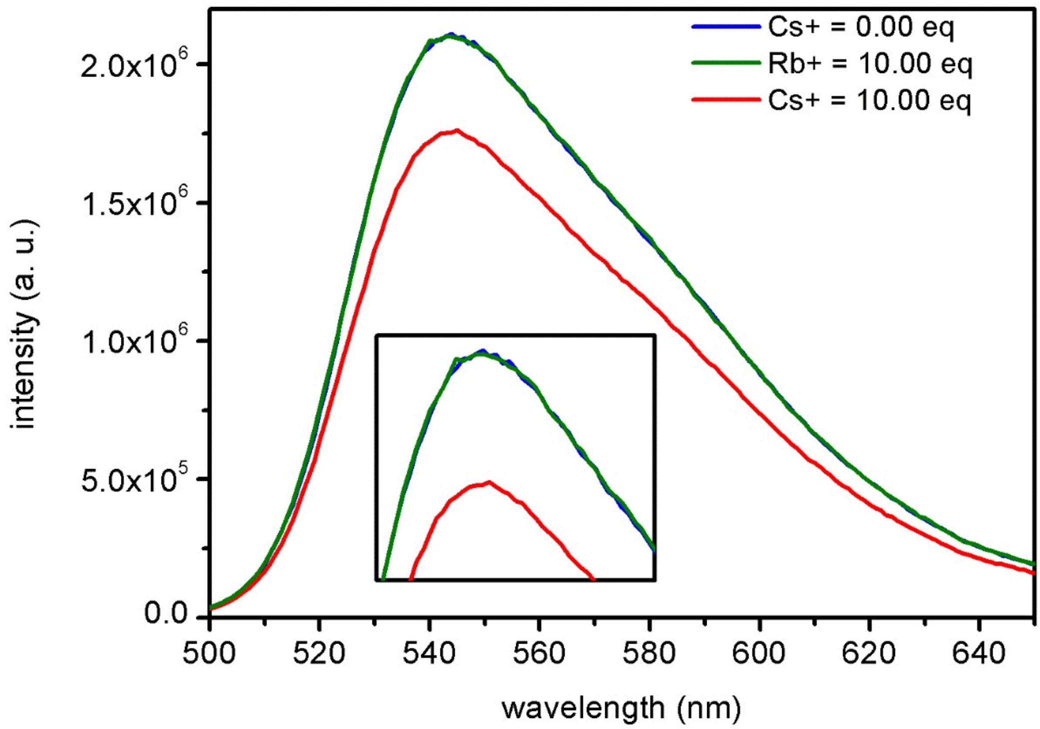

Figure S8. Emission spectra (λ_{ex} = 475 nm) of octyloxybenzene sumanene derivative **3** in the absence and in the presence of rubidium cations (10 eq); spectrum of octyloxybenzene sumanene derivative **3** in the presence of caesium cations (10 eq) is also presented for comparison (the inset of the spectrum is also presented).

Potentiometric selectivity coefficients

The potentiometric selectivity coefficients are introduced in the Nikolski-Eisenman equation, describing the EMF response of ion-selective electrodes in solution containing primary and interfering ions:

$$E = E^{o} + \frac{RT}{z_i F} \ln \left(a_i + K_{i,j}\, a_j^{z_i/z_j}\right)$$

where: E is the measured potential of an ion-selective electrode, E^{o} is a constant, a_i and a_j are the activities of the primary ion (i) and interfering ion (j), z_i and z_j are the charges of the primary ion and interfering ion, $K_{i,j}$ is the potentiometric selectivity coefficient for the primary ion against the interfering ion (R – gas constant, F – Faraday constant, T – absolute temperature).

According to the Nikolski-Eisenman equation, the values of the selectivity coefficients express quantitatively the influence of a given interfering ion (in our case: Na^+, K^+ or Rb^+) on the potential of the ion-selective electrode sensitive towards the primary ion (in our case: Cs^+); the smaller the value of the selectivity coefficient, the less interference.

If the value of $\log K_{Cs,X} = 0$, caesium ions and given interfering ions (X) have the same impact on sensor potential (equal sensor selectivity for caesium and interfering ions), whereas

$\log K_{Cs,X} < 0$ means that the sensor responds to caesium ions more selectively than to interfering ions (*e.g.*, $\log K_{Cs,X} = -1$ indicates tenfold higher sensor selectivity towards caesium against interfering cations, whereas $\log K_{Cs,X} = 1$ means tenfold higher sensor selectivity towards interfering against caesium cations). In other words, if the value of $\log K_{Cs,X} = -1$, the impact of interfering ions on sensor potential will be tenfold smaller than the influence of caesium cations (the sensor will exhibit the same value of potential in solution of interfering cations, that is tenfold more concentrated than the solution of caesium cations).

The term RT/z_iF, present in the Nernst as well as Nikolski-Eisenman equation, defines the theoretical sensor sensitivity, i.e., the theoretical value of the response slope of an ion-selective electrode (for an electrode responding to a monovalent cation, the theoretical response slope is 59.16 mV/dec in 25 ^{o}C).

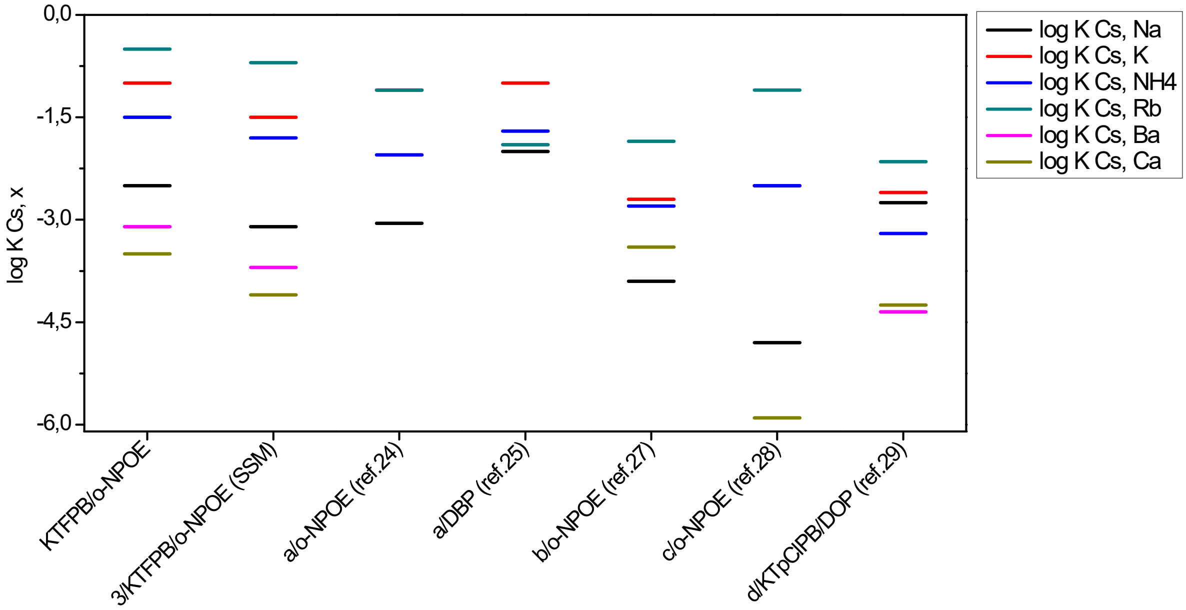

Figure S9. Graphical representation of values of selectivity coefficients (log $K_{\mathrm{Cs,\,X}}$) of potentiometric sensors formulated with octyloxybenzene sumanene derivative **3** and 20 mol% KTFPB (calculated using SSM and FIM method) and without sumanene receptor in PVC/o-NPOE membranes (mean values calculated for 3 electrode specimens). Values of selectivity coefficients of ion-selective electrodes reported in the literature were also presented for comparison. For references 24, 25, 27-29, see main article. Legends: a – dibenzo-18-crown-6 with various spacers; b – calix[6]arene hexaethyl ester; c – 1,3-calix[4]-bis-crown-6; d – p-isopropylcalix[6]arene; o-NPOE – o-nitrophenyl octyl ether; DBP – dibutyl phthalate; DOP – bis(2-ethylhexyl) phthalate, KTFPB – potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; KTpClPB – potassium tetrakis(4-chlorophenyl)borate.

References:

[1] H. Sakurai, T. Daiko, T. Hirao, A Synthesis of Sumanene, a Fullerene Fragment, Science, 301, 2003, 1878.

[2] H. A. Benesi, J. H. Hildebrand, A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons, J. Am. Chem. Soc., 71, 1949, 2703.

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[4] A. Kasprzak, H. Sakurai. Site-selective cation–π interaction as a way of selective recognition of the caesium cation using sumanene-functionalized ferrocenes, Dalton Trans., 48, 2019, 17147.

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