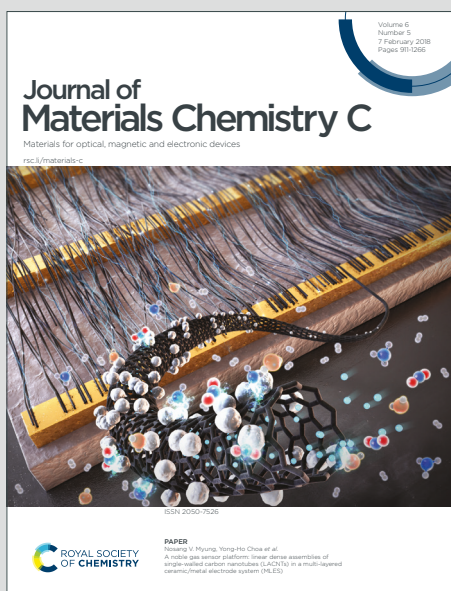


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FULL PAPER

Sumanene-Based Triazole-Linked Receptors

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Designing molecular receptors featuring the bowl-shaped sumanene motif and dedicated to the detection of metal cations constitute an emerging field of applied supramolecular chemistry of this bucky bowl. In this work, we achieved the successful synthesis of a new class of sumanene-based receptors, which key-structural feature was the presence of two or three sumanene units linked via 1,2,3-triazole skeletons generated in the 1,3-dipolar cycloaddition reaction (*click chemistry* approach). The designed compounds were found to recognize metal cations both in solution (spectrofluorometric studies) as well as in heterogeneous system (polymeric membrane of potentiometric sensors). In terms of optical studies in solution, title molecules featured fluorescence quenching behaviours upon addition of metal cations, with Stern-Volmer constant values at the level of 10^6 M^{-1} . The spectrofluorometric and potentiometric results were generally in a good agreement, revealing the preferential binding of lithium (Li^+), caesium (Cs^+) or copper(II) (Cu^{2+}) cations depending on the receptor structure. This work also includes the density functional theory (DFT) computational studies on the structure and receptor properties of the title molecules. The results indicated attractive possibilities for the design of novel organic materials based on sumanene scaffold and toward tuning the recognition properties of the sumanene based receptors for different metal cations.

Supramolecular chemistry of sumanene (**1**, Figure 1), being a bowl-shaped and π -conjugated fragment of fullerene C_{60} , has

developed remarkably in the last several years.^{1–5} The most representative examples include the design of functional materials dedicated to dielectric devices^{6–8}, (metal)organic frameworks and organized molecules^{9,10} or molecular receptors^{11–13}. The last application area might be considered as a natural evolution within sumanene science over the years, which began from numerous computational studies on the cation- π interactions between sumanene and metal cations^{14–17}, as well as demonstrated sumanene possibilities toward formation of organometallic complexes.^{18–21}

In terms of sumanene-based molecular receptors science, recent reports revealed mostly the possibility of selective detection of caesium (Cs^+) cations by means of site-selective cation- π interactions with the inclusion of concave sites of sumanene bowls (formation of sandwich complexes). From the structural viewpoint, these studies employed receptors based on mono^{11,13,22,23}-, tris^{12,22,24–27}- or tetra^{27,28}-substituted sumanene derivatives functionalized with various moieties, mostly aromatic skeletons. Molecular recognition process could be tracked spectroscopically and electrochemically, using both voltammetric^{11,13,24,28} and potentiometric^{22,26} methods. The potentiometric method could be considered especially attractive since on the contrary to the voltammetric sensors, potentiometric technique does not require the presence of redox active moiety in the receptor molecule, what potentially expands the scope of derivatives to be used as ionophores. Previous studies demonstrated that sumanene derivatives might serve as ionophores in potentiometric sensors, featuring good selectivity toward Cs^+ with satisfactory limit of detection (LOD) parameter value at the micromolar concentration level.

The copper-catalysed azide-alkyne cycloaddition (CuAAC) is an efficient *click chemistry* reaction that can be applied, among others, to the synthesis of complex receptors molecules coupling the recognition unit with the reporter probe.²⁹ As a result of *click* reaction, 1,4-disubstituted 1,2,3-triazoles products are formed, where the 1,2,3-triazole ring often plays the role of simple covalent linker of macromolecular

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FULL PAPER

Journal Name

structures.³⁰ However, the 1,2,3-triazole skeleton can be also employed as a building block for the design of functional receptors.³¹ These specific binding properties result from the presence of nitrogen atoms with lone electron pairs, providing binding sites to coordinate transition metal cations, as well as C–H hydrogen bond donor in the heteroaromatic system, enabling CH...anion hydrogen bonding interactions.^{31,32} Therefore, 1,2,3-triazole-based compounds were widely reported as highly effective chromogenic or fluorogenic receptors for cations, anions and neutral molecules sensing.^{33,34} Potentiometric cation and anion-detection was attempted using 1,2,3-triazole-based ionophores introduced into polymeric membranes of ion-selective electrodes (see, e.g. tetratriazole-linked calix[4]arene³⁵ or triazolophane derivatives³⁶ displaying high selectivity toward Cu²⁺ cations or halide anions, respectively). On the other hand, the introduction of ferrocene unit (*via* click reaction) into receptor structure led to development of voltammetric sensors, where the redox properties of ferrocene were affected by cation or anion binding to the triazole moiety.^{33,37,38}

Herein we report on the synthesis of bis- and tris-*sumanenes* (compounds **2-4**, **Figure 1**), as well as spectrofluorimetric and potentiometric studies on their receptor properties towards detection of selected metal cations. The binding mode of the designed receptors relies on the cation- π interactions with the inclusion of *sumanene* skeletons, as well as N-donor binding sites of 1,2,3-triazole moieties. From the synthetic viewpoint, we selected *click chemistry* (1,3-dipolar cycloaddition) approach for the design of target receptors not only taking into account versatility of this methodology toward generation of various applied materials, but also considering prospectively attractive receptor properties of 1,2,3-triazoles in conjunction with *sumanene* motif, as noted above. Inspired by the report³⁹ on the unexpected Li⁺-detection property of *sumanene*-based bis(terpyridine)–ruthenium(II) complexes, among which several molecules were based on two linked *sumanene* skeletons, we anticipated tuned receptor properties of compounds **2-4** in comparison to known Cs⁺ receptors composed of one *sumanene* skeleton in the formula. According to our studies reported in this work bis- and tris-*sumanenes* feature tuned selectivity toward Cs⁺, Li⁺ or Cu²⁺, what not only revealed structure-receptor property relationship but also might be considered as a next step in expanding the scope of possible analytes to be detected by carefully designed *sumanene*-based receptors. Our studies also demonstrated that the location of the 1,2,3-triazole unit in the designed receptors (direct attachment to the *sumanene* skeleton or via a linker) is crucial in terms of the selectivity of the receptor, what is an important outcome for further studies in the discussed area.

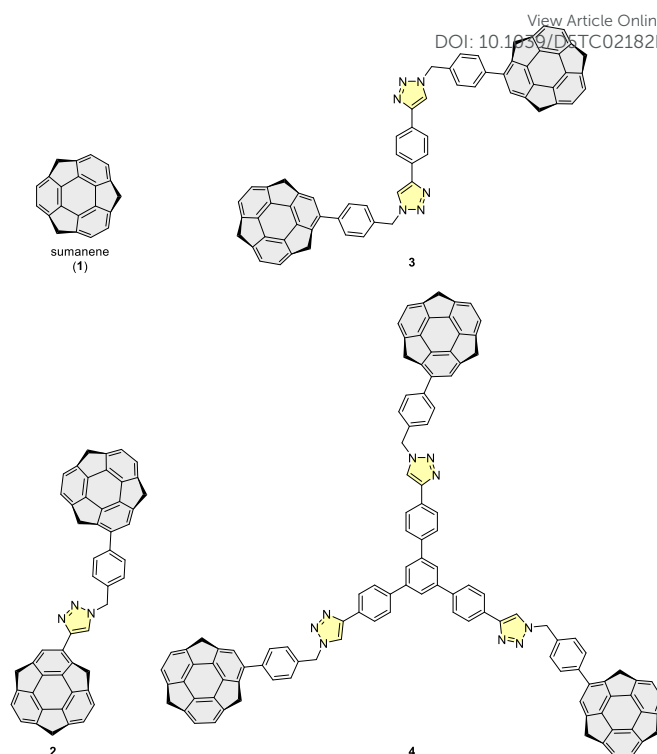


Figure 1. Structures of *sumanene* (**1**) and target compounds **2-4** (*sumanene* skeleton - grey, 1,2,3-triazole skeleton – yellow).

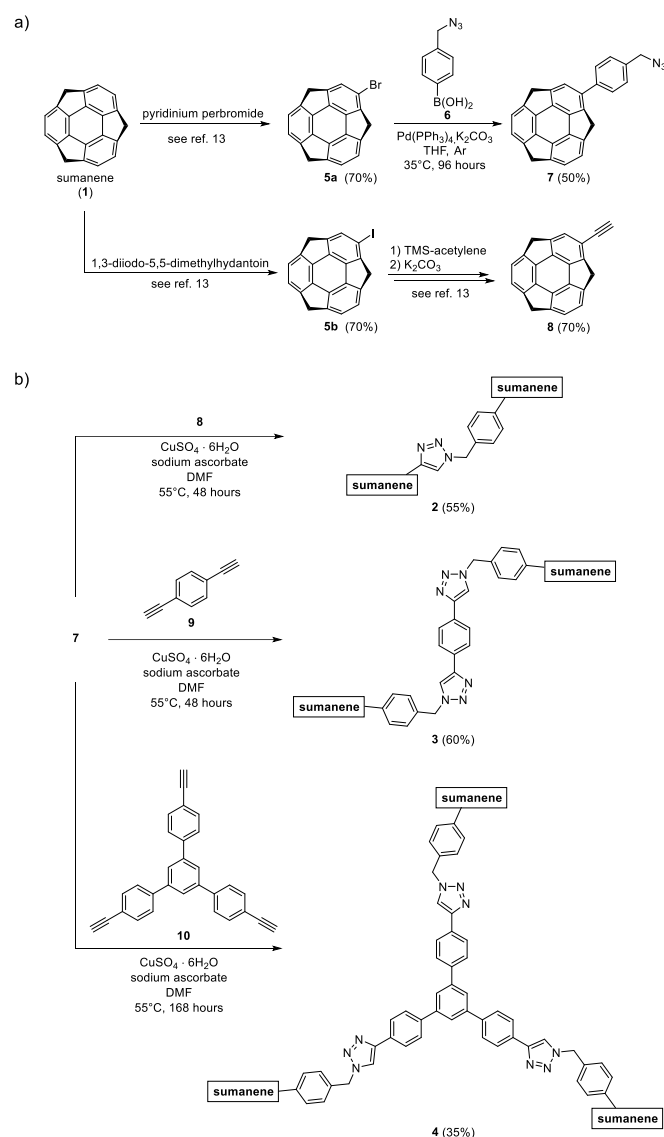
Results and discussion

Synthesis and photophysical characterization of compounds **2-4**

Full experimental details on the synthesis are presented in Electronic Supporting Information (ESI), Section S1. **Scheme 1** shows synthesis paths toward **2-4**. Starting material for the synthesis of compounds **2-4**, namely *sumanene* derivative bearing an azide moiety (compound **7**), was synthesized (60%) by means of the Suzuki-Miyaura cross-coupling between 2-bromosumanene (**5a**)⁴⁰ and (4-(azidomethyl)phenyl)boronic acid (**6**)⁴¹. Optimization experiments revealed that the highest reaction yield was observed for conducting the reaction at 35°C for 96 hours under argon atmosphere and with the usage of tetrakis(triphenylphosphine)palladium(0) as the catalyst. Synthesis paths toward **2-4** were based on the similar conditions of 1,3-dipolar cycloaddition reaction (*click chemistry* approach) using starting material **7** in each case and employing copper(II) sulphate pentahydrate with sodium ascorbate as the catalytic mixture, in *N,N*-dimethylformamide (DMF) as the solvent and at 55°C. 2-Ethynylsumanene (**8**)⁴⁰, 1,4-diethynylbenzene (**9**) or 1,3,5-tris(4-ethynylphenyl)benzene (**10**)⁴² were subjected to reaction to obtain compound **2**, **3** or **4**, respectively. During optimization experiments towards compounds **3-4**, we were able to identify the formation of side products comprising unreacted ethynyl moieties (compounds of mono- or di-substitution; see details on optimization experiments in ESI, Section S1). The highest isolated yield for compounds **2-3** (55-60%) and **4** (35%) were observed for conducting the reaction for 48 hours and 168 hours,



respectively. Longer reaction times have not provided higher yields of target products. Interestingly, we observed that the highest yield for transformation of **7** to *click chemistry* derived **2-4** were achieved when the starting material **7** was subjected to the reaction just after its preparation, suggesting that longer storage times of compound **7** (even for storing the sample under argon atmosphere at -28°C) was not beneficial.



Scheme 1. Synthesis of compounds **2-4**.

1D and 2D NMR spectroscopy, as well as HRMS spectrometry supported the formation of pure compounds **2-4** and **7** (refer to ESI, Sections S1-S3, for the compounds characterization data). **Figure 2** presents the comparison of the ^1H NMR spectra of **2-4** (in $\text{DMSO}-d_6$). In brief reading NMR spectra of compounds **2-4**, the most diagnostic changes between the spectra of starting materials (**7-10**) and target products **2-4** were the lack of the signals coming from the ethynyl moieties (from starting materials **8-10**) in the spectra of

compounds **2-4**, along with the presence of characteristic ^1H NMR signals of 1,2,3-triazole moieties (δ_{H} between 8.82 and 8.73 ppm). Additionally, ^1H and $\{^1\text{H}\}^{13}\text{C}$ NMR spectra of compounds **2-4** not only featured signals coming from the aromatic moieties, but also characteristic ^1H NMR signals for sumanene H-benzylic,endo (δ_{H} between 3.62 and 3.28 ppm) and H-benzylic,exo (δ_{H} between 5.04 and 4.67 ppm) protons, as well as ^{13}C NMR signals of C-benzylic ^{13}C nuclei (δ_{C} between 52.8 and 41.2 ppm). Notably, NMR spectra of **3-4** suggested that these compounds were chemically equivalent in solution. It could be also observed that resonances for benzylic protons of **3-4** were relatively similar to each other and different than those for **2**, what could be ascribed to different sumanene skeleton substitution in **2** (two sumanene bowls feature different substituents at the aromatic position) in comparison to **3-4** (two sumanene bowls feature the same substituent at the aromatic position). Additionally, ^1H DOSY NMR experiments revealed that the signals observed in the NMR spectra of **2-4** came from one molecule, what constituted the further support of samples composition. Hydrodynamic radius ($r_{\text{solv,H}}$)⁴³ for compound **4** (ca. 1.3 nm) was found to be higher than hydrodynamic radii of **2** (ca. 0.8 nm) and **3** (ca. 0.5 nm). Finally, HRMS spectra analyses revealed that experimental and computed isotopic patterns for **2-4** and **7** were consistent with each other, which ultimately confirmed the successful isolation of target sumanene derivatives.

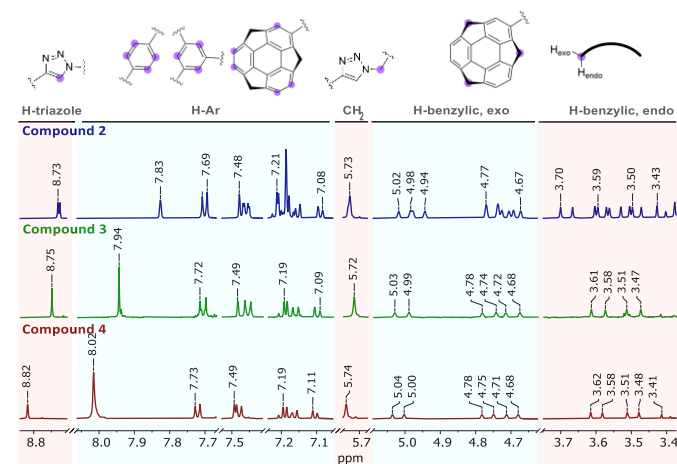


Figure 2. Selected insets of the ^1H NMR spectra (600 MHz, $\text{DMSO}-d_6$) of compounds **2-4**. Graphical representation of the structural moieties ascribed to given groups of signals are also presented. Selected peaks are marked for the image clarity. The same colour does not correspond to the same chemical shift in the NMR spectrum.



Figure 3 shows the summary of UV-vis and fluorescence spectra of compounds **2-4** (in THF; see 3D fluorescence spectra of **2-4** in Section S4, ESI). UV-vis spectra of compounds **2-4** featured absorption maxima (λ_{max}) located between 250–375 nm with molar absorption coefficient (ϵ) values ranging from $1.5 \cdot 10^4$ to $5.5 \cdot 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. Fluorescence spectra of compounds **2-4** showed one emission maximum (λ_{em}) located at ca. 400 nm. The highest ϵ and fluorescence intensity values were found for compound **4**, whereas the lowest for compound **3**. Density functional theory (DFT) and time-dependent DFT (TD-DFT) computations^{44–48} (B3LYP⁴⁹/3-21G⁵⁰) with compounds **2-4** revealed in general good accordance between observed and calculated transitions in the UV-vis spectra (refer to ESI, Section S7 for data). Additionally, HOMO-LUMO energy gaps for compounds **2-4** were very similar (4.42–4.43 eV), which is consistent with the observed lack on significant differences in their experimental fluorescence spectra (λ_{em} between 394–397 nm).

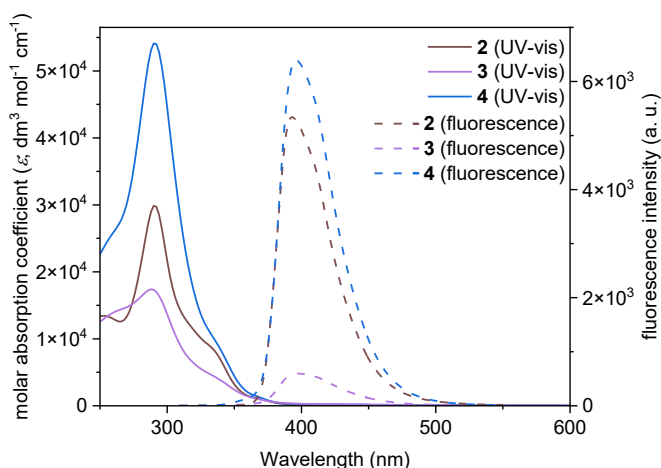


Figure 3. UV-vis (THF) and fluorescence spectra (THF, $\lambda_{\text{ex},2} = 290 \text{ nm}$, $\lambda_{\text{ex},3} = 288 \text{ nm}$, $\lambda_{\text{ex},4} = 290 \text{ nm}$) of compounds **2-4** ($C = 2 \times 10^{-5} \text{ M}$).

Receptor properties of compounds **2-4**

Supramolecular interactions between bis- and tris-*sumanenes* **2-4** and selected metal cations were investigated in solution using fluorescence spectroscopy. Due to the limited solubility of the *sumanene* derivatives in water, the experiments were carried out in 1:1 mixture of THF and water (see full experimental details for spectrofluorimetric titrations in Subsection S1.4, ESI).

Figure 4 presents the results of fluorescence spectra titration curves of receptors **2-4** with various metal cations (Li^+ , Cs^+ and Cu^{2+} were included in the comparison taking into account previous reports on Li^+ and Cs^+ oriented *sumanene* receptors, and the presence of 1,2,3-trizole moieties in **2-4** structures, regarding Cu^{2+}). The addition of further portions (molar equivalents) of metal cations caused a systematic decrease in the intensity of fluorescence signal ($\lambda_{\text{em}} = 400 \text{ nm}$), but different behaviour of signal quenching by particular cations

was observed for the studied receptors. The presence of Li^+ cations resulted in fluorescence quenching of all tested receptors, which was ascribed to the dynamic formation of cation- π systems. However, high selectivity of Li^+ complex formation was noticed only for receptor **2**, whereas derivatives **3** and **4** exhibited comparable affinity toward copper and Cs^+ cations, respectively. Moreover, the most significant changes in intensity of fluorescence signal upon addition of Li^+ and Cs^+ cations was noticed for tris-*sumanene* receptor **4** (see Figures S37 and S38, ESI, presenting emission spectra of **4** during titrations with Li^+ and Cs^+ cations). It should be also emphasized that similar turn-off fluorescence behaviour was found during our previous studies on *sumanene* based Cs^+ cation receptors.²²

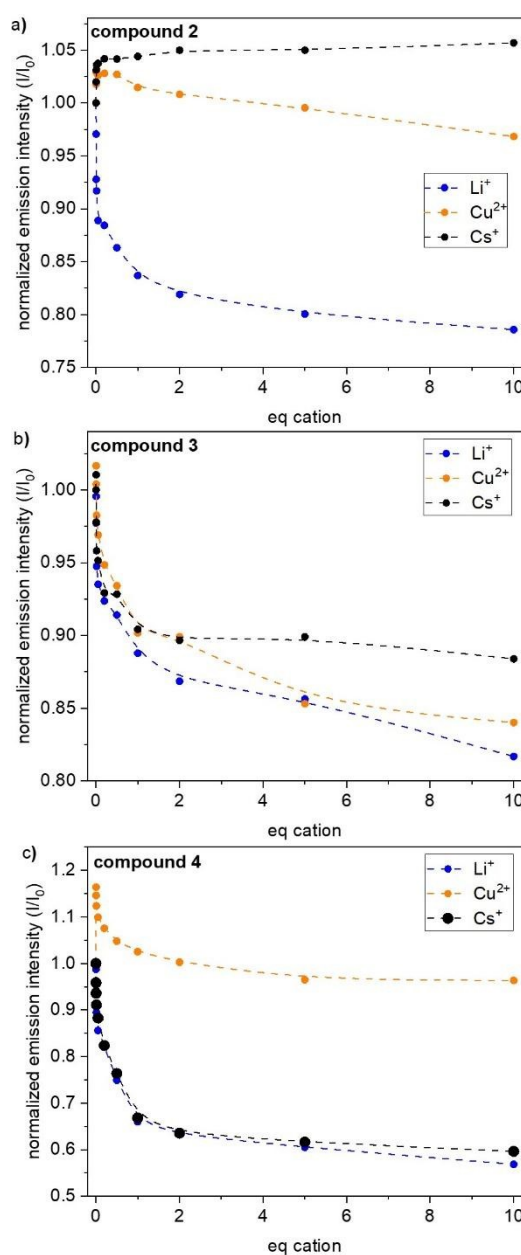


Figure 4. Fluorescence spectra titration curves for receptors **2-4** with Li^+ , Cs^+ and Cu^{2+} cations (THF:water = 1:1 v/v, $C = 0.02 \text{ mM}$).



Stern-Volmer constants were determined using non-linear curve fitting of fluorescence titration data to modified Stern-Volmer equation (1). This equation describes fluorescence quenching in a system, in which only a fraction of fluorophore is accessible to the quencher (e.g. due to partial aggregation of the receptor molecules in solution).^{51–53} The calculated Stern-Volmer constants (K_{SV}), reflecting the strength of interactions between metal cations and receptors **2–4** observed during spectrofluorimetric experiments, were collected in **Table 1** (plots depicting non-linear curve fitting of fluorescence titration data and fitting parameters were presented in Section S6, ESI).

$$\frac{I_0}{I_0 - I} = \frac{1}{f_a \cdot K_{SV} \cdot c} + \frac{1}{f_a} \quad (1)$$

where: I_0 , I – fluorescence intensities of the receptor molecule in the absence and presence of quencher, respectively; c – quencher concentration; K_{SV} – Stern-Volmer constant; f_a – fraction of the fluorophore accessible to the quencher.

Table 1. Values of Stern-Volmer constants determined for derivatives **2–4** using a non-linear curve fitting of fluorescence titration data presented in **Figure 3**.

Compound	Li ⁺ K_{SV} [10^6 M ⁻¹]	Cs ⁺ K_{SV} [10^6 M ⁻¹]	Cu ²⁺ K_{SV} [10^6 M ⁻¹]
2	12.6	-	-
3	2.6	6.7	1.0
4	2.48	3.87	-

The selectivity of metal cation recognition was also studied in a heterogeneous system, i.e., the bis- and tris-sumanene derivatives **2–4** have been introduced into polymeric membranes based on plasticized poly(vinyl chloride) (PVC), used commonly as a membrane matrix of ion-selective electrodes. Potentiometric selectivity coefficients, reflecting the influence of a given interfering cation (Me) on the signal of the ion-selective sensitive towards chosen primary ion, were determined in this regard. Assuming that the tested sumanene derivatives **2–4** work as neutral carriers, lipophilic anionic additive (potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; KTFPB) has been added to the membranes to achieve their permselectivity and provide proper operation of the sensors.^{54–56} The ion-selectivity of the polymeric membranes containing studied receptors **2–4** were graphically presented in **Figure 5** and collected in **Table 2** (the values of selectivity coefficients have been calculated for Na⁺ as an arbitrary chosen primary ion). It should be noted that the presence of anionic sites (TFPB⁻) induces enhanced membrane selectivity toward lipophilic cations (e.g. Cs⁺), characterized by less negative values of standard molar Gibbs free energy of hydration.⁵⁷ Therefore, the reliable evaluation of the results requires the comparison of the selectivity of polymeric layers doped with receptors **2–4** with the same values determined for blank membranes, containing only KTFPB.

According to the results of our previous studies on sumanene molecular receptors^{22,26}, high Cs⁺ selectivity of PVC/2-nitrophenyl octyl ether (o-NPOE) membranes doped with receptors **2–4** was found. However, the specific structures of herein designed bis- and tris-sumanenes **2–4** provided increased membrane selectivity toward Li⁺ cations over alkali metals cations in comparison with blank membranes (an increase of log $K_{Na, Li}$ with simultaneous decrease of log $K_{Na, Me}$ values for other alkali metals cations⁵⁸). Moreover, an enhanced affinity toward Cu²⁺ cations was also noticed, with the most pronounced effect observed for membrane based on receptor **3**, for which a highest selectivity for Cu²⁺ cations was obtained (better even with respect to highly lipophilic Cs⁺ cations). This result was consistent with spectrofluorimetric titrations of the studied receptors, where a strong fluorescence quenching was registered for derivative **3** in the presence of Cu²⁺ cations. Despite the fact that potentiometric selectivity coefficients were determined in a heterogeneous system (membrane/water solution) and therefore did not strictly reflect the ion-binding properties of studied receptors in solution, good correlation of electrochemical and spectroscopic results was noticed.

As mentioned above, 1,2,3-triazole-based compounds are widely used as molecular receptors for selective recognition of Cu²⁺ cations.^{33–35} Therefore, the selectivity of membranes doped with truncated subunit of bis-sumanene **3**, namely 1,4-bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)benzene (**11**; see structure in **Figure 5**)⁵⁹, was studied, to establish the role of 1,2,3-triazole sites in Cu²⁺ binding by receptor **3**. The incorporation of **11** into polymeric membranes led to a complete loss of their Cu²⁺ selectivity, since a selectivity pattern similar to that obtained for blank membranes containing only the ion-exchanger was obtained. Such effect was in good agreement with spectrofluorimetric experiment, where no significant change in the intensity of fluorescence signal was observed during the titration of derivative **11** with copper cations (**Figure S39**, ESI). These results clearly indicate that the affinity of the receptor **3** toward Cu²⁺ was not due to the interactions of the cations solely with the N-donor atoms of 1,2,3-triazole moiety, but resulted from complementary engagement of sumanene bowl(s) and 1,2,3-triazole binding sites in metal cation coordination (enhanced affinity for divalent metal was not observed for sumanene molecular receptors without 1,2,3-triazole moiety, reported in our previous work²²).

Concluding, experimental results pointed out that the presence of multiple sumanene units linked via 1,2,3-triazole skeletons strengthened the receptor affinity for Li⁺ over other alkali metals cations. Moreover, different cation selectivity of receptors **2–4** resulted from the specific location of the 1,2,3-triazole unit in the receptor structure (directly attached to the sumanene skeleton or via a linker). This unique arrangement of the binding sites in **3** was necessary to achieve high Cu²⁺ selectivity, whereas various geometrical feature of core skeleton in structure of **3** (1,4-phenylene) in comparison to **4** (1,3,5-triphenylbenzene) might have influenced the observed selectivity. According to potentiometric and spectrofluorimetric studies with reference molecule **11**, the presence of sumanene skeleton, providing cation- π interaction phenomenon in the



designed molecules, was essential to tune their selectivity profiles. It also means that the binding mode for the studied receptors is related to the existence of cation- π interactions in conjunction with N-oriented interactions with the inclusion of 1,2,3-triazole units.

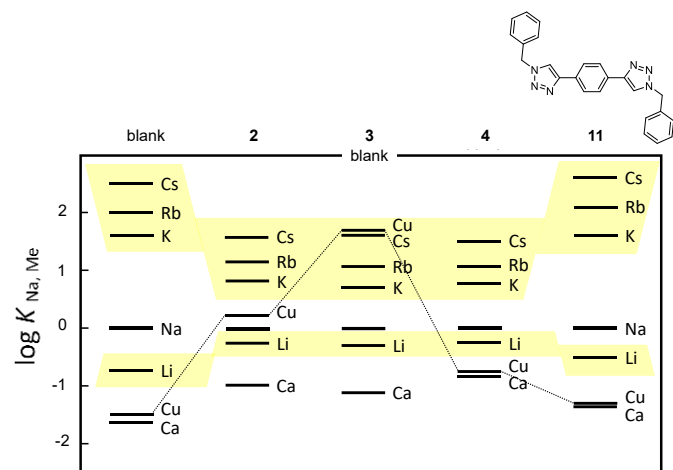


Figure 5. Graphical presentation of the selectivity (values of $\log K_{Na, Me}$) of PVC/o-NPOE membranes formulated with receptors **2-4** and **11** (10 mol% KTFPB) and without receptor (blank membrane); mean values were calculated for 3 electrode specimens. The structure of compound **11** is also presented.

Table 2. Values of selectivity coefficients ($\log K_{Na, Me}$) of potentiometric sensors formulated with receptors **2-4** and **11** (10 mol% KTFPB) and without receptor (blank membrane) in PVC/o-NPOE membranes (mean values calculated for 3 electrode specimens).

	$\log K_{Na, Li}$	$\log K_{Na, K}$	$\log K_{Na, Rb}$	$\log K_{Na, Cs}$	$\log K_{Na, Ca}$	$\log K_{Na, Cu}$
blank	-0.75	1.60	2.00	2.50	-1.65	-1.50
2	-0.25	0.80	1.15	1.55	-1.00	0.25
3	-0.30	0.70	1.05	1.60	-1.15	1.70
4	-0.25	0.75	1.05	1.50	-0.80	-0.75
11	-0.45	1.60	2.10	2.60	-1.35	-1.30

To additionally study the role of sumanene bowl and 1,2,3-triazole binding sites in metal cation coordination, DFT calculations (B3LYP/3-21G) were conducted for Li^+ complexes of receptor **2**, exhibiting the highest affinity toward Li^+ cations among studied receptors. Three different complex arrangements were subjected to DFT calculations, including Li^+ cation concave or convex bound to the bowl-shape parts of the receptor and assuming 1:1 complex stoichiometry (see **Table 3**, where free energies (ΔG) of complex formation and DFT optimized structures were presented). According to our computations, the most energetically favoured was the binding of Li^+ at the concave-oriented system including the engagement of 1,2,3-triazole moiety (arrangement **2_A**). It revealed a

complementarity factor of sumanene and 1,2,3-triazole bindings sites in receptor **2** structure towards metal cation binding. On the other hand, the ΔG values of complex formation for convex-bound (arrangement **2_B**) and concave-bound Li^+ cation but with 1,2,3-triazole moiety separated from the bowl by a phenyl ring (arrangement **2_C**) were significantly higher; ΔG for arrangement **2_B** was *ca.* twice higher as for **2_A**, whereas ΔG for arrangement **2_C** was positive, suggesting thermodynamically unfavoured formation of such complex. Notably, the obtained results also justify the lower values of Stern-Volmer constants determined for derivatives **3** and **4**, in which the complementary engagement of sumanene bowl and 1,2,3-triazole in metal cation coordination could not occur. It should be stressed that the above-noted experimental results from both techniques (spectrofluorimetry, potentiometry) are in good agreement and support highly specific **2**- Li^+ binding over other studied systems. In this sense, performed DFT computations enabled an insight into the preferential binding mode for the studied system, revealing the crucial role of the presence of 1,2,3-triazole moiety directly attached to a sumanene skeleton (via aromatic position) what influenced the improved cation- π interactions in the system. Such insight into Li^+ selectivity for sumanene-based receptors was not reported before.

Table 3. DFT computed (B3LYP/3-21G) interaction energies (ΔG) and DFT optimized (B3LYP/3-21G) structures of complexes formed of receptor **2** and Li^+ cation (hydrogen atoms are omitted for clarity).

Arrangement	Geometry	ΔG [kJ/mol]
2_A		-112.7
2_B		-58.5
2_C		76.6

The coordination chemistry of sumanene-based derivatives has been studied in recent years by many groups involved in the synthesis of these compounds. Depending on their structure, the complexation of various transition metal cations, with a preference for metal binding to a concave surface versus a convex one was reported.⁴ Nevertheless, the receptor properties, especially the selectivity and sensitivity of recognition of target molecules, were determined only for a limited number of sumanene derivatives dedicated for spectroscopic or electrochemical analyte sensing (see **Table 4**). According to the first published computational and



experimental studies high affinity of sumanene receptors towards caesium cations was observed, whereas functionalisation of sumanene bowl with large terpyridine-ruthenium(II) moiety or the design of aggregation-induced emission active (AIE) sumanene-1,1,2,2-tetraphenylethene derivative favored the complexation of lithium cations, predominantly at the convex side according to results of reported DFT computations. The results reported in this work demonstrate an important advancement in the design of new generation of sumanene-based molecular receptors, since a careful tuning of their structure may provide enhanced sensing capabilities toward lithium, copper or caesium cations with satisfactory binding parameters.

The results reported in this work demonstrate an important advancement in the design of new generation of sumanene-based molecular receptors, since a careful tuning of their structure may provide enhanced sensing capabilities toward lithium, copper or caesium cations with satisfactory binding

parameters. Although the aim of the research was to synthesize and determine the coordination properties of new bis- and tris- sumanene derivatives, the electrochemical experiments carried out in a heterogeneous system emphasized their relevance in the development of modern electroanalytical tools. Polymeric membranes are the key element of potentiometric sensors, whose high selectivity results from the recognition abilities of appropriate molecular receptors, enabling their application in the monitoring of complex environmental samples. Therefore, the possibility of adapting the receptor structure based on the same sumanene motif, and thus the selectivity and sensitivity of a designed sensor, to a specific analytical task is particularly important.

Table 4. Comparison of sensing performance for reported sumanene-based receptors.

Receptor	Selectivity	Physicochemical parameter (M ⁻¹)	Analytical technique(s)	Ref.
bis-sumanene (compound 2)	Li ⁺	K_{sv} : 1.26×10^7	fluorimetry potentiometry	This work
tris-sumanene (compound 3)	Cu ²⁺ / Li ⁺	K_{sv} : from 1.0×10^6 to 2.6×10^6		
tris-sumanene (compound 4)	Cs ⁺ / Li ⁺	K_{sv} : from 3.87×10^6 to 2.48×10^6		
trisubstituted sumanenes	Cs ⁺	K_a : from 2.88×10^4 to 7.35×10^6	fluorimetry potentiometry voltammetry (ferrocene derivatives)	12,22,24–27
monosubstituted sumanenes	Cs ⁺	K_{sv} : from 1.70×10^4 to 4.50×10^5	fluorimetry potentiometry	11,22,40
		K_a : from 5.90×10^5 to 8.70×10^5	voltammetry (ferrocene derivatives)	
tetrasubstituted sumanenes	Cs ⁺	K_a : from 3.90×10^3 to 1.20×10^5	fluorimetry voltammetry (ferrocene derivatives)	27,28
sumanenes featuring aggregation-induced emission effect	Cs ⁺ / Li ⁺	K_{sv} : from 4.54×10^8 to 4.68×10^{10}	fluorimetry	23
sumanene-based terpyridine-ruthenium(II) complexes	Li ⁺	K_{sv} : from 0.73 to $\times 10^3$ to 5.05×10^3	fluorimetry	39



Conclusions

In conclusion, our work demonstrated the possibility to synthesize bis- and tris-sumanene derivatives using the *click chemistry* approach. The obtained molecules were applied to the optical and potentiometric detection of metal cations, which revealed structure-receptor property relationship of the designed sumanene-based receptors. Depending on the receptor structure, directly related to the type and geometrical features of a linker between the sumanene skeletons, as well as the method of attachment of a 1,2,3-triazole unit to a sumanene core, different recognition properties toward Cs⁺, Li⁺ or Cu²⁺ cations were found. Results from spectrofluorimetric titrations and potentiometric experiments were in a good accordance, which were further supported with the DFT computations with the representative system. This work opens new horizons in the design of sumanene-based organic materials with tuned receptor properties toward detection of metal cations, ranging from small Li⁺ cations and big Cs⁺ cations, or d-block Cu²⁺ cation.

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Author contributions

J.A. performed synthesis, characterization, receptor (potentiometric, spectroscopic) experiments and DFT computations under the supervision of A.K. and W.W., analysed the data, prepared the manuscript text dealing with spectrofluorimetric titrations and DFT computations, as well as compiled supporting information regarding these parts.

S.K. performed the calculations of Stern-Volmer constants and prepared the text regarding this part of work, commented on the manuscript during the preparation of the final version.

H.S. provided sumanene, funding for research from the Japanese side, and commented on the manuscript during the preparation of the final version.

W.W. co-conceived the project, designed and supervised potentiometric and spectrofluorimetric experiments by J.A., analysed the data, prepared draft of manuscript text dealing with the potentiometric studies, as well as compiled supporting information regarding this part, wrote part of the introduction section, co-conceptualized and commented on the manuscript during the preparation of the final version.

A.K. co-conceived the project, designed structures of all compounds, designed and supervised synthetic, spectrofluorimetric and DFT computational experiments by J.A.,

performed and compiled the results of TD-DFT computations, analysed the data, prepared draft of synthesis and characterization sections in the manuscript, compiled manuscript and supporting information, wrote most parts of introduction section, co-conceptualized and commented on the manuscript during the preparation of the final version, provided funding for research from the Polish side, corresponded with the Editor and Reviewers.

Conflicts of interest

There are no conflicts to declare. All authors have approved the final version of the manuscript.

Data availability

The data supporting this article have been included as part of the supplementary information.

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Data availability

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The data supporting this article have been included as part of the supplementary information.

