Communication

Controlled Anchoring of (Phenylureido)sulfonamide-Based Receptor Moieties: An Impact of Binding Site Multiplication on Complexation Properties

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Abstract: The repetition of urea-based binding units within the receptor structure does not only lead to monomer properties multiplication. As confirmed by spectroscopic studies, UV-Vis and 1H-NMR in classical or competitive titration mode, the attachment to a carrier allocates the active moieties to mutual positions predetermining the function of the whole receptor molecule. Bivalent receptors form self-aggregates. Dendritic receptors with low dihydrogen phosphate loadings offer a cooperative complexation mode associated with a positive dendritic effect. In higher dihydrogen phosphate concentrations, the dendritic branches act independently and the binding mode changes to 1:1 anion: complexation site. Despite the anchoring, the dendritic receptors retain the superior efficiency and selectivity of a monomer, paving the way to recyclable receptors, desirable for economic and ecological reasons.

Keywords: host-guest chemistry; dendrimers; supramolecular chemistry

1. Introduction

Shortly after synthesis of the first compounds with dendritic structure [1,2], features accompanying the defined multiplication of structural subunits were recognized. The fascination of the scientific community with observed unexpected generation-dependent properties of dendrimers led to a broad range of reports on so-called “dendritic effect” [3–5]. After a deeper examination of its origin, Tomalia published a study relating structure parameters to prediction of dendrimer properties [6,7]. Then, advantageously, the concept of formation of microenvironment with locally modified characteristics was employed in drug delivery [8,9], catalysis [10–12] or material [13,14] and supramolecular chemistry [15,16]. Although all these applications are based on an interaction of the dendritic molecule with a guest, the studies concerning dendritic effects in anion recognition are rather rare. In this context, Astruc et al. observed an enhancement in affinity of ferrocene-based dendritic molecules toward anions in comparison with monovalent receptors [17,18]. Dendritic ureas and thioureas prepared by Boas showed an increase in carboxylate binding affinity with increasing number of binding units [19]. Vögtle’s ureas in higher generation showed positive dendritic effect in ATP binding [20]. In our recent work we studied dihydrogen phosphate recognition in a series of carbosilane dendrimers with isophthalamide-based binding sites and we observed an enhanced, generation-dependent complexation ability at higher receptor concentrations [21]. The dendrimers prepared by Losada et al. with amidoferrocenyl units attached poly(propylene imine) dendrimers showed generation-dependent electrochemical responses to inorganic anions [22,23].
Here we report a systematic study of dendritic effects associated with anion recognition by receptor series with increasing number of the active units. We focused on the molecules carrying potent binding sites based on urea moieties conjugated to sulfonamide group. Such moiety has a superior affinity to anions with preferential 1:1 binding stoichiometry [24], even when two binding sites are present in close proximity within one molecule [25]. To induce a multiplication effect, the number of complexation sites within the receptor molecule was gradually increased, finally using their attachment to the periphery of carbosilane dendrimers. This study attempts to exploit the phenomenon of the multivalency in design of potent and possibly recyclable receptors.

2. Results

The influence of binding sites accumulation on anion complexation was studied in a series of receptors differing in the number of receptor moieties. A receptor moiety 4 was synthesized, comprising following structural elements: (i) a urea-based complexation site, capable of donation of highly directional hydrogen bonds, (ii) a sulfonamide group, promoting an electron withdrawal from the complexation sites and (iii) a triple bond, serving as an anchoring group. Although the synthesis of amine 3 was previously described [26], we used an alternative method (Scheme 1).

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\begin{align*}
\text{Scheme 1. Synthesis of receptor moiety 4 and its crystal structure:} & \ (a) \ CH_3NH_2, \ pyridine, \ 93 \% ;
\text{(b) propargyl bromide, K_2CO_3, 33 \% ; (c) SnCl}_2 \ 2H_2O, \ EtOH, \ quantitative, (d) PhNCO, \ 42 \%.}
\end{align*}
\]

4-Nitrophenylsulfonylchloride was reacted with methylamine in water in the presence of pyridine providing 1 in almost quantitative yield. The propargyl group was introduced to the molecule via alkylation with propargyl bromide in the presence of base resulting in the formation of 2. The nitro group was reduced using tin(II) chloride in ethanol, leaving the triple bond intact. The ureido group, serving as a complexation site, was formed in the reaction of the amino group of 3 with phenyl isocyanate providing compound 4 as orange crystals suitable for single crystal X-ray diffraction analysis. Apart from the structure approval, the crystallography confirmed the L-shape of 4, typical for sulfonamides. The hydrogen-binding capability of the ureido moiety is suggested by a non-covalently bound molecule of dimethylsulfoxide (DMSO).

The carriers for attachment of the receptor moieties were based on carbosilane molecules differing in the number of azido groups within the structure (Scheme 2). The respective starting azides were prepared according to published procedures [27–29], except 7 and 9a. The synthesis of compound 7 started with reaction of butyllithium with chloro(3-chloropropyl)dimethylsilane, giving 5 in 91\% yield. The silane 5 was either converted to iodo-derivative 6 by Finkelstein reaction or directly reacted with sodium azide to obtain
The compound 9a was obtained in two steps from (3-chloromethyl)dimethyl silane. Its Ir-catalyzed addition to allylchloride gave 8a together with 8b in approx. 1:1 ratio. The subsequent treatment of the obtained mixture with sodium azide under the conditions of nucleophilic substitution yielded a mixture of the corresponding azides 9a and 9b.

Scheme 2. Synthesis of azide carriers 7, 9a and 9b.

The prepared azide-derivatized carriers were reacted with intermediate 4 providing receptors 11–14 (Scheme 3). In all cases, the copper(I) catalyzed click reaction was employed [30,31]. In the case of bivalent carriers, the mixture of 9a and 9b was subjected to click reaction with 4. The resulting mixture of receptors 11 and 12 in 1:1 ratio was easily separable by preparative thin layer chromatography (TLC).

Scheme 3. Synthesis of receptors 10–14.
The insight into the complexation behavior of prepared receptors when exposed to anions was provided by UV-Vis and/or NMR titration experiments [32,33]. To determine the selectivity and efficiency of the concerned complexation site, the monovalent receptor 10 offering the simplest complexation mode with 1:1 stoichiometry was titrated with a series of anions in the form of their tetrabutylammonium (TBA⁺) salts using ¹H-NMR technique; the association constants [34] with higher uncertainty were specified also by UV-Vis titration. (Table 1).

Table 1. Association constants of 10 with a series of TBA⁺ salts of anions ¹.

| Anion     | ¹H-NMR K_{Ass} [M⁻¹] (Error %) | UV-Vis K_{Ass} [M⁻¹] (Error %) |
|-----------|---------------------------------|---------------------------------|
| H₂PO₄⁻    | 5700 (36)                       | 6100 (20)                       |
| AcO⁻      | 1300 (13)                       | 1730 (7)                        |
| BzO⁻      | 2060 (14)                       | 2200 (6)                        |
| HSO₄⁻     | 190 (1.5)                       | -                               |
| Cl⁻       | 70 (4)                          | -                               |
| Br⁻       | 9 (0.8)                         | -                               |

¹ UV-Vis spectra were measured in DMSO, ¹H-NMR in DMSO-d₆.

The influence of binding site multiplication on anion complexation was studied on the series of receptor stock solutions with the same concentration of binding sites. Based on the above-mentioned preliminary study, the ¹H-NMR titration experiments were performed with TBA⁺H₂PO₄⁻, as a strongly bound anion, and TBA⁺Cl⁻, as a weakly bound one. All receptors showed significant complexation-caused shifts of signals in ¹H-NMR spectra, which were used to construct binding isotherms. In the case of bivalent receptors 11 and 12, the binding isotherms did not have smooth shapes (see Supporting Material, Figures S52 and S53), revealing the presence of multiple ongoing processes. The signals of NH groups were located unexpectedly high (10.60 and 10.14 for 12, compare to 9.43 and 9.06 for 10) and shifted with dilution; with 10-fold dilution the NH signals of 12 moved to 9.36 and 9.19, respectively. The receptor 11 showed similar behavior. On the other hand, in the case of receptors 10, 13, and 14 the dilution-induced changes in respective ¹H-NMR spectra were negligible.

As the complexation constants of systems with higher stoichiometry are not conveniently available, individual systems were compared considering the progress of complexation (expressed as percentage of maximal complexation induced shift (CIS)) at the same level of added anion with respect to concentration of available binding sites. The value of CIS for strong dihydrogen phosphate complexes was easily determined as a shift value reached in equilibrium and was similar for all the tested compounds. For weaker complexes with chloride, the value of CIS was approximated based on the calculation of association constant for 10/Cl⁻ and adjusted to 600 Hz for NH signal (Figure 1).

To further investigate the given systems, we used a competitive approach recently introduced by Haav et al. [35]. The stock solutions were prepared, containing 10/13, and 10/14, with equal amount of monovalent and dendrimer-bound complexation sites, respectively. These mixtures were titrated with an anion according to the standard procedure. The complexation properties of both involved receptors were compared within the same titration experiment, excluding many of the possible uncertainty sources. The shifts of selected signals belonging to receptor 10 in the mixture were followed during the titration experiment and the results were compared to the receptor responses observed during standard titration.

In the case of weakly bound chloride, the differences between curves measured for 10 alone and 10 in the mixture with 13 or 14 are negligible. When 10 is titrated by dihydrogen phosphate in the presence of 13 or 14 (Figure 2), notable differences can be found when compared to sole 10. At lower concentrations of H₂PO₄⁻, 10 seems to have less than one half of the whole amount of anions available for complexation. At higher levels of a guest, the receptor 10 returns to the binding isotherm obtained by the standard methodology or
even higher. The addition of more $\text{H}_2\text{PO}_4^-$, beyond the concentration of available binding sites leads to the same equilibria in all the monitored cases.

**Figure 1.** Comparison of complexation progress in DMSO solutions of receptors 10, 13 and 14 with respect to concentration of binding sites with (a) TBA$^+\text{Cl}^-$, shift of NH (H at N15 in the crystal structure, Figure S64), (b) TBA$^+\text{H}_2\text{PO}_4^-$, shift of ArH (H at C3/5 in the crystal structure, Figure S64).

**Figure 2.** Comparison of $\text{H}_2\text{PO}_4^-$ binding isotherm of pure 10 with the corresponding binding isotherms of 10 in the presence of 13 and 14, respectively (shift of ArH; H at C3/5, Figure S64). For clarity, lines are used to connect the experimental data points.
3. Discussion

The receptor 10 showed a remarkable selectivity toward dihydrogen phosphate anion and carboxylates over halides, as expressed by two orders of magnitude difference in binding constants. Addition of the second complexation site to the structure of receptor and formation of bivalent hosts 11 and 12 significantly altered the complexation behavior. From the high positions of NH signals in 1H-NMR spectra, which changed with dilution, the intermolecular hydrogen bonding can be deduced. Such behavior cannot be attributed to the presence of disiloxane oxygen in 12, as the receptor 11 formed similar aggregates. The inclusion of two urea moieties into the structure of 11 or 12 probably enables the development of enthalpically preferred folded structures, where both the binding sites are involved in the intramolecular interaction. As the anion complexation has to compete with this self-association, the bivalent receptors 11 and 12 were excluded from further studies.

The dilution-induced changes in 1H-NMR spectra of 10, 13, and 14 were negligible from structural reasons; in monovalent 10, these interactions should be much weaker than in 11 or 12, due to the absence of the second interacting moiety. In the case of 13 and 14, the steric hindrance plays the role preventing the molecules from mutual interaction. Therefore, all the changes in 1H-NMR signal positions during titration experiments can be attributed to complexation.

The comparable changes of the signal positions for receptors 10, 13 and 14 at low concentrations of dihydrogen phosphate anion indicate that the role of lower homogeneity of binding sites or salt accumulation in the localized areas is negligible and the establishment of equilibria is quick (Figure 1). In the case of 14, a significantly different behavior can be observed compared to 10; after addition of 0.1 equiv. of H2PO4−, the % CIS corresponds to 20% binding sites occupancy. This implies that until the concentration of anion reaches one half of the available complexation sites, two sites cooperate on binding of one anion. This effect is not so pronounced for the dendrimer 13, but the stoichiometry of the H2PO4− complexation also exceeds the 1:1 binding site:anion ratio. This behavior is evident, although the cooperation between two binding sites comprising the sulfonamide group conjugated to urea is reported to be quite unusual [25].

The assumption of cooperative binding of dihydrogen phosphate in 13 and 14 is supported by the shape of binding isotherms (see Supporting Material, Figure S43) exhibiting a plateau after addition of two or four receptor concentration equivalents of H2PO4−, respectively. Moreover, in the 1H-NMR spectra of 13 and 14, the signals of triazole proton and the nearby protons move significantly with the complexation to the higher field, indicating an increased shielding caused by dendritic branches coming closer upon complexation. Naturally, no such shielding is visible in the case of 10 (Appendix A).

Considering the uncertainty in CIS determination, the titration of receptors 10, 13 and 14 with TBA+Cl− led to very similar results in all cases, regardless the count of binding sites per one molecule (Figure 1). The weakly bound chloride probably does not have a convenient shape and size for cooperative bonding to the dendritic receptors and no effects similar to those observed for dihydrogen phosphate can be followed. The same results were obtained by the competitive experiments; the binding isotherms for sole 10 did not differ much from those measured for 10 in the mixture with a dendritic receptor, confirming low influence of binding sites cumulation on chloride complexation.

On the contrary, in the case of dihydrogen phosphate at low loadings, the dendritic molecules offer a possibility of advantageous cooperative binding of one H2PO4− anion to two branches. This is consistent with competitive study results, where complexation of H2PO4− by 10 was initially hindered by the presence of dendritic molecule (Figure 2). This feature, although also present in 13, is particularly pronounced in the case of 14, which is in accordance with the titration data obtained for the sole receptors. At higher levels of a guest the complexation sites of the dendrimer offering possibility of 1:2 binding mode become saturated. Adding more anion, the dendritic complexes undergo a dissociation step, where the hydrogen bonds of a branch toward the anion are disrupted and another anion is bound forming 1:1 complex. Receptor 10 does not undergo such a process and profits from the
dendritic receptor binding mode change, using more than a half of total present H₂PO₄⁻. When the concentration of H₂PO₄⁻ exceeds the concentration of available binding sites, both the monovalent and dendrimer-bound complexes are equally stable.

To regenerate the dendritic receptors, the methodology of nanofiltration was used. After addition of methanol, which destabilized the complexes and lowered the viscosity of feed solutions, the pressure of nitrogen was used to filtrate the mother liqueurs through the corresponding membranes; 1 kDa cut-off for 13 and 3 kDa for 14, with 60–70% receptor recovery.

In conclusion, the (phenylureido)sulfonamidic moieties were successfully anchored to carbosilane carriers providing multivalent receptors for anions. Notwithstanding the bivalent receptors, which formed self-aggregates in DMSO solution, the multivalent host molecules proved to retain the selectivity and efficiency of monovalent ones. Moreover, the attachment to dendritic scaffold fits the binding sites into a suitable position for cooperative binding of H₂PO₄⁻ anion, particularly pronounced in the second generation of dendrimer. At low molar fractions of dihydrogen phosphate, a positive dendritic effect was observed due to advantageous formation of 2:1 complexes between anchored receptor moieties and dihydrogen phosphate. Despite the weak negative dendritic effect observed at H₂PO₄⁻ molar fractions between 0.5 and 1 caused by the change of binding mode, the overall affinity and selectivity of the binding sites is not affected by the anchoring. No dendritic effects were observed for weakly bound chloride and all binding sites work similarly, regardless the carrier. Such knowledge opens access to potent receptors of anions suitable for multiple use, considering the feasible recycling by nanofiltration.

4. Materials and Methods
4.1. General

The reagents were purchased from commercial sources and used without further purification. The starting carbosilane dendrimers were prepared by the standard iterative procedure [36,37]. n-Butyllithium solution (2.5 M in hexanes), bis(1,5-cyclooctadiene)diiridium(I) dichloride ([IrCl(COD)]₂), (1Z,5Z)-cycloocta-1,5-diene (COD) were purchased from Merck KGaA. Chloro(3-chloropropyl)dimethylsilane was purchased from Gelest, Inc. The solvents used for synthesis and chromatography were purchased from commercial sources and distilled before use. Anhydrous solvents were dried by standard procedures; DCM was dried over calcium hydride, pyridine was stored above NaOH(s), and DMF was stored over molecular sieves.

The ¹H (400.1 MHz), ¹³C (100.6 MHz) and ²⁹Si (79.5 MHz) NMR spectra were recorded using a Bruker Avance 400 spectrometer (Bruker Biospin, Rheinstetten, Germany) at 25 °C. Used solvents (DMSO-d₆, chloroform-d) were stored over molecular sieves. The ¹H and ¹³C-NMR spectra were referenced to the line of the solvent (δ/ppm; δ_H/δ_C: DMSO-d₆, 2.50/39.52, chloroform-d, 7.26/77.16). The ²⁹Si spectra were referenced to the line of external standard hexamethyldisilane (δ/ppm; −19.79). To assign all proton and carbon signals, a combination of 1D and 2D experiments (H,H-COSY, H,C-HSQC and H,C-HMBC) was used. The high-resolution mass spectra (HRMS) were measured on a MicrOtof III spectrometer (Bruker Daltonic, Bremen, Germany) with electrospray (ESI) and atmospheric pressure chemical ionization (APCI) source in positive or negative mode. For calibration of accurate masses, ESI-APCI Low Concentration Tuning Mix (Agilent, Santa Clara, CA, USA) was used. The samples were delivered into the ion source in methanol solution; the ionization in 14 had to be enhanced by addition of ammonium formate buffer. The FTIR analysis was performed on a Nicolet 6700 spectrometer (Thermo-Scientific, Waltham, MA, USA) connected with a GladiATR diamond ATR adapter (PIKE-Technologies, Madison, WI, USA), reflectance measurement, DTGS KBr detector, with following parameters: spectral range: 4000–400 cm⁻¹, resolution: 4 cm⁻¹, number of spectra accumulations: 64, apodization: Happ-Genzel. The spectra were collected and processed by Omnic 9 (Thermo-Scientific, Waltham, MA, USA) including baseline correction. Diffraction data were collected on a Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS with the monochromatic Cu-Kα.
radiation (Bruker AXS, Karlsruhe, Germany). The crystal structure of 4 was solved by charge flipping methods in Superflip [38] and refined by full-matrix least-squares on $R^2$ values in Crystals [39]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms could be localized from electron density maps, but according to common practice, hydrogen atoms bonded to carbon were repositioned geometrically, initially refined with soft restraints and afterwards refined using riding constraints. Hydrogen atoms bonded to nitrogen were localized from electron density maps and refined with restrained geometry. Mercury [40] was used for structure visualization. The crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as a supplementary publication. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures (accessed on 12 August 2021).

Nanofiltration: for purification and recycling of dendritic receptors, a solvent resistant stirred cell (Merck Millipore, Burlington, MA, USA) equipped with 1 kDa or 3 kDa MWCO regenerated cellulose ultrafiltration membrane disk (Merck Millipore) and sealed with fluorinated ethylene propylene (FEP) coated O-rings (Eriks, Rychnov nad Kněžnou, ČR) was used. The filtration was driven by nitrogen under a pressure of 4.5 bar. Solutions of complexes were diluted by methanol to 20 mL total volume and filtered to a target volume of 1 mL of retentate; this run was repeated five times. Evaporation of the retentate gave the dendritic receptor.

4.2. Determination of Complexation Constants

Complexation constants were measured in DMSO-$d_6$ by standard $^1$H-NMR titration methodology. A solution of tetrabutylammonium salt of a selected anion (purchased from commercial sources, stored in a dry box) was gradually added in aliquots into a solution of a given receptor to reach at least a 1:5 ratio of binding group to anion. Concentrations of respective receptors were about 4 mmol/L and were kept constant during the titrations to avoid the effects of dilution. The corresponding complexation constants were calculated based on the analysis of binding isotherms obtained from the complexation induced shifts of $NH$ or aromatic protons. For non-linear curve fitting of experimental data, the freely available software Bindfit [34] was used.

The competition experiments were carried out in the mixtures of receptors with concentration of binding sites of 4 mmol/L of monovalent 10 and 4 mmol/L of respective dendritic molecule 13 or 14, i.e., the mixture contained 4-fold molar excess of 10 compared to 13 or 8-fold molar excess of 10 compared to 14, respectively. The concentration of TBA$^+$ salt of an anion was twofold higher than in the case of a sole receptor.

The UV-Vis titrations were performed in DMSO using double beam UV-1800 spectrophotometer Shimadzu. All UV spectra were taken in the wavelength region from 260 to 800 nm, with steps of 1 nm using cuvettes with pathlength of 1 mm. The stability constants of the resulting complexes were evaluated by employing the freeware program Bindfit using the whole parts of the absorption curves where the changes in absorbance were the most significant.

4.3. Synthesis

4.3.1. Synthesis of Precursors

$N$-methyl-4-nitrobenzene sulfonamide 1

$p$-Nitrophenylsulfonylchloride (1 g, 4.5 mmol) was added into a stirred solution of methyamine (0.4 mL, 40% aqueous solution) in pyridine (20 mL). The reaction was stirred for 2 days at ambient temperature. After this time period, the reaction mixture was poured into aqueous HCl (5 M, 100 mL) and the product was extracted to ethyl acetate ($2 \times 50$ mL). The combined organic layers were dried over magnesium sulfate, filtered and the filtrate was evaporated to give a title compound as a yellow solid (0.9 g, 93% yield).
\[^{1}\text{H-NMR}\ (400 \text{ MHz, DMSO-}\text{d}_6):\ 8.43\ (d, \ J = 8.8 \text{ Hz, 2H}), \ 8.03\ (d, \ J = 8.8 \text{ Hz, 2H}), \ 1.98\ (s, 3\text{H}) \text{ ppm.}\ ^{13}\text{C-NMR}\ (100 \text{ MHz, DMSO-}\text{d}_6):\ 150.2, 145.2, 128.7, 125.1, 29.1 \text{ ppm.}\ \text{HRMS (ESI) calc for \left[C_2\text{H}_2\text{N}_2\text{O}_3\text{S}\right]^+: 215.0132 found 215.0136, [M+H]^+.}\]

\(N\)-methyl-\(N\)-propargyl-4-nitrobenzene sulfonamide 2

\(N\)-methyl-4-nitrobenzene sulfonamide 1 (0.8 g, 3.6 mmol) was dissolved in 30 mL of acetonitrile and 0.6 g (4.3 mmol) of anhydrous potassium carbonate was added. The mixture was stirred for 0.5 h before propargyl bromide (0.6 mL, 4.3 mmol, 60% solution in toluene) was added. Resulting mixture was refluxed for 2 days. After cooling, the solvent was removed in vacuo. The residue was taken up with 50 mL of ethyl acetate, aqueous HCl (1 M, 200 mL) was added and the product was extracted into ethyl acetate (3 × 50 mL). The combined organic layers were dried over magnesium sulfate, filtered and the filtrate was evaporated to give a title compound as a yellow solid (0.3 g, 33% yield).

\[^{1}\text{H-NMR}\ (400 \text{ MHz, DMSO-}\text{d}_6):\ 8.43\ (d, \ J = 8.9 \text{ Hz, 2H}), \ 8.08\ (d, \ J = 8.9 \text{ Hz, 2H}), \ 4.10\ (d, \ J = 2.5 \text{ Hz, 2H}), \ 3.11\ (t, \ J = 2.5 \text{ Hz, 1H}), \ 2.81\ (s, 3\text{H}) \text{ ppm.}\ ^{13}\text{C-NMR}\ (100 \text{ MHz, DMSO-}\text{d}_6):\ 150.1, 142.4, 129.3, 124.5, 77.0, 76.2, 39.3 \text{ ppm.}\ \text{HRMS (APCI) calc for \left[C_{10}\text{H}_11\text{N}_2\text{O}_3\right]^+: 255.0434, found 255.0436, [M+H]^+.}\]

\(N\)-methyl-\(N\)-propargyl-4-aminobenzene sulfonamide 3

\(N\)-methyl-\(N\)-propargyl-4-nitrobenzene sulfonamide 2 (0.3 g, 1.2 mmol) was suspended in ethanol (50 mL). Tin(II) chloride dihydrate (2.65 g, 12 mmol) was added and the reaction mixture was refluxed overnight. After cooling, the solvent was removed in vacuo, the residue was taken up with ethyl acetate (100 mL) and aqueous potassium hydroxide (5 M, 100 mL) was added. The product was extracted to ethyl acetate (2 × 50 mL). The combined organic layers were washed with brine (100 mL) and, after separation, dried over magnesium sulfate, filtered and the filtrate was evaporated. The crude product was filtered through the silica (20 g) where the impurities were eluted by ethyl acetate/hexane 1/4 (3 column volumes). The product was obtained as a yellow slowly crystalizing syrup.
1H-NMR (400 MHz, chloroform-d): 3.49 (t, J = 7.1 Hz, 2H), 1.79–1.71 (m, 2H), 3.5–1.24 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H), 1.49 (m, 2H), 0.63–0.57 (m, 2H), −0.02 (s, 6H) ppm. 13C-NMR (100 MHz, chloroform-d): 48.2, 27.9, 26.7, 26.2, 14.9, 13.9, 13.1, –3.4 ppm.

Butyl(3-azidopropyl)dimethylsilane 6

Mixture of butyl(3-chloropropyl)dimethylsilane 5 (1.00 g, 5.19 mmol) and sodium azide (0.674 g, 10.37 mmol) in 20 mL of DMF were heated to 90 °C for 12 h. The reaction mixture was allowed to cool to room temperature. The crude product was passed twice through a short column filled with silica gel using diethyl ether as an eluent. The resulting solution was dried over anhydrous MgSO4. The solvent was removed on the rotary evaporator and the rest of volatiles under high vacuum giving the title compound (0.97 g, 94%) as a colorless liquid.

1H-NMR (400 MHz, chloroform-d): 3.21 (t, J = 7.1 Hz, 2H), 1.61–1.53 (m, 2H), 1.29–1.22 (m, 4H), 0.54–0.47 (m, 4H), −0.0 (s, 6H) ppm. 13C-NMR (100 MHz, chloroform-d): 54.7, 26.7, 26.2, 23.8, 14.9, 13.9, 12.5, −3.4 ppm. 29Si-NMR (79 MHz, chloroform-d): 2.74 ppm.

bis(3-Chloropropyl)dimethylsilane 8a and bis(3-chloropropyl)dimethyldisiloxane 8b

A mixture of allylchloride (0.56 g, 7.32 mmol), [IrCl(COD)]2 and COD was stirred at 40 °C for 10 min in a reaction flask equipped with a reflux condenser. At this temperature, (3-chloropropyl)dimethylsilane (1 g, 7.32 mmol) was added dropwise. The reaction mixture is further stirred for next 10 h at 40 °C and then passed through short column of silica gel with dichloromethane as an eluent. Solvents and unreacted substrates were evaporated using rotary evaporator giving the 1:1 mixture of 8a and 8b (1.48 g, 89%) as colorless liquid.

1H-NMR (400 MHz, chloroform-d): 3.51 (t, J = 6.7 Hz, 4H), 1.82–1.71 (m, 4H), 0.65–0.60 (m, 4H), 0.01 (s, 6H) ppm. 13C-NMR (100 MHz, chloroform-d): 48.1, 27.7, 12.9, −3.5 ppm. 29Si-NMR (79 MHz, chloroform-d): 3.25 ppm. NMR data for 8a are in accordance with literature [35].

bis(3-Azidopropyl)dimethylsilane 9a and bis(3-azidopropyl)dimethyldisiloxane 9b

Mixture of 8a and 8b (1.48 g) from previous reaction and sodium azide (1.77 g, 11.82 mmol) in 30 mL of DMF were heated at 90 °C for 12 h. The reaction mixture was allowed to cool to room temperature. The crude product was passed twice through a short column filled with silica gel using diethyl ether as an eluent. Resulting solution was dried over anhydrous MgSO4. The solvent was removed on the rotary evaporator and the rest of volatiles under high vacuum giving the 1:1 mixture of 9a and 9b (1.49 g, 96%) as a colorless liquid.

1H-NMR (400 MHz, chloroform-d): 3.23 (t, J = 7.0 Hz, 4H), 1.63–1.54 (m, 4H), 0.58–0.53 (m, 4H), 0.01 (s, 6H) ppm. 13C-NMR (100 MHz, chloroform-d): 54.6, 23.7, 12.3, −3.5 ppm. 29Si-NMR (79 MHz, chloroform-d): 3.28 ppm.
4.3.2. Preparation of Receptors—A General Procedure

In the 10 mL microwave vial was contacted an azide-carrier molecule with intermediate 4 (1.2 equivalents per azide group) in DMF (6 mL) in the presence of copper(I) iodide (0.5 equiv. per azide group) and DIPEA (10 equiv. per azide group). The vial was sealed and irradiated by microwaves for 1.5 h at 120 °C. After cooling, the contents of vial were poured to 1M HCl and the mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over magnesium sulfate, filtered and the filtrate was evaporated giving the crude products.

Receptor 10

The receptor 10 was prepared following the general procedure. The crude product was purified using preparative TLC (ethyl acetate/hexane 1/1) giving the receptor 10 as a yellow semi-solid in 70% yield.

1H-NMR (400 MHz, DMSO-d6): 9.43 (s, 1H), 9.06 (s, 1H), 8.02 (s, 1H), 7.71–7.66 (m, 4H), 7.48 (d, J = 8.5 Hz, 4H), 7.29 (dd, J = 8.5, 7.3 Hz, 2H), 6.99 (t, J = 7.3 Hz, 1H), 4.26 (t, J = 7.1 Hz, 2H), 4.21 (s, 2H), 2.59 (s, 3H), 1.80–1.73 (m, 2H), 1.29–1.17 (m, 4H), 0.83 (t, J = 7.0 Hz, 3H), 0.47–0.43 (m, 2H), 0.41–0.36 (m, 2H), −0.07 (s, 6H) ppm. 13C-NMR (100 MHz, DMSO-d6): 152.25, 144.17, 141.56, 139.33, 128.82, 128.66, 127.96, 123.87, 122.21, 118.40, 117.60, 52.24, 44.96, 34.59, 25.97, 25.55, 24.64, 14.20, 13.66, 11.36, −3.50 ppm. 29Si-NMR (79 MHz, DMSO-d6): 7.63 ppm.

Receptor 11

The receptor 11 was prepared following the general procedure. The crude product was purified using preparative TLC (ethyl acetate/hexane 1/3) giving the receptor 11 as a more polar fraction in the form of a yellow syrup in 35% yield.

1H-NMR (400 MHz, DMSO-d6): 9.80 (s, 2H), 9.42 (s, 2H), 7.99 (s, 2H), 7.68 (s, 8H), 7.49 (d, J = 8.5 Hz, 4H), 7.28 (dd, J = 85, 7.3 Hz, 4H), 6.98 (t, J = 7.3 Hz, 2H), 4.24 (t, J = 7.1 Hz, 4H), 4.20 (s, 4H), 2.59 (s, 6H), 1.76–1.68 (m, 4H), 0.40–0.36 (m, 4H), −0.07 (s, 6H) ppm. 13C-NMR (100 MHz, DMSO-d6): 152.5, 144.5, 141.6, 139.7, 128.8, 128.6, 128.3, 123.9, 122.0, 118.4, 117.6, 52.2, 45.0, 34.6, 24.5, 11.1, −3.7 ppm. 29Si-NMR (79 MHz, DMSO-d6): 3.13 ppm. IR: 3336; 3287; 3135; 2952; 2927; 1713; 1310; 1155 cm−1. HRMS (ESIpos) calc for [C26H39N6O3Si]+: 543.2568, found 543.2572, [M + H]+, calc for [C26H37N6O3SiNa]+: 565.2387 found 565.2388, [M + Na]+.

Receptor 12

The receptor 12 was prepared form the reaction mixture of intermediates 9a and 9b following the general procedure. The crude product was purified using preparative TLC (ethyl acetate/hexane 1/3) giving the receptor 12 as a less polar fraction in the form of an orange syrup in 42% yield.

1H-NMR (400 MHz, DMSO-d6): 10.60 (s, 2H), 10.14 (s, 2H), 8.01 (s, 2H), 7.72–7.66 (m, 8H), 7.51 (d, J = 8.5 Hz, 4H), 7.27 (dd, J = 8.5, 7.3 Hz, 4H), 6.96 (t, J = 7.3, 1.2 Hz, 2H), 4.27 (t, J = 7.1 Hz, 4H), 4.20 (s, 4H), 2.58 (s, 6H), 1.80–1.73 (m, 4H), 0.42–0.37 (m, 4H), 0.00 (s, 12H) ppm. 13C-NMR (100 MHz, DMSO-d6): 152.69, 144.70, 141.61, 139.7, 128.8, 128.6, 128.3, 123.9, 122.0, 118.4, 117.6, 52.2, 45.0, 34.6, 24.5, 11.1, −3.7 ppm. 29Si-NMR (79 MHz, DMSO-d6): 3.50 ppm. IR: 3341; 3284; 3196; 2950; 2927; 1713; 1310; 1155 cm−1. HRMS (ESIpos) calc for [C42H53N12O2Si2Si]+: 935.3235, found 935.3233, [M + Na]+, calc for [C42H53N12O2Si2Si]+: 913.3416, found 913.3412, [M + H]+.

Receptor 13

The receptor 13 was prepared following the general procedure, except form extraction. Due to low solubility of 13 in majority of organic solvents, after pouring the reaction mixture toaq. HCl, the solids were filtered off. The filtrate was depleted and the filtration
obtained solids were sonicated in DMSO for 15 min. The insoluble matter was filtered off and to the filtrate was added Chelex® 100 sodium (Sigma Aldrich) to remove the residual Cu. After stirring overnight, Chelex® was removed by filtration and the solution was concentrated by lyophilization. The crude product was purified by nanofiltration (MWCO 1 kDa, MeOH) giving the receptor 13 as a brownish syrup in 84% yield. The receptor can be recovered from the complexes with anions by nanofiltration (MWCO 1 kDa, MeOH) in 60–70% yields.

$^1$H-NMR (400 MHz, DMSO-d$_6$): 9.16 (s, 4H), 8.80 (s, 4H), 8.01 (s, 4H), 7.73–7.60 (m, 16H), 7.46 (d, $J = 8.0$ Hz, 8H), 7.28 (dd, $J = 8.0, 7.3$ Hz, 8H), 6.99 (t, $J = 7.3$ Hz, 4H), 4.24 (t, $J = 5.7$ Hz, 4H), 4.19 (s, 8H), 2.58 (s, 12H), 1.77–1.73 (m, 8H), 1.31–1.22 (m, 8H), 0.52–0.48 (m, 16H), 0.39–0.35 (m, 8H), $-0.09$ (s, 24H) ppm. $^{13}$C-NMR (100 MHz, DMSO-d$_6$): 152.1, 144.0, 141.7 (from HMBC), 139.1, 128.7, 123.9, 122.2, 118.4, 117.6, 52.2, 44.9, 34.5, 24.6, 19.2, 18.5, 18.3, 18.2, 18.0, 17.2, 11.6, 11.5, $-3.6$ ppm. $^{29}$Si-NMR (79 MHz, DMSO-d$_6$): 2.04 (4Si), 0.78 (1Si) ppm. IR: 3344; 3298; 3136; 2954; 2922; 1711; 1175 cm$^{-1}$. HRMS (ESIpos) calc for [C$_{10}$H$_{31}$N$_2$O$_2$Si$_3$Na]$^{+}$: 2138.8907, found 2138.8898, [M + H]$^+$. Receptor 14

The receptor 14 was prepared following the general procedure, except from extraction. Due to low solubility of 14 in majority of organic solvents, after pouring the reaction mixture to aq. HCl, the solids were filtered off. The filtrate was depleted and the filtration obtained solids were sonicated in DMSO for 15 min. The insoluble matter was filtered off and to the filtrate was added Chelex® 100 sodium (Sigma Aldrich) to remove the residual Cu. After stirring overnight, Chelex® was removed by filtration and the solution was concentrated by lyophilization. The crude product was purified by nanofiltration (MWCO 3 kDa, MeOH) giving the receptor 14 as a brownish syrup in 75% yield. The receptor can be recovered from the complexes with anions by nanofiltration (MWCO 3 kDa, MeOH) in 60–70% yields.

$^1$H-NMR (400 MHz, DMSO-d$_6$): 9.76 (s, 8H), 9.34 (s, 8H), 7.97 (s, 8H), 7.69–7.64 (m, 32H), 7.48 (d, $J = 8.0$ Hz, 16H), 7.26 (dd, $J = 8.0, 7.2$ Hz, 16H), 6.96 (t, $J = 7.2$ Hz, 8H), 4.22 (t, $J = 5.7$ Hz, 16H), 4.17 (s, 16H), 2.56 (s, 24H), 1.73 (br s, 16H), 1.29–1.25 (m, 24H), 0.48 (br s, 48H), 0.38–0.36 (m, 16H), $-0.11$ (s, 48H), $-0.15$ (s, 12H) ppm. $^{13}$C-NMR (100 MHz, DMSO-d$_6$): 152.3, 144.3, 141.5, 139.4, 128.8, 128.7, 128.4, 123.8, 122.1, 118.3, 117.5, 52.2, 45.0, 34.5, 24.6, 19.2, 18.5, 18.3, 18.2, 18.0, 17.2, 11.6, $-3.5$ ppm. $^{29}$Si-NMR (79 MHz, DMSO-d$_6$): 2.00 (8Si), 1.03 (4Si) ppm, Si$^0$ not detected. IR: 3344; 3275; 2950; 2922; 1711; 1311; 1155 cm$^{-1}$. HRMS (ESIpos) calc for [C$_{216}$H$_{316}$N$_{48}$O$_{24}$Si$_{13}$Na]$^{2+}$: 2317.9790, 100%, found 2317.9803, [M + 2Na]$^{2+}$, calc for [C$_{216}$H$_{317}$N$_{48}$O$_{24}$Si$_{13}$Na]$^{2+}$: 2306.9881, 100%, found 2306.9904 [M + H + Na]$^{2+}$.

**Supplementary Materials:** The following are available online: Spectral characterization of building blocks 7 and 9 and of receptors 10–14, UV-Vis and $^1$H-NMR titration data, X-ray single crystal diffraction analysis.

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Sample Availability: Samples of the reported compounds are available from the authors.

Appendix A

The triazole moiety can in some cases play a role of a donor of hydrogen bond. In the case of the receptor 10, due to the presence of more efficient complexation site, this moiety did not exhibit any complication induced changes in $^1$H-NMR spectra upon addition of anions. In the case of dendritic receptors 13 and 14, upon addition of dihydrogen phosphate the signals of triazole proton and the nearby protons broaden and move to the higher field as the dendritic branches come closer in the 1:2 complexation mode (Figure S48, Supplementary Material).

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