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Ion pair binding by an L-tyrosine based polymerizable molecular receptor

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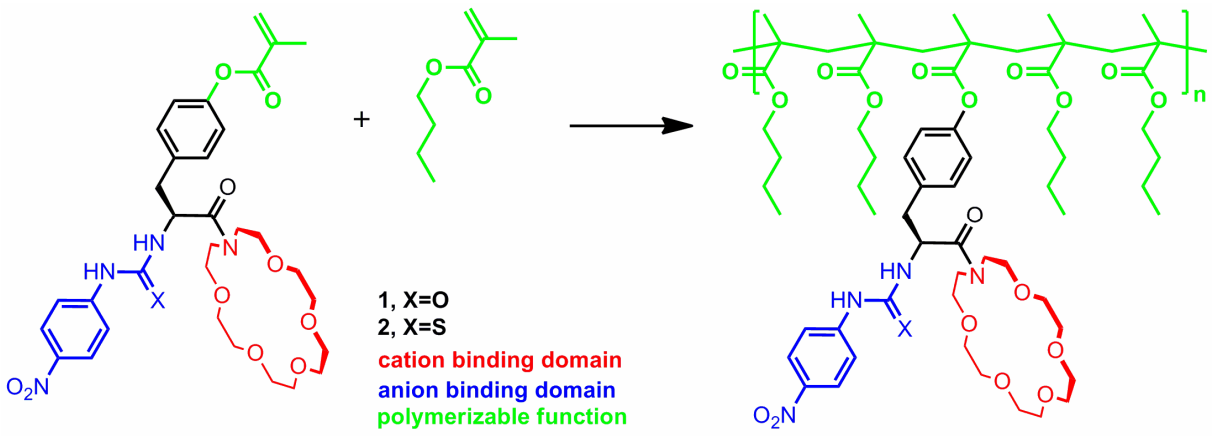
Graphical Abstract:

A polymerizable molecular receptor able to bind in pairs and new functional polymers containing the receptor units were synthesized and characterized.



Abstract. Two new multitopic salt receptors based on the L-tyrosine scaffold were synthesized in a simple approach. Both receptors consist of cation and anion binding domains, as well as a polymerizable function. The anion, cation and salt binding properties of these receptors were measured spectrophotometrically, in acetonitrile solution. The collected data revealed stronger association of receptors with ion pairs relative to single anions. The highest enhancement in salt binding was found for receptor **1**, equipped with a urea based anion binding site. Sodium coordination with the cation binding domain and carbonyl urea group of the receptor was found to be responsible for salt binding enhancement. New functional polymers containing the receptor units were synthesized and characterized. A preliminary extraction study of these receptors and copolymers is also presented.

INTRODUCTION

Over the past few decades anion recognition has been a highly explored area of supramolecular chemistry. Numerous homotopic receptors have been proposed and shown to effectively associate with ions accompanied by non-coordinated counterions.[1] Recently, much more attention has been directed to ion pair recognition, with the advantage of ion pair

receptors over simple ion receptors being widely demonstrated. It has been found that simultaneous complexation of both a cation and an anion by ditopic receptors can enhance their binding strength relative to simple ion receptors, enabling them to operate more effectively.[2] This advantage is especially desirable in real-life situations, where salts exist as ion pairs with coordinated counterions and simple ion receptors cannot be used. Salt receptors that interact with ions to result in electrically neutral complexes have proven advantageous in such practical applications as salt recognition and solubilization, facilitating extraction or transport through membranes.[3] Therefore, designing heterotopic receptors able to bind ion pairs strongly and selectively remains an area of great interest in supramolecular chemistry.

Although the most effective, macrocyclic salt receptors are difficult to synthesize and modify, there is a group of open chain receptors that can also efficiently bind ion pairs and are accessible to structural modifications.[4,5] The latter feature can be utilized to tune the binding properties of receptors by introducing additional binding sites or reinforcing existing ones. Moreover, the presence of a functional group amenable to further modification can be utilized to immobilize receptors in polymeric materials, possibly yielding additional advantages in extraction or transport processes and at the same time facilitating regeneration of the receptors.[6]

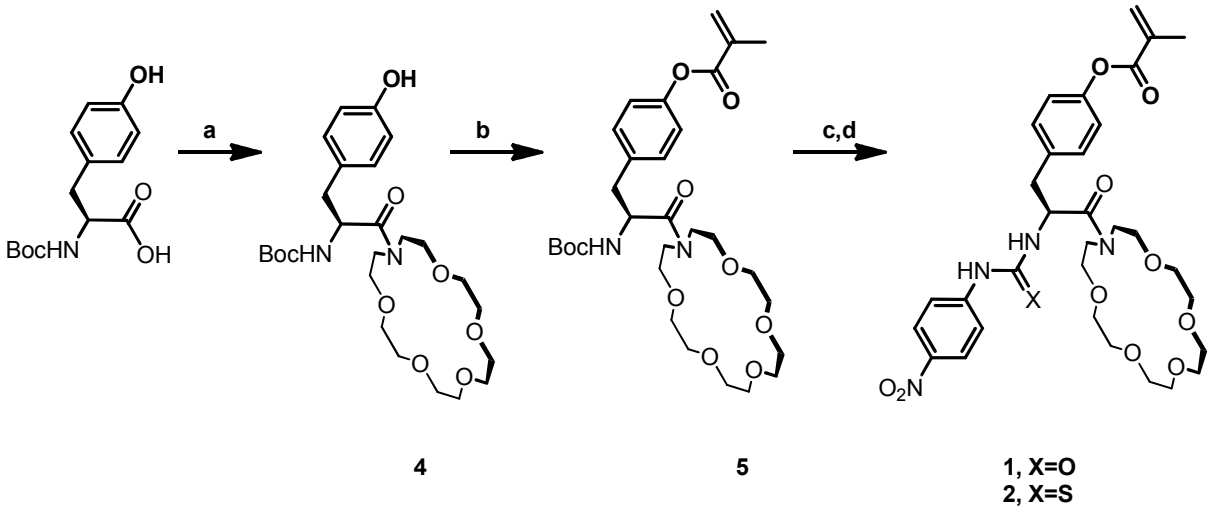
In this context we recently synthesized a family of electrically neutral salt receptors based on the L-ornithine scaffold which are able to cooperatively and selectively bind ion pairs. The functional groups located in ornithine enabled us to introduce an anion and cation binding site through subsequent modification of the a-amino and carboxylic group. The receptors consists of 4-nitrophenylthiourea group responsible for anion binding and aza-18-crown-6 ether unit responsible for cation association. We have proved that arrangement of this domains in amino acid molecular scaffold allows for cooperative binding of ion pairs.[7] In the course of our studies on this type receptor, we found that replacement of 4-nitrophenylthiourea domain with nitrophenylurea counterpart resulted, contrary to anions, in stronger binding of ion pairs.[8] Further enhancement in salt binding was achieved by introducing additional, strong anion binding site in side arm of L-ornithine. Thanks to the double cooperative effects, namely cation and anion binding domains cooperation and induced simultaneous anion binding by two anion binding sites, highly selective receptor for $NaNO_2$ was achieved.[9] Finally, we demonstrated that strong salt recognition can result from high cooperation of cation and anion binding as well as a combination of strong anion coordination at the cost of smaller cation and anion binding cooperativity.[10] This previous study resulted in the development of new molecular receptors able to associate with ion pairs strongly and selectively. Moreover, one of

those receptors was equipped with a polymerizable function, allowing the salt receptors to be embedded in a polymeric chain. We showed, in that previous study, that unlike the salt receptor alone, the polymer containing that receptor is able to effectively extract salt from aqueous to organic media.[7]

Encouraged by these results, in the present study we decided to analyze the synthesis and binding properties of a new L-tyrosine based salt receptors that are equipped with a polymerizable function. Unlike the previously reported L-ornithine based receptors, the present study describes L-tyrosine heterotopic salt receptors containing a methacrylate (rather than methacrylamide) function. This modification was expected to facilitate copolymerization of the receptors with other methacylates.

RESULTS AND DISCUSSION

Receptor synthesis. Receptors **1** and **2** were synthesized in a simple approach in four steps starting from commercially available N-(*tert*-Butoxycarbonyl)-L-tyrosine. Reaction of the carboxylic group of the amino acid with 1-aza-18-crown-6 in the presence of dicyclohexylcarbodiimide allowed a cation binding domain to be introduced into the L-tyrosine platform. Simple acylation of the OH group of L-tyrosine derivative **4** with methacrylic anhydride yielded a modified receptor with polimerizable function. Finally, after deprotection of the amine group and subsequent reaction with 4-nitrophenyl isocyanate or 4-nitrophenyl isothiocyanate, two polymerizable receptors **1** and **2** containing cation (crown ether) and anion (urea or tiourea) binding domains were synthesized (Scheme 1).



Scheme 1 Synthesis of receptors **1** and **2**. Reagents and conditions: a) DCC, 1-aza-18-crown-6, CH_2Cl_2, 0˚C to r.t., 78%; b) methacrylic anhydride, Et_3N, CH_2Cl_2, 0˚C to r.t., 68%; c) TFA- CH_2Cl_2 (1:1), r.t., 95%; d) 4-nitrophenyl isocyanate or 4-nitrophenyl isothiocyanate, Et_3N, THF, 70% for receptor **1** and 65% for receptor **2**.

Anion binding study. The presence of chromophoric 4-nitrophenyl substituent in the receptor skeleton allowed the association constants to be determined using the UV-Vis titration method.[11] These experiments were performed in an acetronitrile solution. To confirm that self-association did not occur in the range of concentration under investigation, dilution studies were first conducted, finding no evidence of self-association for receptors **1** and **2**. The 1:1 binding stoichiometry of receptors **1** and **2** was confirmed by Job plot analyses. Then the affinity of receptors **1** and **2** towards selected anions accompanied with non-coordinated tetrabuthylammonium cation were tested. We found that both receptors associated to these anions moderately, in the order $Br^- < NO_2^- < Cl^- < PhCOO^- < Ac^-$ (Table 1). As expected, receptor **1**, containing a urea based anion binding domain, interacts with anions more weakly than receptor **2**, possessing a thiourea binding site. This is in agreement the with lower acidity of urea relative to thiourea protons and the weaker hydrogen bonding interaction with anions (pKa = 21.1 and 26.9, respectively, in DMSO).[12] For the same reason the more basic, Y-shaped carboxylate anions were bound to the urea domain much more strongly than nitrite anions or the spherical bromide or chloride. The highest association was observed for receptor **1**, with acetate anions. Moreover, upon complexation of benzoate or acetate the deprotonation of receptor **2**, containing a thiourea anion binding site, was observed.

Ion pair binding study. To show that receptors **1** and **2** interact with ion pairs more strongly than with the anions, titration experiments were performed in the presence of one equivalent of sodium cations (added as sodium hexafluorophosphate). It was found that, with the exception of acetate, all anions were associated to receptors in the presence of sodium cation more strongly than in the presence of tetrabuthylammonium countercation. The enhancement in sodium salt binding is even more pronounced in the case of the urea supported receptor **1**, which binds sodium chloride 2.67-fold more strongly than tetrabuthylammonium chloride (Table 1). Higher enhancement in sodium salt binding for the urea equipped receptor **1** can be rationalized in terms of the spatial demands of the binding sites as well as in terms of the hard and soft acid and bases theory.[13] We assumed that the hard sodium cation is coordinated to the crown ether unit and additionally interacts with lone pairs of (thio)urea group. Therefore the hard sodium cation interacts more strongly with urea than with the thiourea function, thus reinforcing the hydrogen bonding of the anion binding site of receptor **1** more effectively than that of receptor **2**.

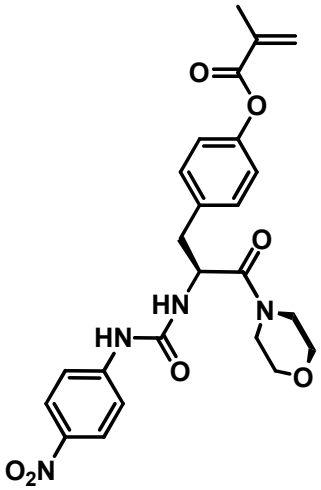
Table 1. Association constants (K_a) for interactions between receptors **1** and **2** and selected anions in the absence or presence of one equivalent of sodium cations[a]

	Receptor 1			Receptor 2		
	TBA^+	**Na^+**	**K_{Na}/K_{TBA}**	**TBA^+**	**Na^+**	**K_{Na}/K_{TBA}**
Br^-	250	590	2.36	280	430	1.53
NO_2^-	750	1500	2.00	800	1450	1.81
Cl^-	1400	3750	2.67	2950	4650	1.57
$PhCOO^-$	31 200	33 300	1.07	-[b)]	-[b)]	-
CH_3COO^-	53 000	18 000	0.34	-[b)]	-[b)]	-

[a] UV-Vis, solvent CH_3CN, temperature 293 K, [**1**] = 6.06×10^{-5} M, [**2**] = 6.37×10^{-5} M, anions added as TBA salts [TBAX] ~2 mM; M^{-1}, Errors < 10%. [b] deprotonation

To establish the role of the cation binding domain in salt binding, a molecular receptor **3** lacking a crown ether binding domain was synthesized and tested (Fig. 1). The crown ether based cation binding domain was here replaced with a morpholine unit. This receptor binds chloride anion a bit more strongly than receptor **1**, with association constant 1700 M^{-1}. The stronger association of receptor **3** with chloride anion can be attributed to lower steric hindrance in close proximity of the anion binding domain. As expected, titration experiments performed for chloride anion in the presence of one equivalent of sodium cation revealed that receptor **3** is not able to bind ion pairs more strongly than anions (K_{NaCl}= 1650 M^{-1}). This supports the conclusion that the 1-aza-18-crown ether based binding site in receptor **1** and **2** is responsible for the enhancement in salt association.

Fig. 1 Structure of reference receptor **3**.



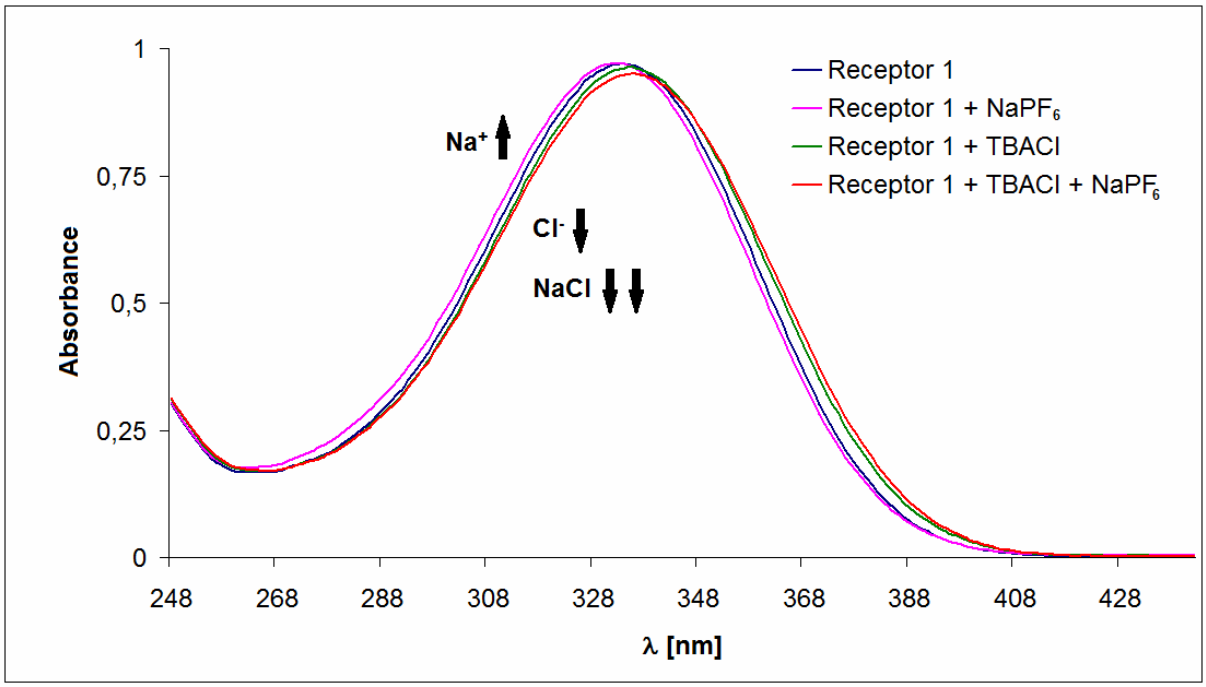
Cation binding study. In order to further verify the hypothesis that sodium cation is responsible for the enhancement of anion binding, we carried out additional UV-Vis experiments, applicable only to receptor **1** equipped with a urea binding domain. The UV-vis spectra for this receptor underwent changes upon addition of sodium cations. The addition of 1.5 equivalents of sodium cations resulted in a slight hypsochromic shift of the absorption maximum of receptor **1** (from 334 to 332 nm). These spectral changes can be attributed to the coordination of the sodium cation not only to the crown ether unit but also to the lone pair of the urea group. Upon addition of 1.5 equivalents of chloride anions, on the other hand, the absorption band was shifted toward longer wavelengths, up to 335 nm. This red-shift band change is a consequence of the interaction of chloride anion with the urea binding domain. Interestingly, the addition of sodium cations into receptor **1** solution pretreated with 1.5 equivalents of chloride anions caused, contrary to the sodium complexation of receptor **1**, further red-shift movement to 336 nm. The spectral changes are even more pronounced in the bands slope (Fig. 2 and Table 2). This observation is in accordance with the hypothesis that sodium cation is coordinated to the urea carbonyl group. Therefore we initially presumed that the interaction of sodium cations with the urea carbonyl group is responsible for increasing the acidity of urea protons. However, the ^{1}H NMR measurements of [**1**·Na^{+}] complex do not support that assumption; namely, there is no downfield shift of urea protons in respect of receptor **1**. Oppositely, upon addition of sodium cations to the receptor **1** solution the signals assigned to both urea protons were shifted only slightly upfield. Thus the enhancement of salt binding of receptor **1** can be attributed mainly to its sodium cation induced conformational change. We concluded that contrary to receptor **1** in [**1**·Na^{+}] complex the nitrophenylurea protons are exposed outwardly from the molecule and allow thereby stronger association with anions.

Table 2. UV-Vis changes (absorption intensities and λ_{max}) for interactions between receptor **1** and Na^+, Cl^- and NaCl[a]

λ [nm]	Receptor 1	Receptor 1·Na^+	Receptor 1·Cl^-	Receptor 1·NaCl
308	0.644	0.615	0.593	0.584
368	0.365	0.343	0.415	0.437
λ_{max}[nm]	334	332	335	336

[a] Solvent CH_3CN, temperature 293 K, [**1**] = 6.65×10^{-5} M, Na^+ added as PF_6 salt (1.5 eq.), Cl^- added as TBA salt (1.5 eq.), NaCl added as TBACl (1.5eq.) + $NaPF_6$ (1.5 eq.)

Fig. 2 UV-Vis changes for interactions between receptor **1** and Na^+, Cl^- and NaCl[a]

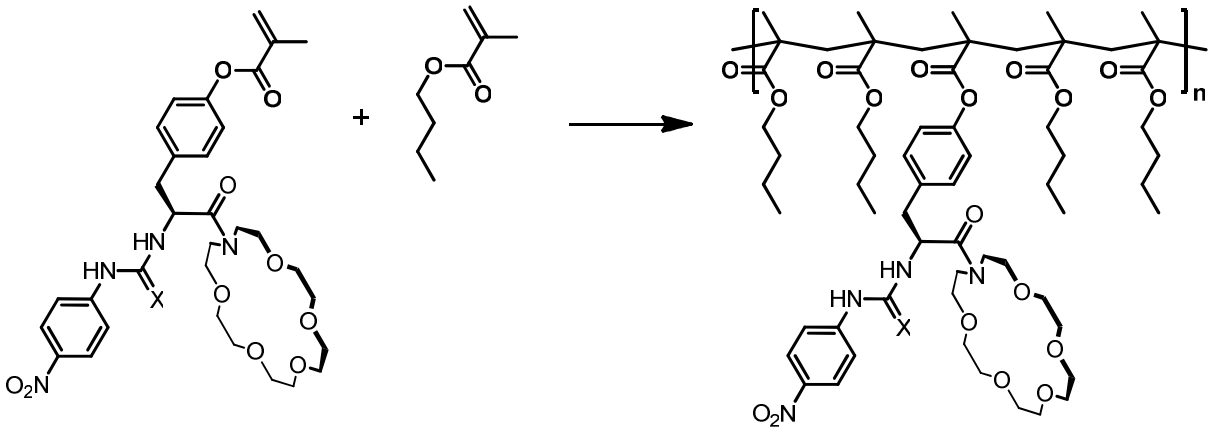


[a] Added as tetrabuthylammonium, hexafluorophosphate or its mixture salts.

Taking advantage of the fact that sodium cation association to receptor **1** causes changes in the UV-Vis absorption band, the stability constant of this [1·Na^+] complex was determined. Upon subsequent addition of sodium hexafluorophosphate a distinct blue-shift movement of receptor **1** band was observed. The association constant of [1·Na^+] complex determined by the nonlinear regression analysis of the binding isotherm was calculated to be 6600 M^{-1}. On the other hand, upon addition of potassium or ammonium cations the receptor **1** spectrum remained unchanged, presumably due to weak interaction with the cation binding domain. Thus to estimate the selectivity of receptor **1** towards cations, titrations were carried out with

chloride anions in the presence of sodium, potassium and ammonium cations. As expected, significant improvement in salt binding was observed only in the presence of sodium cations (K_{TBACl}=1400 M^{-1} vs. K_{NaCl}=3750 M^{-1}). Both potassium and ammonium chlorides were associated to receptor **1** with a strength similar to that of tetrabuthylammonium chloride (K_{KCl}= 1480 M^{-1} and K_{NH4Cl}=1460 M^{-1}). These results, taken together, demonstrate that both receptor **1** and **2** can bind sodium salts more strongly than anions. Moreover, we have established that this enhancement in salt binding is a consequence of the strong affinity of the receptors towards sodium cations.

Copolymer synthesis. Since the presented receptors are equipped with a polymerization function we decided to synthesize new functional copolymers containing salt receptor units. Copolymers **6** and **7** were obtained via reversible addition−fragmentation chain-transfer polymerization utilizing receptors **1** or **2**, butyl methacrylate and 2-cyano-2-propyl dodecyltrithiocarbonate agent with 50 and 54% yield, respectively. Nevertheless the polydispersity indexes of copolymers **6** and **7** were relatively high, at 1.65 and 2.30, respectively. The molecular weight, determined by GPC analyses, was calculated to be 24.8 and 17.1 kDa for **6** and **7**, respectively. The distinguished signals of the crown ether protons of the salt receptor and the -OCH_2- methylene protons of the *n*-buthyl group in the NMR spectra made it possible to determine the content of the receptor units in copolymers. In both cases, similar degrees of receptor incorporation in polymers were observed, calculated to be 9.2 for **6** and 9.5% for **7** (feed ratio of receptor monomers = 10% mol). Combustion analysis confirmed the loading of receptor units in copolymer **7** (1.62% S).



Scheme 2 Synthesis of copolymers **5** and **6**. Reagents and conditions: AIBN, 2-cyano-2-propyl dodecyltrithiocarbonate, THF, 60˚C, 12 h, yield 50% for **6** and 54% for **7**.

Extraction experiments. The ability of the receptors and copolymers to extract solid sodium nitrite and aqueous solution of sodium nitrite into organic phase were examined. Solid and 1M solution sodium nitrite were extracted with 15.2 mM (effective receptor concentration) solution of receptor **1** and its copolymer **6** in chloroform. After phase separation and water extraction of the organic layer, the concentration of nitrite anions in aqueous phase was determined using the UV colorimetric test. The collected data revealed that both receptor **1** and its copolymer **6** extract solid sodium nitrite similarly, with extraction efficiency 19 and 21%. On the other hand receptor **1** and copolymer **6** can extract sodium nitrite from aqueous solution to chloroform phase only weakly (3.5 and 3.4% efficiency, respectively). However, in a recent study of extraction experiments with copolymers containing ornithine based receptor units, we found that such a compolymer is able to extract sodium salts from aqueous media to organic phase more effectively (up to 44%)[7]. Unlike the copolymers in the present study, that copolymer possessed two anion binding domains in its receptor structure unit. Moreover, the copolymer tested here exhibits lower molecular weight than the one previously tested (24.8 vs. 96.1 kDa). Therefore we presume that being able to compete with water to associate with ions in the extraction process requires multiple ion binding sites in the receptor structure as well as higher molecular weight of copolymers.

CONCLUSIONS

Summing up, we have synthesized new multitopic salt receptors **1** and **2**, based on the L-tyrosine molecular scaffold, which are selective for sodium salts. The receptors consist of anion and cation binding domains as well as a polymerizable function. We have demonstrated that both receptors are able to bind sodium salts more strongly than the corresponding anions. The highest enhancement in salt association was observed for receptor **1**, possessing a urea anion binding domain, and sodium chloride. Comparative UV-Vis binding study showed that the presence of the cation binding domain in the receptors' structures is responsible for the enhancement of sodium salt binding. We have established that the sodium cation is coordinated not only to the crown ether unit but also to the carbonyl group of urea, thereby facilitating stronger association with anions. The presence of methacrylate function in the receptor scaffolds enabled us to synthesize new functional copolymers **6** and **7**. A preliminary extraction study of these receptors and copolymers was also presented, finding that both receptors and their copolymers can readily extract solid sodium nitrite to organic phase. Nevertheless, none of the receptors or copolymers can efficiently extract aqueous salt solution

into organic phase. Our future efforts will focus on synthesizing new copolymers with higher molecular weights and containing receptors with multiple or stronger binding domains allowing them to extract salt from aqueous to organic phase more effectively.

EXPERIMENTAL SECTION

1-Aza-18-crown-6 was prepared according to modified literature procedure where instead of potassium at macrocyclization step potassium *tert*-butoxide was used.[14] Other reagents and chemicals were of reagent grade quality and purchased commercially. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz or Varian Unity Plus 200 MHz spectrometer. ^{1}H NMR chemical shifts δ are reported in ppm referenced to residual solvent signal (DMSO-d_6 or $CDCl_3$). UV-Vis titrations were performed in acetonitrile using a Thermo Spectronic Unicam UV500 Spectrophotometer. High resolution mass spectra (HRMS) were measured on a Quattro LC Micromass unit using ESI technique.

Compound 4. To a solution of N-(*tert*-Butoxycarbonyl)-L-tyrosine (843.9 mg, 3 mmol) and 1,3-dicyclohexylocarbodiimide (679.8 mg, 3.3 mmol) in 30 ml of dry dichloromethane, 1-aza-18-crown-6 (789 mg, 3 mmol) at 0 °C (ice bath) was added. The reaction mixture was stirred for 30 min and then left at room temperature overnight. The precipitate was filtered off, washed with dichloromethane and the solvent was evaporated. The residue was purified by silica gel column chromatography (2% methanol in chloroform) to give the title product as a colorless oil (1.23 g, 78% yield).

HRMS (ESI): calcd for $C_{26}H_{42}N_2O_9Na$ $[M+ Na]^+$: 549.2788, found: 549.2784.

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.41 (s, 9H); 2.85–3.00 (m, 2H); 3.35–3.75 (m, 24H); 4.70–4.80 (m, 1H); 5.35 (d, J=9.1, 1H); 6.73 (d, J=8.4, 2H); 7.02 (d, J=8.2, 2H)

^{13}C NMR (50 MHz, $CDCl_3$) δ 28.53, 39.56, 47.47, 48.65, 51.83, 69.45, 69.66, 70.53, 70.73, 70.82, 79.93, 115.73, 127.84, 130.73, 155.27, 155.70, 172.48

Compound 5. To a stirred solution of compound **4** (1.20 g, 2.29 mmol) and triethylamine (0.255 g, 2.52 mmol) in 50 ml of dry dichloromethane at 0 °C a methacrylic anhydride (0.352 g, 2.29 mmol) was added dropwise. The reaction mixture was stirred at that temperature for 1h and then at room temperature overnight. The reaction mixture was washed with 0.5M HCl, with water, then with saturated $NaHCO_3$, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (2% methanol in chloroform) to give the title product as a colorless oil (0.925 g, 68% yield)

HRMS (ESI): calcd for $C_{30}H_{46}N_2O_{10}Na$ $[M+ Na]^+$: 617.3044, found: 617.3050.

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.37 (m, 9H), 2.05 (s, 3H), 2.95–3.00 (m,2H), 3.72–3.40 (m, 24H), 8.43 (dd, 1H), 5.31(d, 1H), 5.74 (s, 1H), 6.32 (s, 1H), 7.02 (d, *J*=8.4, 2H), 7.22 (d, *J*=8.4, 2H).

^{13}C NMR(50 MHz, $CDCl_3$) δ 18.59, 28.51, 39.64, 47.35, 48.76, 51.51, 69.40, 69.70, 70.57, 70.69, 70.75, 70.83, 70.89, 70.93, 76.60, 70.23, 77.87, 121.68, 127.33, 130.65, 134.37, 136.05, 149.99, 155.10, 165.93, 172.07

Receptor 1. Compound **5** (900 mg, 1.51 mmol) was dissolved in 20 ml of dichloromethane and 5 ml of trifluoroacetic acid was added. The reaction mixture was stirred at room temperature until the starting material was consumed (TLC monitoring). The mixture was neutralized with saturated $NaHCO_3$. The water layer was separated and extracted with dichloromethane (2x). The organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The obtained amine (710 mg, 95% yield) was used in the next step without further purification. To the solution of amine (300 mg, 0.607 mmol) in 20 ml of dry THF, the 4-nitrophenyl isocyanate (99.6 mg, 0.607 mmol) was added. After stirring overnight at room temperature, the reaction mixture was concentrated and purified by silica gel column chromatography (2% methanol in chloroform) to give receptor **1** as a pale-yellow oil (280 mg, 70% yield).

HRMS (ESI): calcd for $C_{32}H_{42}N_4O_{11}Na$ $[M+ Na]^+$: 681.2748, found: 681.2781.

^{1}H NMR (300 MHz, DMSO-d_6) δ 1.99 (s, 3H), 2.84-3.09 (m, 2H), 3.40-3.70 (m, 24H), 4.93 (q, *J* = 7 Hz, 1H), 5.89 (s, 1H), 6.26 (s, 1H), 6.81 (d, *J* = 9 Hz, 1H), 7.09 (d, *J* = 9 Hz, 2H), 7.25 (d, *J* = 6 Hz, 2H), 7.58 (d, *J* = 12 Hz, 2H), 8.14 (d, *J* = 12 H, 2H), 9.41 (s, 1H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 18.05, 37.88, 46.52, 48.08, 50.16, 68.23, 69.01, 69.75, 69.88, 69.95, 70.02, 70.08, 116.90, 121.50, 125.19, 127.62, 130.40, 134.57, 135.34, 140.63, 146.71, 149.30, 153.66, 165.27, 171.31.

Receptor 2. Receptor 2 was synthesized analogously to receptor **1**. Instead of 4-nitrophenyl isocyanate the 4-nitrophenyl isothiocyanate (109.2 mg 0.607 mmol) was used. After chromatographic purification the receptor **2** was obtained as a pale yellow oil (293 mg, 65% yield).

HRMS (ESI): calcd for $C_{32}H_{42}N_4O_{11}Na$ $[M+ Na]^+$: 697.2520, found: 697.2509.

^{1}H NMR (300 MHz, DMSO-d_6) δ 2.00 (s, 3H), 2.90-3.20 (m, 2H), 3.38-3.70 (m, 24H), 5.57 (q, *J* = 7 Hz, 1H), 5.89 (s, 1H), 6.27 (s, 1H), 7.12 (d, *J* = 6 Hz, 2H), 7.28 (d, J = 6 Hz, 2H), 7.90 (d, *J* = 9 Hz, 2H), 8.18 (d, *J* = 9 Hz, 2H), 8.42 (d, *J* = 9 Hz, 2H), 10.40 (s, 1H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 18.05, 37.14, 46.52, 48.16, 54.59, 68.17, 68.85, 69.75, 69.87, 69.94, 70.01, 70.07, 79.18, 120.47, 121.62, 124.48, 127.64, 130.36, 134.23, 135.33, 142.07, 146.09, 149.39, 165.27, 170.39, 179.10.

Receptor 3. Receptor **3** was synthesized analogously to receptor **1** and **2**.

HRMS (ESI): calcd for $C_{24}H_{26}N_4O_7Na$ $[M+ Na]^+$: 505.1699, found: 505.1680.

^{1}H NMR (300 MHz, DMSO-d_6) δ 2.00 (s, 3H), 2.84-3.04 (m, 2H), 3.22-3.62 (m, 24H), 4.96 (q, J = 7 Hz, 1H), 5.89 (s, 1H), 6.27 (s, 1H), 6.85 (d, J = 9 Hz, 1H), 7.10 (d, J = 9 Hz, 2H), 7.27 (d, J = 9 Hz, 2H), 7.59 (d, J = 9 Hz, 2H), 8.14 (d, J = 9 Hz, 2H), 9.48 (s, 1H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 18.07, 37.68, 41.91, 45.60, 49.74, 65.90, 79.18, 116.89, 121.57, 125.19, 127.66, 130.56, 134.25, 135.32, 140.63, 146.75, 149.37, 153.69, 165.31, 169.53.

General procedure for preparation of copolymers 6 and 7.

Receptor (0.46 mmol), buthyl methacrylate (583 mg, 4.1 mmol), 2-cyano-2-propyl dodecyltrithiocarbonate (31 mg, 0.09 mmol) and azobisisobutyronitrile (7.7 mg, 0.046 mmol) were dissolved in 1.2 ml of dry THF. The solution was degassed and then placed at 70 °C overnight under atmosphere of nitrogen. The resulting viscous solution was added dropwise to excess methanol. The precipitate was isolated, dissolved in small amount of THF and again added dropwise into excess methanol. The copolymers **6** and **7** were subsequently isolated by decantation and dried *in vacuo* to give a light-yellow solids in 50% yield for **6** and 54% yield for **7.**

Copolymer **6**:

^{1}HNMR (200 MHz, $CDCl_3$) δ 0.50-1.10 (bm, 61.14H), 1.10-1.42 (bm, 30.21H), 1.42-1.65 (bm, 23.08H), 1.65-2.15 (bm, 25.59H), 3.56 (bs, 25.12H), 3.87 (bs, 20H), 5.07 (bs, 0.2H), 6.93 (bs, 2.41H), 7.20 (bs, 2.84H), 7.39 (bs, 1.05H), 7.96 (bs, 1.52H), 8.28 (bs, 0.38H).

GPC: M_n: 24.8 kDa, PDI: 1.65

Copolymer **7**:

^{1}HNMR (200 MHz, $CDCl_3$) δ 0.60-1.10 (bm, 57.82H), 1.10-1.42 (bm, 30.33H), 1.42-1.65 (bm, 21.77H), 1.65-2.20 (bm, 26.56H), 3.56 (bs, 24.44H), 3.87 (bs, 20H), 6.95 (bs, 2.82H), 7.21 (bs, 4.51H), 7.54 (bs, 1.82H), 8.03 (bs, 2.30H).

GPC: M_n: 17.1 kDa, PDI: 2.30

Supporting Information. Spectroscopic data for all new compounds, as well as UV-Vis measurements (Job Plots, Dilution curves, Binding isotherms)

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