



Supramolecular Polymers

Counter Cation Dependent and Stimuli Responsive Supramolecular Polymers Constructed by Calix[4]pyrrole Based Host–Guest Interactions

Samet Yuvayapan^[a] and Abdullah Aydogan*^[a]

Abstract: Carboxylate tethered calix[4]pyrroles in the form of their tetrabutylammonium (TBA) and cetyltrimethylammonium (CTA) salts were synthesized via an acid base reaction between the corresponding carboxylic acid functionalized calix[4]pyrrole and tetrabutyl- or cetyltrimethylammonium hydroxide. The host–guest recognition motif based on these calix[4]pyrrole macrocycles and tethered carboxylate units was employed to construct novel A–B type supramolecular polymers from low molecular weight monomers in chloroform. These supramolecular polymers were found to be dependent on the counter cation in terms of the properties of supramolecular polymers. ¹H-,

DOSY-, NOESY-NMR spectroscopic analyses, viscosity measurements, and SEM results were used to characterize supramolecular polymers and revealed that the CTA cation becomes a direct part of supramolecular polymer via cation– π interactions between the ammonium part of CTA and carboxylate-bound calix[4]pyrrole, effecting the overall properties of supramolecular polymers such as viscosity, gel formation, and drawing fibers. Additionally, reversible pH- and thermo-responsiveness of the supramolecular polymers were demonstrated for the first time for an anion recognition induced calix[4]pyrrole based supramolecular polymer.

Introduction

Highly complicated and ordered materials having stimuli-responsiveness are ubiquitous in biological systems, in which the reversible interactions play a critical role. Development of new materials with unique properties requires the understanding of reversibility and responsiveness. At this junction, supramolecular chemistry provides a platform to develop advanced and sophisticated materials with unconventional properties. Supramolecular polymers, constructed from low molecular weight monomers with the aid of reversible noncovalent interactions, are kind of responsive polymers that can be sensitive to solvent, concentration, pH, temperature and chemical stimuli.^[1] Numerous types of forces, such as hydrogen bonding, metal-ligand coordination, and hydrophobic and donor-acceptor interactions are employed to engineer supramolecular polymers.^[2] Among these, host-guest interactions have been widely utilized to construct supramolecular polymers by using various macrocyclic hosts such as crown ethers,^[3] calixarenes,^[4] cyclodextrins,^[5] cryptands^[6] and pillar[5]arenes.^[7] In this context, a number of guest molecules (e.g., adamantane, anthracene, chargednaphthalenes, -amines, -imidazoles, and viologens) have been used as neutral or positively charged guest species when they incorporated into the structures of above mentioned host molecules. Supramolecular chemistry of anionic dimers, trimers and

Supporting information and ORCID(s) from the author(s) for this article are

tetramers are widely investigated.^[8] However, pH- and thermoresponsive high performance supramolecular polymers based on the recognition of anionic guest species have not been fully exploited yet.

Calix[4]pyrroles, known as selective anion receptors that recognize anions (e.g., fluoride, chloride, and acetate) well in organic media, have been widely employed as anion extraction agents,^[9] anion separating solid supports,^[10] ion transporters,^[11] electroactive, optical anion sensors^[12] and ion-pair receptors.^[13] Calix[4]pyrroles have also been used as building blocks to construct functional assemblies with complementary guest species. For instance, Sessler and co-workers reported heterocomplementary subunits consisting of a tetrathiafulvalene-functionalized calix[4]pyrrole and glycol diester-linked bis-2,5,7-trinitrodicyanomethylenefluorene-4-carboxylate or bis(dinitrophenyl)-meso-substituted calix[4]pyrrole.[14] These monomers were found to produce short oligomers stabilized by hydrogen bonding and donor-acceptor charge transfer interactions. An imidazolium-functionalized calix[4]pyrrole in the form of its bromide salt was also used to produce a supramolecular polymer via recognition of both the anion and imidazolium cation. Unfortunately, this system was suffered from low solubility in organic solvents such as CHCl₃ and CH₂Cl₂.^[15] Although the above resulting supramolecular assemblies were found to show dynamic quest dependent structural transformations and good fidelities, these systems suffered from either complicated synthetic steps, low degrees of supramolecular polymerization^[14a,15] or higher critical supramolecular polymerization concentrations (CPC).^[16] Calix[4]pyrrole based, counter cation dependent, dual responsive, and high performance supramolecular polymers with low CPC have not been reported yet.

 [[]a] Department of Chemistry, Istanbul Technical University, Maslak, Istanbul, 34469 Turkey
 E-mail: aydoganab@itu.edu.tr
 http://akademi.itu.edu.tr/en/aydoganab

available on the WWW under https://doi.org/10.1002/ejoc.201801663.





Structural analyses of supramolecular monomers reported earlier reveals that, for an A-B type monomer, favoring the formation of linear supramolecular polymers with low CPC can be achieved by using long and flexible alkyl chain linkers between host and guest moieties.^[17] On the basis of these findings, we report here the design and synthesis of a novel, dual responsive and counter cation dependent supramolecular polymer, which was constructed from a heteroditopic A-B type calix[4]pyrrole monomer (2) by utilizing the reversible host-quest interactions between the calix[4]pyrrole core and its tethered carboxylate unit (Figure 1). The effect of counter cation on the properties of supramolecular polymers was also investigated by using two different ammonium cations, namely tetrabutylammonium (TBA) and cetyltrimethylammonium (CTA). When CTA was used as counter cation, the long alkyl chain was envisioned as the basis of high solubility and enhancements in the properties of supramolecular polymers (e.g., viscosity, drawing fibers and gel formation) via additional hydrophobic interactions between long alkyl chains of CTA which was a direct part of supramolecular polymer through cation- π interactions.



Figure 1. Structures of carboxylic acid (1), carboxylate-functionalized calix[4]pyrroles (2), and the counter cation dependent supramolecular polymerization of **2a** and **2b**.

conditions.^[18] Therefore we followed the click reaction strategy to obtain calix[4]pyrrole 1 starting from an alkyne-functionalized calix[4]pyrrole and an azido compound having a carboxylic acid functionality. To do so, alkyne-functionalized calix[4]pyrrole **3**^[9d] was dissolved in THF and reacted with **4**^[19] in the presence of an aqueous solution of CuSO₄·5(H₂O) and sodium ascorbate at room temperature. After completion of the reaction, crude products were extracted with methylene chloride and precipitated from hexane after workup. This was yielded 1 in 96 % as a pale yellow solid. Once we have the carboxylic acid-functionalized calix[4]pyrrole 1 in hand, it was treated with TBAOH or cetvltrimethylammonium hydroxide (CTAOH)^[20] to obtain 2a and 2b, respectively. For instance, a methanol solution of 1 treated with equimolar TBAOH to give essentially pure 2a guantitatively in 1 h after removal of the solvent. 2b was also obtained in the same manner when 1 reacted with CTAOH.



Scheme 1. Synthesis of 1 and 2. i) $\mbox{CuSO}_4\mbox{-}5(\mbox{H}_2\mbox{O}),$ sodium ascorbate/THF, r.t., 48 h. ii) In MeOH, r.t., 1 h.

Characterizations of the precursor **1** and carboxylate-functionalized target compounds (**2a** and **2b**) were carried out using ¹H and ¹³C NMR spectroscopy, as well as low- and highresolution mass spectroscopy. For example, ¹H NMR analysis of compound **1** revealed the *CH* protons of triazole ring at 7.59 ppm as a singlet peak. Pyrrole NH proton signals were observed at 7.23 and 7.12 ppm as two distinctive resonance signals, reflecting the asymmetric nature of the compound **1**.

Results and Discussion

Preparation of carboxylate-functionalized calix[4]pyrroles **2a** and **2b** starts with the synthesis of corresponding carboxylic acid functionalized calix[4]pyrrole **1** as illustrated in Scheme 1. Sharpless and co-workers introduced the "Click Chemistry" as a term describing the reactions displaying high yields with tolerance to a wide range of substrates and solvents under mild





Similarly, the presence of multiplet and triplet peaks at 5.92 and 5.67 ppm was attributed to the CH protons of pyrrole ring (Figure 2a and S2).



Figure 2. Partial ¹H NMR spectra (500 MHz) of (a) **1**, (b) **2a**, (c) **2b**, and (d) CTAOH recorded in CDCl₃ at 25 °C. * denotes residual solvent peaks.

¹H NMR measurements can also be used to obtain important information regarding the complexation behavior of supramolecular monomers.^[21] Therefore, ¹H NMR spectra of **2a** and **2b** in CDCl₃ (12 mM) were compared with the ones that of precursor 1 and CTAOH. As shown in Figure 2, while pyrrole NH resonance signals of 1 were observed as two distinct peaks at 7.12 and 7.23 ppm, in the case of 2a they were found to be shifted downfield to 9.55 ppm as a single broad peak. In contrast, pyrrole CH proton signals of 2a appeared to be shifted upfield from 5.91 ppm to 5.78 ppm (cf. Figure 2a and 2b). When a calix[4]pyrrole was bound to an anion these lower and upper field peak shifts are known as typical.^[22] Parallel to the above results, similar peak shifts were observed in the case of 2b. For instance, pyrrole NH peaks of 2b were observed at 11.09 and 11.27 ppm, pyrrole CH proton resonances gave rise around 5.66 ppm (cf. Figure 2a and 2 d). These results clearly indicate that 2a and 2b exhibit intermolecular interactions via complexation of pyrrole NHs and tethered carboxylate units.

Since the counter cations of 2a and 2b are different, their effect on the self-assembly process was investigated by using ¹H NMR spectroscopy. An inspection of Figure 2b reveals that while the methylene protons connected to the nitrogen atom of TBA resonate at 3.06 ppm, in the case of CTA resonance signals of the same protons appear as a broad peak at 2.23 ppm. Similar to this observation, resonance signals belonging to the methyl protons of CTA gave rise as a very broad peak at 1.90 ppm (Figure 2c). On the other hand, methyl and methylene protons connected to the nitrogen atom of CTAOH gave resonance signals originally at 3.38 and 3.26 ppm, respectively (Figure 2d). When a calix[4]pyrrole is bound to an anion it adopts a cone conformation while forming a "cup-like" π electron cloud by means of oriented pyrrole rings.^[16] Upfield chemical shifts belonging to methyl and methylene protons of CTA clearly indicate that calix[4]pyrrole core of 2b acts as an ion pair receptor for both tethered carboxylate unit and CTA, binding the ammonium cation of CTA via cation $-\pi$ interactions and

the tethered carboxylate via hydrogen bonding.^[15,23] This was also supported by the existence of correlated 2D-NOESY signals between the methyl protons of CTA and pyrrole CH protons of calix[4]pyrrole core (Figure S22).

Variable concentration ¹H NMR analyses provide important insights into the self-assembly behavior of supramolecular agaregates in solution.^[24] Although the calix[4]pyrroles **2a** and **2b** were expected to form monomers and short oligomers at low concentrations, they were anticipated to self-assemble into higher order aggregates at elevated concentrations to give supramolecular polymers. This is because of an association constant ($K_a = 1.77 \times 10^3 \pm 24.6 \text{ M}^{-1}$ in CDCl₃, Fig. S15) between calix[4]pyrrole and tethered carboxylate unit and the existence of a long flexible alkyl chain linker. In accordance, concentration-dependent ¹H NMR analyses of 2a and 2b were carried out in CDCl₃. As shown in Figure 3 and Figure 4, calix[4]pyrroles 2a and 2b behave differently when their NMR spectra were compared under the same concentrations. For instance, while pyrrole NH proton resonance signals of 2a were observed at 9.55 ppm, in the case of 2b these signals were found to resonate at 11.09 and 11.27 ppm at 12 mm concentrations (cf. Figure 3a and Figure 4a). The corresponding signals undergo a downfield shift (10.70 ppm) as the concentration of 2a was increased to 191 mм. These peaks were found to resonate at 11.09 and 11.27 ppm and not to be affected over the course of the above concentration increment in the case of 2b (cf. Figure 3d and Figure 4d). Another result that can be inferred from the concentration-dependent ¹H NMR spectra is that as the concentrations of 2a and 2b were increased gradually, all proton signals become broader, indicating the formation of higher order supramolecular aggregates in solution. In the case of 2b these peak broadenings were significantly enhanced when compared to 2a.



Figure 3. ¹H NMR spectra (CDCI₃, 500 MHz, 25 °C) of **2a** at different concentrations: (a) 12, (b) 35, (c) 125, (d) 191 mm. * denotes residual solvent peaks.





Figure 4. Partial ¹H NMR spectra (CDCl₃, 500 MHz, 25 °C) of **2b** at different concentrations: (a) 12, (b) 35, (c) 125, (d) 190 mm. * denotes residual solvent peaks.

Eurjoc Full Paper



Figure 5. Specific viscosity (Vs) changes of 2a and 2b plotted against monomer concentration in CHCl₃ at 25 °C.

Two-dimensional diffusion ordered NMR (DOSY) can be utilized to investigate the self-assembly process of monomers and to compare the sizes of supramolecular aggregates quantitatively by using diffusion coefficients.^[25] Therefore, concentrationdependent DOSY experiments of **2a** and **2b** were performed (Figures S23–26). Specifically, weighted average diffusion coefficients were measured as 6.81×10^{-10} and 4.79×10^{-10} m² s⁻¹ for 12 mM **2a** and **2b** solutions, respectively. When the concentration was increased, diffusion coefficients of the **2a** (300 mM) and **2b** (191 mM) were found to be decreased to 1.20×10^{-10} and 1.04×10^{-10} m² s⁻¹, respectively. These sharp decreases in the diffusion coefficients indicate the existence of higher order supramolecular polymers at elevated concentrations of **2a** and **2b**.

Viscosity is a direct index for the formation of polymers. Therefore, viscosity measurements were also carried out by using an Ubbelohde semi-micro dilution viscometer to analyze further the supramolecular polymers obtained from 2a and 2b. As shown in Figure 5, a double-logarithmic plot of specific viscosity (Vs) vs. concentration changes of monomers exhibited viscosity transitions. At low concentration ranges, the curve has a slop of 1.05. As the concentrations increased gradually, the slopes of curves approach 2.72 and 3.09 for 2a and 2b, respectively. The linear relationship (slope of 1.05) between concentration and viscosity indicates the presence of monomers and oligomers with constant sizes for both 2a and 2b. Whereas, exponential relationships (slopes of 2.72 and 3.09) are indicative for the formation of supramolecular polymers in which the size of supramolecular aggregates exhibited a nonlinear change with concentration increments. The CPCs for the monomers 2a and 2b in CHCl₃ were found to be about 43 and 32 mm, respectively, as evidenced from clear changes of slopes occurring at these concentrations, indicating transition from oligomeric and cyclic species to highly ordered supramolecular polymers.

NMR analyses and viscosity measurements reveal that **2b** exhibits a better performance in the properties of supramolecular polymer when it was compared with **2a**. This is because **2b** exhibits notable enhanced peak broadenings when the ¹H NMR spectra of equimolar high concentration solutions of **2a** and **2b** were compared (cf. Figure 3d and Figure 4d). **2b** also shows

broader peaks than 2a even at low concentrations that can be judged from Figure 3a and Figure 4a and lower diffusion coefficient during DOSY NMR analyses. Additionally, a higher curve slope (m=3.09 and 2.72 for **2b** and **2a**, respectively) was obtained in the case of viscosity measurements. Furthermore, a binding constant because of the interaction between the π electron cloud of cone-shaped carboxylate-bound calix[4]pyrrole 3 and the ammonium cation of cetyltrimethylammonium acetate (CTAOAc) (cf. Figure 2c and Figure 2d) was calculated to be K_a = 1.13 × 10² ± 0.87 M⁻¹ in CDCl₃ (Figure S18), indicating that CTA becomes a direct part of supramolecular polymer. This was also supported by NOESY NMR analyses of 10.2 and 191 mm CDCl₃ solutions of **2b**. The correlated 2D-NOESY signals between methylene units of CTA were found to be enhanced at high concentration (cf. Figures S21 and S22). All of these results let us to conclude that the presence of long alkyl chains of CTA provides additional hydrophobic interactions, as the supramolecular polymer of 2b grows. These enhanced properties were also found to be reflected in the degree of polymerization (DP). DP values of 2b were estimated to be at least 40 % higher than those of 2a (Table S1).

Since 2b exhibits better supramolecular polymerization performance, a high concentration solution of 2b was used to draw rod-like fibers. Scanning electron microscopy (SEM) images of fibers are shown in Figure 6a and revealed fibers with diameters of 9.03 and 4.06 µm, providing direct evidence for the formation of supramolecular polymers with high degree of molecular weights.^[26] After heating to 50 °C, the gel obtained from a 230 mm CHCl₃ solution of **2b** dissociated into a solution. Cooling the solution to 25 °C afforded the reformation of supramolecular gel (cf. Figure 6c and Figure 6d). The SEM image of a freeze-dried gel sample exhibited a paraffin like network structure (Figure 6b). Thermo-responsive behaviour of the supramolecular polymer formed by 2b was also supported by variable temperature viscosity measurements. As illustrated in Figure 6e, Vs. of a 158 mM CHCl₃ solution of **2b** was found to be 4.04 at 25 °C. When the temperature of the solution was increased to 50 °C, it was measured as 1.1. 2a also showed a similar result when it was exposed to variable temperature vis-





cosity measurements (Figure 8b). These sharp viscosity decreases reflects the dynamic nature of noncovalent interactions between calix[4]pyrrole and carboxylate units, and the presence of high molecular weight supramolecular polymers at low temperatures.



Figure 6. SEM images of gold-coated (a) fiber drawn from a 251 mm $CHCI_3$ solution of **2b**, and (b) supramolecular polymer gel obtained via freeze-drying of the same solution. Reversible sol-gel transition of supramolecular gel obtained from a 251 mm $CHCI_3$ solution of **2b** at (c) 25 °C, (d) 50 °C. (e) Temperature dependent viscosity change of a 158 mm $CHCI_3$ solution of **2b**.

Calix[4]pyrroles **2a** and **2b** contains tethered carboxylate units. Carboxylate salts can be protonated by adding an acid, thus destroying the host-guest interaction between calix[4]pyrrole core and the carboxylate unit and making the supramolecular aggregates disassemble. Hence, the reversible supramolecular polymer–monomer transition could be achieved by changing pH. Evidence for this was provided by chemical shift changes in ¹H NMR spectra (Figure 7). When equimolar CH₃SO₃H was added to a CDCl₃ solution of monomer **2a** (100 mM), pyrrole NH resonances were found to be shifted from



Figure 7. Partial ¹H NMR spectra (500 MHz) of (a) **2a** (100 mM, 0.5 mL), after addition of equimolar (b) CH₃SO₃H, (c) TBAOH, and (d) CH₃SO₃H recorded in CDCl₃ at 25 °C.

10.56 to 7.35 and 7.25 ppm, indicating the disruption of host– guest interaction between calix[4]pyrrole and carboxylate units. However, the chemical shift reversed back to 10.33 ppm after addition of equimolar TBAOH, which is an indication of the reestablishment of complexation between the same host–guest units. When the resulting solution was treated with CH₃SO₃H again, the corresponding NH proton signals were observed at 7.19 ppm as a broad singlet, showing that this process can be repeated over the course of consecutive acid base treatments.

The pH responsiveness of **2a** was also confirmed by viscosity measurements which were carried out with a 100 mm CHCl₃ solution of **2a** while increasing the concentration of CH₃SO₃H gradually (Figure 8a). As the concentration of acid was increased, Vs. of the solution decreased gradually, since the H-bonding interactions between calix[4]pyrrole core and the carboxylate unit were broken step by step. These studies clearly indicate that the supramolecular polymerization of **2** can be controlled by changing the pH of solution. DOSY NMR analyses also support these findings. While the diffusion coefficient of a 100 mm CDCl₃ solution of **2a** was determined as 2.62×10^{-10} m² s⁻¹, after treatment with equimolar CH₃SO₃H it was found to be 4.04×10^{-10} m² s⁻¹ (Figures S27 and 28).



Figure 8. Specific viscosity changes of CHCl₃ solutions **2a** (a) (100 mM) upon incremental addition of CH₃SO₃H, (b) (257 mM) upon incremental change in the temperature.

Conclusions

We present the synthesis and characterization of a carboxylic acid-functionalized calix[4]pyrrole with a long alkyl chain linker between the calix[4]pyrrole core and carboxylic acid unit. This calix[4]pyrrole is then converted to its corresponding carboxylate derivatives (as TBA and CTA slats) by treatment with either TBAOH or CTAOH. The resulting heteroditopic A-B type supramolecular monomers consisting of a calix[4]pyrrole core and a tethered carboxylate unit with two different counter cations were found to self-assemble into the higher order aggregates at elevated concentrations to give pH- and thermo-responsive supramolecular polymers, which was evidenced by various techniques such as NMR spectroscopy, viscosity measurements, and SEM analyses. When CTA was used as the counter cation, it was shown to be a direct part of the supramolecular polymer via cation- π interactions, providing enhanced properties to the supramolecular polymers formed. The present work demonstrates the first example of stimuli responsive and counter cat-



ion dependent supramolecular polymers based on calix[4]pyrroles and their anion recognition ability.

Experimental Section

1. General Information: All solvents were dried before use according to standard literature procedures. Unless specifically indicated, all other chemicals and reagents used in this study were purchased from commercial sources and used as received. ¹H, ¹³C, DOSY and NOESY NMR spectra were recorded on Agilent VNMRS 500 spectrometers using TMS as an internal reference. Mass spectra were measured on a Thermo Scientific TSQ Quantum GC and Micromass Autospec Ultima. Viscosity measurements were carried out with an Ubbelohde micro dilution viscometer (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 293 K in chloroform. Melting points were determined using a Gallenkamp instrument with 1 °C/min. temperature increment under ambient conditions. The Compounds **3**,^[9d] **4**⁽¹⁹⁾ and CTAOAc^[27] were synthesized according to previously reported literature procedures.

2. Synthesis

Compound 1: 3 (830 mg, 1.52 mmol) and 10-azidodecanoic acid (4) (328 mg, 1.54 mmol) were dissolved in THF (20 mL). Then, the solution of Na-ascorbate (664 mg, 3.35 mmol) in 1 mL of water was added to reaction mixture dropwise followed by addition of solution of CuSO₄·5H₂O (418 mg, 1.68 mmol) in 1 mL of water. The reaction mixture was stirred at room temperature for 24 h. After the completion of the reaction solvent was removed under reduced pressure. Then the crude mixture was dissolved in DCM (30 mL) and washed with water three times. This was followed by washing the organic phase with 0.1N HCl (30 mL) and brine (30 mL). Excess solvent was removed under vacuum after drying the organic phase with anhydrous Na₂SO₄. Resulting viscous solution was added dropwise into excess hexane, causing the precipitation of 1 as a pale yellow solid (1.11 g, 96 %). Melting point: > 224 °C (decomposes). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ =7.59 (s, 1H, triazole-CH), 7.23 and 7.12 (br s, 4H, NH), 6.94 and 6.86 (d, 4H, benzene-CH), 5.92 (m, 6H, pyrrole CH), 5.67 (t, J=3 Hz, 2H, pyrrole CH), 5.19 (s, 2H, -OCH₂-), 4.36 (t, J=7.2 Hz, 2H, -CH₂-), 2.35 (t, J=7.5 Hz, 2H, -CH₂-), 1.92 (br m, 2H, -CH₂-), 1.86 (s, 3H, -CH₃), 1.64 (br m, 2H, -CH₂-), 1.52 (br s, 18H, $-CH_3$), 1.33 ppm (br m, 10H, $-CH_2$ -). ¹³C NMR (126 MHz, CD₃CN): $\delta =$ 186.56, 144.30, 140.50, 138.50, 136.77, 128.46, 122.37, 113.85, 105.72, 102.79, 62.20, 53.41, 50.40, 44.00, 35.18, 33.31, 31.58, 29.65, 28.56, 26.30, 24.63 ppm. LRMS: m/z 758.26 [M - H]+. HRMS: m/z calcd for C₄₆H₆₀N₇O₃⁺, 758.47578, found 758.48012. Elemental analysis: calculated for C46H59N7O3: C 72.89, H 7.85, N 12.93; found C 72.63, H 8.02, N 12.86.

CTAOH: CTAOH was prepared according to a previously reported procedure with slight changes.^[20b] A glass column (1 cm diameter) packed with 5 g of commercial anion exchange Amberlyst A-26 (OH⁻) form was washed with MeOH (100 mL). Methanol solution of CTABr (100 mg in 10 mL) was passed slowly through the column four times. After washing the column with 10 mL of MeOH, the combined eluates were evaporated, and the obtained residue was dried under high vacuum to give CTAOH quantitatively as a white solid. ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 3.53 (m, 2H, -CH₂-), 3.47 (s, 9H, -CH₃), 1.75 (br m, 2H, -CH₂-), 1.36 (br m, 4H, -CH₂-), 1.26 (br s, 22 H, -CH₂-), 0.88 (t, J=7 Hz, 3H, -CH₃).

Compound 2a: To a methanol solution of **1** (502 mg, 0.66 mmol) tetrabutylammonium hydroxide (1 m, 0.66 mL, in MeOH) was added dropwise. After addition was complete, the reaction mixture was stirred at room temperature for 1 h. Excess methanol was removed



and the resulting solid washed with diethyl ether followed by drying under vacuum afforded **2a** as a white solid (632 mg, 95%). Melting point: > 213 °C (decompose). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 10.42 (br s, 4H, NH), 7.72 (s, 1H, triazole –*CH*), 6.86 and 6.81 (d, 4H, benzene–*CH*), 5.88–5.65 (m, 8H, pyrrole–*CH*), 5.19 (s, 2H, -OCH₂-), 4.40 (t, *J*=7.2 Hz, 2H, -*CH*₂-), 2.92 (m, 8H, -*CH*₂-), 1.91 (t, *J*= 7.5 Hz, 2H, -*CH*₂-), 1.27–1.83 (m, 51H, meso-*CH*₃ and -*CH*₂-), 0.97 ppm (t, *J*=7.3 Hz, 12H, -*CH*₃). ¹³C NMR (126 MHz, CDCl₃): δ = 186.6, 144.3, 140.5, 138.7, 136.8, 128.5, 122.4, 113.9, 105.7, 102.8, 53.4, 50.4, 44.0, 35.2, 33.3, 31.6, 29.7, 28.6, 26.3, 24.6, 22.7, 14.1. ppm. LRMS: *m*/*z* 756.403 [M]⁻. HRMS: *m*/*z* calcd for C₄₆H₅₈N₇O₃⁻, 756.46013, found 758.46125. Elemental analysis: calculated for C₆₂H₉₄N₈O₃: C 74.51, H 9.48, N 11.21; found C 74.93, H 9.79, N 11.14.

Compound 2b: This compound was prepared from 1 (126.5 mg, 0.42 mmol) and CTOH (318 mg, 0.42 mmol) using the same procedure that was used to produce 2a. The product was a white solid (431 mg, 98 %). M.p. > 213 °C (decomp). Melting point: > 198 °C (decomposes). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ = 11.45 and 11.27 (br s, 4H, NH), 7.86 (br s, 1H, triazole-CH), 6.88 (m, 4H, benzene-CH), 5.60-5.83 (br m, 8H, pyrrole-CH), 5.31 (s, 2H, -OCH₂-), 4.40 (t, J= 7.3 Hz, 2H, -CH₂-), 2.33 (t, J= 7 Hz, 2H, -CH₂-), 2.23 (br s, 2H, -NCH₂-), 1.90 (br m, 9H, -NCH₃), 1.84 (s, 3H, -CH₃), 1.69–121 (m, 60H, meso-CH₃ and -CH₂-), 0.89 ppm (t, J= 7 Hz, 3H, -CH₃). ¹³C NMR $(126 \text{ MHz}, \text{CDCl}_3)$: $\delta = 178.0, 156.2, 143.5, 141.3, 140.0, 138.2, 128.8, 128$ 123.9, 114.2, 103.5, 100.8, 66.1, 62.4, 51.0, 44.2, 34.8, 32.0, 29.7, 26.1, 24.9, 22.7 ppm. LRMS: m/z 756.412 [M]-. HRMS: m/z calcd for $C_{46}H_{58}N_7O_3^{-},\,756.46013,\,found$ 758.46084. Elemental analysis: calculated for $C_{65}H_{100}N_8O_3$: C 74.96, H 9.68, N 10.76; found C 75.16, H 9.87, N 10.28.

Acknowledgments

This work was supported by Istanbul Technical University (Grant Number: TDK-2017-40643).

Keywords: Supramolecular polymers · Self-assembly · Hostguest systems · Macrocycles

- [1] a) L. Yang, X. Tan, Z. Wang, X. Zhang, *Chem. Rev.* 2015, *115*, 7196–7239;
 b) X. Yan, F. Wang, B. Zheng, F. Huang, *Chem. Soc. Rev.* 2012, *41*, 6042–6065.
- [2] a) C. Lu, M. Zhang, D. Tang, X. Yan, Z. Zhang, Z. Zhou, B. Song, H. Wang, X. Li, S. Yin, H. Sepehrpour, P. J. Stang, J. Am. Chem. Soc. 2018, 140, 7674–7680; b) A. Lavrenova, D. W. Balkenende, Y. Sagara, S. Schrettl, Y. C. Simon, C. Weder, J. Am. Chem. Soc. 2017, 139, 4302–4305; c) A. Samanta, M. Tesch, U. Keller, J. Klingauf, A. Studer, B. J. Ravoo, J. Am. Chem. Soc. 2015, 137, 1967–1971; d) Y. Han, Y. Tian, Z. Li, F. Wang, Chem. Soc. Rev. 2018, 47, 5165–5176; e) P. Liu, Z. Li, B. Shi, J. Liu, H. Zhu, F. Huang, Chem. Eur. J. 2018, 24, 4264–4267.
- [3] B. Zheng, F. Wang, S. Dong, F. Huang, Chem. Soc. Rev. 2012, 41, 1621– 1636.
- [4] D. S. Guo, Y. Liu, Chem. Soc. Rev. 2012, 41, 5907-5921.
- [5] A. Harada, Y. Takashima, H. Yamaguchi, Chem. Soc. Rev. 2009, 38, 875– 882.
- [6] a) X. Ren, J. Zhang, M. Cheng, Q. Wang, J. Jiang, L. Wang, *Tetrahedron Lett.* **2018**, *59*, 2197–2204; b) C. Yao, J. Zhang, M. Cheng, Q. Sun, Y. Pan, J. Jiang, L. Wang, *Macromol. Rapid Commun.* **2018**, *39*, 1700218.
- [7] a) C. Li, Chem. Commun. 2014, 50, 12420–12433; b) H. Li, W. Chen, F. Xu, X. Fan, T. Liang, X. Qi, W. Tian, Macromol. Rapid Commun. 2018, 39, 1800053.
- [8] Q. He, P. Tu, J. L. Sessler, Chem 2018, 4, 46-93.
- [9] a) A. Aydogan, Supramol. Chem. 2016, 28, 117–124; b) A. Aydogan, D. J. Coady, V. M. Lynch, A. Akar, M. Marquez, C. W. Bielawski, J. L. Sessler, Chem. Commun. 2008, 1455–1457; c) S. K. Kim, J. Lee, N. J. Williams, V. M.





Lynch, B. P. Hay, B. A. Moyer, J. L. Sessler, *J. Am. Chem. Soc.* **2014**, *136*, 15079–15085; d) A. Aydogan, A. Akar, *Chem. Eur. J.* **2012**, *18*, 1999–2005; e) X. Chi, G. M. Peters, C. Brockman, V. M. Lynch, J. L. Sessler, *J. Am. Chem. Soc.* **2018**, *140*, 13219–13222.

- [10] C. Z. Zhou, H. Tang, S. J. Shao, S. X. Jiang, J. Liq. Chromatogr. Relat. Technol. 2006, 29, 1961–1978.
- [11] M. Yano, C. C. Tong, M. E. Light, F. P. Schmidtchen, P. A. Gale, Org. Biomol. Chem. 2010, 8, 4356–4363.
- [12] a) E. Baysak, S. Yuvayapan, A. Aydogan, G. Hizal, *Sens. Actuators B* 2018, 258, 484–491; b) A. Aydogan, A. Koca, M. K. Şener, J. L. Sessler, *Org. Lett.* 2014, 16, 3764–3767; c) D. Sareen, J. H. Lee, H. Hwang, S. Yoo, C.-H. Lee, *Chem. Commun.* 2016, 52, 5852–5855; d) S. K. Kim, H. G. Lee, G. I. Vargas-Zúñiga, J. H. Oh, V. M. Lynch, M. H. Lee, J. L. Sessler, *Supramol. Chem.* 2017, 29, 651–657; e) D. Stefani, M. Perrin, C. Gutiérrez-Cerón, A. C. Aragonès, J. Labra-Muñoz, R. D. Carrasco, Y. Matsushita, Z. Futera, J. Labuta, T. H. Ngo, K. Ariga, I. Díez-Pérez, H. S. van der Zant, D. Dulić, J. P. Hill, *ChemistrySelect* 2018, 3, 6473–6478.
- [13] R. Molina-Muriel, G. Aragay, E. C. Escudero-Adán, P. Ballester, J. Org. Chem. 2018, 83, 13507–13514.
- [14] a) S. Bähring, L. Martín-Gomis, G. Olsen, K. A. Nielsen, D. S. Kim, T. Duedal, Á. Sastre-Santos, J. O. Jeppesen, J. L. Sessler, *Chem. Eur. J.* **2016**, *22*, 1958– 1967; b) J. S. Park, K. Y. Yoon, D. S. Kim, V. M. Lynch, C. W. Bielawski, K. P. Johnston, J. L. Sessler, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 20913–20917.
- [15] A. Aydogan, J. L. Sessler, Chem. Commun. 2014, 50, 13600-13603.
- [16] S. Amharar, S. Yuvayapan, A. Aydogan, Chem. Commun. 2018, 54, 829– 832.
- [17] a) S. Dong, Y. Luo, X. Yan, B. Zheng, X. Ding, Y. Yu, Z. Ma, Q. Zhao, F. Huang, Angew. Chem. Int. Ed. 2011, 50, 1905–1909; Angew. Chem. 2011,

123, 1945; b) F. Wang, J. Zhang, X. Ding, S. Dong, M. Liu, B. Zheng, S. Li, L. Wu, Y. Yu, H. W. Gibson, F. Huang, *Angew. Chem. Int. Ed.* **2010**, *49*, 1090–1094; *Angew. Chem.* **2010**, *122*, 1108; c) N. Yamaguchi, H. W. Gibson, *Chem. Commun.* **1999**, 789–790.

- [18] H. C. Kolb, M. G. Finn, K. B. Sharpless, Angew. Chem. Int. Ed. 2001, 40, 2004; Angew. Chem. 2001, 113, 2056.
- [19] R. Elena, W. Ina, G. Silvia, L. W. Ariel, S. Luke, T. Manuela, Angew. Chem. Int. Ed. 2014, 53, 11944–11949; Angew. Chem. 2014, 126, 12138.
- [20] a) F. Al-Ali, A. Brun, F. Rodrigues, G. Etemad-Moghadam, I. Rico-Lattes, Langmuir 2003, 19, 6678–6684; b) E. Alcalde, I. Dinarès, A. Ibáñez, N. Mesquida, Molecules 2012, 17, 4007–4027.
- [21] Y. Liu, Z. Wang, X. Zhang, Chem. Soc. Rev. 2012, 41, 5922–5932.
- [22] P. A. Gale, J. L. Sessler, V. Kral, V. Lynch, J. Am. Chem. Soc. 1996, 118, 5140–5141.
- [23] C. Caltagirone, N. Bill, D. Gross, M. Light, J. Sessler, P. Gale, Org. Biomol. Chem. 2010, 8, 96–99.
- [24] N. Yamaguchi, D. S. Nagvekar, H. W. Gibson, Angew. Chem. Int. Ed. 1998, 37, 2361–2364; Angew. Chem. 1998, 110, 2518.
- [25] N. L. Strutt, H. C. Zhang, M. A. Giesener, J. Y. Lei, J. F. Stoddart, Chem. Commun. 2012, 48, 1647–1649.
- [26] N. Yamaguchi, H. W. Gibson, Angew. Chem. Int. Ed. 1999, 38, 143–147; Angew. Chem. 1999, 111, 195.
- [27] S. Debnath, A. Dasgupta, R. N. Mitra, P. K. Das, Langmuir 2006, 22, 8732– 8740.

Received: November 7, 2018





- Supramolecular Polymers
- S. Yuvayapan, A. Aydogan* 1-8

 Counter Cation Dependent and
 Stimuli Responsive Supramolecular Polymers Constructed by Calix[4]pyrrole Based Host-Guest Interactions



A host-guest recognition motif based on a calix[4]pyrrole macrocycle and tethered carboxylate unit was employed to construct counter cation dependent supramolecular polymers from low molecular weight A–B type monomers. Reversible pH- and thermo-responsiveness of the supramolecular polymers were demonstrated for the first time for a calix-[4]pyrrole based and anion recognition induced supramolecular polymer.

DOI: 10.1002/ejoc.201801663