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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Supramolecular Polymeric Complexes of Calix[8]arenes

A. V. Ten'kovtsev, L. V. Abramova, and M. M. Dudkina

Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia

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Abstract—Formation of ionic complexes of calix[8]arenes with polymers of various basicities was studied, and previously unknown ternary polymeric complexes of calix[8]arenes of the ion–ion (polymer–calixarene–uranyl ion) and ion–hydrophilic molecule–hydrophobic molecule (polymer–calixarene–fullerene) types were prepared.

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Calixarenes exhibit unique properties from the viewpoint of the host–guest complex chemistry [1, 2]. Firstly, methods have been developed for facile synthesis of calixarenes of the required size under properly chosen condensation conditions. Secondly, calixarenes have internal cavities of different size formed by a belt of phenyl rings; these cavities are capable to accommodate a guest molecule of a definite size, which allows their use in molecular recognition. It should be noted that calixarenes form complexes both with neutral organic molecules and with ions. Furthermore, calixarenes can be readily functionalized, which allows variation of their affinity for a guest molecule. Finally, expenses for the preparation of calixarenes from *p*-substituted phenols and formaldehyde are relatively low, which is an important factor for practical applications. For example, calixarenes can be used as specific ligands in analytical chemistry, sensor techniques, medical diagnostics, and synthesis of new materials in supramolecular chemistry.

For many technical applications, it is desirable to combine in one sample the useful properties of both calixarenes and polymers. Synthesis of polymers based on calixarenes is a challenging problem, because these are polyhomofunctional compounds and preparation of di- and monofunctionalized derivatives suitable as monomers for polymerization or polycondensation is difficult. However, the presence in calixarenes of functional groups capable of deprotonation (e.g., hydroxy groups) suggests the possibility of formation of ionic complexes of calixarenes with basic polymeric carriers.

In this study we examined the possibility of preparation of binary and ternary complexes of calixarenes with ionic monomers of various basicities. As investigation objects we chose octa-*p*-*tert*-butylcalix[8]arene and octa-*p*-nitrocalix[8]arene, polymers of various basicities (polyalkyleneacetamidines and poly-4-vinylpyridine), and fullerene C_{60} and uranyl ions UO_2^{2+} as guest species. The choice of the guest species was governed by the complementarity of their size and the size of the calix[8]arene cavity, and also by the pronounced tendency of many calixarene derivatives to form complexes with uranyl cation. Owing to the latter property, sulfo derivatives of calixarenes were suggested as a sensor element [3] in determination of the uranium content in radiochemical production wastes.

EXPERIMENTAL

p-*tert*-Butylphenol, paraform, and solvents were used without additional purification. To prepare the complexes, we used polyamidines ($M_w = 2 \times 10^3$, $M_w/M_n = 2.2$) and poly-4-vinylpyridine (Acros, $M_w = 1.6 \times 10^4$).

The NMR spectra were recorded on Bruker AC200 (200 MHz) and Bruker AC300 (300 MHz) spectrometers from solutions in DMSO and chloroform. The UV spectra were taken with Varian Cary 100 and SF-26 spectrophotometers. The luminescence spectra were excited with the nitrogen laser radiation (λ = 337 nm, pulse length 6–8 ns) and were recorded during the persistence time of 1 μs after the excitation pulse at T = 300 K. To measure the linear-optical properties of the samples, we used a Nd–garnet pulse laser with the emission wavelength of 1.06 μm. The laser operated in the modulated *Q*-factor mode; the pulse length was 15 ns. The dynamic light scattering was measured with a Brookhaven BI-200SM goniometer and a Brookhaven BI-9000AT correlator. As a light source we used a He–Ne laser (λ = 632.8 nm).

***p*-Nitrocalix[8]arene.** To 10 ml of a 1 : 1 mixture of 65% HNO_3 and 98% H_2SO_4, cooled to +3°C, 1 g (7.7×10^{-4} mol) of *p-tert*-butylcalix[8]arene [4] is gradually added with stirring, keeping the temperature of the reaction mixture in the interval 3–5°C. The product is precipitated by adding 40 ml of water. The yellow precipitate is treated with 20 ml of boiling methanol; the solution is cooled and filtered. This treatment is repeated two times. By so doing, two fractions (soluble and insoluble in methanol) are obtained. As follows from the ^1H NMR data, the fraction soluble in methanol is a mixture of partially degraded or incompletely substituted cyclic and acyclic products. The fraction insoluble in methanol is the target product; yield 0.25 g (27%), mp >360°C. ^1H NMR spectrum (300 MHz, DMSO, 25°C), δ, ppm: 7.97 s (2H, C_{ar}–H), 5.13 br (1H, OH), 4.00 s (2H, CH_2).

Ternary complex poly-1,8-octamethyleneacetamidine–octa-*p*-nitrocalix[8]arene–$UO_2(OH)_2$. Nitrocalix[8]arene (0.02 g, 1.6×10^{-5} mol) is dissolved in 2 ml of acetone, and $UO_2(OH)_2$ (0.015 g, 0.5×10^{-4} mol) is suspended in 2 ml of acetone. Mixing of the solution and suspension results in formation of a soluble binary complex. To the resulting solution, 2 ml of an alcoholic solution of poly-4-vinylpyridine (0.06 g, 0.5×10^{-3} mol) is added. The ternary complex is isolated on cooling as a dark orange precipitate. Films of the complex are obtained by casting onto a rotating support (3000 rpm, 30 s).

Ternary complex polymer–calixarene–fullerene. Such ternary complexes can be prepared by two procedures differing in the order of combining the components.

(1) A solution of *p-tert*-butylcalix[8]arene and poly-1,8-octamethyleneacetamidine (1.2×10^{-3} mol) (calixarene : polymer ratio 1 : 40) in ethanol is prepared. A polymer film is prepared by casting onto a rotating support. After drying over concentrated H_2SO_4, the film is placed in a hot 1.5×10^{-3} M solution of fullerene (2 mg) in toluene (2 ml). The ternary complex is formed within 24 h as a gray-brown film. The product is extracted with two 2-ml portions of boiling toluene and vacuum-dried.

(2) Fullerene (1 mg) is dissolved in 2 ml of toluene on refluxing for 2 h. To the refluxing solution, 2 mg of *p-tert*-butylcalix[8]arene is added to obtain a 1.5×10^{-3} M solution. The solution is filtered while hot and allowed to slowly cool over a period of 24 h. The black precipitate is separated by centrifugation and dissolved in 5 ml of toluene. A polymer film is prepared by casting a solution of 0.2068 g (1.2×10^{-3} mol) of poly-1,8-octamethyleneacetamidine in 1.2 ml of alcohol onto a rotating support; the film is dried over concentrated H_2SO_4, placed in the hot solution of the calixarene–fullerene complex (see above), and allowed to stand for 4–6 h in a closed weighing bottle. The ternary complex is formed as a gray-brown film. The product is extracted with two 2-ml portions of boiling toluene and vacuum-dried.

Octa-*p-tert*-butylcalix[8]arene was prepared as described in [4] by the condensation of *p-tert*-butylphenol with paraform in the presence of sodium oxide. According to published data, the simplest route to octa-*p*-nitrocalix[8]arene is *ipso* nitration of octa-*p-tert*-butylcalix[8]arene with acetyl nitrate [5] or with a mixture of anhydrous HNO_3 and H_2SO_4 [6]. However, we failed to reproduce these procedures. In the case of nitration with acetyl nitrate, it appeared impossible to add the reagent to a solution of octa-*p-tert*-butylcalix[8]arene in methylene chloride because of extremely low solubility of the macrocycle in this solvent (in agreement with data of [4]). Nitration of octa-*p-tert*-butylcalix[8]arene under the conditions described in [6] yields octa-*p*-nitrocalix[8]arene heavily contaminated with decomposition products; the suggested purification procedure, reprecipitation from 2 M Na_2CO_3 into dilute HCl, results in tarring and total decomposition of octa-*p*-nitrocalix[8]arene. In this connection, we suggested a modification of this method, allowing preparation of the desired compound in a reasonable yield (up to 30%). We found that *ipso* nitration does not occur at temperatures below 3°C, whereas above 10°C the reaction becomes uncontrollable and leads to the ring opening. When the reaction is performed in the interval 5–7°C, >97% pure octa-*p*-nitrocalix[8]arene can be isolated by selective extraction with methanol.

The possibility of preparing double polymer–calixarene complexes was examined with octa-*p-tert*-butylcalix[8]arene and octa-*p*-nitrocalix[8]arene as calixarene components, and polyoctamethyleneacetamidine and poly-4-vinylpyridine, differing in the basicity of nitrogen-containing moieties, as polymer components.

p-tert-Butylcalix[8]arene is insoluble in ethanol but soluble in an alcoholic solution of polyamidine (p*K* ~11), which suggests the deprotonation of the macrocycle and formation of an ionic bond between the calixarene and polymer. As seen from Fig. 1, in a rel-

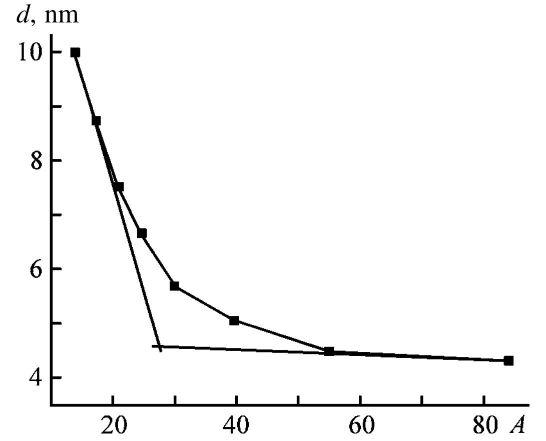


Fig. 1. Diameter *d* of particles of polyoctamethyleneacetamidine–octa-*p*-*tert*-butylcalix[8]arene complex as a function of the polymer : macrocycle ratio *A*.

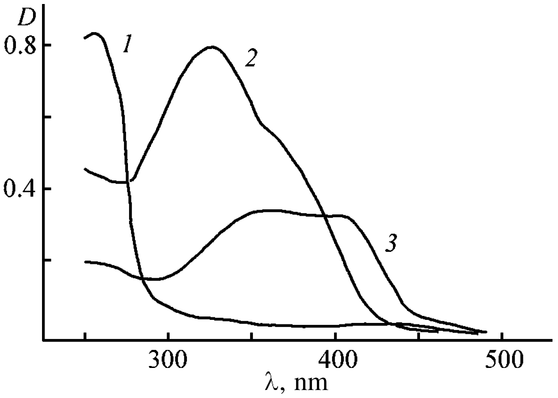


Fig. 2. Absorption spectra of (*1*) polyoctamethyleneacetamidine, (*2*) octa-*p*-nitrocalix[8]arene, and (*3*) their complex. (*D*) Optical density and (λ) wavelength; the same for Figs. 3 and 5.

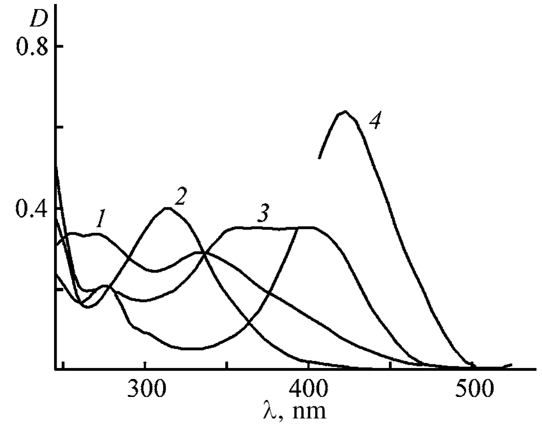


Fig. 3. Absorption spectra of octa-*p*-nitrocalix[8]arene at pH (*1*) 6.0, (*2*) 0, (*3*) 9.7, and (*4*) 13.

atively wide range of calixarene : polyamidine ratios (up to 1 : 40, counting for functional groups), no colloidal particles are formed, which suggests monodeprotonation of the macrocycle and formation of a comb-shaped ionic complex. Apparently, owing to the steric factors associated with the size and shape of the calixarene, the maximal capacity of the polymer for the calixarene should be considerably lower than the theoretical value (1 mol of polymer units per mole of calixarene). Polarization-optical examination of the complexes shows that the system becomes two-phase at polymer : calixarene ratios less than 30 : 1, which is in good agreement with the dynamic light scattering data.

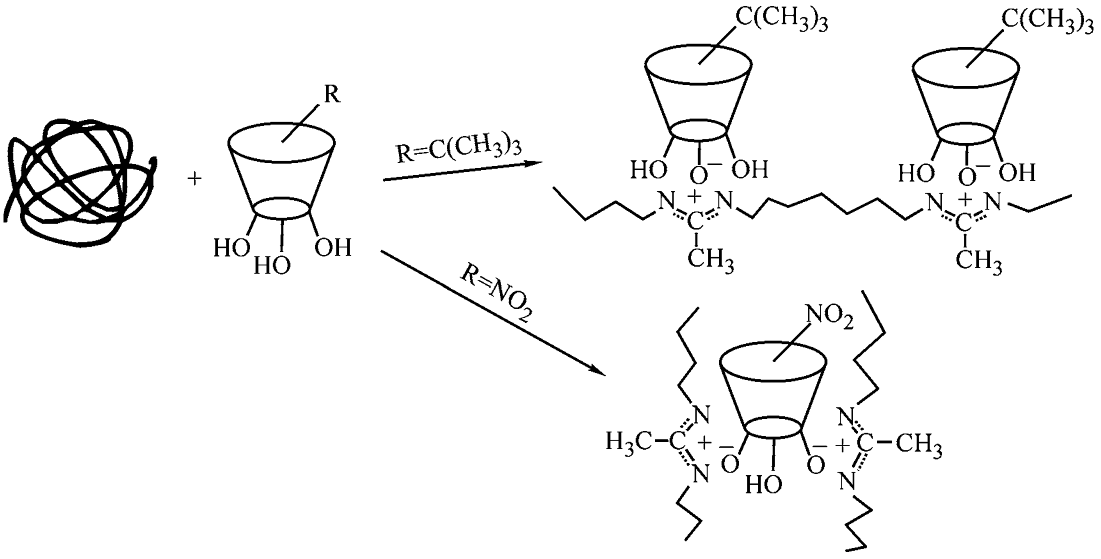
Mixing of an alcoholic solution of poly-4-vinylpyridine with *p*-*tert*-butylcalix[8]arene does not lead to their reaction, because of insufficient basicity of the polymer (p*K* ~9).

Octa-*p*-nitrocalix[8]arene (pK_1 <0, pK_2 2.6, pK_3 7.2 [6]) is sparingly soluble in ethanol (~3.2×10^{-3} M). On mixing alcoholic solutions of the macrocycle and a polymer (both polyamidine and poly-4-vinylpyridine), a polymer–calixarene complex precipitated, suggesting the binding of the polymer with the calixarene via several hydroxy groups and formation of a three-dimensional ionic network. Figure 2 shows the spectra of the starting polyamidine, octa-*p*-nitrocalix[8]arene, and their complex in DMF solutions. As seen, the spectrum of the complex differs essentially from those of the components, confirming the ionic interaction in the system. Figure 3 shows that the electronic spectra of octa-*p*-nitrocalix[8]arene depend on pH strongly and in a complex fashion, suggesting successive deprotonation of several hydroxy groups. It should be noted that the number of deprotonated groups in the nitrocalix[8]arene molecule is as follows [6], at pH 0, 0; at pH 6.0, 1; at pH 9.7, 2 or 3; and at pH 13.0, 4 or more. Comparison of the electronic spectrum of the complex with those of octa-*p*-nitrocalix[8]arene suggests that the interaction involves two or three hydroxy groups of the macrocycle.

Thus, our data show that variation of the basicity of the polymer and acidity of the hydroxy groups of calixarene can lead to the formation of both comb-shaped and cross-linked structures (Scheme 1).

The possibility of formation of ternary ion–ion complexes in a calixarene–polymer–metal ion system was examined with the system poly-4-vinylpyridine–octa-*p*-nitrocalix[8]arene–UO_2^{2+} as example. The choice of this system was governed by the fact that the less acidic octa-*p*-*tert*-butylcalix[8]arene does not form sufficiently stable complexes with uranyl ion, as judged from the identity of the luminescence spectra of a mechanical mixture of octa-*p*-*tert*-butylcalix[8]arene and the residue after evaporation of a solution of

Scheme 1. Formation of binary complexes



the components in DMSO–ethanol. However, the reaction of an alcoholic solution of octa-*p*-*tert*-butylcalix[8]arene with $UO_2(OH)_2$ is accompanied by the dissolution of $UO_2(OH)_2$, formation of a 1 : 1 complex (according to elemental analysis), and disappearance of the characteristic luminescence spectrum of the uranyl ion, consisting of several well-resolved lines (Fig. 4). The high acidity of octa-*p*-nitrocalix[8]arenes (first, pK_1 <0, and second, pK_2 2.6, dissociation steps) suggests that two hydroxy groups of the macrocycle act as anionic ligands for UO_2^{2+}, four less acidic OH groups act as donor–acceptor ligands, and the remaining two phenolic groups do not participate in the complexation. It should be noted that the equivalence of all the hydroxy groups of the macrocycle does not allow us to clearly distinguish the role of each particular OH group of the calixarene in the complexation.

On mixing alcoholic solutions of the polyamidine and UO_2^{2+}–octa-*p*-nitrocalix[8]arene complex, the ternary complex UO_2^{2+}–octa-*p*-nitrocalix[8]arene–polyamidine precipitates. Its qualitative composition is suggested by a broad band with a maximum at about 500 nm, appearing in the luminescence spectrum (Fig. 4). The appearance of the luminescence is probably associated with the electron density redistribution in the interaction of the UO_2^{2+}–octa-*p*-nitrocalix[8]arene complex with highly basic polyamidine, resulting in the deprotonation of the hydroxy groups of the macroring that are not involved in ionic bonding with uranyl ions (Scheme 2).

The possibility of preparing ternary polymeric complexes of calixarenes in which the components are bound by a combination of ionic and hydrophilic–hydrophobic interactions was examined with the octa-*p*-*tert*-butylcalix[8]arene–poly-1,8-octamethyleneacetamidine–C_{60} system as example. The complexes were prepared by two pathways: treatment of the octa-*p*-*tert*-butylcalix[8]arene–poly-1,8-octamethyleneacetamidine complex with a boiling solution of fullerene in toluene and treatment of the polyamidine with a hot solution of the calixarene–fullerene complex in toluene. Both procedures yielded the ternary complexes. Figure 5 shows the electronic spectra of the binary complexes fullerene–octa-*p*-*tert*-butylcalix[8]arene and poly-1,8-octamethyleneacetamidine–octa-*p*-*tert*-butylcalix[8]arene and of the ternary complex. It is seen that the spectrum of the ternary complex fuller-

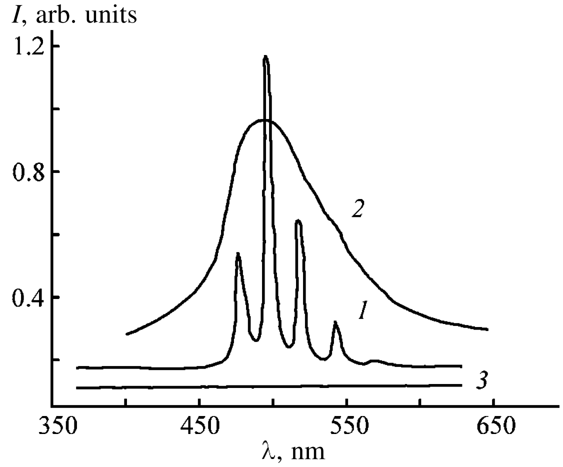
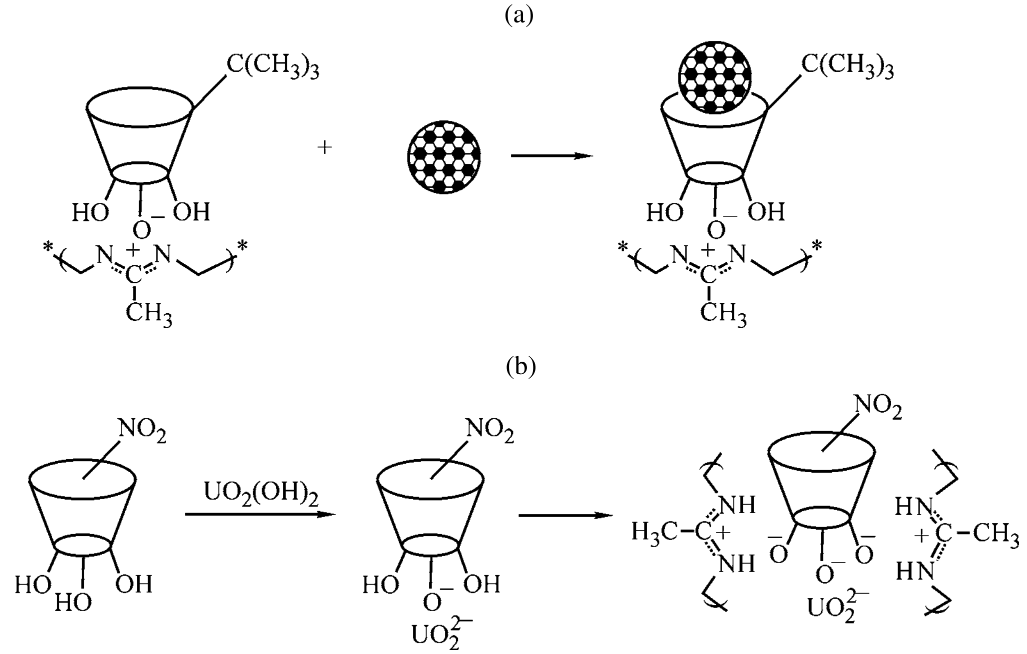


Fig. 4. Luminescence spectra of (*1*) uranic acid, (*2*) complex of UO_2^{2+} with octa-*p*-nitrocalix[8]arene, and (*3*) ternary complex UO_2^{2+}–octa-*p*-nitrocalix[8]arene–polyoctamethyleneacetamidine. (*I*) Intensity and (λ) wavelength.

Scheme 2. Formation of ternary (a) hydrophilic-hydrophobic and (b) ion–ion complexes



ene–poly-1,8-octamethyleneacetamidine–octa-*p*-*tert*-butylcalix[8]arene is a superposition of the spectra of the binary complexes. This fact indicates that both procedures allow preparation of ternary complexes combining the ionic and hydrophobic–hydrophilic binding of the components (Scheme 2).

Both procedures for preparing the ternary complex yield a stable film resistant to the action of boiling hydrocarbons (toluene, xylene) but partially degrading under the action of boiling ethanol. Such a behavior is also indicative of the formation of a ternary complex, taking into account the fact that the fullerene–*p*-*tert*-butylcalix[8]arene complex is soluble in toluene and decomposes in polar solvents [7].

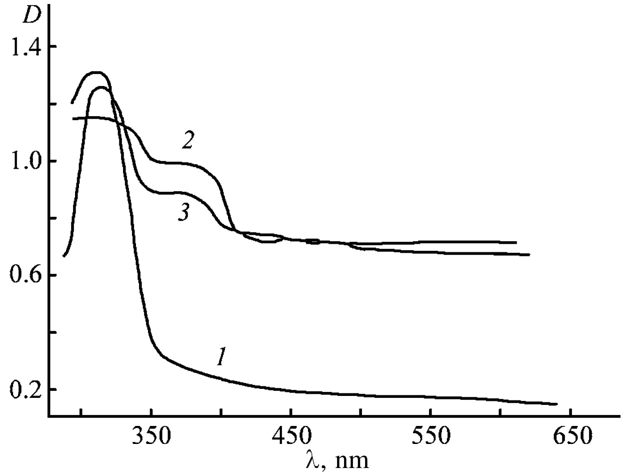


Fig. 5. Electronic spectra of the binary complexes (*1*) fullerene–octa-*p*-*tert*-butylcalix[8]arene and (*2*) poly-1,8-octamethyleneacetamidine–octa-*p*-*tert*-butylcalix[8]arene; (*3*) spectrum of the ternary complex.

Thus, calixarenes are capable of forming ternary complexes by simultaneous interactions with the functional groups of ionic polymers and guest molecules; the acidity–basicity ratio for the polymer–calixarene system strongly affects the possibility of formation of ion–ion and ion–hydrophobic component–hydrophilic component supramolecular structures. We believe that the suggested route to polymer systems containing fullerenes can find use in the development of new materials for optoelectronics and of polymeric sensors for environmental monitoring.

CONCLUSION

The formation of ionic complexes by interaction of ionic polymers with calix[8]arenes was studied in relation to the basicity of functional groups of the polymer and acidity of those of the macrocycle. The possibility of formation of ternary supramolecular complexes ion–ion (polymer–calixarene–uranyl ion) and ion–hydrophilic component–hydrophobic component (polymer–calixarene–fullerene) was shown.

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