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Formation and functioning of electroactive coatings based on fullerenes and their derivatives. The role of non-covalent interactions

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Abstract. Results on the formation of electroactive coatings based on fullerenes and their derivatives and their functioning are presented. Attention is focused on the fullerene – cationic lipid composite films immobilised on electrodes. The role of non-covalent interactions in the formation and functioning of fullerene-containing coatings is discussed. The bibliography includes 124 references.

I. Introduction

Fullerenes are a carbon nano-form.[1] The discovery of carbon clusters with the unique structure and spherical molecules, represented, first of all, by C_{60},[2] and the development of methods for their synthesis[3] have stimulated the studies of these compounds. The remarkable properties of these carbon nanoclusters make them attractive in the production of hybrid materials. Thus fullerenes and their derivatives including fullerenopyrrolidines and methanofullerenes serve as 'building blocks' in the synthesis of multicomponent systems capable of photoinduced electron transfer. Such systems are already used in the development of molecular electronics devices.[4–7] Of no less importance is the use of fullerenes and fullerene-based materials in the catalysis,[8] particularly, for the C–H bond activation.

A recently published review[9] devoted to the chemistry of [60]fullerene deposited on a surface has analysed the main synthetic methods for ordered multilayered fullerene-based coatings and proposed directions for their use in the materials science, predominantly as photovoltaic devices. A tendency of fullerenes to form aggregates due to supramolecular interactions favours the formation of stable and structurally ordered fullerene films. Note that the same non-covalent interactions (hydrogen and coordination bonds, van der Waals forces, electrostatic effects, *etc.*) play the key role in the molecular organisation of biological systems, including selective chemical transformations of substrates in enzymic reactions.

The structural peculiarities and unusual properties of fullerenes as the π-conjugated systems are of great interest for biology as well. Lipophilic compounds of fullerenes and the ways of modifying biomembranes by fullerenes were studied.[10] The spherical shape of a C_{60} molecule, its size and hydrophobicity favour the free diffusion of fullerene within the bilayer of natural lipid membranes.[11] Self-organisation of iron atoms and molecules of trimesic (1,3,5-benzenetricarboxylic) acid on the copper (100) surface produced nanosized cavities that can be considered as the model two-dimensional supramolecular metalloreceptors capable of the reversible binding of fullerenes or biomolecules by non-covalent interactions.[12] Fullerene aggregation based on non-covalent interactions can considerably change their physicochemical properties, thus determining the application fields of fullerene-based materials.

Many laboratories made contributions to the studies of fundamental and applied aspects of chemistry of fullerenes and their derivatives, particularly, the electrochemical properties of these systems. The general problems of electrochemistry of fullerene solutions and fullerene-based films were considered in, *e.g.*, a review.[13] The electrochemical behaviour of C_{60} fullerene in the form of films differs from its behaviour in solutions.† This points to considerable structural changes occurring at the reduction of fullerene-containing coatings and their doping with electrolyte cations.

Thin fullerene-based coatings (films) represent suitable electrode materials for the development of different devices.

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† The redox behaviour of fullerenes and a lot of their derivatives was analysed in a review.[14]

Due to their electrochemical properties, fullerenes find application as new efficient electrocatalysts of various chemical and biochemical reactions. The possibility of designing electrochemical sensors based on fullerenes and carbon nanotubes was examined.[15] Important reactions involving fullerene anionic forms, can be exemplified by, *e.g.*, the reduction of molecular nitrogen.[16,17] Fullerenes dissolve in biological membranes and can take part in the electron transport. Their ability to take part in the reversible redox transfer of electrons allows fullerenes to act both as independent carriers and in combination with other mediators, namely, a C_{60} molecule behaves as an n-type semiconductor (energy gap width of 1.6 eV).[11] Insofar as biomembranes are modelled by planar bilayers of lipids and synthetic lipids formed on the electrode surface, the electrochemically stable electrodes with immobilised fullerenes can find their application as biosensors.

In the present review, results on the formation and functioning of electroactive coatings based on fullerenes and their derivatives are analysed preferentially in aqueous media. Redox transitions on electrodes modified by either films formed by lipid matrices with embedded fullerenes or cast (rubbed-on) fullerene films are considered. The latter are reduced irreversibly in aqueous supporting electrolyte solutions. The behaviour of a fullerene immobilised on the electrode surface in a matrix formed by a quaternary ammonium salt is characterised by stability and reversibility of redox processes in aqueous media and also by a noticeable shift of the reduction potentials to less negative values as compared with fullerene in solution. Insofar as under these conditions, the coating composition and organisation play an important role, attention is focused on the role of supramolecular interactions in the electrochemical transformations of fullerene in a film. Using density functional theory for a series of model complexes tetraoctylammonium bromide – [60]fullerene, the interaction energies of C_{60} and $[C_{60}]^{-\bullet}$ species with the molecules of their nearest environment were calculated as well as the values of C···H contacts between octyl-group hydrogen atoms and fullerene-sphere carbon atoms. This made it possible to judge with more certainty on the packing of fullerene molecules in a cationic matrix and on the role of packing in electrochemical processes involving fullerene that proceed on thus modified electrodes.

II. Fullerene phase films

1. Cast and rubbed-on films

In recent years, attention of scientists was focused on modifying the properties of materials by depositing monomolecular or thin films of structurally organised molecules on their surfaces. The use of fullerenes and their derivatives for these purposes makes it possible to transfer the unique properties of carbon nanoclusters (optical, electrochemical, *etc.*) to different materials, which is important from the viewpoints of both theory and practice.

The main method of preparation of fullerene-containing phase‡ films consist of their casting, *i.e.*, the controlled solvent evaporation from a fullerene solution that wets the electrode surface. The use of known amounts of substance allows one to control the surface concentration of the electroactive component on the electrode. Yet another method used for preparation of such coatings is the electrostatic rubbing-on; it allows only rough assessment of the fullerene surface concentration but is more convenient and fast. The amount of deposited substance is regulated by the rubbing time and assessed based on the voltammetric responses. The rubbing-on procedure provides a qualitative picture of the redox behaviour of rubbed-on films in a medium that does not dissolve the films. Both methods were used in the synthesis of fullerene microaggregates of crystalline or amorphous structures, where the morphology of the cast coating depended on the solvent nature and the way of its removal. The differences between cast and rubbed-on films of C_{60} fullerene observed after their synthesis were levelled down after several electrochemical cycles, for example, in the $MeCN - Bu^n_4NBr$ system.[18,19]

The drop method was also used for synthesising films including those containing fullerenes. In this case, microdroplets of solution of components were placed on the substrate surface and evaporated either in air or in a solvent atmosphere. The important factors in the formation of coatings were the state of the substance to be deposited, the properties of solvent itself (*e.g.*, Ref. 20), the size of the evaporated droplet and its nature, especially, its hydrophilic and hydrophobic properties. Particularly, the role of these factors in the film preparation was demonstrated by the example of tetrathiofulvalene derivatives.[21]

The methods of solvent evaporation by centrifugation (spin coating), developed earlier for polymeric coatings, are used at present in the preparation of thin films and nanostructures from small (non-polymeric) molecules. A solution of a component (or a mixture) is spread on a support that rotates at a high speed. A part of solution remains on the surface due to the surface tension forces, while the excess is removed from the sample. Polymer-containing solutions demonstrated good film-forming properties, providing uniform coatings with high adhesion and cohesion.

Yet another method, namely, film formation by layer-by-layer deposition of solution components (LbL method), was considered in several publications.[22,23] All the listed methods do not exclude self-assembling of components during the coating formation.

a. Redox transformations of films in aqueous solutions

The electrochemical properties of fullerene-containing films were studied by cyclic voltammetry (CV). In an aqueous medium, a deposited (cast or rubbed-on) fullerene coating demonstrated the cathodic reduction current only in the first cycle (curve *1* in Fig. 1).[24–27] In the course, supporting-electrolyte cations penetrated into the fullerene layer thus doping the coatings (incorporation of cations during the reduction for charge compensation). After the reduction, the C_{60} films prepared by casting a fullerene solution in CH_2Cl_2 onto the electrode (*e.g.*, gold) surface exhibited sufficiently high hydrophilicity and stability with respect to water and air oxygen. Such films were also characterised by high reproducibility of electrochemical responses.[27] Comparing the electrochemical behaviour of fullerene films in aqueous salt solutions showed that the potential of C_{60} reduction shifts in the cathodic direction as the hydration heat of the entering cation increases.[28,29] Reduced fullerene films were prepared with different cations,[28,29] including films based on mixed fullerides. In an aqueous medium, the reduction of fullerene depended on the presence of proton donors, namely, Brønsted acids.[24] In a dimethylforma-

‡ By a phase film, a sufficiently thick film that remains electroneutral in its bulk during a redox transformation is meant.

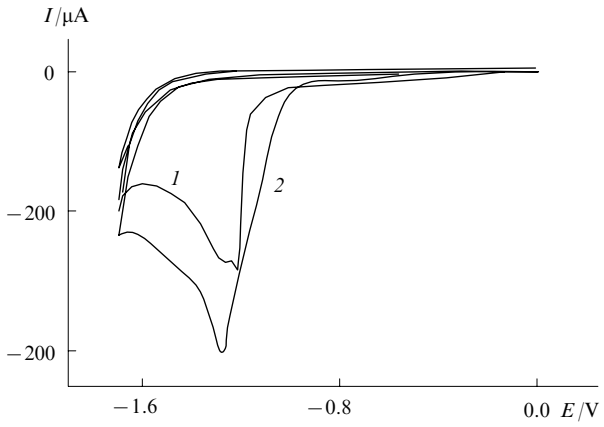
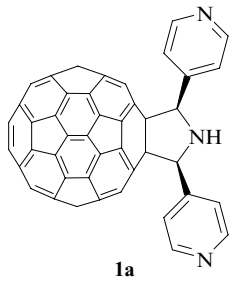


Figure 1. First cycles of CV curves for films of C_{60} (*1*) and **1a** (*2*) fullerenes rubbed onto glassy carbon, recorded in aqueous 0.5 M KCl at the potential scanning rate of 0.1 V s^{-1}.
Electrode surface area (S_{el}) 0.04 cm^2; reference electrode represented aqueous saturated calomel electrode (SCE).[26]

mide–water mixture, in the presence of potassium cations, a [60]fullerene film was reversibly reduced by an intricate mechanism.[30,31]

The cathodic reduction of dipyridyl-substituted fullerenopyridine **1a** was also judged from the first potential scan.[26]



1a

CV curves measured on rubbed-on films of C_{60} and its derivative **1a** showed that the reduction of both compounds occurs at very similar negative potentials (see Fig. 1). However, for C_{60}, the potential corresponding to the beginning of cathodic doping lied at more negative values as compared with compound **1a**. The CV curve shape pointed to the considerable irreversibility of processes, which with the given anodic potential limit (0.0 V), made impossible the reverse process, *i.e.*, dedoping of cathodically doped fullerenes. Shifting the anodic limit to 1.3 V (*vs.* aqueous saturated calomel electrode) allowed the partial anodic dedoping of cathodically doped compound **1a** and the partial redoping of the film to be conducted. For [60]fullerene, no dedoping was observed in this potential range, which suggests that its redox transformations are still more irreversible as compared with fullerenopyridine **1a**. The irreversibility and the high negative potential complicate studies of redox transformations of fullerene coatings in aqueous solutions.

Peculiarities of the cathodic behaviour of coatings based on C_{60} and compound **1a** are determined by their solid-phase nature. Maintenance of electroneutrality requires that the cathodic doping be accompanied by the incorporation of supporting electrolyte cations into the film. This process is closely related to the film restructuring, because the original coating contains no ready voids capable of housing dopants. Energy consumed in film restructuring leads to a high overpotential of the cathodic process.

Phase films of C_{60} were characterised by a close packed crystal structure, whereas films of compound **1a** were amorphous.[32] It is this difference that determines the stronger hindering of the [60]fullerene doping as compared with pyridyl-containing fullerenopyrrolidine. Moreover, the presence of polar substituents in compound **1a** makes it less hydrophobic as compared with C_{60}. The lower hydrophobicity makes easier the penetration of water into the fullerene phase and, hence, the entry of the hydrated inorganic cation-dopant. Chemical reactions that involve C_{60} and occur in cast or rubbed-on films during their reduction in aqueous media can also lead to irreversibility of fullerene redox transitions.[19,33,34]

Thus, CV curves of fullerenes in aqueous solutions demonstrated a reduction peak that could represent an overall reaction with addition of up to 4 electrons to the fullerene moiety. From the viewpoint of thermodynamics, the addition of four electrons at once could be possible as a result of changes in the film structure, because the overpotential was high only at the addition of the first electron. It should be mentioned that a CV curve of [60]fullerene was characterised by a virtually vertical frontal part (see curve *1* in Fig. 1). The site of cation incorporation into the C_{60} lattice depended on its crystallographic radius.[28,29]

b. Redox transitions of fullerene films in aprotic media

When going from aqueous to organic solutions, the electrochemical behaviour of fullerene phase films changes.[19,26,35] The electrochemistry of fullerene films in acetonitrile in the presence of electrolytes containing large (tetrabutyl-, tetrahexyl- or tetraoctylammonium) and small (Na^+, K^+, Cs^+, *etc.*) cations was considered in a review.[13] Salts of tetrabutylammonium (TBA) were used most frequently. Figure 2 shows CV curves of fullerene C_{60} in a solution of a TBA salt in acetonitrile.[26] Acetonitrile was used not only due to the low solubility of C_{60} in it but also because it provides a wide potential interval accessible for electrochemical studies. In the first cycle, only one cathodic peak appeared that corresponded to all possible reduction steps in this potential interval (as in water, all redox transitions 'gathered' together). In the anodic CV branch, two peaks were

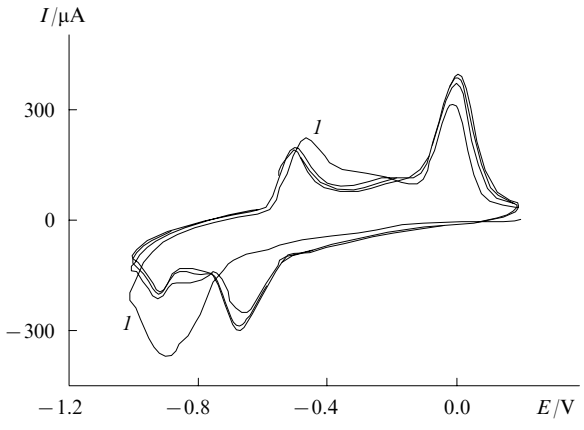


Figure 2. CV curves recorded on a C_{60} fullerene film rubbed onto glassy carbon, recorded in 0.1 M $Bu^n_4NBF_4$ solution in MeCN at the potential scanning rate of 0.1 V s^{-1} (curve *1* shows the first cycle).
S_{el} = 0.04 cm^2; reference electrode represented aqueous SCE.[26]

observed. Starting from the second cycle, the cathodic process splitted into two steps, where each cathodic doping peak corresponded to an anodic dedoping peak, *i.e.*, in the first cycle, the film structure had been prepared for more reversible doping, *e.g.*, had been loosened. As a result, the penetration of supporting electrolyte cations into the film deposited on the electrode became easier. Further reduction led to the coating dissolution, because fullerides, *i.e.*, salts of the $[C_{60}]^{3-}$ anion, are soluble in acetonitrile (see Ref. 27 and references therein). The power (1/2) dependence of the cathodic current peaks on the potential scanning rate in the range of 0.025–0.20 V s^{-1} suggested that the penetration of cations-dopants into the C_{60} film was controlled by diffusion.

The increase in the reversibility of C_{60} redox transitions in phase films when going from water to acetonitrile can be associated with the fact that compared to water, the organic solvent penetrates more easily into the hydrophobic fullerene phase. Moreover, an organic cation TBA^+ is capable of easier incorporation into the hydrophobic matrix as compared with inorganic hydrated cations from the aqueous solution.

The use of fullerenopyridine **1a** in place of C_{60} produced a radically new picture of redox transitions (Fig. 3).[26] In the cathodic branch, two poorly pronounced reduction steps were observed. These processes occurred at much less negative potentials as compared with C_{60}. The curve contained no indication of sharp changes in the structure of a solid film of substituted fullerenopyridine **1a**. Apparently, the amorphous structure of the coating based on compound **1a** was the main reason for the observed deviations in CV curves.

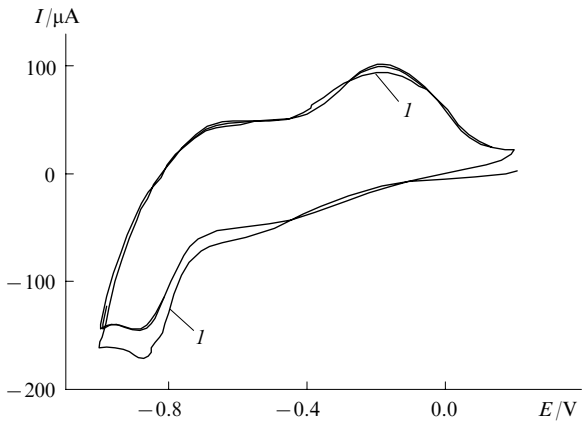
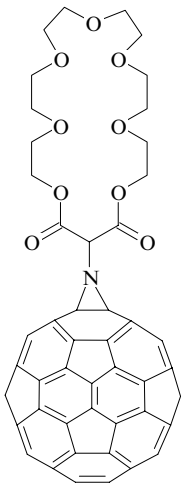
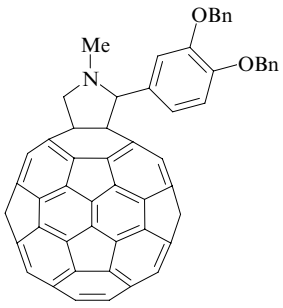


Figure 3. CV curves recorded on a film of compound **1a** rubbed onto glassy carbon, recorded in 0.1 M $Bu^n_4NBF_4$ solution in MeCN at the potential scanning rate of 0.1 V s^{-1} (curve *1* shows the first cycle). S_{el} = 0.04 cm^2; reference electrode represented aqueous SCE.[26]

Reduction of cast coatings prepared from compounds **2** and **3** proceeded irreversibly (most probably, due to their complete dissolution in the first cathodic cycle).[36] Note that the reduction of a structurally more ordered (according to X-ray diffraction data) film of fullerenopyrrolidine **3** required a higher negative potential.



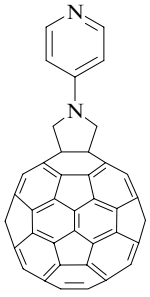
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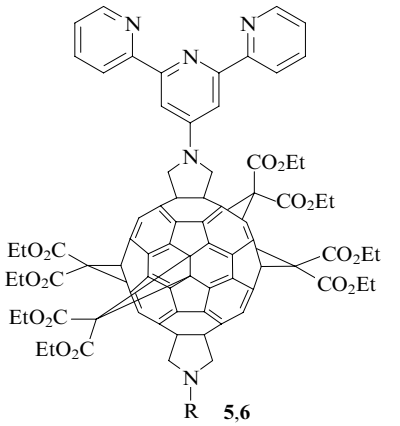
3

In a composite film compound **3**–poly(3-hexylthiophene) (PHT), the reduced fullerene forms were stabilised by the interaction of fullerene anions with the conjugated double bonds of the polymer. This gave rise to reversible redox transformations of the substituted fullerenopyridine. The number of ordered domains of fullerene **3** decreased with an increase in the concentration ratio PHT : fullerene, which was accompanied by deterioration of photovoltaic properties of the film.

The number of addends in a fullerene molecule affected the redox properties of fullerene derivatives. Thus for pyridyl and terpyridyl derivatives of fullerene **4**–**6,** an increase in the number of addends was the reason for irreversibility of the reduction of these compounds in acetonitrile on an Au electrode.[37] In this case, self-assembling of the electroactive layer could proceed due to specific adsorption interaction of addend's nitrogen atoms with the gold surface.

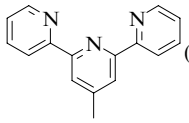


4



5,6

R is 4-pyridyl (**5**),

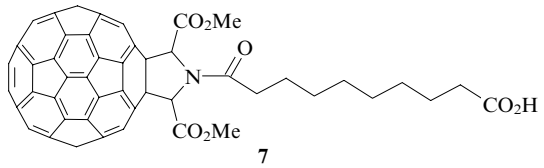


(**6**).

Immobilisation of C_{60} fullerene on an ITO (alloy of indium and tin oxides) support included the use of diamines $H_2N(CH_2)_nNH_2$ (n = 8–12). A method of preparation of self-assembled diamine–fullerene layers was developed. Diamines are adsorbed on the electrode surface and react

with fullerenes as follows: one amino group binds a diamine to the support and the other adds covalently to fullerene to form a fullerene monolayer. As the number of layers increased, the films acquired insulating properties.[38]

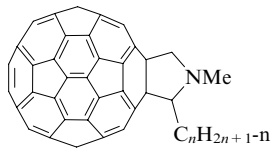
Based on fullerenopyridine **7** containing a long alkyl substituent with the end carboxyl group, the oriented films were formed[39] at the water–air interface.



7

The layer formed on the water surface represented a closely packed monolayer that contained no aggregates and could be transferred to a support. Repeated successive operations on the formation and transfer of layers (layering) produced multilayered coatings. The absorption spectra of these films pointed to the presence of interactions between fullerene fragments of neighbouring molecules. The electrochemical properties of such a film were studied in an aqueous $Fe(CN)_6^{3-}$ solution; it was shown that as the number of layers increased, the coating acquired ion-selective properties.

The nature of electrolyte cations was shown to affect the properties of fullerene coatings obtained as a result of electroreduction.[13] Fullerene films doped with large cations proved to be less soluble. As in the case of fullerene,[13] the films of 2-(n-alkyl)fullerenopyrrolidines **8a–e** prepared by the drop method were sufficiently stable in the course of their reduction in acetonitrile in the presence of TBA salts.[40]

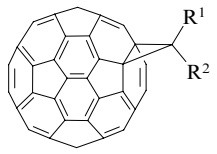


8a–e

n = 4 (**a**), 6 (**b**), 8 (**c**), 10 (**d**), 12 (**e**).

Solubility of doped films of compounds **8a–e** in acetonitrile increased with the increase in both the number n in the alkyl substituent of pyrrolidine ring and the reduction degree of the fullerene fragment in a molecule. Moreover, the stability of such a film depended on the solvent acidity.

Studies of redox properties of films formed by substituted methanofullerenes **9a–h** have shown[41] that their reduction in MeCN in the presence of tetrabutylammonium salts was virtually irreversible.

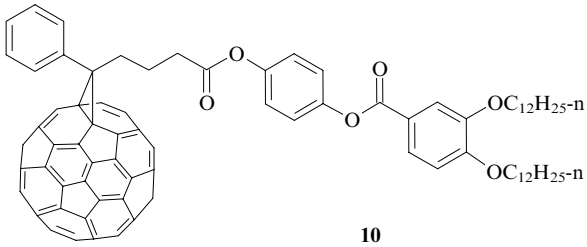


9a–h

$R^1 = R^2 = CO_2Me$ (**a**), CO_2Bu^n (**b**), $CO_2C_8H_{17}$-n (**c**), $CO_2(CH_2)_2OMe$ (**d**), $(CH_2)_2Ph$ (**e**);
R^1 = Ph: $R^2 = (CH_2)_3CO_2C_nH_{2n+1}$-n [$n$ = 1 (**f**), 4 (**g**), 12 (**h**)].

For all studied cations, namely, $Bu_4^nN^+$, K^+, Na^+ and Li^+, the first reduction potential of methanofullerene **9h** with the longest alkyl chain in the ester group shifted to negative values. This suggested that the electron-withdrawing properties of the fullerene moiety of molecule **9h** weakened, because the addend contained long hydrocarbon substituents with electron-donating properties.

Moreover, the length of alkyl chain in the addend had a considerable effect on the stability of methanofullerene coatings, namely, a film of compound **9h** did not dissolve up to the third reduction potential. Apparently, long hydrocarbon substituents shielded the electrode surface, thus preventing the diffusion of cations. A similar behaviour was also typical of methanofullerene **10** deposited on electrodes as cast films.[42,43]

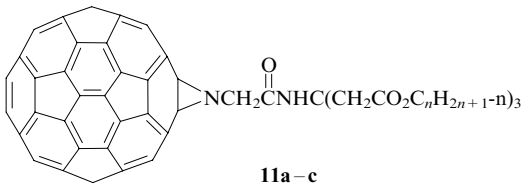


10

This compound is a covalently bound dyad, where the PCBM (phenyl-C_{61}-butyric acid methyl ester) derivative and the di(dodecyloxy)phenyl moiety act as the accepting and donating components, respectively. Partial charge separation in the ground state favoured the self-assembling of this compound in media with different polarity. The mechanism of aggregation of methanofullerene **10** molecules, which included their self-assembling to form, first, a bilayer and, then, vesicles, was considered.[42] Irreversibility of electroreduction of compound **10** was associated with the high degree of organisation of its cast coating due to the formation of coarse spherical particles, when the deposition on the electrode surface was carried out from a $THF-H_2O$ mixture.

c. Coatings based on lipid-like fullerene compounds

As regards their physicochemical properties, synthetic bilayer lipid membranes resemble natural membranes and can be deposited on a surface to form molecular films. A series of water-insoluble fullerene derivatives **11a–c** containing an aziridine ring annelated to a 6,6-bond of fullerene was characterised.[44]



11a–c

n = 11 (**a**), 13 (**b**), 15 (**c**).

In an aqueous 0.5 M TBA chloride solution heated to 55 °C, a film of fullerene **11c** was stable only at the first redox transition potential.[45] Scanning at the second potential led to a decrease in the reduction current and its complete disappearance after 10 cycles, which may point to the formation of an inert film of lipid-like fullerene on the electrode surface. Although fullerenes **11a–c** contained different numbers of carbon atoms in their alkyl chains, the potentials of their cathodic and anodic peaks differed

insignificantly at 60 °C. Thus the formal potentials (E_f)§ of compounds **11a–c** were −0.44, −0.41 and −0.43 V, respectively. At the first redox transition, the cathodic and anodic currents depended on the potential scanning rate according to the linear (in the range of 0.010–0.030 V s^{-1}) and square root (in the range of 0.1–3.0 V s^{-1}) laws.

The amount of electroactive fullerene in a coating increased as the number n in the lipid part of compounds **11** decreased. For example, up to 50% of compound **11a** was electroactive at 60 °C, *i.e.*, its molecules in the film were arranged in a way that provided their optimal electrochemical contact.[45] The temperature affected differently the redox processes of fullerenes **11a–c**; only for compound **11c,** a clear dependence on the phase transition temperature was observed.[45]

The optical spectrum of compound **11b** in hexane contained intense bands at 209.5, 255.5, 323 nm and a weak band at 421.5 nm. A cast film based on compound **11b** exhibited absorption even at 215.5, 262.5 and 329.5 nm, which pointed to the interaction between fullerene fragments of neighbouring molecules. At temperatures above the phase transition, the further shift of absorption bands occurred. The shift of symmetrical and asymmetrical stretching bands of CH_2 groups in compound **11b** that formed a film at ~35 °C was attributed to the *trans–gauche* conformation conversions of long alkyl chains, which led to the phase transition. The X-ray diffraction spectrum of compounds **11b** contained several peaks, which pointed to the presence of a well organised polylayered structure. However, the calculated distance between peaks (48.1 Å) was longer that the estimated length of the molecule (35.4 Å). This allows one to speak of self-assembling of the lipid-like fullerene in the film to form a poly(bilayer) structure with the molecules lying at an angle of 42.8° to the layer surface. At temperatures above the phase transition point, the diffraction peaks disappeared, which pointed to the destruction of the ordered film structure. The temperature dependence of the diffraction pattern was reversible.[45]

In aqueous media, the thermodynamics of binding of supporting electrolyte cations to the electrochemically generated radical anions and dianions of compound **11b** that existed in the form of a molecular-bilayer film on the graphite electrode surface, was studied.[46] Constant (K_1) of its binding to a radical anion increased with the length of alkyl substituents in ammonium cations, *i.e.*, as the cations that entered the film from solution became 'softer'. For example, for 1:1 complexes, K_1 was 7.93×10^3 and 1.71×10^8 litre mol^{-1} for Et_4N^+ and $Bu^n_4N^+$, respectively. In addition, the binding constants of ion pairs 'tetraalkylammonium (or tetraalkylphosphonium) cation of electrolyte–reduced form of fullerenes **11a,c**' were measured.[45] For a wide spectrum of Alk_4N^+ and Alk_4P^+ cations with similar alkyl groups, K_1 values differed by an order of magnitude. Apparently, the more pronounced 'softness' of the tetraalkylphosphonium cation determines its higher K_1 value, because fullerene anions are 'soft' anions. The constants of binding of compounds **11a–c** with cations decreased with a decrease in the number of carbon atoms in the lipid moiety of fullerene-containing molecules. Moreover, the π–σ interactions between the anion of compound **11** and the alkyl chains of a cation also contributed to their binding.[46]

Crystalline salts containing fullerene cations were obtained for the first time[47] and their structure was studied. Salt **12** was synthesised by the reaction

$$C_{60}(N(CH_2CH_2)_2N) + HCl + 1/2\ Rh_2(\mu\text{-}Cl)_2(CO)_4 \xrightarrow{CS_2} [C_{60}(N(CH_2CH_2)_2NH)]^+[Rh(CO)_2Cl_2]^-.$$

12

In a crystal of the (**12**·2 CS_2) solvate, the polar part is formed by the positively charged piperazine fragment of the cation together with the anion, whereas the hydrophobic part consists of the fullerene sphere and solvent molecules (Fig. 4). Hence, in contrast to a solvate of a neutral compound $C_{60}[N(CH_2CH_2)_2N]\cdot 1.5\,CH_2Cl_2$ (Ref. 48), the cationic derivative of fullerene **12** formed a bilayer. This is the first example of the crystallographicaly proved bilayered structure of a fullerene derivative. This can be considered as evidence for the possible formation of bilayers of fullerene compounds containing long alkyl substituents.

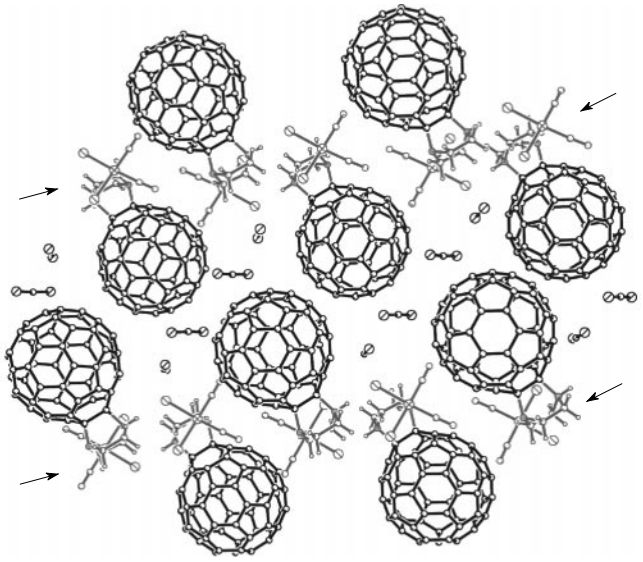


Figure 4. Packing of a cations and anions in a layer of solvate **12**·2 CS_2.[47]

Deposited on a graphite electrode, fullerenopyrrolidines **13a–e** formed a coating with the layered structure (Fig. 5), which was associated with the presence of long-chain alkyl groups.[49] The structure of layers and the distance between them were determined by the number of alkyl groups in the addend and their length, respectively.

CV curves of films formed by compounds **13a,b** (graphite, 0.1 M $Bu^n_4NClO_4$, MeCN, potential scanning rate 0.1 V s^{-1}, reference electrode Ag/Ag^+) showed a single redox transformation corresponding to the formation of a fullerene radical anion with the half-wave potentials ($E_{1/2}$) at −1.29 and −1.30 V, respectively. Based on the reduction current values, the electroactive substance was calculated to amount to 25% for compound **13a** and 63% for compound **13b** and decrease with cycling.

§ E_f is determined as a half-sum of the potentials of anodic and cathodic peaks of the corresponding redox transition.

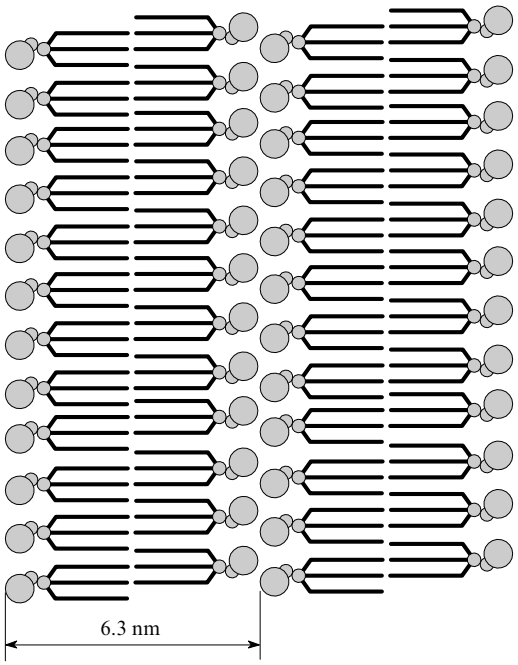
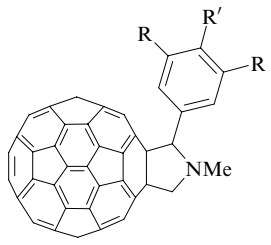


Figure 5. Illustration of molecular organisation of a film of compound **13a** on graphite.[49]



13a–e

R = R′ = $OC_{16}H_{33}$-n (**a**), $OC_{20}H_{41}$-n (**b**), $OC_{12}H_{25}$-n (**c**);
R = $OC_{16}H_{33}$-n, R′ = H (**d**); R = H, R′ = $OC_{16}H_{33}$-n (**e**).

Self-assembling of fullerene derivatives with long alkyl substituents (*e.g.*, fullerenopyrrolidine **13a**) occurred in solvents of different polarity to form ordered supramolecular ensembles with the 1D, 2D or 3D architecture such as vesicles, disks and cones, containing bilayers as the fundamental structural unit (Fig. 6).[50, 51] Absorption spectra of such ensembles showed bands at 330, 270 and 214 nm, which were shifted to the long wavelength range by 21, 15 and 5 nm, compared to absorption of compound **13a** in hexane. As in the previous cases, the observed red shift pointed to the strong $\pi-\pi$ interactions between fullerene moieties.

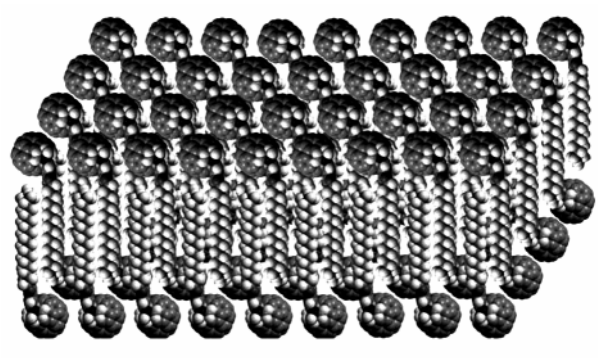
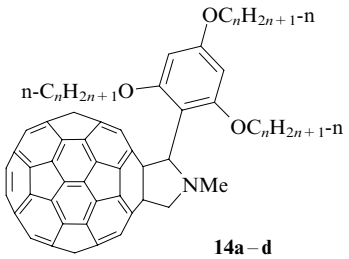


Figure 6. Hypothetical model structure of a 3D-aggregate of compound **13a** isolated from its solution in dioxane.[51]

In an X-ray diffraction spectrum of a film of compound **13a**, the distance between peaks was 4.28 nm, which was consistent with the calculated distance ($d = 4.3$ nm) between the centres of fullerene fragments of two opposite molecules. Based on the data of atomic force microscopy (AFM), a similar value was also obtained for a single bilayer. The supermolecular organisation of such fullerene derivatives was largely associated with $\pi-\pi$ interactions between fullerene fragments and van der Waals interactions between asymmetrically arranged alkyl chains.[51] Such compounds are promising as the capacitors in which the upper and lower conducting layers (fullerene fragments) are divided by an insulating layer formed by alkyl groups.

The nature of alkoxy groups in the phenyl substituent of fullerenopyrrolidines **14** affected the phase state of the compound.[52] Thus at room temperature, fullerenopyrrolidines **14b–d** containing 2,4,6-tris(alkoxy)phenyl group with $n = 12$, 16, 20 are liquids in contrast to compound **14a** with octyl residues (melting point at 147–148 °C). Hence, there is a correlation between the phase state of a compound and the length of its alkyl substituent.



14a–d

n = 8 (**a**), 12 (**b**), 16 (**c**), 20 (**d**).

For all CH_2 groups in the *trans*-conformation, the octyl chain length in compound **14a** was assessed to be 9.0 Å and the dodecyl group length in compound **14b** was estimated to be 14 Å. Hence, with the C_{60} diameter equal to 7.1 Å, the dodecyl groups in compound **14b** now acted as the effective stabilisers that prevented the aggregation typical of fullerene molecules. The longer the alkyl chain in the addend, the more 'plastic' the fullerene derivative **14**.

Films cast from compounds **14a–d** proved to be electrochemically active. However, their state and behaviour depended on the solvent used in the coating preparation. A film of compound **14d** cast from methylene chloride was liquid at room temperature and its redox transformations retained all the basic features typical of this compound in CH_2Cl_2 solutions. Two redox transformations (at -0.74 and -1.02 V, Ag/Ag^+ reference electrode) corresponded to the formation of mono- and dianions. A film of the same compound **14d** prepared from hexane was solid at room temperature. It demonstrated a single transformation. The reduction potential (-0.73 V) of a metastable solid film of compound **14d** was close to the reduction potential of fullerene in the liquid state, but the peak current was much lower. Electroactive fullerenes in the liquid state were characterised by easy diffusion of electrolyte, molecules of the medium (in this case, water) and the substance itself. This determined quite a number of advantages including the enhanced mobility of charge carriers, comparable with the

analogous characteristic of modified films of conducting polymers.

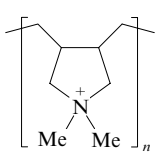
2. Fullerene films synthesised by electrophoresis

In addition to the methods of solvent evaporation (casting) and electrostatic rubbing, it was proposed to use electrophoresis for preparing C_{60} phase films (see Ref. 53 and bibliography therein). This involved the use of fullerene solutions in low-polarity toluene. The addition of an excess of acetonitrile or ethanol to this solution led to salting-out of fullerene to form a suspension. Applying a constant potential difference to the suspension containing no supporting-electrolyte salts resulted in the deposition of a coating of fullerene nanocrystals on the positive electrode. The grain size was easily controlled by changing the conditions of suspension synthesis. The fullerene amount deposited on the electrode increased with the increase in the applied potential difference; however, the spectral characteristics of films were independent of the deposition rate.[54] Studying the electrochemical behaviour of electrophoretic C_{60} films in TBA salt solutions in acetonitrile has shown that the redox behaviour of such coatings resembles that of a fullerene deposited on an electrode as a cast or rubbed-on film in the analogous medium. CV curves of films showed C_{60} reduction peaks at -0.63 and -0.98 V (*vs.* SCE). According to spectroelectrochemical data, in the solid phase, a radical anion and a [60]fullerene dianion were formed depending on the applied potential difference.[54]

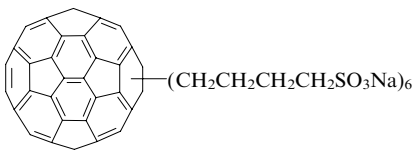
3. Atomic force microscopic studies of fullerene films

The electrochemical properties of thin coatings substantially depend on their morphology, namely, the shape of particles, their contacts with one another and the electrode surface, and also on the coating defects. Analysing films with an atomic force microscope allows one to acquire necessary information on the coating structure, including the surface coverage of the support, the coating uniformity and thickness, whereas the analysis of the surface itself makes it possible to conclude on the film morphology.

According to the AFM data, on the surface of electrophoretic C_{60} films, spherical particles with the diameter of 500 nm were present.[54] In turn, these entities consisted of three-dimensional ensembles of C_{60} nanoclusters of different shapes and the diameter of up to 100–200 nm. Insofar as such ensembles had cavities,[55] the dense packing of fullerene clusters should determine the shape of individual particles. The film morphology was shown to depend on the potential and time of electrophoretic deposition.[53] A film based on a composition hexa(sulfobutyl)fullerene **15**–PDDA [PDDA is poly(diallyldimethyl)ammonium chloride], which was synthesised by layer-by-layer deposition of components, had a granular structure. Its average roughness equal to 1.04 nm pointed to its relative uniformity.[56]



PDDA



15

According to AFM data, the adsorption of fullerene **13a** on highly oriented pyrolytic graphite resulted in the formation of layered structures approximately 100 nm long with the linear (1D) architecture.[49] The orientation of alkyl chains along the graphite basal plane axes determined the packing of fullerene fragments on the surface. The layer height was 6.3 nm. Bearing in mind the the length of molecule **13a** assessed as 3.1 nm (all CH_2 groups in the *trans*-configuration), this corresponded to two molecules in a layer. The derivatives **13a**–**c** formed a bilayer with the 'head-to-tail' structure (see Fig. 5), where the fullerene fragments of molecules were arranged in the zigzag fashion, while compound **13e** with a single alkyl group formed an interdigital layer. Such an organisation of fullerene structure in the coating suggested the involvement of two different types of intermolecular interactions, namely, between C_{60} fragments (sp^2 carbon atoms) and between alkyl groups (sp^3 carbon atoms).[51]

Figure 7 shows an AFM image of a part of the cast C_{60} film surface.[32] The coating was fine grained (with the particle size of 0.2–0.5 μm in the horizontal direction) and closely packed (see also Ref. 24). The surface of a cast film of fullerenopyrrolidine **1a** synthesised under similar conditions[32] was more uniform, namely, R_{rms} values¶ for the coatings of C_{60} and compound **1a** were 17.88 and 0.82 nm,

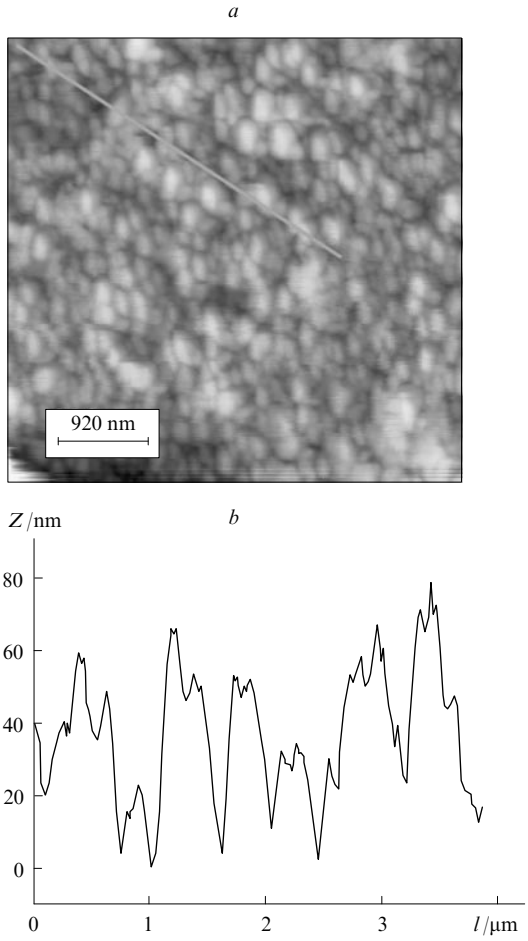


Figure 7. AFM images of a surface area (*a*) and the linear profile of a C_{60} film deposited on ITO (*b*).

¶ R_{rms} is a characteristic of surface roughness found based on AFM data.

respectively. Taking into account the surface topography and the amorphous nature (according to X-ray diffraction data) of compound **1a** and also the presence in it of polar substituents, it is possible to explain the observed difference between the electrochemical behaviour of films of unsubstituted C_{60} fullerene and its derivative **1a**.

By the example of films of mono- and bisanthracene adducts to C_{60}, it was shown that the number of addends and their position in molecules affect the coating morphology; the relationship of the latter with the electrochemical properties of films was also demonstrated.[57] Atomic force microscopy allows one to carry out studies of not only the initial film but also the changes in its state, *in situ* because the size of fullerene clusters in a coating usually changes during its electrochemical reduction (*e.g.*, see Refs 33 and 58).

According to AFM data, the surface structure of a reduced coating of fullerene **9h** depends on the nature of the cation-dopant.[41] Thus, for $Bu^n_4N^+$, a uniform and structurally ordered film (grains of $\sim$240 nm) was obtained, whereas for Li^+ cations, heterogeneities shaped as loose flakes were present of the film surface. No information was given[41] on the degree of ordering of the initial coating of methanofullerene **9h**.

III. Fullerenes dispersed in lipid matrices

Studying the electrochemical properties of hydrophobic fullerenes in aqueous solutions is possible only after their solubilisation. Solubilitisation is a result of chemical functionalisation, *i.e.*, the addition of highly polar addends to a fullerene, the formation of supramolecular complexes (*e.g.*, with cyclodextrins, calixarenes), or due to the formation of colloids at sonication of fullerenes in polar solvents. The first vesicular C_{60} solutions in aqueous medium were prepared using lipids and lipid-like compounds (dimethyldioctadecylammonium bromide, dipalmitoylphosphatidylcholine and dihexadecyl phosphate).[59] Changes in the spectra observed at the formation of vesicles pointed to the fullerene clusterisation. In the chemical reduction of fullerene, the yield of its radical anion $[C_{60}]^{-\bullet}$ was the highest when a cationic lipid, *e.g.*, a quaternary ammonium salt, was used.

Redox transformations of fullerene phase films, especially those with the compact crystal structure are strongly hindered (see Fig. 1). To remove this hindrance, the fullerenes should be dispersed to molecules or small associates.[60] One of the simplest effective methods of fullerene dispersion in the solid phase is their incorporation into a matrix formed by a surfactant,† particularly, a matrix formed by a quaternary ammonium salt (QAS) with long alkyl groups.[61] This method is very mild, because compared to, *e.g.*, chemical functionalisation, it virtually does not involve the electronic systems of the fullerene molecule. Moreover, such a matrix serves as a polar medium for the electroactive component.

The number of alkyl groups in the ammonium cation and their length determined the structure of supramolecular aggregates (see Ref. 64). The formation of bilayers led to film ordering due to the electrostatic interactions of dipoles positively charged quaternised nitrogen atom – anion. In the preparation of salt matrices for fullerene dispersion, Br^- served most often as the anion, apparently due to its polarisability and the large size. This requires that additional conditions be fulfilled, namely, the salt should be poorly soluble in water and, like fullerenes, be soluble in nonpolar media. In this very case, the evaporation of a solution containing a fullerene and a QAS made it possible to prepare water-stable poly(bilayer) fullerene films. In the deposition of coatings, different solvents were used, namely, benzene, toluene, xylenes, dichlorobenzene, dichloromethane, *etc.*

1. Compositions fullerene – asymmetrical quaternary ammonium salts

In an aqueous solution, salts $(n\text{-}C_{12}H_{25})_3MeN^+Br^-$ (Refs 65, 66), $(n\text{-}C_{14}H_{29})_2Me_2N^+PSS^-$,[61] $(n\text{-}C_{16}H_{33})_2Me_2N^+PSS^-$ (Refs 61, 66, 67) where $PSS^- = [CH_2CH(C_6H_4SO_3^-)]_n$ were used as the fullerene matrices. The lipid to fullerene molar ratio in the cited studies was 19 : 1. In the general case, it could be varied from 10 : 1 (predominant) to 50 : 1. The electrochemical responses for fullerene C_{60} in a film of synthetic lipid $(n\text{-}C_{14}H_{29})_2Me_2N^+PSS^-$ proved to be the most stable.[61] In the absence of QAS, fullerene could be reduced neither the electrochemically in the potential range accessible in aqueous solutions nor chemically under the action of $Na_2S_2O_4$.[66]

Using an X-ray diffraction technique, it was shown[67] that a C_{60} – QAS film with non-equivalent alkyl substituents at the nitrogen atom [*e.g.*, $(n\text{-}C_{16}H_{33})_2Me_2N^+PSS^-$] had a poly(bilayer) structure with molecular layers located at an angle 47° to the surface. The presence of C_{60} in the matrix of such QAS did not change the structure of the latter.

Figure 8 illustrates the formation of poly(bilayer) structures from asymmetrical QAS on a negatively charged electrodes or on surfaces containing negatively charged groups. It can be assumed that on a positively charged electrode, the first layer is formed by bromide anions. For a zero-charged electrode, the first layer most probably contains fullerene molecules.

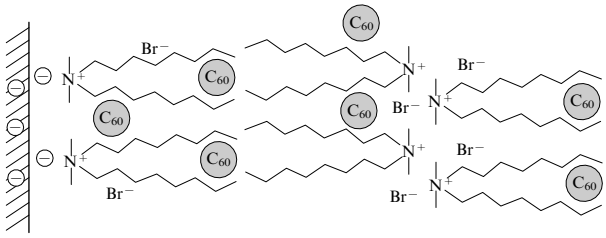


Figure 8. Schematic structure of electroactive layers based on fullerene and asymmetrical tetraalkylammonium salts.[60]

Characteristic features of the electrochemical behaviour of C_{60} in a matrix of an asymmetrical QAS are listed below.

1. Reversible and stable electrochemical formation of singly, doubly and sometimes triply charged fullerene anions. In a QAS films, fullerene radical anions are stable, which is untypical of a $[C_{60}]^{-\bullet}$ species in aqueous solutions.

† The role of surfactants in electrochemistry was considered in, *e.g.*, Refs 62 and 63.

The formation of fullerene radical anions was confirmed by the spectroelectrochemical method.[66]

2. A considerable positive shift (as compared with solutions) of fullerene reduction potentials due to the binding of formed fullerene anions by the matrix cations. This was confirmed by the loss of fullerene susceptibility to reduction with the substitution of an anionic or zwitter-ionic lipid for cationic one under the chosen experimental conditions.[68] The presence of QAS probably prevents the formation of the fullerene crystalline phase as the solution involved in the coating formation dries out and a film forms on the electrode surface. In the process, the long alkyl substituents of cations form the microenvironment for C_{60}, which favours the realisation of reversible electrochemical processes.

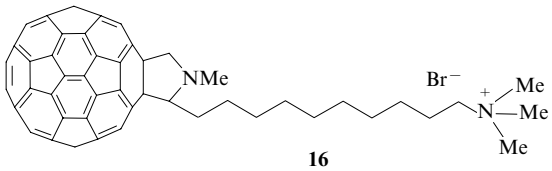
3. As a rule, for lipid films with incorporated fullerene, to retain the electroneutrality of the film bulk at the reduction of C_{60}, the salt matrix anions leave the matrix rather than the supporting salt cations enter it.[66]

4. The rate of fullerene redox transformations in a sufficiently thick film is controlled by diffusion of ions in it, as follows from the square root dependence of the current on the potential scanning rate. However, at very low rates, this dependence becomes linear, and the transformations involve the largest part of fullerene in the film.

5. The presence of the phase transition between the solid and liquid-crystalline states is one of fundamental properties of lipid membranes. Analysis of ^{13}C NMR spectra of the higher homologues of tetraalkylammonium bromides $(n\text{-}C_nH_{2n+1})_4NBr$ (n = 8, 10, 12, 18), carried out in a wide temperature range containing all phase transitions, has shown[69] that the conformational changes that give rise to disordering and motion in crystals begin (gradually or stepwise) from the terminal methyl group in the alkyl chain (see also Ref. 70). At temperatures below the phase transition point, the rigid conformation of alkyl chains in a QAS cation prevents the C_{60} diffusion, and the fullerene–QAS composition becomes electrochemically inactive. At the same time, at temperatures above the phase transition, two or three reversible fullerene redox transformations were observed. As was mentioned above, a fullerene introduced into a matrix formed by a synthetic lipid $(n\text{-}C_{14}H_{29})_2Me_2N^+PSS^-$ did not affect the characteristic bilayer membrane structure, because the phase transition occurred at $\sim$27 °C for both the ammonium salt and the C_{60}–$(n\text{-}C_{14}H_{29})_2Me_2N^+PSS^-$ composition.

The changes that occur in a C_{70}–didodecyldimethylammonium bromide film during its preparation and reduction in an aqueous solution were studied.[71] The authors provided the spectral evidence that the chemical and reversible electrochemical reduction of C_{70} fullerene in a lipid film did occur[66,71] to form the anionic forms, the same as for the C_{60}–tetraoctylammonium bromide (TOAB) composition.[72]

In contrast to C_{60} films that were not reduced in aqueous KCl solutions on pyrolytic graphite in the potential range from −1.0 to 0 V, the CV curves of a cast coating of fullerenopyrrolidine **16**‡ contained a single, albeit broadened, peak which corresponded to the reduction of the fullerene moiety (at −0.5 to −0.6 V, SCE) to the radical anion.[73]



16

Further cycling led to a decrease in the current. The CV shape allowed assuming the heterogeneity of the film formed by compound **16**, which among other things, was associated with the set of bilayer-based structures observed in the X-ray diffraction experiments (Fig. 9). Substitution of tetraethyl-, tetrapropyl- and, especially, tetrabutylammonium chlorides for KCl favoured redox processes in the film. This effect was probably associated with the increase in the constant of binding (as in the electrochemical reactions of lipid-like fullerenes[45,46]) of the electrolyte cation with the anion of compound **16** formed in the reduction and the concomitant changes in the film structure.[74]

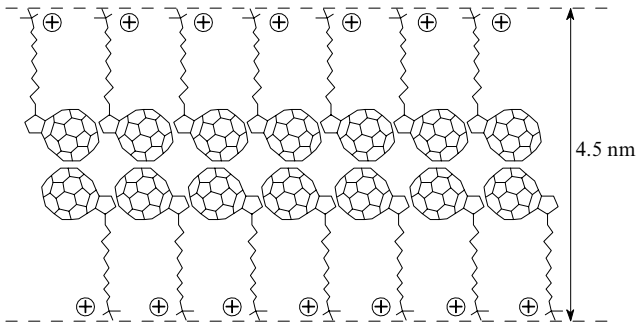


Figure 9. A scheme of a bilayer for compound **16**.[72]

The redox properties of fullerenopyrrolidine **16** embedded in a cationic lipid matrix [*e.g.*, a composition **16**–$(n\text{-}C_{12}H_{25})_3MeN^+Br^-$] were similar to the electrochemical properties of a film with C_{60} incorporated into the same matrix (see above). At the same time, the first reduction potential of compound **16** shifted in the cathodic direction when a zwitter-ion (*e.g.*, dioleylphosphatidylcholine) and, particularly, a negatively charged lipid (didodecyl phosphate) served as the matrix. Thus, the cathodic shifts of the first and second reduction potentials were 0.3 and 0.26 V for compound **16** in the **16**–zwitter-ion lipid composition as compared with the **6**–$(n\text{-}C_{12}H_{25})_3MeN^+Br^-$ composition. The reduced coating of the **16**–didodecyl phosphate composition was extremely unstable. The analysis of the behaviour of compound **16** demonstrated that the reaction of its reduced forms with the supporting electrolyte cations plays a significant role for both zwitter-ionic and negatively charged lipids.[73,74]

Thus, the alkylammonium group in the addend of fullerene **16** was not apparently directly involved in the stabilisation of reduced forms of this compound. Its effect on the redox processes in the film manifested itself in an increase in the coating polarity due to its salt-like nature, which made easier the entry of molecules of the medium and electrolyte cations into the film at its electrochemical doping in an aqueous solution. The observed dependence of the redox

‡ Compound **16** represents a fullerene-containing QAS derivative and exhibits hydrophilic properties due to the presence of a cationic ammonium group. This determines its reduction in a cast film in aqueous solutions at a lower [as compared with C_{60} (Ref. 26)] negative potential.

process direction on the electrolyte cation structure confirms this conclusion. It is also known that the nature of the counter-ion in fullerenopyrrolidine with a positively charged ammonium group on the short spacer turns out to be crucial for the morphology of the material.[75]

The electrochemical properties of the incorporated fullerene did not depend on the method of film preparation when a QAS was used as the matrix. For example, a stable Langmuir monolayer consisting of C_{60} (or C_{70}) fullerene and a synthetic lipid was prepared at the air–water interface and then transferred to a pyrolytic graphite electrode as a Langmuir–Blodgett film.[68,76] It was shown that in such a film, the electrochemical reduction of fullerene in an aqueous solution is possible only in the presence of a cationic component. The film turned out to be stable when cycled at the first C_{60} reduction potential but exfoliated with the further fullerene reduction.

2. Higher fullerenes, endometallofullerenes and metallocomplexes in lipid films

Reversible redox transformations of fullerenes embedded into a QAS matrix are typical of not only C_{60} and C_{70} fullerenes but also of the higher fullerenes and endometallofullerenes. For example, [84]fullerene was reduced to form multicharged anions.[77] In aqueous solutions, the electrochemical properties of electrodes modified with films of endometallofullerene La@C_{82} or La@C_{82} embedded into a matrix of a synthetic lipid, namely, tridodecylmethylammonium bromide, was studied.[78] As for C_{60} and C_{70}, redox transformations of La@C_{82} occurred only in the presence of a QAS matrix. Thus on an electrode coated with a film of La@C_{82}–tridodecylmethylammonium bromide, the reduction peaks observed at -0.28, -0.69 and -1.0 V (*vs.* SCE) corresponded to endometallofullerene anion, dianion and trianion, respectively. Being embedded in a lipid film deposited on an electrode, La@C_{82} was sufficiently stable in air.

Insofar as the oxidation potential of lower fullerenes (and, correspondingly, films on their basis) is very high, they are characterised by electroreductive rather than electrooxidative properties. For endometallofullerenes, a possibility emerges for their oxidation in a film. Thus a CV curve (glassy carbon, gold, or ITO electrode, aqueous solution) of Dy@C_{82} endometallofullerene embedded into a cationic lipid (didodecyldimethylammonium bromide) film demonstrated four pairs of reversible redox peaks. One pair ($E^1_{1/2} = 0.471$ V) corresponded to the oxidation and three pairs corresponded to the reduction ($E^2_{1/2} = 0.234$ V, $E^3_{1/2} = -0.405$ V and $E^4_{1/2} = -1.08$ V).[79,80] It is worth mentioning that in lipid films, Dy@C_{82}, its anion and also di- and trianions were resistant to the action of oxygen and water but their further reduction was accompanied by chemical reactions. Under identical conditions, the $[Dy@C_{82}]^-$ anion turned out to be more stable than the $[Dy@C_{82}]^+$ cation. At the Dy@C_{82} reduction in a cationic matrix, its anions get bound with the matrix cations [*e.g.*, with $(n\text{-}C_{12}H_{25})_2Me_2N^+$], whereas at the oxidation, the supporting electrolyte anions are incorporated into the coating to compensate the charge.

Redox transformations of Dy@C_{82} were studied by using a spectrophotometric method in the near IR range. The behaviour of an electrode modified with endometallofullerene Gd@C_{82} in a cationic lipid matrix resembled that of electrodes modified with other endometallofullerenes, particularly, it was stable in aqueous solutions. In the potential range from 0.6 to -1.0 V, redox processes of Gd@C_{82} metallofullerene were observed. The electron transfer rate in reductive transitions involving Gd@C_{82} increased due to the presence of a lipid matrix.[81]

The considered approach, *viz.*, the incorporation of an electroactive material into a surfactant matrix, was extended to metal complexes. On pyrolytic graphite modified by a film ruthenium complex–surfactant [ammonium salts with long alkyl chains served as surfactants, for example, a synthetic lipid $(n\text{-}C_{14}H_{29})_2Me_2N^+PSS^-$], the electrochemical behaviour of ruthenium ions was studied in aqueous solutions.[82] As in the case of fullerene[65,66,72] or its derivatives,[26] the role of the QAS matrix consisted in developing the necessary environment for the electroactive substance, *i.e.*, a metal complex.[82] It this case too, the degree of binding of the reduced forms of a metal complex to the matrix cations affected the electrochemical properties. This allowed redox processes that do not occur in non-aqueous solutions or in aqueous media for films containing no lipid cations to be observed. As in the case of fullerene–lipid films, the electrochemical reactions of ruthenium complexes in a QAS matrix and their reactions with carbon dioxide depended on the phase transition in the lipid film.[83] A composition ruthenium complex–lipid was proposed as a model for developing catalytically active materials and gas sensors.

For the reduction of a lutecium complex $[(n\text{-}C_6H_{13}S)_8Pc]_2Lu$ or $[(n\text{-}C_{12}H_{25}S)_4Pc]_2Lu$ (Pc is phthalocyanine) embedded into a cationic tetraoctylphosphonium bromide matrix, it was shown that the stepwise addition of electrons to metallophthalocyanines is acompanied by an increase in the number of matrix cations bound with it. Their ratio varied from 1:1 {for single-charged anionic derivatives of phthalocyanine) to 1:5 [for five-charged derivatives, $[(n\text{-}C_6H_{13}S)_8Pc]_2Lu^{5-}$ or $[(n\text{-}C_{12}H_{25}S)_4Pc]_2Lu^{5-}$}. This validates the fact that at the reduction of metallophthalocyanines embedded in a $(n\text{-}C_8H_{17})_4P^+Br^-$ matrix, the formed anions get bound with phosphonium cations. The same as for fullerenes, this very bonding was responsible for the observed positive shift of reduction potentials as compared with the electrode reaction in non-aqueous solutions.[84,85]

3. Fullerenes embedded in films of tetraalkylammonium and -phosphonium bromides

The electrochemical reduction of fullerenes in aqueous solutions was also studied for symmetrical quaternary ammonium salts with alkyl groups containing from 5 to 8 carbon atoms and also 10, 12 and 16 atoms.[66,72,86] A cationic matrix acquired the functional properties of a lipid film only if each alkyl residue contained no less than seven carbon atoms.[66] In this matrix, the immobilised fullerene could undergo up to three reversible reductions; moreover, the formation of mono- and dianions was confirmed by spectroelectrochemical studies.[72] The matrices usually represent bromides of quaternary ammonium salts (most often, tetraoctylammonium bromide) and tetraoctylphosphonium bromide.[86] The electrochemical behaviour of C_{60} was virtually identical in these two matrices, although TOAB has a crystalline structure, whereas the phosphonium salt forms a gel-like phase. The general mechanism of the C_{60} behaviour in matrices of symmetrical QAS was similar to that in matrices formed by asymmetrical QAS with very long alkyl substituents (see above). In the absence of TOAB,

no C_{60} reduction occurred in the potential range accessible in aqueous solutions.[72]

Figure 10 shows CV curves for [60]fullerene in a TOAB film. In 0.5 M KCl aqueous solution, C_{60} fullerene underwent two reversible redox transitions.[26, 66, 72] In a TOAB film, for potential scanning rate of 0.05–1.0 V s^{-1}, the fullerene reduction was controlled by diffusion, whereas at the rate < 0.01 V s^{-1}, the current was proportional to the scanning rate. In the latter case, when the whole film bulk 'worked', fullerene was active by 97%.[86] In lipid films with embedded fullerene, the coating electroneutrality during the C_{60} reduction was maintained as a result of the exit of QAS anions from the salt matrix.[66, 72] The presence of a prepeak in the first C_{60} reduction cycle pointed to structural changes in the C_{60}–TOAB film[72] that could occur as the result of the removal of solvent captured by the film during its preparation, the formation of ion pairs of lipid cations with fullerene anionic forms and also the partial exchange of anions in the film.

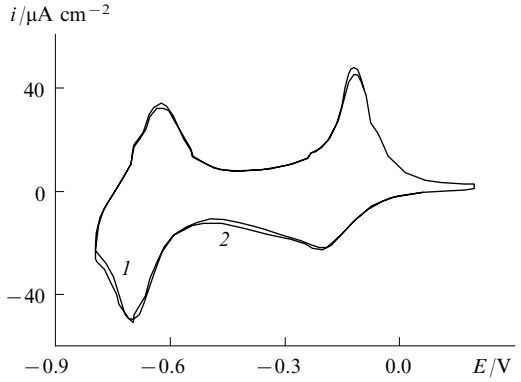
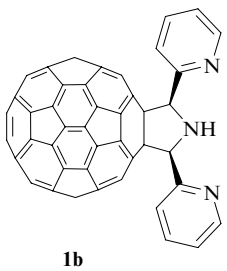
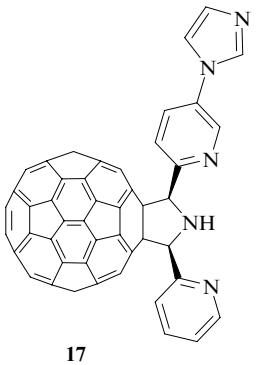


Figure 10. CV curves measured on a C_{60} fullerene film (curves *1* and *2* correspond to the 3rd and 6th cycles) in aqueous 0.5 M KCl with the potential scanning rate of 0.1 V s^{-1}.
The compound was immobilised in a TOAB salt matrix (salt : C_{60} = 10 : 1), ITO as the working electrode, aqueous SCE as the reference electrode.[26, 32]

The electrochemical transformations of fullerenopyrrolidines in salt matrices were similar to those of C_{60}, particularly, for compounds **1a**,**b**, two redox steps were observed. However, in contrast to fullerene-containing coatings, films **1b**–TOAB gradually lost their redox activity with cycling (Fig. 11). This process was even faster for compound **17**.



1b



17

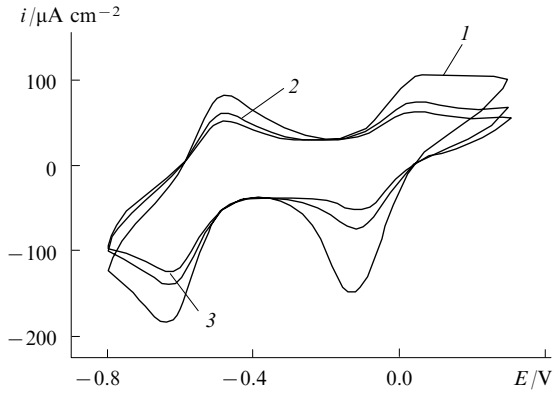
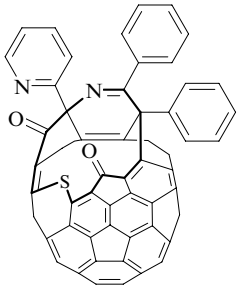


Figure 11. CV curves measured on a film of fullerenopyrrolidine **1a** (curves *1*–*3* pertain to the corresponding cycles) in aqueous 0.5 M KCl at the potential scanning rate of 0.1 V s^{-1}.
The compound was immobilised in a TOAB salt matrix (salt : **1a** = 10 : 1), ITO as the working electrode, aqueous SCE as the reference electrode.[32]

The possible reasons for such a drop of activity can include dissolution of the reduced coating (when radical anions and double-charged anions of compounds **1a**,**b** and **17** pass to solution), and also a decrease in the degree of stabilisation of pyridyl-substituted fullerenopyrrolidines in the salt matrix, for example, due to the steric hindrances and electronic effects of addends. Apparently, the stability of reduced forms of fullerenopyrrolidines decreased as the nitrogen atom in the addend became more spatially accessible and the addend volume (molecular mass) increased, *i.e.*, when going from **1** to compound **17**.

The electrochemical properties of substituted fulleroid **18** with the 'open' structure were studied in both its phase film and a TOAB matrix.[87] As in the previous cases, the cationic matrix played the key role in the reversible reduction of this compound. The first reduction potentials of compound **18** approached the formal potentials of the C_{60} reduction in the TOAB matrix.[72] However, as compared with [60]fullerene, the radical anions and dianions of compound **18** proved to be less stable. The electrochemical behaviour of compound **18** was closer to pyridyl-substituted fullerenopyrrolidines **1a**,**b**.



18

For better understanding of the lipid functions of symmetrical QAS cations, their packing types should be considered. The crystal structures of tetraalkylammonium and tetraalkylphosphonium halides with four identical n-alkyl groups containing from 10 to 18 carbon atoms were obtained.[88] Based on the data on the crystal structure of such salts and also on their molecular simulation, it was concluded that depending on the alkyl group length, the

following cation conformations can be realised: with alkyl chains associated in pairs ('biradial' conformation) or with separately oriented alkyl chains ('tetraradial' conformation) (Fig. 12). In both cases, the first carbon atoms of alkyl chains formed the tetrahedral environment around the nitrogen atom of a cation. The transitions between these forms of symmetrical QAS occurred when the energy gained due to the association of two alkyl residues (as in the paraffin packing) exceeded the energy consumed in the point disordering of the zigzag structure of one of alkyl substituents. This was observed when the number of carbon atoms in a chain reached 12, for instance, TOAB exists in the tetraradial form.

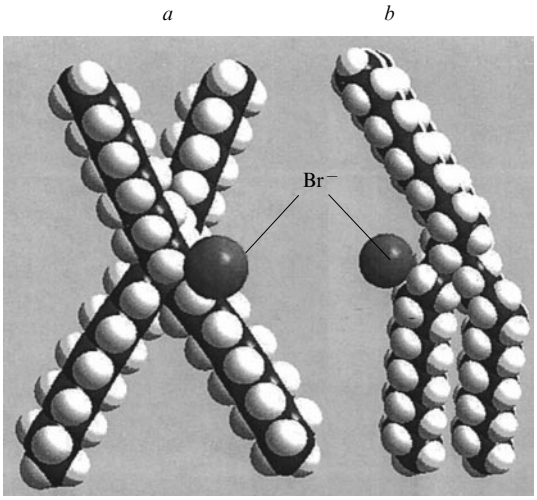


Figure 12. Molecular structure of $(n\text{-}C_{10}H_{21})_4PBr$ (*a*) and $(n\text{-}C_{12}H_{25})_4NBr$ (*b*). [86]

From the standpoint of the hard-soft acid-base (HSAB) principle, large lipophilic quaternary cations are 'soft' acids. Hence, they can form ion pairs with the 'softest' anions. Thus a symmetrical tetraalkylammonium cation $(n\text{-}C_nH_{2n+1})_4N^+$ in xylene exists as an ion pair $(n\text{-}C_nH_{2n+1})_4N^+\cdots X^-$ partially dimerised to form $\{(n\text{-}C_nH_{2n+1})_4N^+\cdots X^-\}_2$.[89] Dimerisation of such pairs was observed in other solvents with low dielectric constants. For the TOAB concentration $>10^{-3}$ mol litre^{-1}, this was the main process. Inorganic anions X^- in a dimeric ion pair were surrounded by alkyl groups of cations.[90] We used these data when developing a model of the TOAB film structure with embedded fullerene.

Optical spectra of films of compound **1a** and composition **1a**–TOAB (1 : 10) on quartz demonstrated bands at 223, 267, 336 nm and 215, 260, 329 nm, respectively.[32] By the absorption at 400 nm, it was possible to judge the type of addend addition to C_{60} and the fullerene physical state.[39,91] Figure 13 shows that the spectra of films of compound **1a** and composition **1a**–TOAB lack a characteristic band of fullerenopyrrolidines at 430 nm. This was probably due to its broadening as a result of inhomogeneity of the environment and pointed to the presence of interactions between fullerene fragments of neighbouring molecules. The analogous behaviour was typical of other fullerene compounds. The decrease in the bulk molar concentration of fullerene for the **1a**–TOAB composition and the ability of fullerene molecules to concentrate the matrix

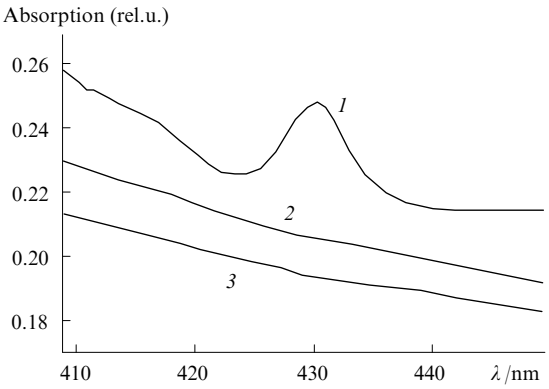


Figure 13. Absorption spectra of compound **1b** dissolved in CH_2Cl_2 (*1*) and also of quartz-deposited films of compound **1a** (*2*) and its composition with TOAB (*3*).[32]
Concentration of compound **1b** was 2×10^{-5} mol litre^{-1}, the ratio **1a** : TOAB = 1:10.

hydrophobic parts around them decreased the aggregation of the electroactive substance and favoured its more uniform distribution throughout the film bulk. This was reflected in the position of absorption bands in spectra of coatings based on compound **1a** and the **1a**–TOAB composition.

A diffraction pattern of a coating based on compound **1a** contained a broad peak corresponding to the interplanar distance of 4.149 Å.[32] Based on the data for other C_{60} derivatives,[92] this peak was attributed to the amorphous phase. The interplanar distance of 9.408, 6.259, 4.695 and 3.754 Å for TOAB in a **1a**–TOAB (1 : 10) coating virtually corresponded to their position in the diffraction pattern of the individual salt. This suggests that the TOAB film structure remained unchanged, being close to the layered structure according to some conclusions.[93,94] The conservation of the structure is the general property of matrices based on quaternary ammonium salts.[67]

As was mentioned above, for cast films of C_{60}, the resulting coatings were fine grain and closely packed. Figures 7 and 14 show how the surface of films formed by individual fullerenes and TOAB changed with the incorporation of C_{60} into a tetraoctylammonium bromide matrix (fullerene : TOAB = 1 : 10).[32]

A question arises of how important is the layered onium-salt structure for the reversible functioning of an electroactive fullerene-based coating in an aqueous solution. The fulleride $(Ph_4P)_2C_{60}Br$ structure is stabilised due

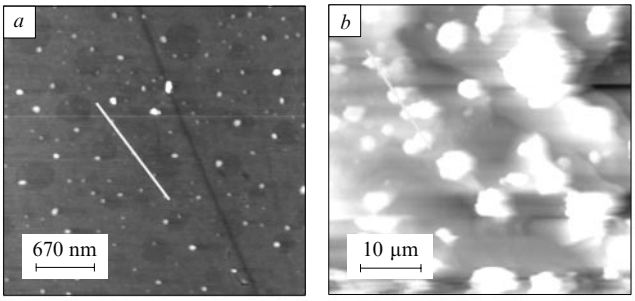


Figure 14. AFM images of the surface TOAB films (*a*) and a C_{60}–TOAB composition (*b*), which were deposited on ITO.

to the interaction between p-orbitals of carbon atoms at fullerene double bonds and appropriately oriented benzene rings of the cation.[95] It seems helpful to compare the behaviour of two electrode-supported compositions, TOAB–fullerene and tetraphenylphosphonium bromide–fullerene, in the C_{60} redox transformations, namely, the involvement of the CH/π (see below) and π–π interactions in the organisation of an electroactive layer and its functioning for TOAB and PPh_4Br, respectively. CV curves of C_{60} fullerene immobilised in a matrix of tetraphenylphosphonium bromide, measured in 0.5 M KCl aqueous solutions, demonstrated a single virtually irreversible redox transformation.[32] The procedure of measurements included recording the 1st and 2nd cycles, then, 10 cycles were allowed to pass, and the 13th cycle was recorded (Fig. 15).

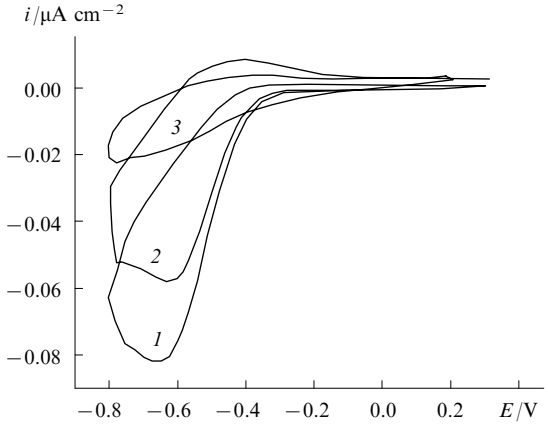


Figure 15. CV curves of a cast C_{60}–Ph_4PBr film, recorded in aqueous 0.5 M KCl at the potential scanning rate of 0.1 V s^{-1} (Ref. 32). S_{el} = 1 cm^2, ITO as the working electrode.

A considerable increase in the potential scanning rate allowed the oxidation of a radical anion of C_{60} to be observed in the anodic scan (Fig. 16). The first redox transition of fullerene C_{60} (according to the data on the cathodic and anodic branches recorded at different rates) in the PPh_4Br matrix took place at the formal potential from −0.53 to −0.55 V, *i.e.*, considerably shifted in the cathodic direction as compared with the analogous C_{60} transformation in a TOAB matrix [E_f = −0.16 V (SCE)]. Nonetheless, fullerene was dispersed in the PPh_4Br matrix, as follows from the comparison of formal potentials of the C_{60}–PPh_4Br composition with the reduction potential of a rubbed-on C_{60} film ($E \sim -1.2$ V). Hence, the observed deviations in the redox properties of C_{60} incorporated into a film of tetraphenylphosphonium bromide or TOAB (or tetraoctylphosphonium bromide[86]) pointed to the important role played by the layered structure of the TOAB matrix in the realisation of reversible electrochemical processes involving fullerene in aqueous solutions.

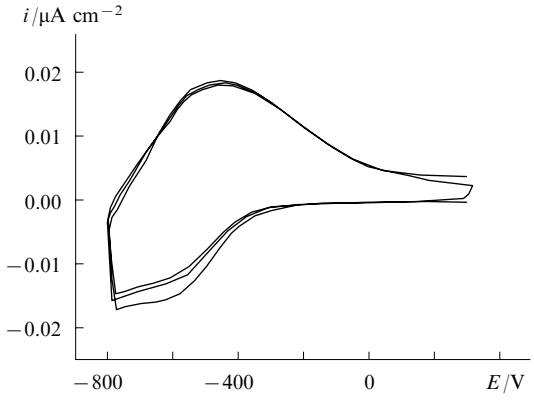


Figure 16. CV curves of a cast C_{60}–Ph_4PBr film (ITO as the working electrode, surface area 1 cm^2), recorded in aqueous 0.5 M KCl at the potential scanning rates of 0.05 and 0.4 V s^{-1} in the cathodic and anodic direction, respectively.[32] S_{el} = 1 cm^2, ITO as the working electrode, aqueous SCE as the reference electrode.

The mechanism of fullerene reduction in a cationic lipid film differed from that for electrodes modified with films of pure fullerene and lipid-like fullerene derivative **16**. For the latter, the electrolyte cation regulated the fullerene reduction potentials,[27,74] whereas for an electrode with fullerene embedded into a cationic lipid matrix, this process was controlled by the electrolyte anion.[66,72] Thus X-ray photoelectron spectra of fullerene reduced in a didodecyldimethylammonium bromide matrix in aqueous 0.5 M KCl solution showed a peak with the binding energy (E_b) typical of chlorine atoms, whereas the peak with E_b typical of potassium atoms was absent. This means that tetraalkylammonium cations present in the film served as counter-ions for fullerene radical anions and dianions, and the fullerene reduction process was accompanied by the anion exchange between coating and solution.[96]

IV. The role of non-covalent interactions

For compositions fullerene–cationic lipid (quaternary ammonium salts), the self-organisation of coating components should be considered. This is a spontaneous process that proceeds with a gain in the free energy and occurs due to the universal forces of dispersion, polarisation and induction and also due to specific non-covalent interactions. The latter include the CH/π (see §) and π–π interactions. Although the formed bonds are weak (0.2–2.5 kcal mol^{-1} for CH/π interactions[97]), they make an additional contribution to the energy of self-organisation, particularly, in combination with the other molecular interactions, which, apparently, is important for system functioning. Such interactions may be increased by the electron transfer to the fullerene molecule.

Indeed, in fulleride complexes, in contrast to fullerene complexes, the closer CH/π contacts were observed.[98] When lipid-like fullerene compounds were reduced in a film, the interaction responsible for their binding with the cations supplied from solution depended on the hydration energy of cations and could include the electrostatic interactions between the formed fullerene anion and alkyl chains of Alk_4N^+ cations involved in the coatings.[46] The hierarchical organisation of fullerene derivative **13a** was the reason for the formation of supramolecular ensembles with the 1D, 2D and 3D architecture. The same as for superhydrophobic materials based on other fullerene derivatives (*e.g.*, compound **13b** containing three eicosyloxyaliphatic groups),

§ CH/π Interactions are the interactions of a hydrogen bond in a 'soft' CH-acid with a 'soft' base (π-system).[97]

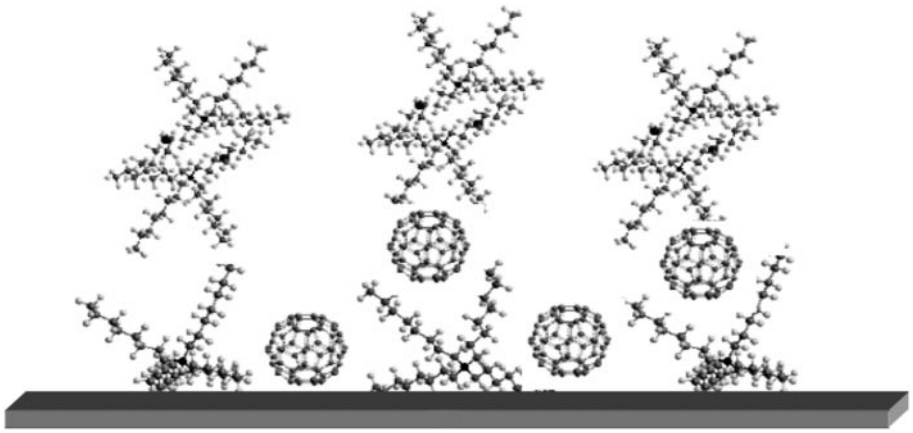


Figure 17. Illustration of molecular organisation of a polylayer C_{60}–TOAB coating.

this was associated with the π–π and van der Waals interactions of the fullerene fragments in molecules and the asymmetrical alkyl chains, respectively.[51] The intensity of interaction of fullerene fragments with alkyl groups of an addend depended on the environment. The processes of self-organisation and aggregation of fullerene derivatives can be controlled by selecting appropriate solvent systems.[99]

In supramolecular chemistry of fullerene, an important role is played by the hydrogen CH/π bonds in addition to the van der Waals interactions.[98] The analysis of structural data for molecular complexes of fullerene has shown that aliphatic groups and aromatic fragments interact with the spherical fullerene molecule as the CH donors. The frequencies of trypticene (TPC) C–H bond vibrations in the TPC–C_{60} complex were sensitive with respect to the TPC coordination to fullerene.[100] Thus, the C–H_{arom} stretching frequencies in the range of 3000–3100 cm^{-1} shifted by ~6 cm^{-1} and the vibrational frequencies of tertiary C–H_{aliph} bonds in the range of 2950–2980 cm^{-1} shifted by 20 cm^{-1}. Co-deposition of fullerene C_{60} with 1,3,5,7-tetraphenyladamantane (TPA) onto the gold surface produced nanostructures with each C_{60} molecule surrounded by three TPA molecules.[101] The role of TPA was dual, namely, on the one hand, it favoured the weakening of C_{60}–metal interactions and, on the other hand, stabilised C_{60} in nanostructures. The observed stabilisation was the result of a gain in energy due to local intermolecular interactions.

No direct evidence of the interaction of TOAB alkyl chains with a C_{60} molecule in a film was obtained so far; however, indirect confirmations of such a possibility are known. First of all, this is the reversibility of redox transformations of fullerene embedded in a TOAB matrix observed in aqueous solutions,[26, 66, 72] which is impossible without the formation of a specific microenvironment for fullerene molecules in the film. Such a possibility was also evidenced by the separation of carbon nanotube bundles, observed in the presence of TOAB, and the stabilisation of the resulting suspension (as compared with aggregation and deposition in polar solvents), which cannot be explained except as the TOAB binding with the nanotube surface due to hydrophobic interactions.[102] The difference in the band position in absorption spectra of cast films of individual fullerenes and fullerene–TOAB coatings also pointed to the fullerene dispersion in a solid matrix as a result of interactions with the hydrophobic components of the latter.[32] Finally, the involvement of C_{60} in the electron transfer through bilayer membranes was shown to be possible only at its dissolution in membrane hydrophobic layer.[11] All these factors point to the involvement of non-covalent, particularly, CH/π interactions, in the structural organisation of fullerene–lipid (TOAB) coatings and make it possible to put forward the model of a solid polylayer coating shown in Fig. 17.

1. Fullerene interactions with environment molecules in the C_{60}–TOAB composition

Our calculations carried out by an *ab initio* density functional method PBE[103] with the use of an extended basis for the SBK pseudopotential[104] and a program PRIRODA[105] (in these calculations, the computer power of the Interdepartmental Computing Centre of the Russian Academy of Sciences was used) allowed us to acquire information on the energy and structural manifestations of the fullerene interaction with environment molecules. As an example, Fig. 18 shows the structure of complex $\{[C_{60}]^{-\bullet}(n\text{-}C_8H_{17})_4N^+\}$. Such a complex can be present in the boundary lipid layer at its interface with the aqueous phase, because Br^- anions pass to solution at the reduction of fullerene embedded into a TOAB matrix. Apparently, in this complex, three sufficiently close contacts (about 2.77–2.81 Å) between full-

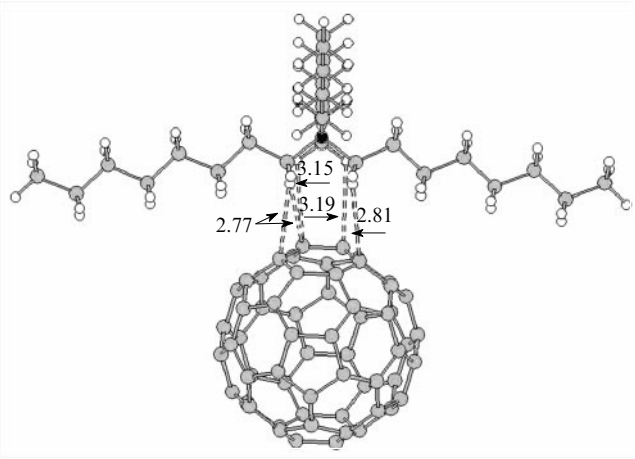


Figure 18. Structure of $\{[C_{60}]^{-\bullet}(n\text{-}C_8H_{17})_4N^+\}$ complex according to the PBE/SBK data (here and in Fig. 19, distances are shown in Å).

erene carbon atoms and H atoms of alkyl substituents are realised. These are forced contacts due to the strong Coulomb interactions between oppositely charged ions. It is interesting that the interaction energy of 43.2 kcal mol^{-1} coincided sufficiently accurately with its formal estimate based on the Coulomb law (42.7 kcal mol^{-1}) for a distance of 7.76 Å between the fullerene centre and the nitrogen atom of a tetraoctylammonium cation in this complex. Apparently, this coincidence is accidental, because in this system, other interactions are realised in addition to Coulomb interactions. Thus a considerable effect of polarisation of $[C_{60}]^{-\bullet}$ ions in the electric field of $(n\text{-}C_8H_{17})_4N^+$ cations was observed, which increased the electron density on fullerene carbon atoms located most closely to the N atom, *i.e.*, to the centre of positive charge distribution. Simultaneously, a part of electron density (0.13 e) was transferred from a radical anion $[C_{60}]^{-\bullet}$ to a tetraoctylammonium cation. As a result, the electron density on each of two H atoms located at the closest distances to $[C_{60}]^{-\bullet}$ (Fig. 18) increased by a half of this value, while the total electron density localised on three C atoms in the close contact with H atoms was 0.15 e higher than the density on a free fullerene anion. The mentioned charge transfer to the C–H bonds did not change their lengths within the accuracy of 0.001 Å as well as the charges on the corresponding carbon atoms.

The energy of interaction of a radical anion $[C_{60}]^{-\bullet}$ with an ion pair $(n\text{-}C_8H_{17})_4N^+Br^-$ decreased to 7.8 kcal mol^{-1}, while the length of C···H contacts decreased to 3.20–3.56 Å. Correspondingly, the transferred electron density decreased to 0.05 e. In this case, formal estimation of the interaction energy based on the charge–dipole N^+Br^- scheme produced a value of 12.8 kcal mol^{-1}, which was 5 kcal mol^{-1} higher than the calculated value. This discrepancy was associated with the fact that the corrections to the Coulomb law for different effects, namely, for polarisation interactions and molecular repulsion, that approximately compensated one another in the previous case, depended differently on the distance. In the absence of charge on the C_{60} molecule (C_{60}–TOAB composition before the reduction), the energy of its interaction with $(n\text{-}C_8H_{17})_4N^+Br^-$ decreased to a typical value of 4.9 kcal mol^{-1} for van der Waals C···H contacts with the length of 3.72–3.89 Å (the length of CH/π contacts taken in supramolecular chemistry [106]), which increased in parallel with the distance between the fullerene centre and the N atom, namely, from 8.21 Å in the $\{[C_{60}]^{-\bullet}$–$(n\text{-}C_8H_{17})_4N^+Br^-\}$complex to 8.71 Å.

At the interaction of $[C_{60}]^{-\bullet}$ with two TOAB ion pairs, the local motif and the length of C···H contacts did not change. Figure 19 shows the structure of a $\{Br^-.$ $.(n\text{-}C_8H_{17})_2N^+(n\text{-}C_8H_{17})_2[C_{60}]^{-\bullet}(n\text{-}C_8H_{17})_2N^+(n\text{-}C_8H_{17})_2Br^-\}$ complex which may exist in the film bulk during the electron transfer to a fullerene molecule. As follows from this figure, in fullerene–QAS compositions containing QAS with sufficiently long alkyl substituents, namely, twice longer than the fullerene molecular size, due to steric hindrances, $[C_{60}]^{-\bullet}$ can only interact with two $(n\text{-}C_8H_{17})_4N^+Br^-$ molecules. The overall interaction energy of 13.6 kcal mol^{-1} was approximately the double energy of radical anion interaction with an ion pair. This made it possible to conclude that in the absence of steric hindrances, a fullerene surrounding by the largest possible number of QAS molecules is more advantageous. Apparently, such a possibility arises with a decrease in the length of hydrocarbon substituents.

At more complete shielding of C_{60} with ion pairs, *i.e.*, with an increase in the number of inorganic counter-ions, the formation of an external layer of halide ions becomes highly probable. This leads to an increase in the distance between fullerene molecules so that the probability of electron jump between them during a redox process

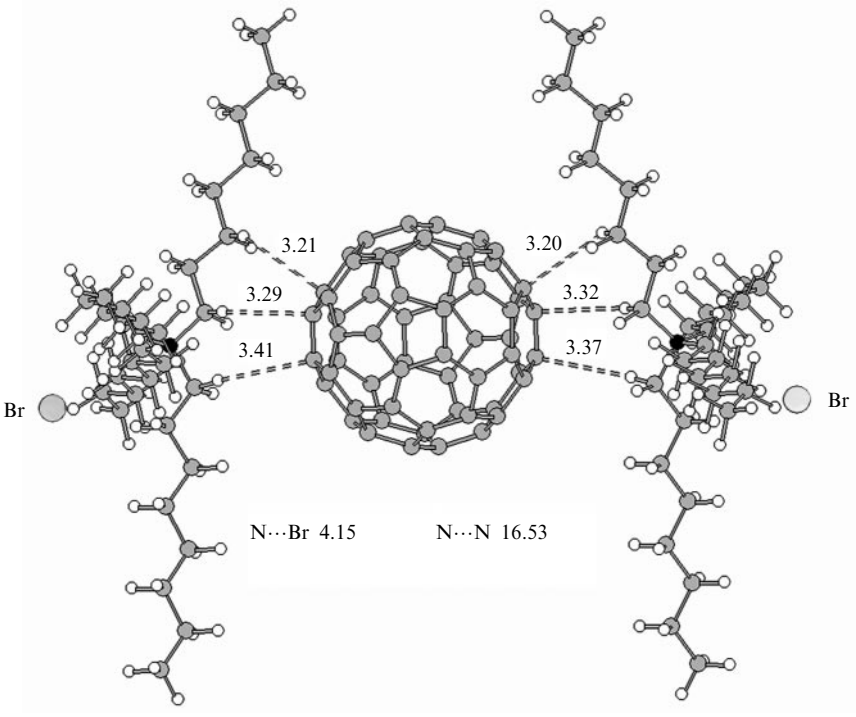


Figure 19. Structure of $\{Br^-(n\text{-}C_8H_{17})_4N^+[C_{60}]^{-\bullet}$ $(n\text{-}C_8H_{17})_4N^+Br^-\}$ complex according to the PBE/SBK data.

becomes extremely low. This agrees with the absence of reduction of fullerene embedded in a matrix of QAS with less than 7 carbon atoms in an alkyl group.[66] Under certain conditions, for asymmetrical tetraalkylammonium cations with two long and two short alkyl substituents, it was possible to achieve more complete C_{60} shielding with the retention of sufficiently short distances between fullerene molecules. Probably, this is among the factors that determine the wide use of didodecyldimethylammonium bromide for immobilising fullerenes on the electrode surface.

Based on performed calculations, it is possible to determine changes in the electron affinity of a C_{60} fullerene in the tetraalkylammonium salt environment. In the presence of one or two $(n\text{-}C_8H_{17})_4N^+Br^-$ ion pairs, the affinity increased by 124 and 334 meV, respectively. These values are the reasonable contribution of the nearest environment to the redox-potential shift (by $\sim$0.5 V) of the fullerene C_{60}–quaternary ammonium salt compositions with respect to the solution (Table 1).

Table 1. Formal potentials of redox transitions for C_{60} and **1a**,**b** in solutions and films (*vs.* Fc/Fc^+).[60]

Fullerene	System	$-E_f^I$/V	$-E_f^{II}$/V
In solution			
C_{60}	$Bu_4^nNBF_4$–PhMe–DMF	0.87	1.36
1a	$Bu_4^nNBF_4$–PhMe–DMF	0.99	1.48
1b	$Bu_4^nNBF_4$–PhMe–DMF	1.02	1.51
In TOAB matrix			
C_{60}	KCl–H_2O	0.31	0.81
1a	KCl–H_2O	0.24	0.79
1b	KCl–H_2O	0.17	0.70

The distance between nitrogen atoms of two ion pairs and the C···H contacts in the $\{Br^-N^+(n\text{-}C_8H_{17})_4C_{60}\cdot(n\text{-}C_8H_{17})_4N^+Br^-\}$ complex decreased by 0.9 and 0.5 Å, respectively, after the electron withdrawal by fullerene. Moreover, the distance between the fullerene sphere centre and nitrogen atoms equal to 8.27 Å and the set of short C···H contacts with the lengths of 3.20–3.57 Å were approximately the same as in an adduct with one ion pair. However, these changes in the molecule geometry led only to an insignificant weakening (by 65 meV) of the vertical electron affinity as compared with the adiabatic one. For the reverse electron withdrawal from $[C_{60}]^{-\bullet}$, the difference between the vertical and adiabatic energies of electron elimination was still smaller (53 meV). Thus, these differences were of the order of magnitude of kT, and the reorganisation effects in the coating could not substantially reduce the electron transfer rate. In connection with this, it should be noted that the reversibility of the redox process characterised by the difference between the potentials of cathodic and anodic peaks ($\Delta E_{c/a}$), considerably deteriorated when going from the systems C_{60}–salt matrix and C_{60}–solution ($\Delta E_{c/a}$ equal to 0.08 and 0.06 V, respectively) to a system with a rubbed-on C_{60} film (glassy carbon, $Bu_4^nNBF_4$, MeCN) for which $\Delta E_{c/a} = 0.73$ V.[26]

2. Peculiarities of functioning of C_{60}–TOAB compositions in the fullerene electrochemical transformations

Fullerenes contained in rubbed-on coatings and matrices of tetraalkylammonium bromide, *e.g.*, tetraoctylammonium bromide, exhibited substantially different electrochemical properties in aqueous solutions. This was manifested in the reversibility and high stability of electrochemical processes and a substantial shift of the cathodic doping formal potential to less negative values for fullerenes in matrices.[26, 66, 72] Such effects were also observed for other types of immobilised systems. Thus the presence of K^+ near a crown-ether cavity containing a fullerene led to a substantial anodic shift (90 mV) in the first reduction step $C_{60} \rightarrow [C_{60}]^{-\bullet}$ (Ref. 107).

The conformational differences between the alkyl groups of QAS with long hydrocarbon substituents and TOAB made it possible to understand why the functioning of a cationic coating with embedded fullerene requires a phase transition only in the former case. The conformational rigidity of long alkyl chains of a cation at temperatures below the phase transition point prevents the approach of the fullerene being reduced to a nitrogen atom and creates conditions unfavourable for electron hopping during the redox transition. The matrix phase transition into the liquid crystal state promoted the fullerene diffusion in it and, provided that the requisite fullerene microenvironment remained unchanged, made possible the reversible redox transformation of fullerene.[66] For TOAB, the spatial arrangement of shorter chains and the geometrical dimensions of its molecule (the octyl chain length is 9.0 Å) allowed a fullerene to immediately occupy the position optimal for both the interaction of a neutral fullerene with alkyl radicals and the binding of a fullerene anion with the cation nitrogen atom (see above).

It can be assumed that the ability of TOAB to form layered structures and develop an appropriate microenvironment due to non-covalent CH/π interactions favours the formation of extended ordered structures in sufficiently thick layers of synthetic cationic lipids as well (see Fig. 17). At the fullerene reduction, the electron is transferred *via* these supramolecular structures from the support–lipid to lipid–solution interfaces. With QAS of the suitable molecular structure, the presence of fullerene in the tetraalkylammonium salt matrix did not disturb the layered structure of the latter and its interaction with the hydrophobic matrix parts provided the necessary microenvironment for fullerene and favoured reversible electrochemical reactions. The further process could follow two routes. If solution contained a species capable of withdrawing an electron, the latter passed to it as to the final acceptor. This involved no composition changes, and fullerene acted as the electron carrier. The hopping mechanism is one of the most probable routes of electron transfer in planar bilayer membranes.[11, 108] According to calculations,[109] the presence of aggregated fullerene forms, even its dimers, in a lipid bilayer favoured destruction of the bilayer.

When solution contains no species capable of reduction at the potentials of fullerene redox transformations, the electron remains in the coating as part of the fullerene anion the formation of which was confirmed by spectral methods (see Ref. 72). To maintain the solid phase electroneutrality, the more hydrophilic inorganic anion of the lipid matrix leaved the latter and passed to solution.[66, 72] As a result, the solution-adjacent QAS layer contained [60]fullerene anion electrostatically bound with a QAS cation (see Fig. 17). In the X-ray photoelectron spectrum of such a coating, a peak appeared with a binding energy identified as the binding energy of the nitrogen atom in the ion pair formed.[96] A similar picture was also typical of the C_{70}–lipid composition.[71]

During the coating formation, an important role was played by non-covalent interactions as a result of which a fullerene (individual molecules or small clusters) finds itself in a channel with walls of hydrophobic alkyl groups of TOAB, whereas in the reduction step, the degree of binding between the nitrogen atom of a cation and the reduced fullerene form acquired great importance. This exactly was demonstrated in calculating the structure and the interaction energy of film components (see above). Fullerene C_{60} and its derivatives **1a**,**b** undergo two-step reduction. Table 2 shows the formal potentials of these processes. For both fullerene reduction steps in a lipid film, E_f shifted in the negative direction in the order **1b** → **1a** → C_{60}. The latter is opposite to the formal potential variation order for these compounds in solution (see Table 2).[110] The changes in the E_f variation order when going to matrices can be associated with the fact that the presence of donor substituents in a fullerene molecule enhances the interaction energy of fullerene reduction products (radical anions and dianions) with tetraalkylammonium cations. Strengthening of interaction resulted in an anodic shift of E_f, which increased with the strengthening of the donor capacity of fullerene derivatives.

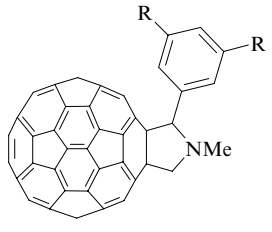
Table 2. Formal potentials of redox transitions of C_{60} and **1a**,**b** in solution and films (*vs.* aqueous SCE).[26,110]

Fullerene	$-E_f^I$/V	$-E_f^{II}$/V
In solution [a]		
C_{60}	0.302	0.791
1a	0.407	0.898
1b	0.439	0.930
In TOAB matrix [b]		
C_{60}	0.160	0.663
1a	0.100	0.647
1b	0.032	0.558

[a] Working electrode was made of glassy carbon, solvent represented a toluene and DMF mixture; [b] working electrode was made of ITO.

3. Spectral manifestations of non-covalent interactions in coatings based of miscellaneous fullerene derivatives

Non-covalent interactions are widespread in chemistry of fullerenes. Thus, irrespective of preparation methods, the absorption spectra of fullerene-containing monolayer films are generally characterised by the band broadening and a bathochromic shift, pointing to the presence of the π–π interactions in the coating. Absorption spectra of phase films (thickness ~2–3 μm) formed by clusters of C_{60} fullerenes and fullerenopyrrolidines **13f**,**g** deposited on ITO–SnO_2 supports were similar to the spectra of solutions of clusters, demonstrating unstructured absorption in the visible and near IR ranges, combined with a high molar extinction coefficient.[111]



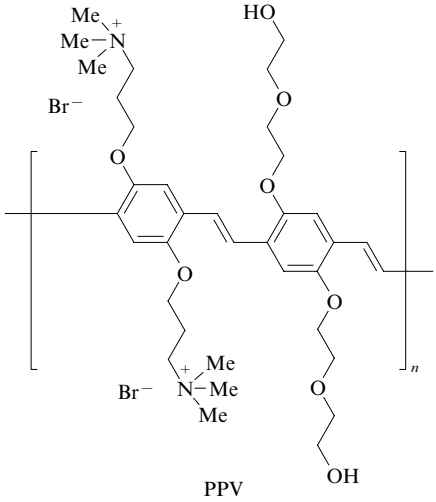
13f,**g**

R = H (**f**), $OC_{18}H_{37}$-n (**g**).

According to the AFM data, in coatings based on fullerenopyrrolidine **13g** containing two $C_{18}H_{37}$ groups, the formation of disk-like structures was observed. Despite the hydrophobic structure of both fragments (C_{60} and C_{18} alkyl groups), the latter formations could represent two-bilayer-thick vesicles. With the introduction of bulky substituents (when going from fullerene **13f** to compounds **13g**), the efficiency of electron phototransfer in the coatings decreased.

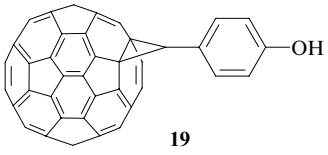
Coatings with the ordered structure synthesised by layer-by-layer deposition of poly(diallyldimethylammonium) chloride and hexa(sulfobutyl)fullerene **15** (see Section II.3) were characterised by broad absorption in the UV range with λ_{max} = 225 nm and non-linear optical properties.[56]

Changes in the absorption spectra of Langmuir–Blodgett films of pyrrolidinofullerene **7** containing an alkyl chain with the terminal carboxyl group, compared to spectra recorded in solutions in $CHCl_3$ and its composition with polyphenylvinylene (PPV), pointed to the presence of interactions between components. Particularly, for films of compound **7**, the interactions were the result of contacts between the neighbouring fullerene-containing molecules in the layer bulk.



PPV

In this case, the bathochromic shift and the broadening of absorption bands were attributed to the formation of *J*-like aggregates.[39,112] Interactions in a composite film **7**–PPV can point to the contacts between fullerene fragments of compound **7** and phenyl fragments of PPV, *i.e.*, to the presence of π–π interactions within the layers.[113]



19

The observed absorption band broadening and red shift for *p*-hydroxyphenylmethano[60]fullerene **19** in a film (227, 267 and 333 nm) as compared with solution (210, 266 and 330 nm) were associated with the close packing of molecules in a layer and the interactions between molecules.[114]

The absorption spectrum of compound **1a** in solution was virtually independent of the TOAB presence. However, the absence of the absorption band at 430 nm in spectra of films formed by compound **1a** and composition **1a** – TOAB (see Fig. 13) directly pointed to the interaction between neighbouring molecules in the coating.[32]

V. Conclusion

In this review, conditions for the formation and functioning (preferentially in aqueous media) of electroactive coatings based on fullerene and its compounds are analysed. The behaviour of a fullerene embedded into a cationic lipid matrix is characterised by reversibility of redox properties and a high degree of reduction. Calculations carried out using density functional theory for the system fullerene C_{60} – TOAB emphasised the role of supramolecular interactions in the self-organisation and subsequent performance of a fullerene-containing coating and qualitatively agreed with the experimental data. Thus, the interaction energy of C_{60} fullerene with the environment molecules decreased in a sequence $\{(n\text{-}C_8H_{17})_2N^+(n\text{-}C_8H_{17})_2[C_{60}]^{-\bullet}\} > \{Br^-(n\text{-}C_8H_{17})_2N^+(n\text{-}C_8H_{17})_2[C_{60}]^{-\bullet}\} > \{Br^-(n\text{-}C_8H_{17})_2N^+ . .(n\text{-}C_8H_{17})_2C_{60}(n\text{-}C_8H_{17})_2N^+(n\text{-}C_8H_{17})_2Br^-\}$. In contrast, the distances (contact lengths) between hydrogen atoms of a TOAB octyl group and carbon atoms of a fullerene sphere increased in the same order, falling in the ranges of 2.77 – 2.81, 3.20 – 3.56 and 3.72 – 3.89 Å, respectively. It is these interactions that provide the microenvironment for fullerene molecules, which is necessary for functioning of coatings in aqueous solutions.

Non-covalent interactions such as $\pi-\pi$ and CH/π between micelles of Triton X-100 [non-ionic detergent, (*tert*-octyl)phenylpolyethylene glycol] and C_{60} molecules led to solubilisation of the latter to form a stable aqueous dispersion.[115] This was accompanied by the shifts (by 7 – 10 cm^{-1}) of C – H stretching bands for the phenyl ring and CH_2 groups in Triton X-100, located at 3066 and 2823 cm^{-1}, respectively, which points to the presence of interactions of these groups with C atoms of fullerene, *i.e.*, suggests that C_{60} is located inside the hydrophobic core of a micelle.

For electrodes based on fullerene immobilised in a cationic type matrix, the ability to operate in aqueous solutions finds practical applications. Due to its unique properties, namely, spherical molecule, hydrophobicity, semiconducting properties and also its susceptibility to reduction, fullerene C_{60} was used as the electron carrier in bilayer lipid membranes.[11, 116, 117] Electrochemically stable electrodes modified with fullerenes (C_{60} or C_{70}) or endometallofullerenes embedded in a lipid film turned out to be efficient electrocatalysts of the reduction of chloroorganic acids (mono- and trichloroacetic acids)[118] and biological macromolecules (haemoglobin,[71, 96] myoglobin and cytochrome *c*[81]) in aqueous solutions. Such reactions became possible because fullerene acts as an active mediator of electron transport. The involvement of endometallofullernes in such electrocatalytic transformations is particularly interesting from the viewpoint of their potential use in medicinal chemistry. Thus the electrocatalytic reduction of oxygen proceeded much more efficiently in the presence of $Hb - Dy@C_{82} - (n\text{-}C_{12}H_{25})_2Me_2N^+Br^-$ as compared with $Hb - (n\text{-}C_{12}H_{25})_2Me_2N^+Br^-$ (Hb is haemoglobin), which points to the effective electron-transport properties of $Dy@C_{82}$ in a cationic matrix.[80] Immobilisation of biomolecules in films of self-organised layers, namely, Langmuir – Blodgett layers and LbL ensembles was considered in a review,[119] as well as the development of studies in this field.

Cationic lipid matrices play an important role in electrochemical processes involving carbon nanostructures to be used as electroactive materials. The function of a cationic lipid consists of changing the microenvironment and also increasing the electron transfer rate to an electroactive species incorporated into the film on an electrode. For example, an electrode modified with a film of single-walled carbon nanotubes (SWNT) in a didodecyldimethylammonium matrix demonstrated high electrocatalytic activity in the anodic oxidation of ascorbic acid. The presence of SWNT considerably accelerated the electron transfer in an electrochemical process.[120]

In the synthesis of molecular nanostructures on solid surfaces, an important role belongs to fullerene molecules with long alkyl substituents. The molecular design of such compounds makes it possible to control the conducting layer structure and opens up prospects for the practical application of new materials based on carbon nanomaterials.[49, 99, 121, 122]

The high sensitivity and selectivity of voltammetric determination of paracetamol[123] and atenolol[124] were achieved on a glassy carbon electrode modified with C_{60}. Deviations in the electrochemical behaviour of fullerene derivatives as compared with the original carbon clusters harbour new possibilities for their use as the mediators in electrocatalytic processes. Moreover, the variations in both structural and electronic properties of fullerene derivatives are of considerable importance. It is studying and simulating the processes involving these derivatives that open up wide prospects for the molecular design of electrodes aimed at the development of highly sensitive and selective biosensors of different types.

References

1. J L Delgado, M A Herranz, N Marttn *J. Mater. Chem.* **18** 1417 (2008)
2. H W Kroto, J R Heath, S C O'Brien, R F Curl, R E Smalley *Nature (London)* **318** 162 (1985)
3. W Krätschmer, L D Lamb, K Fostiropoulos, D R Huffman *Nature (London)* **347** 354 (1990)
4. H Hoppe, N S Sariciftci *J. Mater. Chem.* **16** 45 (2006)
5. H Hoppe, N S Sariciftci *J. Mater. Res.* **19** 1924 (2004)
6. P A Troshin, R N Lyubovskaya, V F Razumov *Ross. Nanotekhnol.* **3** 242 (2008) [a]
7. S Fukuzumi, T Kojima *J. Mater. Chem.* **18** 1427 (2008)
8. N F Goldshleger *Full. Sci. Technol.* **9** 255 (2001)
9. D Bonifazi, O Enger, F Diederich *Chem. Soc. Rev.* **36** 390 (2007)
10. M Braun, A Hirsch *Carbon* **38** 1565 (2000)
11. K Asaka, A Ottova, H T Tien *Thin Solid Films* **354** 201 (1999)
12. S Stepanow, N Lin, J V Barth, K Kern *Chem. Commun.* 2153 (2006)
13. J Chlistunoff, D Cliffel, A J Bard *J. Thin Solid Films* **257** 166 (1995)
14. L Echegoyen, L E Echegoyen *Acc. Chem. Res.* **31** 593 (1998)
15. B S Sherigara, W Kutner, F D'Souza *Electroanalysis* **15** 753 (2003)
16. Y Nishibayashi, M Saito, S Uemura, S-i Takekuma, H Takekuma, Z-i Yoshida *Nature (London)* **428** 279 (2004)
17. L Pospíšil, J Bulíčková, M Hromadová, M Gál, S Civiš, J Cihelka, J Tarábek *Chem. Commun.* 2270 (2007)
18. M F Suárez, F Marken, R G Compton, A M Bond, W Miao, C L Raston *J. Phys. Chem. B* **103** 5637 (1999)

19. W T Tan, E B Lim, A M Bond *J. Solid State Electrochem.* **7** 134 (2003)
20. J Puigmartí-Luis, A Minoia, A Pérez del Pino, G Ujaque, C Rovira, A Lledòs, R Lazzaroni, D B Amabilino *Chem. – Eur. J.* **12** 9161 (2006)
21. E Gomar-Nadal, J Puigmartí-Luis, D B Amabilino *Chem. Soc. Rev.* **37** 490 (2008)
22. X Zhang, H Chen, H Y Zhang *Chem. Commun.* 1395 (2007)
23. K Ariga, J P Hill, Q M Ji *Phys. Chem. Chem. Phys.* **9** 2319 (2007)
24. Á Szücs *J. Electroanal. Chem.* **505** 159 (2001)
25. W T Tan, E B Lim, J K Goh *J. Solid State Electrochem.* **9** 30 (2005)
26. N F Goldshleger, E V Ovsyannikova, A N Lapshin, O N Efimov, R N Lyubovskaya, N M Alpatova *Elektrokhimiya* **42** 853 (2006) [b]
27. Á Szücs, A Loix, J B Nagy, L Lamberts *J. Electroanal. Chem.* **397** 191 (1995)
28. Á Szücs, M Tölgyesi, M Csiszár, J B Nagy, M Novák *J. Electroanal. Chem.* **442** 59 (1998)
29. e Szmcs, A Loix, J B Nagy, L Lamberts *J. Electroanal. Chem.* **402** 137 (1996)
30. Á Szücs, V Budavári, J B Nagy, M Novák *J. Electroanal. Chem.* **528** 153 (2002)
31. Á Szücs, M Novák *J. Solid State Electrochem.* **9** 304 (2005)
32. N F Goldshleger, V I Zolotarevsky, A M Kolesnikova, E V Ovsyannikova, N M Alpatova. *Synth. Met.* **157** 876 (2007)
33. M Krause, D Deutsch, P Janda, L Kavan, L Dunsch *Phys. Chem. Chem. Phys.* **7** 3179 (2005)
34. Á Szücs, V Budavári, O Berkesi, M Novák *J. Electroanal. Chem.* **548** 131 (2003)
35. W-J Wang, H-S Chiu, L-J Yu, B-C Wang *Synth. Met.* **70** 1465 (1995)
36. G Ridolfi, N Camaioni, G Casalbore-Miceli, A M Fichera, M Maggini, G Possamai *J. Solid State Electrochem.* **8** 277 (2004)
37. S Zhang, O Lukoyanova, L Echegoyen *Chem. – Eur. J.* **12** 2846 (2006)
38. S-Y Oh, S-H Han *Langmuir* **16** 6777 (2000)
39. S-Z Kang, S-L Xu, H-M Zhang, L-B Gan, C Wang, L-J Wan, C-L.Bai. *Surf. Sci.* **536** L408 (2003)
40. W Kutner, K Noworyta, G R Devipasad, F D'Souza *J. Electrochem. Soc.* **147** 2647 (2000)
41. H Zhang, X Huang, L Z Fan, B Nin, Y Q Wu, L P Zheng, Y Cao *J. Appl. Polym. Sci.* **100** 3634 (2006)
42. S S Gayathri, A Patnaik *Langmuir* **23** 4800 (2007)
43. S S Gayathri, A Patnaik *J. Chem. Phys.* **124** 131104 (2006)
44. H Murakami, Y Watanabe, N Nakashima *J. Am. Chem. Soc.* **118** 4484 (1996)
45. T Nakanishi, M Morito, H Murakami, T Sagara, N Nakashima *Chem. – Eur. J.* **8** 1641 (2002)
46. T Nakanishi, H Murakami, T Sagara, N Nakashima *J. Phys. Chem. B* **103** 304 (1999)
47. C J Chancellor, A A Thorn, C M Beavers, M M Olmstead, A L Balch *Cryst. Growth Des.* **8** 976 (2008)
48. K-D Kampe, N Egger *Liebigs Ann. Chem.* 115 (1995)
49. T Nakanishi, N Miyashita, T Michinobu, Y Wakayama, T Tsuruoka, K Ariga, D G Kurth *J. Am. Chem. Soc.* **128** 6328 (2006)
50. T Nakanishi, W Schmitt, T Michinobu, D G Kurth, K Ariga *Chem. Commun.* 5982 (2005)
51. T Nakanishi, K Ariga, T Michinobu, K Yoshida, H Takahashi, T Teranishi, H Möhwald, D G Kurth *Small* **3** 2019 (2007)
52. T Michinobu, T Nakanishi, J P Hill, M Funahashi, K Ariga *J. Am. Chem. Soc.* **128** 10384 (2006)
53. W Kutner, P Pieta, R Nowakowski, J W Sobczak, Z Kaszkur, A L McCarty, F D'Souza *Chem. Mater.* **17** 5635 (2005)
54. S Barazzouk, S Hotchandani, P V Kamat *Adv. Mater.* **13** 1614 (2001)
55. S Q Zhou, C Burger, B Chu, M Sawamura, N Nagahama, M Toganoh, U E Hackler, H Isobe, E Nakamura *Science* **291** 1944 (2001)
56. H Li, Y Zhou, Y Li, Y Song, H Fang, S Xiao, H Liu, H Gan, T Jiu, D Zhu *Chem. Phys. Lett.* **383** 230 (2004)
57. M Rendón, M E Hyde, M F Suárez, A Duarte-Ruiz, R G Compton. *Synth. Met.* **149** 99 (2005)
58. D Deutsch, J Tarübek, M Krause, P Janda, L Dunsch *Carbon* **42** 1137 (2004)
59. H Hungerbühler, D M Guldi, K D Asmus *J. Am. Chem. Soc.* **115** 3386 (1993)
60. N M Alpatova, N F Gol'dshleger, E V Ovsyannikova *Elektrokhimiya* **44** 85 (2008) [b]
61. N Nakashima, T Tokunaga, Y Nonaka, T Nakanishi, H Murakami, T Sagara *Angew. Chem., Int. Ed.* **37** 2671 (1998)
62. A-E F Nassar, J M Bobbitt, J D Stuart, J F Rusling *J. Am. Chem. Soc.* **117** 10986 (1995)
63. R Vittal, H Gomathi, K-J Kim *Adv. Colloid Interface Sci.* **119** 55 (2006)
64. T Kunitake, N Kimizuka, N Higashi, N Nakashima *J. Am. Chem. Soc.* **106** 1978 (1984)
65. N Nakashima, T Kuriyama, T Tokunaga, H Murakami, T Sagara *Chem. Lett.* **27** 633 (1998)
66. T Nakanishi, H Ohwaki, H Tanaka, H Murakami, T Sagara, N Nakashima *J. Phys. Chem. B.* **108** 7754 (2004)
67. N Nakashima, Y Nonaka, T Nakanishi, T Sagara, H Murakami *J. Phys. Chem. B.* **102** 7328 (1998)
68. T Nakanishi, K Ariga, M Morita, H Kozai, N Taniguchi, H Murakami, T Sagara, N Nakashima *Colloids Surf., A* **284** – **285** 607 (2006)
69. J Cheng, A Xenopoulos, B Wunderlich *Mol. Cryst. Liq. Cryst.* **225** 337 (1993)
70. M A Osman, M Ernst, B H Meier, U W Suter *J. Phys. Chem. B* **106** 653 (2002)
71. M Li, M Xu, N Li, Z Gu, X Zhou *J. Phys. Chem. B* **106** 4197 (2002)
72. F Song, L Echegoyen *J. Phys. Chem. B* **107** 5844 (2003)
73. H Murakami, M Shirakusa, T Sagara, N Nakashima *Chem. Lett.* **28** 815 (1999)
74. N Nakashima, T Ishii, M Shirakusa, T Nakanishi, H Murakami, T Sagara *Chem. – Eur. J.* **7** 1766 (2001)
75. P Brough, D Bonifazi, M Prato *Tetrahedron* **62** 2110 (2006)
76. T Nakanishi, H Kozai, M Morita, H Murakami, T Sagara, K Ariga, N Nakashima *J. Nanosci. Nanotechnol.* **6** 1779 (2006)
77. N Nakashima, N W B Wahab, M Mori, H Murakami, T Sagara *Chem. Lett.* **30** 748 (2001)
78. N Nakashima, M Sakai, H Murakami, T Sagara, T Wakahara, T Akasaka *J. Phys. Chem. B* **106** 3523 (2002)
79. Y Wu, L Fan, S Yang *J. Phys. Chem. B* **109** 17831 (2005)
80. L Fan, S Yang, S Yang *J. Electroanal. Chem.* **574** 273 (2005)
81. M X Li, J X Wang, B Y Sun, N Q Li, Z N Gu *J. Electrochem. Soc.* **151** E271 (2004)
82. T Nakanishi, A Thuriere, J L Bear, K M Kadish *Electrochem. Solid-State Lett.* **7** E6 (2004)
83. T Nakanishi, K Ariga, A Thuriere, J L Bear, K M Kadish *Thin Solid Films* **499** 349 (2006)
84. K M Kadish, T Nakanishi, A Gmrek, V Ahsen, I Yilmaz *J. Phys. Chem. B* **105** 9817 (2001)
85. T Nakanishi, I Yilmaz, N Nakashima, K M Kadish *J. Phys. Chem. B* **107** 12789 (2003)
86. T Nakanishi, H Murakami, T Sagara, N Nakashima *Chem. Lett.* **29** 340 (2000)
87. K Watanabe, M Komatsu, Y Niidome, M Murata, Y Murata, K Komatsu, N Nakashima *J. Phys. Chem. C* **111** 6500 (2007)
88. D J Abdallah, R E Bachman, J Perlstein, R G Weiss *J. Phys. Chem. B* **103** 9269 (1999)
89. K Sawada, T Sohara, Y Kikuchi *J. Chem. Soc., Faraday Trans.* **91** 643 (1995)
90. K Sawada, E Takahashi, T Horie, K Satoh *Monatsh. Chem.* **132** 1439 (2001)
91. H Liu, G-H Tao, D G Evans, Y Kou *Carbon* **43** 1782 (2005)
92. G Possamai, N Camaioni, G Ridolfi, L Franco, M Ruzzi, E Menna, G Casalbore-Miceli, A-M Fichera, G Scorrano, C Corvaja, M Maggini *Synth. Met.* **139** 585 (2003)
93. S Wu, F Zeng, H Zhu, Z Tong, *Macromolecules* **39** 2606 (2006)
94. A F Thünemann *Prog. Polym. Sci.* **27** 1473 (2002)

95. V V Gritsenko, O A D'yachenko, G V Shilov, N G Spitsyna, E B Yagubskii *Izv. Akad. Nauk, Ser. Khim.* 1982 (1997) [c]
96. M Li, N Li, Z Gu, X Zhou *Electroanalysis* **15** 982 (2003)
97. M Nishio *Tetrahedron* **61** 6923 (2005)
98. H Suezawa, T Yoshida, S Ishihara, Y Umezawa, M Nishio *Cryst. Eng. Commun.* **5** 514 (2003)
99. T Nakanishi, T Michinobu, K Yoshida, N Shirahata, K Ariga, H Möhwald, D G Kurth *Adv. Mater.* **20** 443 (2008)
100. D V Konarev, Ya V Zubavichus, E F Valeev, Yu L Slovokhotov, Yu M Shul'ga, R N Lyubovskaya *Synth. Met.* **103** 2364 (1999)
101. K J Franke, G Schulze, N Henningsen, I Fernandez-Torrente, J I Pascual, S Zarwell, K Rück-Braun, M Cobian, N Lorente *Phys. Rev. Lett.,* **100** 036807 (2008)
102. G Girishkumar, K Vinodgopal, P V Kamat *J. Phys. Chem. B* **108** 19960 (2004)
103. J P Perdew, K Burke, M Ernzerhof *Phys. Rev. Lett.* **77** 3865 (1996)
104. W J Stevens, H Basch, M J Krauss *J. Chem. Phys.* **81** 6026 (1984)
105. D N Laikov, Yu A Ustynyuk *Izv. Akad. Nauk, Ser. Khim.* 804 (2005) [c]
106. M Nishio, in *Encyclopedia of Supramolecular Chemistry* (Eds J L Atwood, J W Steed) (New York: Marcel Dekker, 2004) p. 1576
107. F Diederich *Angew. Chem., Int. Ed. Engl.* **27** 362 (1988)
108. H Shiba, K Maeda, N Ichieda, M Kasuno, Y Yoshida, O Shirai, S Kihara *J. Electroanal. Chem.* **556** 1 (2003)
109. L Li, H Davande, D Bedrov, G D Smith *J. Phys. Chem. B* **111** 4067 (2007)
110. N F Goldshleger, A N Lapshin, E I Yudanova, N M Alpatova, E V Ovsyannikova *Elektrokhimiya* **42** 19 (2006) [b]
111. H Hotta, S Kang, T Umeyama, Y Matano, K Yoshida, S Isoda, H Imahori *J. Phys. Chem. B* **109** 5700 (2005)
112. H Imahori, H Yamada, Y Nishimura, I Yamazaki, Y Sakata *J. Phys. Chem. B* **104** 2099 (2000)
113. S-Z Kang, S L Xu, M J Han, S Lei, C Wang, L J Wan, C L Bai *Colloids Surf., A* **257** – **258** 195 (2005)
114. A Gulino, S Bazzano, G G Condorelli, S Giuffrida, P Mineo, C Satriano, E Scamporrino, G Ventimiglia, D Vitalini, I Fragala *Chem. Mater.* **17** 1079 (2005)
115. I Ramakanth, A Patnaik. *Carbon* **46** 692 (2008)
116. H T Tien, L-G Wang, X Wang, A L Ottova *Bioelectrochem. Bioenerg.* **42** 161 (1997)
117. H Gao, G Luo, J Feng, A L Ottova, H T Tien *J. Electroanal. Chem.* **496** 158 (2001)
118. M X Li, Z Li, F F Wang, Z W Zhu, N Q Li, Z N Gu, X H Zhou *Chin. J. Anal. Chem.* **33** 1211 (2005)
119. K Ariga, T Nakanishi, T Michinobu *J. Nanosci. Nanotechnol.* **6** 2278 (2006)
120. W Cheng, G Jin, Y Zhang *Elektrokhimiya* **41** 1193 (2005) [b]
121. K Ariga, T Nakanishi, J P Hill *Curr. Opin. Colloid Interface Sci.* **12** 106 (2007)
122. T Nakanishi, H Takahashi, T Michinobu, M Takeuchi, T Teranishi, K Ariga *Colloids Surf., A* **321** 99 (2008)
123. R N Goyal, S P Singh *Electrochim. Acta* **51** 3008 (2006)
124. R N Goyal, S P Singh *Talanta* **69** 932 (2006)

[a] — *Nanotechnol. Russ. (Engl. Transl.)*
[b] — *Russ. J. Electrochem. (Engl. Transl.)*
[c] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*