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Radical anion and coordination compounds of polyconjugated molecules: potential organic materials with unusual magnetic, conducting and optical properties

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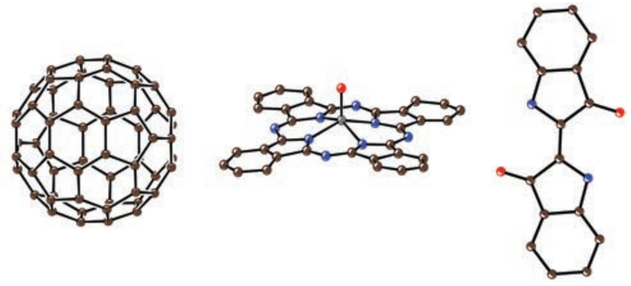
Radical anion salts and coordination complexes of fullerenes, macrocycles and organic dyes obtained by reduction are considered. The reduction transfers an electron to these molecules enabling their participation in magnetic coupling of spins and/or high conductivity as well as modifies essentially their optical properties. Different types of electron transfer between the components have also been observed for these compounds. This review presents new approaches to the syntheses of these salts and complexes as well as their structural and physiochemical properties. Prospects for the development of this area are discussed.



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Introduction

Organic functional materials occupy an extending area in modern technologies.[1] New promising materials based on organic polyconjugated molecules, whose specific aromatic systems define their key photophysical and electrochemical properties, are now of great interest.[2] Our research area comprises molecular design of multifunctional materials based on radical anion salts as well as charge transfer complexes and coordination compounds. The structural assemblies of organic, organometallic molecules and carbon clusters, linked by relatively weak bonds, constitute an important field of material science. The properties of these assemblies can be unusual compared with classical organic compounds due to the unique crystal and electronic structure. For the preparation of this type of compounds, various molecules with conjugated bonds system can be employed, for example carbon fullerene clusters, heteroaromatic compounds such as metal-free and metal-containing phthalocyanines, porphyrins and other macrocycles, as well as organic dyes (Figure 1). This research is associated with the development of methods for chemical reduction of these compounds to obtain them in radical anion, anion or dianion state. They can form salts in this state with functional cations or coordination complexes with transition metals. Unpaired electron of the radical anion appeared under reduction can lead to the magnetic coupling of spins of different types (ferro-, ferri- or antiferromagnetic), metallic conductivity or even superconductivity, as well as reversible electron transfer between the components of salts and coordination complexes. Acceptance of an electron can also modify optical properties of the molecules. In the solid state, different chemical transformations are possible for their anions, for example they potentially can coordinate to metal atoms, dimerize or polymerize.

The preparation of molecular assemblies in the form of single crystals allows one to characterize their structure and deduce its correlation with their properties. More than 300 compounds have been obtained till now with the molecules of different classes. This work started from fullerenes. However, methods of the reduction and crystal growth developed for preparation of fullerene compounds[3] were found to be applicable to other polyconjugated organic molecules as well (see Figure 1). Different reducing agents have been employed depending on the redox properties of the polyconjugated molecules (Table 1). Using these agents, investigations have been extended to the radical anion salts and coordination compounds of metal-free

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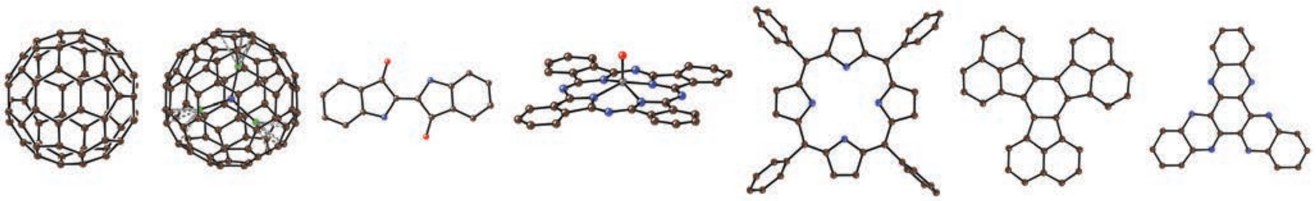

Fullerenes Endometallofullerenes Organic dyes, for example indigo Metallophthalocyanines Porphyrins and metalloporphyrins Aromatic hydrocarbons Polyacenes

Figure 1 Selected types of molecules with conjugated π-electron systems as components of the structural assemblies investigated. Atoms are shown in brown for C, blue for N, red for O, green for Sc and grey for V.

and metal-containing macrocycles[4] as well as organic dyes[5] and aromatic hydrocarbons and nitrogen-containing polyacenes. Note that the approaches developed have been also employed for the preparation of inorganic compounds, such as negatively charged carbonyl containing clusters of Co, Ru, Ir and Rh.[6]

Reducing agents and methods for the preparation of single crystals

In general, reduction of organic compounds is widely used in chemical synthesis and numerous reducing agents are considered in the corresponding reviews.[7] Alkali metals are the most strong reducing agents, which can be utilized in coordinating solvents like THF, 1,2-dimethoxyethane or dioxane for reduction of various organic compounds including fullerenes[8] and aromatic hydrocarbons.[9] Doping of the starting compounds by alkali metals in gas phase has been also developed and initially employed for fullerenes,[10] with later extension to aromatic hydrocarbons[11] and metal phthalocyanines.[12] The disadvantage of this method is the powder state of the product, with the only possibility to solve its structure using the Rietveld method.

We investigated reduction of organic molecules (L) in non-coordinating solvents like *o*-dichlorobenzene and toluene, which had moderate polarity and, therefore, were mixible with *n*-hexane. The solvents were purified from any traces of water and oxygen. Most of the reducing agents employed contained alkali metal cations M$^+$ (Table 1), and the addition of a salt of organic cation as Cat$^+$Hal$^-$, where Hal = Cl, Br or I, into the reaction mixture allowed the alkali metal cation to exchange for organic cation during the reduction process. Then more soluble salt Cat$^+$L$^-$ dissolved, whereas the insoluble salt M$^+$Hal$^-$ precipitated from the solution. Slow mixing of the solution of the obtained salt Cat$^+$L$^-$ with *n*-hexane for one–two months resulted in precipitation of the salt as single crystals. All the syntheses were carried out in a glove box with the content of water vapor and oxygen less than one ppm. Note that coordinating solvents are not suitable for the reactions, since M$^+$Hal$^-$ salt cannot be precipitated from this solution and the resulting mixture of cations prevents the preparation of perfect single crystals. We also used crown ethers to dissolve the reducing agents, which contained alkali metal cations, in nonpolar solvents. We found that [2.2.2]cryptand was the most suitable reagent among different crown ethers tested. It forms cations of the {[2.2.2]cryptand(M$^+$)} composition and the salts of these cations are readily soluble not only in *o*-$C_6H_4Cl_2$ but sometimes in toluene as well. That is especially useful for the preparation of anionic species in a crystalline state.

Commercially available sodium thiolate Na$^+$EtS$^-$ can reduce fullerenes to the radical anion state in the presence of organic cations.[17] It represents relatively weak reducing agent and is highly active since the thiolate anions can serve as ligands for metals. For example, reduction of manganese or zinc phthalocyanines by this reagent yielded [M$^{\mathrm{II}}$(EtS$^-$)(Pc^{2-})]$^-$ anions (M = Mn, Zn)[17(*c*)] as one of products, alternatively, thiolate can be added to some cations as a nucleophile.[17(*d*)]

Sodium fluorenone ketyl Na$^+$$C_{13}H_8O^-$ is rather strong reducing agent with E_{ox} = –1.30 V *vs.* SCE.[13] It can be used in *o*-$C_6H_4Cl_2$ solution to obtain salts of fullerenes, phthalocyanines and organic dyes with the organic and alkali metal–crown ether cations.[18,19] In general, ketyls are not stable in *o*-$C_6H_4Cl_2$ for a long time most probably due to dimerization and the formation of inactive species. Typically, intense red color of the reducing agent disappears in *o*-$C_6H_4Cl_2$ for 20–30 min. Ketyls and their

Table 1 Reducing agents, limitations of the method and types of compounds to be reduced.

Reducing agent and its E_{ox} if available	Reduction conditions	Limitations	Compounds to be reduced			
			Fullerenes	Metal macrocycles	Organic dyes	Hydrocarbons
Sodium thiolate, EtSNa	Cat$^+$Hal$^-$ in *o*-$C_6H_4Cl_2$	Active EtS$^-$ group can add to cations and metals	+	Thiolates formation	–	–
Sodium fluorenone ketyl, Na$^+$($C_{13}H_8O^{\bullet-}$) E_{ox} = –1.30 V[13]	Cat$^+$Hal$^-$ or crown-ethers in *o*-$C_6H_4Cl_2$	Ketyls are stable in *o*-$C_6H_4Cl_2$ for 20–30 min	+	+	+	–
Zinc E_{ox} = –0.76 V[14]	Cat$^+$Hal$^-$ or Ni$^{\mathrm{II}}$LCl_2 in *o*-$C_6H_4Cl_2$	$ZnCl_2$ formed can coordinate to ligand	–	+	–	–
Potassium graphite, KC_8	Cryptand in *o*-$C_6H_4Cl_2$ or toluene, good solubility of salts	Reaction runs appropriately with cryptand only	+	+	+	–
Na$^+$[CpCo(CO)$_2$]$^-$ [a] E_{ox} = –1.90 V[15]	Cat$^+$Hal$^-$ or crown-ethers in *o*-$C_6H_4Cl_2$	Metal-containing moieties can coordinate or be inserted into the crystals	+	+	+	–
Metallocenes[16] Cp^*_2Cr,[b] E_{ox} = –1.04 V Cp^*_2Co, E_{ox} = –1.47 V	In *o*-$C_6H_4Cl_2$	Solubility of salts is limited in $C_6H_4Cl_2$, so addition of PhCN is needed	+	+	–	–
Cs$^+$(anthracene$^{\bullet-}$) E_{ox} = –1.95 V	In toluene with cryptand or Cat$^+$Hal$^-$	Reagent is stable only in toluene, can reduce cations	Salts are not soluble	+	Salts are not soluble	+

[a] Cp is cyclopentadienyl. [b] Cp* is pentamethylcyclopentadienyl.

dimers represent effective ligands and are capable of coordinating through their oxygen atom to the metal one. For example, phthalocyanines $\mathrm{M^{III}ClPc}$ (M = B, Al, Ga; Pc = phthalocyanine) reduced by ketyls contain the ketyl dimers or protonated ketyl coordinated to the metal atom.[20]

Zinc dust with $E_{\mathrm{ox}} = -0.76$ V *vs.* SCE[14] can reduce metal phthalocyanines and fullerenes in $o\text{-}\mathrm{C_6H_4Cl_2}$ solution in the presence of organic cations affording the corresponding radical anions.[21]

Commercially available potassium graphite $\mathrm{KC_8}$ is a highly effective reducing agent that can react in $o\text{-}\mathrm{C_6H_4Cl_2}$ with different compounds having redox potential up to values of –1.2 to –1.3 V. For example, tetra(4-pyridyl)porphyrin free base with $E_{\mathrm{red}} = -1.26$ V *vs.* SCE[22] can be reduced by $\mathrm{KC_8}$ in the presence of cryptand.[23] Since $\mathrm{KC_8}$ is completely insoluble in $o\text{-}\mathrm{C_6H_4Cl_2}$ or toluene, it serves as a reducing agent only in the presence of crown ethers. It is possible to control the reaction stoichiometry using an exact amount of the crown ether, cryptand being the most suitable reagent. Graphite formed after oxidation of $\mathrm{KC_8}$ is insoluble in the solvents used, and the reduction proceeds without byproducts.

$\mathrm{Na^+[CpCo(CO)_2]^-}$ as an example of an organometallic compound salt is a strong reducing agent[15] (see Table 1). It can be employed for the reduction of fullerenes[24] or metallomacrocycles with very negative reduction potentials.[16]

Decamethylchromocene $\mathrm{Cp_2^*Cr}$ with $E_{\mathrm{ox}} = -1.04$ V and decamethylcobaltocene $\mathrm{Cp_2^*Co}$ with $E_{\mathrm{ox}} = -1.47$ V[25] are effective organometallic reducing agents suitable for preparation of charge transfer complexes. $\mathrm{Cp_2^*Cr^+}$ cation can exchange one of its two Cp* ligands for other anionic ligands such as indigo,[5(a)] thioindigo[19(c)] or even chloride anions released in the reduction of $\mathrm{[Sn^{IV}Cl_2(Pc^{2-})]}$ by $\mathrm{Cp_2^*Cr}$.[26]

Reduced hydrocarbon salts, for example $\mathrm{Cs^+(anthracene^{\bullet-})}$ with $E_{\mathrm{ox}} = -1.95$ V *vs.* SCE[27] are strong reducing agents, which can be used in toluene only. They are not stable in $o\text{-}\mathrm{C_6H_4Cl_2}$ most probably due to the reduction of the solvent, E_{red} for $o\text{-}\mathrm{C_6H_4Cl_2}$ being –1.85 V *vs.* Ag/AgBr in DMF.[28] In the presence of organic cation salt $\mathrm{Cat^+Hal^-}$ or cryptand, the $\mathrm{Cs^+(anthracene^{\bullet-})}$ salt is capable of reducing any porphyrin to the radical anion and dianion states as well as some aromatic hydrocarbons with their first reduction potential more positive than –1.8 V. Salts of porphyrins and aromatic hydrocarbons with large cations, like $\mathrm{Bu_4P^+}$, $\mathrm{Bu_3MeP^+}$ or $\mathrm{[cryptand(Cs^+)]}$, are moderately soluble in toluene and can be precipitated as single crystals.

Compounds with negatively charged fullerenes

Fullerenes $\mathrm{C_{60}}$ and $\mathrm{C_{70}}$ are characterized by rich reduction chemistry and generate anions of different types, namely radical anions, dianions, radical trianions and others.[3,29] In these anion states they demonstrate promising physical properties, including metallic conductivity,[30] superconductivity[10] and organic ferromagnetism.[31] Besides, fullerene anions are able to coordinate,[32] dimerize[32,33] and polymerize,[33] affording various types of structures.

Fullerene dimerization, polymerization and coordination accompanied by formation of single C–C or C–Co bonds

Studies of the salts with fullerene radical anions $\mathrm{C_{60}^{\bullet-}}$ in the solid state revealed that they were able to dimerize with generation of negatively charged single-bonded dimers $\mathrm{(C_{60}^-)_2}$ [Figure 2(*a*)]. The dimerization occurs when short enough Van der Waals contacts are formed between $\mathrm{C_{60}^{\bullet-}}$ moieties in a crystal and is accompanied by transition from paramagnetic to diamagnetic state.[34] The transition is reversible and the dissociation temperature of $\mathrm{(C_{60}^-)_2}$ dimers depends on their environment varying from 120 K up to room temperature. In some cases, the process depends on the crystal cooling rate. Fast cooling can result in a mixture of monomers and dimers or even pure monomeric phases at low temperature.[35] Stability of these negatively charged single-bonded dimers as well as their dissociation temperature go up essentially with an increase in the size of fullerene to $\mathrm{C_{70}}$[36] and further to endohedral trimetallonitridofullerene $\mathrm{Sc_3N@\mathit{I}_h\text{-}C_{80}}$ (ref. 37). Thus, single-bonded dimers $\mathrm{(Sc_3N@\mathit{I}_h\text{-}C_{80}^-)_2}$ [Figure 2(*b*)] are stable and dissociate only at 400–460 K.[37(b)] The radical anions of chemically modified fullerenes also can generate single-bonded dimers if the fullerenes have a surface free from substituents and large enough to enable their close approach to each other. For example, radical anions $\mathrm{C_{70}(CF_3)_{10}^{\bullet-}}$ with ten $\mathrm{CF_3}$ groups form stable single-bonded dimers $\mathrm{[C_{70}(CF_3)_{10}^-]_2}$ [Figure 2(*c*)],[38] while their $\mathrm{C_{60}(CF_3)_{12}^{\bullet-}}$ counterparts with twelve $\mathrm{CF_3}$ substituents more or less evenly distributed over the $\mathrm{C_{60}}$ surface do not generate such dimers.[39]

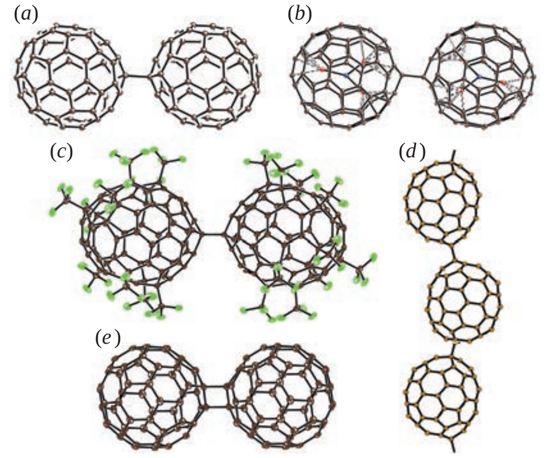


Figure 2 Single- and double-bonded fullerene dimers as well as polymer formed in the radical anion and dianion fullerene salts: (*a*) single-bonded dimer $\mathrm{(C_{60}^-)_2}$,[34(a)] (*b*) single-bonded dimer $\mathrm{(Sc_3N@\mathit{I}_h\text{-}C_{80}^-)_2}$,[37(b)] (*c*) single-bonded dimer $\mathrm{[C_{70}(CF_3)_{10}^-]_2}$,[38] (*d*) polymer $\mathrm{(C_{70}^{2-})_n}$[44] and (*e*) double-bonded dimer $\mathrm{(C_{60}^-)_2}$.[45(b)]

Coordination of $\mathrm{C_{60}^{\bullet-}}$ to cobalt(II) tetraphenyl- (TPP) or octaethylporphyrin (OEP) is similar to the dimerization. Here an electron from d_z^2 orbital of cobalt(II) is involved in the formation of coordination σ-bond with $\mathrm{C_{60}^{\bullet-}}$. As a result, coordinated anions $\mathrm{[Co^{II}porphyrin(C_{60}^-)]}$ are diamagnetic and EPR-silent.[17(d),40] Reversible dissociation of the $\mathrm{Co\text{–}C(C_{60}^-)}$ bonds is promoted by heating.[41] Additional coordination of nitrogen-containing cations, for example *N*-methyl-1,4-diazabicyclo[2.2.2]octanium cation ($\mathrm{MDABCO^+}$) with a nitrogen atom available for coordination, from the opposite side of cobalt(II) porphyrin destabilizes the $\mathrm{Co\text{–}C(C_{60}^-)}$ bonds in the $\mathrm{[(MDABCO^+)(Co^{II}porphyrin)(C_{60}^-)]}$ compound.[42] Dissociation of these bonds restores the paramagnetic $\mathrm{C_{60}^{\bullet-}}$ and $\mathrm{Co^{II}}$ porphyrin species and their contribution (with two unpaired $S = 1/2$ spins) to the magnetic susceptibility.[41,42] Note that the formation of double salt from $\mathrm{C_{60}^{\bullet-}}$ and phthalocyanine anions $\mathrm{[Co^{I}(Pc^{2-})]^-}$ is not accompanied by coordination of $\mathrm{C_{60}^{\bullet-}}$ to cobalt(I) phthalocyanine anion, and both anions are crystallized far from each other.[43] Therefore, only $\mathrm{Co^{II}}$ is capable of forming σ-bond with $\mathrm{C_{60}^{\bullet-}}$.

Fullerene dianions have two additional electrons, which can participate in the formation of intercage single bonds. As a result, dianions $\mathrm{C_{70}^{2-}}$ even can polymerize, affording one-dimensional zigzag polymer [Figure 2(*d*)]. Since both electrons participate in the formation of bonds, this polymer exists in diamagnetic state.[44]

Fullerene structures connected by two C–C bonds

Negatively charged fullerenes can dimerize or polymerize also with formation of two single intercage C–C bonds *via* the [2+2] cycloaddition reaction accompanied by the emergence of cyclobutane ring.[30,33,45] Unpaired spin persists on the fullerene cage, and such dimers and polymers can reveal a strong magnetic coupling of spins and high conductivity. For example, it is known that $C_{60}^{\bullet-}$ polymerizes in the salts MC_{60} (M = K, Rb, Cs), which have been obtained by the doping of fullerene in the gas phase. The polymers $[M^+(C_{60}^{\bullet-})]_n$ demonstrates metal-type conductivity, which can be quasi-one- or three-dimensional, depending on the size of alkali metal cation. Strong antiferromagnetic correlations are observed in these polymers at low temperature.[30] The first negatively charged dimer $(C_{60}^-)_2$ connected by two single bonds [Figure 2(*e*)] was obtained in the salts $[(MDABCO^+)(M^{II}TMPP)]_2(C_{60}^-)_2$, where M = Co, Zn and TMPP = tetrakis(4-methoxyphenyl)-porphyrin.[45] A center-to-center interfullerene distance for the dimers $(C_{60}^-)_2$ connected by two bonds is 9.07 Å, which is shorter than those for the single-bonded dimers $(C_{60}^-)_2$, where the distance is ~9.30 Å. Therefore, the negatively charged dimers with two bonds can be generated due to ‘chemical pressure’ of the porphyrin cage on the $C_{60}^{\bullet-}$ pairs. These dimers have a triplet state with magnetic moment of 2.69 μ_B at 300 K and reveal EPR signal characteristic of triplets, especially at low temperature when the concentration of triplets decreases.[45(*b*)] Their magnetic susceptibility reaches a maximum at 50 K and below this temperature decreases due to transition of the dimer to its singlet ground state. The estimated exchange interaction J/k_B between two $S = 1/2$ spins in the dimer is –44.7 K.[45(*b*)] Fullerene dimers can also be obtained by chemical modification, when an organic bridge brings two fullerene cages together so closely, that they dimerize forming two single bonds, such type of dimerization being typically observed for neutral fullerenes.[46] Reduction of these dimers introduces spins on the fullerene cages, and they reveal a triplet state with magnetic moment of 2.61 μ_B at 300 K. EPR data supports the triplet state existence by a specific triplet signal, especially at low temperature. Introduction of an additional organic bridge between two paramagnetic fullerene cages adds a new channel for magnetic exchange and enhances the magnetic coupling between spins, J/k_B being –78 K.[47] Numerous salts with closely packed fullerene radical anions in a crystal, which represent one-, two- and three-dimensional structures, have been obtained by now. Exploration of these salts under pressure results in new negatively charged fullerene polymers. Recently it has been shown that anionic compounds can also be obtained from chemically modified fullerenes and endometallofullerenes, which makes the synthesis and investigation of these negatively charged dimers and polymers a promising field of research.

Note, that the single-bonded fullerene dimers, typically formed in the radical anion salts, are diamagnetic, and in most cases the dimerization excludes fullerenes from the electronic interactions. To observe effective magnetic coupling of spins or high conductivity in the fullerene subsystem, the dimerization of fullerene radical anions should be suppressed with preservation of short distances between them and overlapping of their π-orbitals.

Complexes with partial charge transfer

One of the ways to suppress dimerization is the preparation of complexes with partial charge transfer to fullerene.[48] Since dimerization requires the participation of both electrons from two radical anions, the degree of charge transfer to fullerene moiety δ = –0.5 or less excludes the dimerization even at close packing of fullerene anions in a crystal. In this case, the complexes are formed by partial oxidation of fullerene radical anions by the derivatives of porphyrazine or phthalocyanine. Thus, complex $[\text{cryptand}(Na^+)](C_{60})_3^-{\cdot}2\,C_6H_4Cl_2$ with $\delta = -0.33$ reveals a metallic type of conductivity.[48] A Dysonian shape of EPR signal for its oriented single crystal confirms two-dimensional character of conductivity, which persisted in the air environment for a long time. This compound transfers to non-metallic state below 100 K, and the Dysonian EPR signal changes its shape to the Lorentzian one. The cations $[\text{cryptand}(M^+)]$ and anions C_{60} form the complexes with partial charge transfer having another composition and correspondingly different δ values of –0.50 and –1.33, however charge disproportionation suppresses metallic conductivity in these complexes. The formation of such complexes is possible due to the close sizes of the $[\text{cryptand}(M^+)]$ and C_{60} ions which can interchange each other in crystal.[48]

Triangular lattices formed by $C_{60}^{\bullet-}$ radical anions

Some special components, which preclude a too close approach of fullerene moieties to each other but preserve the short distances between them, can help to avoid the dimerization, examples of these moieties with C_3 symmetry are neutral triptycene molecule [Figure 3(*a*)][49] and tributyl(methyl)-phosphonium cation [Figure 3(*b*)].[50] These components arrange the fullerene radical anions in triangular lattices, which are important for the emergence of metallic conductivity[49] or strong magnetic interactions with spin frustration.[50] The arrangement of spins in the triangular lattices does not enable their ordering, in spite of strong magnetic coupling between them. Strong spin frustration can result in so-called quantum spin liquid state at very low temperature for some inorganic and organic compounds.[51] It has been shown that this state is close to the metallic one, and even superconductivity has been demonstrated for the radical cation salts with bis(ethylenedithio)tetrathia-fulvalene (ET).[52]

Fullerene moieties are nearly spherical large molecules with a minimal interfullerene distance in the salts of ~10 Å, whereas the salts of ET and $M(dmit)_2$, where M = Ni, Pd and dmit = 4,5-dimercapto-1,3-dithiole-2-thione, consisting of planar molecules, have minimal distances between the centers of the $(ET)_2^{\bullet+}$ or $[M(dmit)_2]_2^{\bullet-}$ pairs in the triangular lattices, which are typically shorter than 7.2 Å.[52] As a result, magnetic coupling of spins is stronger for the salts of ET or $M(dmit)_2$ compared with the fullerene salts, the corresponding Weiss temperatures being up to –375[52] and –120 K, respectively.

In complex $(MDABCO^+)(C_{60}^{\bullet-}){\cdot}TPC$, fullerene moieties are separated by triptycene (TPC) molecules,[49] which do not allow them to form dimers. Structure of this compound has rhombohedral symmetry and contains hexagonal fullerene layers [Figure 3(*a*)] of two types with equilateral fullerene triangles and

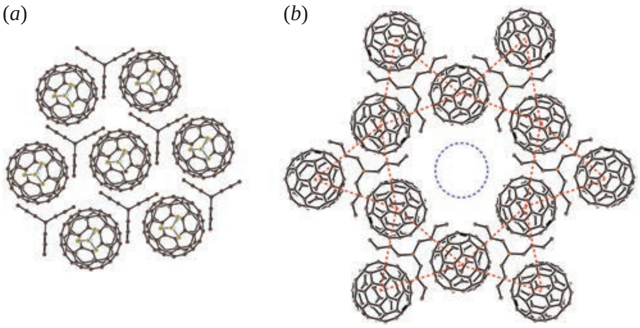


Figure 3 (*a*) Projection of TPC–$MDABCO^+$ layer on the hexagonal closely packed fullerene $C_{60}^{\bullet-}$ layer in $(MDABCO^+)(C_{60}^{\bullet-}){\cdot}TPC$,[49] carbon atoms of the $MDABCO^+$ cation are shown in olive color; (*b*) the Kagome lattice of $C_{60}^{\bullet-}$ moieties with equilateral fullerene triangles in $(Bu_3MeP^+)(C_{60}^{\bullet-}){\cdot}0.33\,C_6H_4Cl_2$ (red dashed lines),[50] the channel occupied by disordered Bu_3MeP^+ cations and *o*-$C_6H_4Cl_2$ solvent molecules is shown by blue dashed circle.

a short interfullerene distance of 10 Å. Difference between the two fullerene layers appears due to various orientation of $MDABCO^+$ cations relative to these layers. Below 180 K, this compound undergoes a transfer from high-symmetry rhombohedral unit cell to low-symmetry triclinic one, however the asymmetry in fullerene layers is low. Measurements of conductivity by several methods for the oriented single crystal support the metallic character in a wide temperature range, namely from 400 down to 1.9 K. At that fullerene layers with different properties coexist in a high-symmetry phase from 400 down to 180 K. The ordered layer is metallic, while the layer with disordered fullerenes is non-metallic and reveals antiferromagnetic coupling of spins with Weiss temperature of –30 K. This represents a rare example of solid compound containing layers of different functionality. The replacement of cation in this compound by *N*-methylquinuclidinium (MQ^+) yields salt $(MQ^+)(C_{60}^{\bullet-})\cdot TPC$[53] with interfullerene distances increased to 10.15–10.17 Å at 250 K due to different orientation of the MQ^+ moieties. As a result, this salt transfers to the Mott insulator state having antiferromagnetic coupling of spins with Weiss temperature of –27 K but without magnetic ordering down to 1.9 K. Substitution of trypticene moieties in $(MDABCO^+)(C_{60}^{\bullet-})\cdot TPC$ in position 9 with Br or I atoms suppresses the phase transition to low-symmetry triclinic phase and affects behavior of the fullerene layers.

Cations with C_3 symmetry also can prevent the dimerization of fullerene fragments, affording triangular fullerene lattices. Two examples of this type[54] are considered below. In general, compounds can transfer to the quantum spin liquid state if magnetic coupling of spins is essential, in this case the Weiss temperature is from about –100 up to –375 K, and antiferromagnetic ordering of spins must be suppressed down to very low temperatures.[51,52] Essential magnetic coupling of spins with the Weiss temperature of –100 to –120 K is possible in the fullerene salts with close $C_{60}^{\bullet-}$ packing. For example, the Weiss temperature is –118 K for salt $(MDABCO^+)(C_{60}^{\bullet-})$. However, due to the absence of equilateral triangles, the spins are antiferromagnetically ordered in this compound below 50 K, estimated J/k_B being –25.3 K.[15(*a*)] Tri-*n*-butyl(methyl)-phosphonium cations Bu_3MeP^+ yield salt $(Bu_3MeP^+)(C_{60}^{\bullet-})\cdot 0.33\,C_6H_4Cl_2$[50] [Figure 3(*b*)] containing Kagome fullerene layers of two types with different interfullerene distances, since methyl groups of both Bu_3MeP^+ cations are directed towards only one of the two fullerene layers. This salt has trigonal symmetry down to 20 K and probably at lower temperatures. Therefore, the Kagome lattice contains equilateral fullerene triangles, whose symmetry is supported by high trigonal symmetry of the crystal. The compound reveals strong magnetic coupling of spins with the Weiss temperature of –108 K but without antiferromagnetic ordering down to 1.5 K. Therefore, this salt represents the most promising candidate with the possible quantum spin liquid state at very low temperatures. Note that the radical anions $C_{70}^{\bullet-}$ and $Sc_3N@I_h\text{-}C_{80}^{\bullet-}$[50] also form salts with Bu_3MeP^+ cations, which are isostructural with $(Bu_3MeP^+)(C_{60}^{\bullet-})\cdot 0.33\,C_6H_4Cl_2$. These radical anions demonstrate high capacity to dimerize, but according to magnetic measurements they are in paramagnetic monomeric state in these salts down to 1.9 K. That is a first example of closely packed fullerene salts with the monomeric radical anions $C_{70}^{\bullet-}$ and $Sc_3N@I_h\text{-}C_{80}^{\bullet-}$ in solid state. The endometallofullerene moiety has the larger cage size, resulting in enlarged interfullerene distances and weaker magnetic coupling of spins, the Weiss temperature being only –47 K.[50] In the absence of dimerization, it becomes possible to investigate the optical and magnetic properties of radical anions $Sc_3N@I_h\text{-}C_{80}^{\bullet-}$ in the solid state.[37(*b*),50] These anions reveal unusual EPR spectrum with splitting of a signal into 22 lines due to hyperfine interaction of spin with three scandium nuclei ($I = 7/2$). Besides, each of these 22 lines is additionally split into six lines, and as a result, 132 lines are observed. From the analysis of EPR and optical spectra of $Sc_3N@I_h\text{-}C_{80}^{\bullet-}$ it has been concluded, that the additional electron is localized mainly in the $Sc_3N@I_h\text{-}C_{80}^{\bullet-}$ moiety at the central Sc_3N fragment.[37(*b*)] Variation in the cation size and investigation of the salts as crystals under pressure can result in further progress in the field of compounds with triangular fullerene lattices.

Coordination compounds of fullerenes

Coordination of fullerenes to transition metals results in compounds with promising optical and magnetic properties.[55,56] Double bonds in fullerenes are of olefinic nature, and fullerenes interact with transition metals like electron-deficient olefins rather than typical aromatic hydrocarbons. Various methods for the preparation of transition metal–fullerene complexes have been described,[55,56] while our approach is based mainly on reduction. An example for the synthesis of coordination compound from fullerene C_{60} and $Ni^{II}(dppe)Cl_2$, where dppe = = 1,2-bis(diphenylphosphino)ethane, in the presence of sodium fluorenone ketyl as a reducing agent is the following:

$$C_{60} + Ni^{II}(dppe)Cl_2 + 2\,Na^+(C_{13}H_8O^{\bullet-}) \rightarrow$$

$$\rightarrow [Ni^0(dppe)(\eta^2\text{-}C_{60})] + 2\,NaCl\downarrow + 2\,C_{13}H_8O.$$

In this reaction fullerene replaces two chloride anions at the metal center, whereas metal is reduced to zero oxidation state. NaCl byproduct precipitates from non-coordinated *o*-$C_6H_4Cl_2$ solvent. Besides sodium flurenone ketyl, reducing agents like zinc dust, sodium tetraphenylborate and chromium(II) acetylacetonate can be used in this type of reactions.[3(*d*)] Here we consider mainly coordination complexes with fullerene C_{60} anions as well as metal-bridged fullerene dimers and polymers. Several other mononuclear η^2-complexes of C_{60} and C_{70} have been described in our review.[3(*d*)]

No electron transfer from metal to fullerene has been found in binuclear complex $\{[Cp^*Rh(\mu_2\text{-}Cl)]_2(\eta^2,\eta^2\text{-}C_{60})\}\cdot C_6H_{14}$,[57] where two Cp*Rh units bridged by two μ_2-Cl anions are coordinated to two adjacent 6–6 bonds of C_{60} moiety. Deeper two-electron reduction of the $[Cp^*Rh^{III}(\mu\text{-}Cl)Cl]_2$ and C_{60}

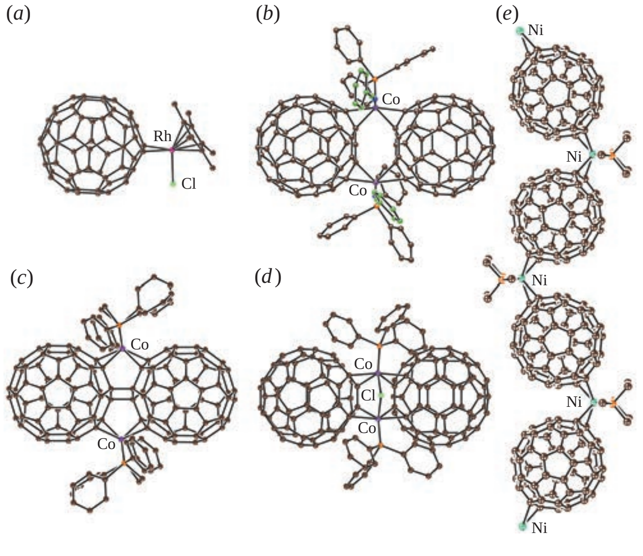


Figure 4 Structures of the synthesized coordination units: (*a*) monomeric anion $[Cp^*RhCl(\eta^2\text{-}C_{60})]^-$;[57] (*b*) dimer $[Co(Ph_3P)(PhCN)C_{60}]_2$,[62] carbon atoms of PhCN are shown in green color; (*c*) dimer $[Co(dppe)C_{60}]_2$ with two additional C–C bonds;[63] (*d*) dimeric anion $\{[Co(Ph_3P)C_{60}]_2Cl\}^-$;[64] and (*e*) polymer $[Ni^0(Me_3P)_2(C_{60})]_n$.[67]

mixture yields salt $(Bu_4N^+)[Cp^*RhCl(\eta^2\text{-}C_{60})]^-$ [Figure 4(*a*)].[57] In the EPR spectrum, this compound shows only a signal from impurity below 120 K, while a broad signal grows in intensity above this temperature together with magnetic moment, which reaches the value of 2.16 μ_B at 300 K, this value being intermediate between those characteristic of the systems with one and two $S = 1/2$ spins, and the corresponding spin-only values being 1.73 and 2.45 μ_B, respectively. Such behavior is in agreement with the presence of diamagnetic Rh^I and C_{60}^0 species below 120 K as well as the appearance of a contribution from paramagnetic Rh^{II} and C_{60}^- above this temperature. Characteristic feature of this compound is an emergence of an intense absorption band at 1030 nm in its NIR spectrum, which is generally attributed to fullerene anion. Compounds with anions $[(Cp^*IrX)(\eta^2\text{-}C_{60})]^-$, where X = Cl or I, reveal similar NIR spectra. In contrast to the rhodium counterpart, the iridium-containing anions are diamagnetic.[58] Similar anions can be obtained with cyclopentadienyl or pentamethylcyclopentadienyl molybdenum dicarbonyl moieties, namely $[CpMo(CO)_2(\eta^2\text{-}C_{60})]^-$ and $[Cp^*Mo(CO)_2(\eta^2\text{-}C_{60})]^-$,[59] both anions being diamagnetic. The former anion has weak absorption in the NIR range, and the latter reveals intense bands at 936 and 1088 nm characteristic of C_{60}^-. DFT calculations support similar electronic structure for the two anions. However, negative electron density is delocalized in the latter anion mainly over the fullerene ligand due to stronger π-back donation from metal to fullerene. The reason for that is essentially stronger donor properties of the Cp* ligand compared with its Cp counterpart. Thus, the two anions have different distribution of negative charge within the coordination unit. Probably, the similar reason can explain the charge transfer in coordination complexes with rhodium and iridium, which contain the donor Cp* ligand.

Dimers with metal bridges between two fullerene moieties had been obtained only with clusters like Ir_4 or Rh_6.[60] We have found that such dimers can also be prepared with transition metals like nickel(0) or cobalt(0). Initially, $Co^{II}(dppe)Cl_2$ and C_{60} did not form coordination complexes under reduction conditions. However, an addition of benzonitrile resulted in mononuclear complex $[Co^0(dppe)(PhCN)(\eta^2\text{-}C_{60})]$[61] with coordination number for cobalt equal to five, or dimer $[Co(Ph_3P)(PhCN)(\eta^2\text{-}C_{60})]_2$ with the coordination number equal to six [Figure 4(*b*)].[62] In this latter dimer, two cobalt(0) atoms are bridged with two fullerene cages coordinated to them by η^2-type to the 6–6 bonds. The $Co–C(C_{60})$ bond length is 2.05–2.13 Å. There is no electron transfer from metals to C_{60} in this dimer, however two closely located Co^0 centers ($S = 1/2$) are strongly coupled. Its excited triplet state has magnetic moment of 2.83 μ_B at 300 K and reveals a half-field signal characteristic of triplets but transfers to singlet ground state below 50 K. Exchange interaction J/k_B has been estimated as –28.6 K.[62] Therefore, essential magnetic coupling of spins can be attained in dimers of this type.

Two $Co^0(dppe)$ units function as bridges between fullerene moieties in dimer $[Co(dppe)C_{60}]_2$ [Figure 4(*c*)].[63] Fullerenes are close to each other in this dimer, and they are arranged in such a way that the 6–6 π-bond of one fullerene moiety is positioned opposite to analogous π-bond of another one providing their dimerization with formation of a cyclobutane ring [see Figure 4(*c*)]. The reason for dimerization is ‘chemical pressure’ on the fullerenes, which emerges during formation of the two metal bridges. Similar dimerization has been found later for some fullerene derivatives, when an organic bridge brings fullerene cages so close that they dimerize.[46(*a*)]

Two Co^0 atoms also function as bridges between two fullerene cages in anionic dimer $\{[Co(Ph_3P)C_{60}]_2Cl\}^-$, but instead of benzonitrile molecules like in dimer $[Co(Ph_3P)(PhCN)(\eta^2\text{-}C_{60})]_2$, one chloride anion is coordinated by μ_2-type to two cobalt atoms [Figure 4(*d*)].[64] Magnetic behavior below 150 K indicates the contribution from two independent $S = 1/2$ spins from Co^0, magnetic moment being 2.43–2.48 μ_B. In contrast to the previously discussed dimers, here the spins interact weakly, affording the positive Weiss temperature of 2 K. The magnetic moment reversibly increases above 150 K up to 3.03 μ_B at 300 K. Since this elevation is accompanied by the growth of broad EPR signal with $g_1 = 2.2672$ from Co^I as well as the narrower signal with $g_2 = 1.9979$ from C_{60}^-, it can be concluded that the reversible temperature-induced charge transfer from Co^0 to C_{60}^0 occurs in the dimer, affording high-spin state with Co^I ($S = 1$) and $C_{60}^{\bullet -}$ ($S = 1/2$).[64] Such behavior is similar to the spin crossover transitions from low- to high-spin state. Thus, different phenomena are observed in the metal-bridged fullerene dimers, including singlet–triplet magnetic transitions, coordination-induced dimerization of fullerenes and temperature-induced charge transfer from metal to fullerene moieties.

Coordination compounds of fullerenes with nickel(0) can also be obtained in monomeric,[65] dimeric[66] as well as polymeric form [Figure 4(*e*)].[67] Metal bridged polymers with carbon clusters occur rarely. In the polymer, fullerene moieties are closely packed with the center-to-center interfullerene distance of 9.92 Å only. Thus, the investigation of fullerene complexes with diamagnetic nickel(0) or paramagnetic cobalt(0) reveals their high synthetic potential for the development of functional compounds, and among them negatively charged fullerene polymers are of special interest due to their diverse chemistry.[33] Addition of metal bridges to these polymers results in introduction of a magnetic component as well as can lead to the charge transfer from metal to fullerene within the polymer. The existence of unpaired electrons on the fullerene allows them to participate in conductivity or magnetic coupling between the paramagnetic metal atoms.

Radical anion and coordination compounds of metallomacrocycles

Metal-free and metal-containing macrocyclic compounds have found an application as dyes, pigments, catalysts as well as components for solar cells and semiconductors.[68] Their oxidation or reduction leads to appearance of an unpaired electron on the macrocycle and thus affects the properties of the compounds.[69]

It is known that the metal-type conductivity stable down to the liquid helium temperatures can appear in metal phthalocyanines at their chemical and electrochemical oxidation, and in some cases these compounds can exhibit a giant magnetoresistance. In general, these compounds contain one-dimensional stacks or two-dimensional layers of partially oxidized macrocycles.[69] Substances with magnetic ordering of spins can be prepared through the oxidation of manganese(II) macrocycles by π-acceptors such as tetracyanoethylene or tetracyanoquinodimethane. The resulting coordination polymeric chains contain alternating high-spin Mn^{III} ions ($S = 2$) and radical anions of π-acceptors ($S = 1/2$), affording ferrimagnetic ordering of spins within the chains.[70]

Reduction of metallomacrocycles and free bases with an addition of electron results in the formation of $[M^{II}(Macrocycle^{\bullet 3-})]^{\bullet -}$ or $(H_2Macrocycle)^{\bullet -}$ radical anions. It was deduced from calculations[71] that non-transition metal phthalocyanines could exhibit metallic conductivity or even superconductivity in the reduced state. However, active investigations in this area are still limited due to weak acceptor properties of the macrocycles and, as a result, anaerobic conditions requirement for their reduction. The acceptor ability of macrocycles is mainly determined by a number of nitrogen atoms. For example, phthalocyanine with eight nitrogen atoms is reduced at –0.70 V *vs.* SCE in DMF.[72] A decrease in the number of N atoms in porphyrin and corrole macrocycles to four ones weakens essentially their acceptor properties, since H_2TPP, H_2OEP and H_3T(Me-Ph)Cor [TPP is tetraphenylporphyrin, OEP is octaethylporphyrin, T(Me-Ph)Cor is tri(4-methylphenyl)-corrole] are reduced *vs.* SCE at –1.26,–1.46 V in CH_2Cl_2[73] and –1.36 V in PhCN,[74] respectively. Sixteen nitrogen atoms in tetrapyrazinoporphyrazine macrocycles increase the acceptor ability and result in the shift of reduction potentials of the corresponding metal complexes to positive values by ~0.2–0.4 V relative to Pc.[75] Acceptor substituents, such as fluoro, chloro or cyano groups at peripheral positions of the macrocycles can additionally shift the reduction potentials to positive values by 0.3–0.6 V.[76] Thus, the redox potentials of macrocycles can be adjusted in a wide range.

A challenge in the exploration of unsubstituted metal-free and metal-containing phthalocyanines, porphyrazines and naphthalocyanines consists in their poor solubility in organic solvents. However, our investigation has demonstrated that in the reduced state nearly all these macrocycles and even larger ones can be dissolved in the non-coordinating *o*-$C_6H_4Cl_2$ solvent. In this case, the methods developed allow one to synthesize these compounds in a crystalline form.

Packing and properties of metal phthalocyanine radical anions

Physical properties of negatively charged metallomacrocycles depend on their packing in a crystal, which for metallophthalocyanines is in turn determined by axial substituents at the central metal atom. Radical anions of metal phthalocyanines lacking axial ligands typically form salts with two large countercations like Bu_4N^+, and halogen anions are introduced into these compounds to compensate the excessive positive charge. As a result, these isolated macrocyclic salts demonstrate only weak magnetic interactions.[4]

Titanyl and vanadyl phthalocyanine derivatives with one axial oxygen ligand tend to form π-stacking dimers characterized by effective π–π interactions between the $Pc^{\bullet 3-}$ planes [Figure 5(*a*)].[77] Macrocycle moieties in such dimers can be shifted somehow relative to each other depending on the cation size, which affects the overlap integrals between radical trianions $Pc^{\bullet 3-}$. Magnetic coupling between the π-stacked radical trianions as well as the charge transfer between them in dimers are highly dependent on the overlap integrals. Therefore, it is possible to tune the magnetic and optical properties by simple variation in cation size. Indeed, the increase in the cation size from Et_4N^+ to Bu_4N^+ and then to Hex_4N^+ changes the overlap integral values from large for Et_4N^+, characterized by strong exchange interaction between the $Pc^{\bullet 3-}$ macrocycles ($J/k_B = -255$ K), to nearly zero ones for Hex_4N^+ with the absence of any magnetic coupling between the macrocycles. The same trend has been found for the intensity of charge transfer bands.[4,77] Increase in the size of macrocycles to naphthalocyanine (Nc) results in additional enlargement of the overlap integrals and magnetic coupling between radical trianions $Nc^{\bullet 3-}$.[78]

Tin(IV) dichloride phthalocyanine has two axial ligands. The corresponding radical anions $[Sn^{IV}Cl_2(Pc^{\bullet 3-})]^{\bullet -}$ are packed in one-dimensional chains,[79] which in turn can be arranged in double chains[26] as well as two-dimensional layers[19(*a*)] [Figure 5(*b*)], depending on the size and shape of cations. Magnetic coupling between radical anions increases essentially for two-dimensional systems such as salt $\{[2.2.2]cryptand(Na^+)\}[Sn^{IV}Cl_2(Pc^{\bullet 3-})]^{\bullet -}\cdot C_6H_4Cl_2$, in which the exchange interaction J/k_B is –18 K and antiferromagnetic ordering of spins is observed below 35 K.[19(*a*)] Macrocycles of larger size with sixteen halogen substituents form π-stacks with efficient π–π interactions [Figure 5(*c*)]. However, in most cases these stacks are not uniform.[21(*a*),80] Thus, our investigations have revealed, that effective π–π interactions are present in some packing patterns of the macrocycles, resulting in strong magnetic coupling of spins.

Analysis of properties of the synthesized salts demonstrated the absence of metallic conductivity in them. For oxidized macrocycles, the metallic properties are revealed only by compounds with partial degree of macrocycle oxidation, *i.e.* at δ from +0.33 to +0.50, whereas full charge transfer typically results in semiconducting properties only.[69(*b*)] However, compounds with partial macrocycle reduction are still unavailable, since the neutral metallomacrocycles and their radical anion counterparts have different solubility, and therefore the neutral species precipitate from solution.

Besides free-base phthalocyanines,[4,81(*a*)] other free-base macrocycles, including porphyrin,[23] corrole,[82] naphthalocyanine,[83] tetrapyrazinoporphyrazine,[81(*b*),(*c*)] and trithiadodecaazahexaphyrin,[84] have been investigated in the radical anion and dianion states and their molecular structure, optical and magnetic properties have been elucidated.

Properties of reduced metallomacrocycles

Considering the properties of compounds with negatively charged metallomacrocycle moieties, the following should be noted. Reduction of macrocycles by decamethylchromocene Cp_2^*Cr allows one to obtain molecular magnets, which are somewhat similar to the known compounds containing manganese(III) macrocycles and π-acceptors.[70] The first compound of this type was obtained by reduction of iron(II) phthalocyanine with Cp_2^*Cr.[85] The formed iron(I) phthalocyanine anions and $Cp_2^*Cr^+$ cations alternate in the

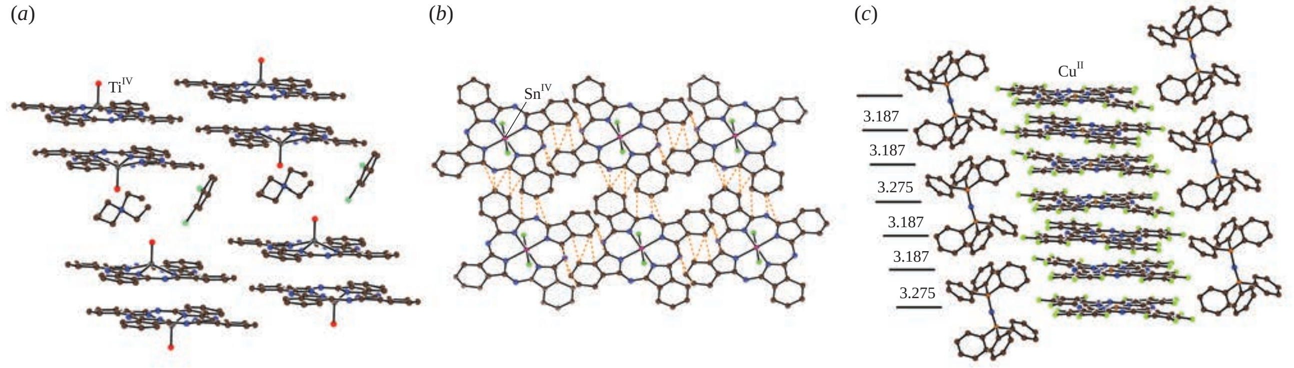


Figure 5 Packing of the components of metal phthalocyanine derivatives: (*a*) salt $(Et_4N^+)[Ti^{IV}O(Pc^{\bullet 3-})]^{\bullet -}\cdot C_6H_4Cl_2$ with π-stacked Pc dimers;[4,77(*b*)] (*b*) anions of the salt $\{[2.2.1]cryptand(K^+)\}[Sn^{IV}Cl_2(Pc^{\bullet 3-})]^{\bullet -}\cdot C_6H_4Cl_2$ with closely packed Pc layer, the short van der Waals contacts between macrocycles are shown by orange dashed lines;[19(*a*)] and (*c*) salt $(PPN^+)_3[Cu^{II}(F_{16}Pc)]_3^{3-}\cdot 2\,PhCN$ with stacked F_{16}Pc moieties, PPN^+ = bis(triphenylphosphoranylidene)ammonium.[80(*b*)]

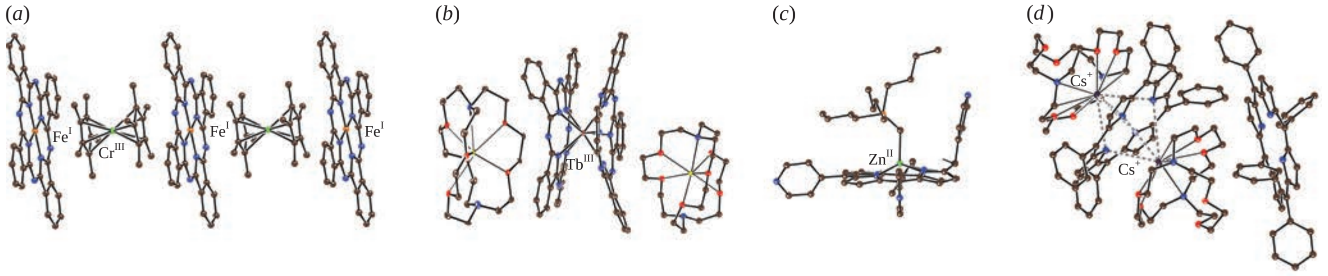


Figure 6 Molecular structures of (*a*) ferrimagnet $(Cp^*_2Cr^+)[Fe^I(Pc^{2-})]^-\cdot 4\,C_6H_4Cl_2$,[85] (*b*) $\{[2.2.2]cryptand(Na^+)\}_2[(Pc^{2-})Tb^{III}(Pc^{\bullet 3-})]^{2-}$ as the first salt containing radical trianion $Pc^{\bullet 3-}$ species,[16] (*c*) anion $[Zn^{II}(Bu_3PCH_2)(TPyPH)^{3-}]^-$ obtained by abstraction of hydrogen atom from Bu_3MeP^+ by dianion $[Zn^{II}(TPyP^{4-})]^{2-}$,[88] and (*d*) salt $\{[2.2.2]cryptand(Cs^+)\}(H_2TPP^{\bullet -})$ with asymmetry in the cationic environment of $H_2TPP^{\bullet -}$ and charge disproportionation.[90]

π-stacks [Figure 6(*a*)]. This alternation of ions Fe^I and Cr^{III} with different spin states $S = 1/2$ and $3/2$, respectively, results in ferrimagnetic ordering of spins below 5 K.[85] More charge transfer complexes of $Cp^*_2Cr^+$ containing paramagnetic metal-free phthalocyanine radical anions and corrole radical dianions, which revealed a similar alternation of ions in π-stacks, were obtained,[82,86] however essentially weaker magnetic coupling was observed in these complexes, and the strongest interactions were found for the corrole-based system with the Weiss temperature of –31 K.[86]

Double-decker phthalocyanines $[(Pc^{2-})M^{III}(Pc^{\bullet -})]$ of terbium(III) and dysprosium(III) in their neutral, oxidized or monoreduced state demonstrate single-ion magnetism (SIM) with relatively high spin-reversal energy barriers U_{eff} up to 652 cm^{-1}.[87] Compounds showing the SIM properties can find applications in high-density information storage, quantum computing and spintronics. Reduction of complex $[(Pc^{2-})Tb^{III}(Pc^{\bullet -})]$ by hydrazine under mild conditions leads to dianionic Pc^{2-} macrocycles in anion $[Tb^{III}(Pc^{2-})_2]^-$. Reduction by sodium fluorenone ketyl also produces only monoanionic salt $(PPN^+)[Tb^{III}(Pc^{2-})_2]^-\cdot 2.5\,C_6H_4Cl_2$.[16] However, effective spin-reversal energy barrier U_{eff} for this salt equal to 538 cm^{-1} is higher as compared with salt $(Bu_4N^+)[Tb^{III}(Pc^{2-})_2]^-$ having U_{eff} = 230 cm^{-1}.[87(*a*)] The use of essentially strong reducing agent $NaCpCo(CO)_2$ results in the formation of salt $\{[2.2.2]cryptand(Na^+)\}_2[(Pc^{2-})Tb^{III}(Pc^{\bullet 3-})]^{2-}$,[16] which is the first double-decker phthalocyanine with radical trianion $Pc^{\bullet 3-}$ [Figure 6(*b*)]. However, this compound does not reveal SIM properties. Considering geometry around the Tb^{III} atom in this salt, it is clear that rotation angle between the two Pc macrocycles is the least among the $Tb^{III}Pc_2$ compounds investigated, and this can be the reason for the disappearance of SIM properties.[16] Thus, changes in the cationic environment of anions $(Tb^{III}Pc_2)^{n-}$ (n = 1, 2) can affect geometry of the Tb^{III} atoms and SIM properties of the compounds, and characteristics of SIMs for complexes $M^{III}Pc_2$ can be tuned by the molecular design approach. Formation of radical trianionic $Pc^{\bullet 3-}$ macrocycles in salt $\{[2.2.2]cryptand(Na^+)\}_2[(Pc^{2-})Tb^{III}(Pc^{\bullet 3-})]^{2-}$ leads to low-energy absorption in the IR range at 4700 cm^{-1} (or 2130 nm), this absorption is also manifested at ~1600 nm in complex $[(Pc^{2-})Tb^{III}(Pc^{\bullet -})]$ with one oxidized $Pc^{\bullet -}$ macrocycle.[16]

Reduced porphyrins have almost not been investigated up to now due to very negative reduction potentials. Nevertheless, the use of strong reducing agents like potassium graphite or cesium anthracene allows one to prepare both their radical anions and dianions. We have found that porphyrin anions and especially dianions are highly chemically active.

An attempt to obtain salt of dianions $[Zn^{II}(TPyP^{4-})]^{2-}$ [TPyP = tetra(4-pyridyl)porphyrin] with tri-*n*-butyl(methyl)-phosphonium (Bu_3MeP^+) cations resulted in the abstraction of proton from one Bu_3MeP^+ cation and formation of neutral ylide coordinated to zinc atom. Proton was attached to the porphyrin macrocycle, affording finally salt $(Bu_3MeP^+)[Zn^{II}(Bu_3PCH_2)(TPyPH)^{3-}]^-$ [Figure 6(*c*) shows only structure of its anion].[88] Thus, the first ylide complex of metalloporphyrin has been obtained in this reaction and unusual $TPyPH^{3-}$ trianion has been investigated. These anions are similar to phlorins[89] and reveal promising optical properties. Visible spectrum of salt $(Bu_3MeP^+)[Zn^{II}(Bu_3PCH_2)(TPyPH)^{3-}]^-$ is similar to that of starting complex $[Zn^{II}(TPyP^{2-})]$, in spite of interruption of the cyclic π-conjugation in $TPyPH^{3-}$. An intense and very broad absorption band at 850 nm is present in the NIR spectrum, its intensity being comparable with that of the Soret band. The $TPyPH^{3-}$ and $TPyP^{2-}$ macrocycles with 18 π-electron systems are isoelectronic, which results in similarity of their spectra in the visible range. The intense NIR absorption can originate from essential decrease of symmetry in the macrocycle due to protonation. The parent porphyrin represents a highly symmetric molecule with two degenerated LUMO orbitals. Distortion or reduction of the molecule resulting in splitting these orbitals into two closely located levels, the splitting being ~0.2 eV for complex $[Zn^{II}(TPyP^{4-})]^{2-}$. The lowest LUMO orbital is occupied in dianions and therefore it can be considered as a new HOMO, while direct transition to the next LUMO level is symmetrically forbidden for dianion $[Zn^{II}(TPyP^{4-})]^{2-}$. Protonation increases the HOMO–LUMO splitting essentially in trianions $TPyPH^{3-}$ (splitting is 1.55 eV), but here direct transition from the occupied HOMO to the vacant LUMO levels becomes possible, and this transition has high oscillator strength according to calculations.[88] This approach demonstrates how compounds with strong NIR absorption can be obtained after distortion of the anions of initially highly symmetrical molecules.

Molecular structure and properties of metal-free porphyrin radical anions were investigated in salt $\{[2.2.2]cryptand(K^+)\}(H_2TPyP^{\bullet -})$.[23] Reduction of porphyrins by cesium anthracene in the presence of cryptand affords radical anion salts of tetra(pentafluorophenyl)- or tetraphenylporphyrin (H_2TPP) with cation $[cryptand(Cs^+)]$.[90] These cations can exist in two conformations with cesium atom in a center of the cryptand cage or cesium atom outside the cryptand cage. For the latter arrangement, the two $[cryptand(Cs^+)]$ cations are close to only one of the two $H_2TPP^{\bullet -}$ radical anions [Figure 6(*d*)]. As a result, reversible charge disproportionation is observed in salt $\{[2.2.2]cryptand(Cs^+)\}(H_2TPP^{\bullet -})$ below 260 K with the formation of diamagnetic H_2TPP^0 and H_2TPP^{2-} species and transition of initial salt into diamagnetic state. Note that cooling of compound $\{[2.2.2]cryptand(Cs^+)\}(H_2TPP^{\bullet -})$ in magnetic field partially suppresses this transition, thus stabilizing the paramagnetic $H_2TPP^{\bullet -}$ radical anions.[90]

Coordination compounds of metallomacrocycles

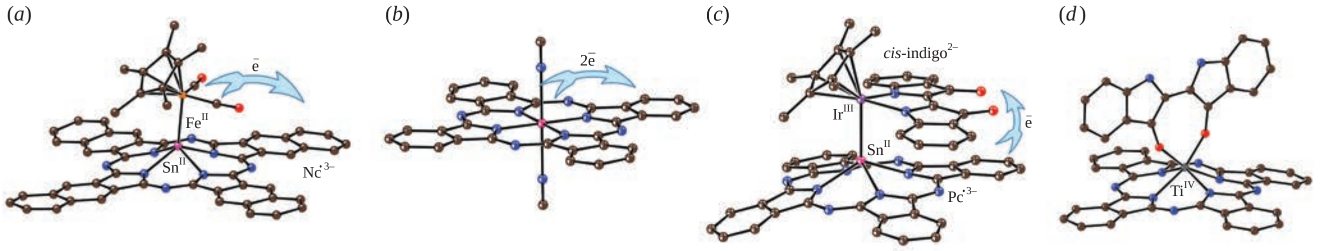
Tin or indium macrocycles are capable of generating coordination compounds with transition metals. Such complexes with tin(II) phthalocyanine are obtained regardless of the charge state of the macrocycle, which can be dianion, radical trianion or even tetraanion.[91] To achieve strong magnetic coupling of spins, coordination of transition metals to $[Sn^{II}(Pc^{\bullet 3-})]^{\bullet -}$ is most promising. An alternative is presented by tetrapyrazinoporphyrazines (TPyzPz), which can coordinate with transition metals by nitrogen atoms at the macrocycle periphery positions. Thus, reduction of $Fe^{II}(TPyzPzEt_8{}^{2-})$ by zinc dust in the presence of bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) yields salt $(PPN^+)_2[Fe^{II}(TPyzPzEt_8)^{4-}(ZnCl_2)_2]^{2-}$ with two $ZnCl_2$ moieties coordinated to imine and pyrazine nitrogen atoms of macrocycle $TPyzPzEt_8{}^{4-}$.[92]

Coordination of ligands to tin(II) phthalocyanine leads to compounds with various properties. For example, dissolution of $[Sn^{II}(Pc^{2-})]$ together with complex $(Cp^*Ir^{III}I_2)_2$ gives formally neutral coordination product $\{Cp^*Ir^{III}I_2[Sn^{II}(Pc^{2-})]\}^0\cdot 2\,C_6H_4Cl_2$, in which macrocycles Pc^{2-} preserve their dianion state.[58] Similarly, interaction of $[Sn^{II}(Pc^{2-})]$ with dimer $[CpFe^I(CO)_2]_2$ or $[Cp^*Fe^I(CO)_2]_2$ results in formally neutral complex $[CpFe^{II}(CO)_2Sn^{II}(Pc^{\bullet 3-})]^0$ or $[Cp^*Fe^{II}(CO)_2Sn^{II}(Pc^{\bullet 3-})]^0$, where the intrinsic charge transfer from Fe^I to macrocycle Pc^{2-} leads to formation of Fe^{II} and paramagnetic radical trianion $Pc^{\bullet 3-}$.[93] Tin(II) naphthalocyanine (Nc) or tetraphenylporphyrin (TPP) also form this type of complexes with intrinsic charge transfer, where the macrocycles are reduced to the radical trianion state [Figure 7(*a*)].[93] Analogous charge transfer has been found in the interaction of $CpFe^I(CO)_2$ with radical anion $[Sn^{II}(Pc^{\bullet 3-})]^{\bullet -}$, affording anions $[CpFe^{II}(CO)_2Sn^{II}(Pc^{4-})]^-$ with tetraanionic Pc^{4-} macrocycles.[91] Molecules of neutral complexes $[Cp^{(*)}Fe^{II}(CO)_2Sn^{II}(Mac^{\bullet 3-})]^0$, where Mac is Pc or Nc, do not contain cations and are closely packed in dimers with effective π-stacking between the $Mac^{\bullet 3-}$ moieties.[93] These π–π interactions between the neighboring dimers can also appear due to essential shift of the macrocycle fragments in the dimers, which results in formation of one-dimensional chains. Magnetic behavior of the dimers and chains composed of $Mac^{\bullet 3-}$ moieties are well described by the Heisenberg model for dimers and chains with large intradimer interaction J/k_B value of –54 to –85 K. The largest coupling is observed for the naphthalocyanine compound $[CpFe^{II}(CO)_2Sn^{II}(Nc^{\bullet 3-})]^0$ with intra- and interdimer interactions J/k_B of –140 and –40 K, respectively.[94] The absence of effective π–π interaction between the macrocycles in complex $\{CpFe^{II}(CO)_2Sn^{II}(TPP^{\bullet 3-})\}^0$ results in weak magnetic coupling of spins with the Weiss temperature of –5 K. The charge transfer has also been observed in a similar coordination compound with indium(III) phthalocyanine, namely $[CpFe^{II}(CO)_2In^I(Pc^{2-})]^0$, however in this complex diamagnetic indium(I) is formed, which preserves diamagnetic Pc^{2-} macrocycles.

An example of charge transfer has been found for tin(II) phthalocyanines and naphthalocyanines coordinated with anionic cyano, cyanato or imidazolato ligands. Because of too large size, the tin(II) atom deviates from the center of macrocycle and is arranged outside the Pc plane by 1.275 Å.[94] For this reason, the tin(II) atom cannot be coordinated with two ligands on the different sides of the macrocycle. Contrary to that, in complex $[Sn^{IV}Cl_2(Pc^{2-})]$, tin(IV) atom is positioned in the center of the phthalocyanine macrocycle.[95] Thus, coordination of two ligands requires the position of the central tin atom exactly in the center of macrocycle, and transition from tin(II) to tin(IV) is needed for that. Indeed, coordination of two ligands to tin(II) provides two electron transfer from metal to dianionic Pc^{2-} macrocycle, with the formation of tin(IV) and tetraanionic Pc^{4-} macrocycles in salts $\{[2.2.2]cryptand(M^+)\}_2[Sn^{IV}L_2(Pc^{4-})]^{2-}$, where M = Na, K and L = CN^-, CNO^-, Im^- [Figure 7(*b*)].[96] Such a transition is supported by essential distortion of macrocycles, manifested in the blue shift and appearance of new bands in the NIR spectrum and confirmed as well by DFT calculations. In addition, it has been found that the orientation of cyano ligand is defined by cationic environment and the close approach to the cation results in coordination of cyano group by the nitrogen atom. Thus, the Sn–N bond elongates [2.339(1) Å] as compared with the Sn–C bond [2.266(3) Å] but electrostatic interaction of NC^- ligand with the cationic environment is enhanced due to larger negative charge on cyano group in its isocyano coordination.[96]

Considering the coordination compounds with two different ligands at one metal center, we have found that indigo dye[97] and tin(II) phthalocyanine[58] form complexes with Cp^*Ir^{III}, *e.g.* $(Bu_4N^+)[Cp^*(cis\text{-indigo}^{2-})Ir^{III}Sn^{II}(Pc^{\bullet 3-})]^{\bullet -}$, where *cis*-indigo^{2-} is doubly deprotonated indigo dianion in *cis*-configuration and $[Sn^{II}(Pc^{\bullet 3-})]^{\bullet -}$ is tin(II) phthalocyanine radical anion [Figure 7(*c*)].[97] Due to the presence of $[Sn^{II}(Pc^{\bullet 3-})]^{\bullet -}$ moiety, this complex has magnetic moment of 1.71 μ_B and reveals a broad low-temperature EPR signal characteristic of $Sn^{II}(Pc^{\bullet 3-})$ coordinated to transition metal.[91] Narrow EPR signals of reduced indigo are also observed for compound $(Bu_4N^+)[Cp^*(cis\text{-indigo}^{2-})Ir^{III}Sn^{II}(Pc^{\bullet 3-})]^{\bullet -}$, but their intensity does not exceed 6% of that of the broad signal. At temperatures above 160 K intensity of the narrow signals increases, while the broad signal becomes weaker, which indicates the transfer of spin density from $[Sn^{II}(Pc^{\bullet 3-})]^{\bullet -}$ to *cis*-indigo^{2-} with the temperature increase and formation of $[Sn^{II}(Pc^{2-})]^0$ and radical trianion *cis*-indigo$^{\bullet 3-}$. This charge transfer does not change magnetic moment of the complex, but delocalization of spin and electron density between the two ligands obviously varies with temperature. Thus, it has been established that different types of electron density transfer occur in the coordinated metallomacrocycle systems.

Properties of metallomacrocycles can be also modified by organic dyes which can coordinate to the central metal atoms. They become especially strong ligands when the additional electron density appears in radical anions or dianions of dyes. The configuration of indigo and thioindigo can change in the reduced state, resulting in coordination of both oxygen atoms of the dye to one metal center. Dyes in dianion state easily substitute



$\{Sn^{II}(Nc^{2-})\}^0 + Fe^I \xrightarrow{CT} \{Sn^{II}(Pc^{\cdot 3-})\}^{\cdot -} + Fe^{II}$

$\{Sn^{II}(Pc^{2-})\}^0 + 2\,CN^- \xrightarrow{CT} \{Sn^{IV}(CN)_2(Pc^{4-})\}^{2-}$

$\{Cp^*Ir^{III}Sn^{II}(Pc^{\cdot 3-})(cis\text{-indigo}^{2-})\}^{\cdot -} \xrightarrow{CT} \{Cp^*Ir^{III}Sn^{II}(Pc^{2-})(cis\text{-indigo}^{\cdot 3-})\}^{\cdot -}$

Figure 7 Different types of coordination moieties originated from tin(II) macrocycles and resulted from the charge transfer: (*a*), (*b*) from metal to macrocycle[93,96] (*c*) between the ligands,[97] and (*d*) neutral $[(cis\text{-indigo}^{2-})Ti^{IV}(Pc^{2-})]^0$ unit.[98]

chloride anions in complexes $\mathrm{Ti^{IV}Cl_2(Pc^{2-})}$ and $\mathrm{In^{III}Cl(Pc^{2-})}$, affording the corresponding neutral $\{(cis\text{-indigo}^{2-})\mathrm{Ti^{IV}(Pc^{2-})}\}$ [Figures 7(*d*)] and anionic $\{(cis\text{-thioindigo}^{2-})\mathrm{In^{III}(Pc^{2-})}\}^-$ units.[98] Donor properties of the dye dianions are not strong enough to transfer electron density to the phthalocyanine macrocycles, so these macrocycles are preserved in dianionic state. As a result, these complexes are diamagnetic in the studied temperature range of 1.9–300 K. Phthalocyanine ligand reveals more intense absorption band in the visible range compared with dianions of the dyes, therefore the phthalocyanine bands prevail in the optical spectra of the complexes.[98] Hence, metal phthalocyanines can be combined in complexes with indigo dyes and most probably other vat dyes.

Thus, metallomacrocycles form radical anion salts, so their packing mode and properties can be varied using cations of different size and shape. Complexes of metallomacrocycles can also be used in design of diverse functional compounds. Transition metals or anions of dyes modify the optical and magnetic properties of metallomacrocycles. Coordination compounds demonstrate different types of temperature-induced charge transfer between ligands, metals and macrocycles, with prospective synthesis of materials with configurable properties.

Synthesis of compounds incorporating organic dyes, hydrocarbons and other polyconjugated molecules

The approaches developed for fullerenes and metallomacrocycles are extendable to other classes of π-conjugated organic molecules like organic dyes, aromatic hydrocarbons and polyacenes, which can be involved in chemical transformations, including dimerization and formation of complexes with transition metals in their radical anion and dianion states. These investigations have only been started and their outcomes have not been published in full. Here some of the results are presented.

Indigo and thioindigo have radical anions with $S = 1/2$ spin state, so they can participate in magnetic interactions. Indigo forms intra- and intermolecular hydrogen bonds and its radical anions demonstrate the same capability, *e.g.* chains with four strong N–H···O(C) hydrogen bonds of 2.11–2.17 Å length for radical anions $\text{indigo}^{\bullet-}$ are found in compound $\{[2.2.2]\text{cryptand}(\mathrm{K^+})\}_6(trans\text{-indigo}^{\bullet-})_6(trans\text{-indigo})\cdot 5.5\,\mathrm{C_6H_4Cl_2}$ [Figure 8(*a*)].[5(*b*)] These chains are packed in the layers separated by bulky [cryptand($\mathrm{K^+}$)] cations with no noticeable π–π interaction between the neighboring chains. Therefore, most probably the essential magnetic coupling of spins with the Weiss temperature of –14 K can originate in the chains through strong hydrogen bonds.[5(*b*)]

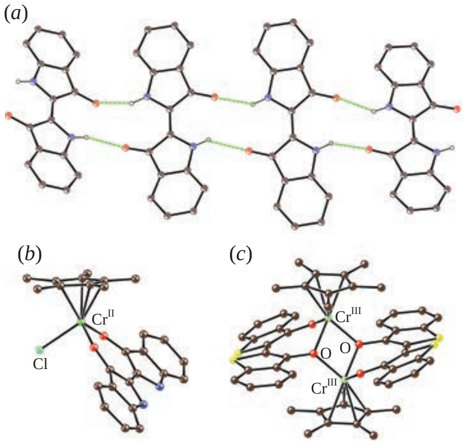


Figure 8 (*a*) Strong hydrogen bonds system (in green dashed lines) of *trans*-indigo radical anions in salt $\{[2.2.2]\text{cryptand}(\mathrm{K^+})\}_6(trans\text{-indigo}^{\bullet-})_6(trans\text{-indigo})\cdot 5.5\,\mathrm{C_6H_4Cl_2}$,[5(*b*)] (*b*) $[\mathrm{Cp^*Cr^{II}Cl}(cis\text{-indigo})^0]$ unit[5(*a*)] and (*c*) dimer $[\mathrm{Cp^*Cr^{III}}(cis\text{-thioindigo}^{2-})]_2$.[19(*c*)]

Reduction of indigo[5(*a*)] and thioindigo[19(*c*)] by decamethylchromocene $\mathrm{Cp^*_2Cr}$ is expected to yield charge transfer complexes of the $(\mathrm{Dye}^{\bullet-})(\mathrm{Cp^*_2Cr^+})$ type in accordance with their redox potentials. The formation of radical anions and especially dianions of these dyes decreases the energy of rotation around the central C–C bond. This enables their transition from *trans*- to *cis*-configuration followed by coordination to chromium atom through both oxygen atoms and replacement of one Cp* ligand. An example is complex $[\mathrm{Cp^*Cr^{II}Cl}(cis\text{-indigo})^0]$ formed in the presence of chloride anions,[5(*a*)] which according to magnetic measurements contains $\mathrm{Cr^{II}}$ with $S = 1$ spin state and neutral indigo moiety in *cis*-conformation [Figure 8(*b*)]. This complex has unusually strong absorption extending up to 1200 nm, which according to calculations can originate from the intramolecular metal-to-ligand charge transfer producing a quintet excited state $[\mathrm{Cp^*Cr^{III}Cl}(cis\text{-indigo}^{\bullet-})]$ with parallel orientation of the $\mathrm{Cr^{III}}$ ($S = 3/2$) and $\text{indigo}^{\bullet-}$ ($S = 1/2$) spins.[5(*a*)] Thioindigo is essentially stronger acceptor than indigo and forms dimeric complex $[\mathrm{Cp^*Cr^{III}}(cis\text{-thioindigo}^{2-})]_2$ [Figure 8(*c*)]. In this complex, chromium(III) atoms have high $S = 3/2$ spin state and are separated only by oxygen atoms, which mediate strong magnetic coupling between the $\mathrm{Cr^{III}}$ centers. The estimated exchange interaction is –34.5 K. It has been supposed that the radical anions of indigo and thioindigo can mediate magnetic coupling between the transition metal atoms. Complexes of this type are now under study.

Conclusions

Design of anion, radical anion salts and coordination complexes of polyconjugated molecules, namely fullerenes and metallomacrocycles with extention to other classes, such as organic dyes, aromatic hydrocarbons and polyacenes, allows one to obtain compounds with promising properties and to explore their chemical transformation, dimerization, polymerization and coordination to various transition metals. The prospective research directions in this area are the following. (i) Triangular lattices formed by radical anions demonstrate essential magnetic coupling with spin frustration, metallic conductivity and superconductivity, transitions between these states being possible as a result of the change in structural parameters or under pressure. (ii) Dimers and especially polymers of fullerenes bonded by two C–C bonds and/or by metal bridges, including paramagnetic ones, reveal promising structural and physical properties, in particular their spins can be delocalized over the fullerene part, which is capable of coexisting and/or interacting with localized spins of paramagnetic metal bridges. (iii) Coordination compounds reveal the temperature-induced charge transfer from low- to high-spin state, similarly to the spin crossover compounds. (iv) Metallomacrocycles can coordinate transition metal-containing moieties or the radical anions and dianions of organic dyes to the central metal atoms, the resulting complexes demonstrate essential magnetic coupling of spins and represent interesting examples of charge transfer between the components. Some of these complexes are obtained as soluble neutral molecules, which can be deposited as films or inserted into composites. (v) Compounds with strong NIR absorption can be obtained as a result of interligand transition or distortion of the anions of initially highly symmetric molecules with degenerated orbitals. (vi) Our preliminary results reveal the possibility to synthesize new magnetic systems through coordination assembly of the radical anions of dyes and polyacenes with several paramagnetic metal atoms. The presence of spin on the ligand can lead to effective magnetic exchange between the coordinated metal centers.

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