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Coordination Compounds in Devices of Molecular Spintronics

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Abstract—Spintronics, being one of the youngest fields of microelectronics, is applied already for several decades to enhance the efficiency of components of computer equipment and to develop units of quantum computer and other electronic devices. The use of molecular material layers in a spintronic device makes it possible to substantially deepen the understanding of the spin transport mechanisms and to form foundation for a new trend at the nexus of physics and chemistry: molecular spintronics. Since the appearance of this trend, various coordination compounds, including semiconductors, single-molecule magnets, complexes with spin transitions, and metal-organic frameworks, are considered as molecular materials of spintronic devices with diverse unusual characteristics imparted by these materials. Specific features of using the earlier described representatives of the listed classes of compounds or their analogs, which are still "kept on the shelves" in chemical laboratories, for manufacturing polyfunctional devices of molecular spintronics are briefly reviewed.

Keywords: vertical spin valve, coordination compounds, metal-organic frameworks, molecular spintronics, molecular magnetism, spin state, "spinterface"

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INTRODUCTION

The further increase in the productivity of computer techniques required enhancing efforts of researchers working in the very different areas of basic research [1, 2], since the computational capability of the modern silicon chips has nearly reached a maximum, including because of restraints related to high heat release and power consumption [3]. One of the possible solutions of the problem implies the use of both charges of electrons moving in electrical circuits and their spins as information carriers [3, 4]. The relatively young area of microelectronics, so-called spintronics [5] born at the late 1980s after the discovery of the giant magnetoresistance effect [6, 7], investigates possible applications of the spin degree of freedom of an electron. This discovery made it possible to produce various spin logical devices [8, 9], quantum computer units [10], magnetic field sensors [11, 12], magnetoresistive random-access memory (MRAM) cells [13–16], and other devices of information recording and red-out [15, 17, 18], which have already found use in the industrial production of modern computers.

For a long time, spintronic devices contained only inorganic materials, such as metals or semiconductors [5, 19]. However, relatively recent attempts to insert some organic and coordination compounds into a spintronic device showed their high potential for spintronics problems, and this gave rise to the appearance of a new research field at the nexus of physics and chemistry: molecular spintronics [20]. Advantages of molecular devices, such as long spin relaxation times [21, 22] and a possibility of individual molecules to interact with the spin of an electron [23, 24], formed a basis for the development of new nanosized electronic devices.

Coming into being of molecular spintronics as a particular area is traditionally associated with the preparation of the first spintronic devices based on aluminum tris(8-hydroxyquinoline) (Alq_3) [25] and further development of coordination chemistry, in particular, including the development of novel approaches to the purposeful design of molecular compounds [26] with conductivity and diverse magnetic properties.

To date, such representatives of coordination compounds as organic semiconductors, single-molecule magnets, transition metal complexes that undergo spin transition under an external action (temperature, pressure, or light irradiation), and metal-organic frameworks (MOFs) of different dimensionalities, found use in molecular spintronics. The study of the spintronic devices containing these compounds as one of the functional layers made it possible to achieve a breakthrough in both understanding of fundamental processes of the interaction of spin carriers with the matter and preparing devices themselves [27].

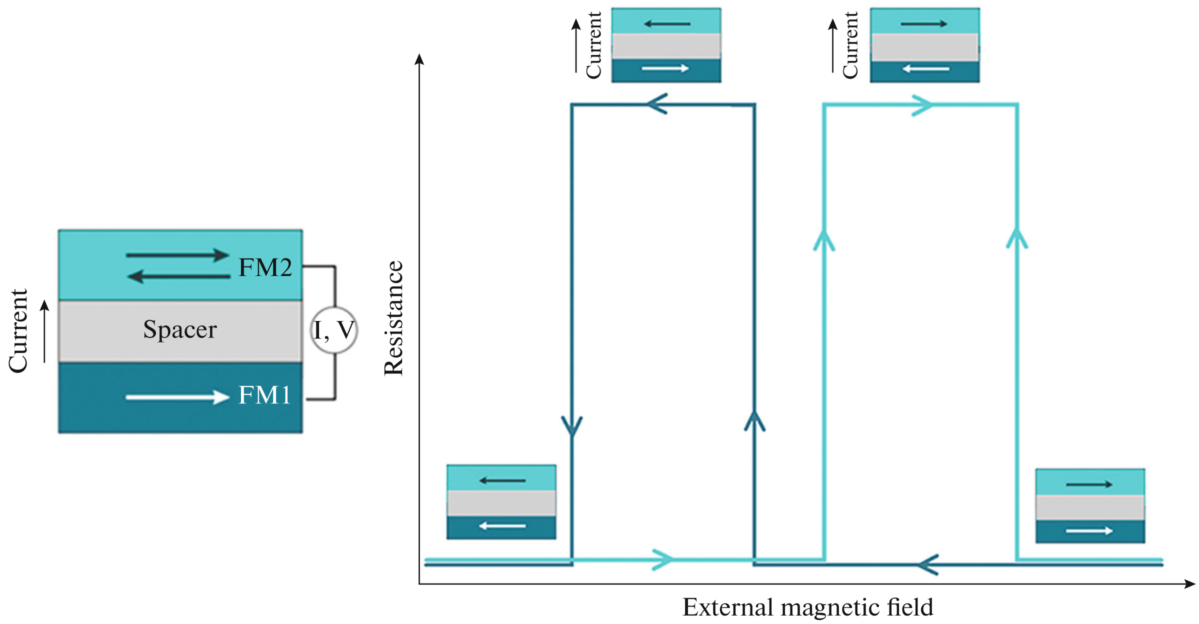

Fig. 1. Scheme of the (a) vertical spin valve and (b) dependence of the resistance on the external magnetic field. Arrows show the magnetization direction of the ferromagnetic electrodes (FM1 and FM2) [24].

This minireview is aimed at familiarizing specialists in the field of coordination chemistry with the most promising compounds that found use in molecular spintronics and at extending the scope of possible applications of new representatives of the listed above classes of compounds that have already been synthesized but are yet kept “on the shelves” of chemical laboratories.

MAIN PRINCIPLES

The operation of all spintronic devices is based on the phenomenon of the so-called spin polarization, which is the predominant orientation of electron spins along one chosen axis. Similar charge carriers with a spin oriented along one direction are named spin-polarized carriers, and their fraction toward the total number of charge carriers in the material makes it possible to quantitatively estimate spin polarization [5]. Any spintronic device traditionally represents a multilayer heterostructure with three or more layers performing three main functions: (i) injection of spin-polarized electrons, (ii) electron transport with the retention of the initial polarization, and (iii) red-out of the resulting spin polarization [4, 19]. The simplest and most popular architecture of similar devices is the so-called vertical spin valve consisting of two ferromagnetic electrodes (FM1 and FM2) separated by the transport layer (Fig. 1) [24, 28, 29]. Such an architecture of the device is the most reliable and simplest for preparation and, hence, is often chosen for studying the properties of various materials served as the electrodes and transport layer [25, 30, 31].

Ferromagnetic electrodes act as a spin “injector” that injects the spin-polarized current into the device and as a detector detecting the polarization of inlet spin carriers using the magnetoresistance effect leading to a sharp increase in the resistance of the device when the magnetizations of the ferromagnetic electrodes are contradirectional [22]. For the correct operation of the vertical spin valve, the electrodes should substantially differ in coercive force, i.e., magnetic field strength necessary for their magnetization or demagnetization. Thus, the application of a weak magnetic field to the device makes it possible to control the magnetization direction of the electrode with a lower coercive force with the retention of the initial magnetization of the second electrode in order to prepare the co- and contradirectional configurations of the device.

The use of molecular compounds (to which MOFs are also referred conventionally by specialists in molecular spintronics) as a transport layer makes it possible to enhance the spin polarization of ferromagnetic materials at the ferromagnet–molecular layer interface, which allows magnetoresistance controlling [32, 33]. A similar interaction of the metallic and molecular materials at the interface can, e.g., enhance the magnetoresistance effect or change its sign due to the hybridization of the molecule on the metal surface [24, 34]. This phenomenon is known as a “spinterface effect” [27, 35] and represents one of the most important problems of modern molecular spintronics, since the mechanisms of its formation and the influence on spin polarization remain unclear [33, 36]. To fill this and many other fundamental gaps in the understanding of spin transport processes, specialists in molecular spintronics focused efforts on the systematic study of various classes of molecular compounds acting as transport layers. For this purpose, approaches of coordination chemistry propose numerous substances with different magnetic properties that can be controlled by molecular design methods in combination with high conductivity and affinity to the electrode material and simplicity of preparing uniform thin films [26].

ORGANIC SEMICONDUCTORS

An important contribution to achievements of modern microelectronics is made by organic semiconductors among which are solid organic or coordination compounds with electron and hole conductivity, i.e., manifesting the properties of traditional inorganic semiconductors [37]. These compounds have found use long ago in diverse fields of microelectronics, including the industrial production of organic light-emitting diodes (OLEDs) [38, 39], and became evident candidates to the role of molecular compounds in spintronic devices.

A stimulus to the formation of molecular spintronics as a particular field of microelectronics was the preparation of the vertical spin valve based on the π-conjugated Alq_3 molecule [25] with a high thermal stability that makes it possible to form uniform thin films [19]. The further active use of this coordination compound in such devices made it possible to propose an optimum architecture of a vertical spin valve [19, 40] and to substantially deepen the understanding of the spin conductivity mechanisms, for instance, to discover a new manifestation of the negative magnetoresistance effect leading to a sharp decrease in the resistance of the device with the contradirectional configuration of electrode magnetizations [26, 30, 41–49]. Hydroxyquinolates of other transition metals of the Mq_3 (M = In(III) [50], Ga(III) [50–52], Fe(III) [53]) and Ln_3q_9 (Ln = Y(III) and Tb(III)) [54] types demonstrated the dependence of the electron transport properties of the vertical spin valve on the ligand environment rather than on the nature of the central metal ion, thus confirming the determining influence of the spinterface on the operation mode and magnetoresistance in devices of this type [50, 54]. It turned out that the choice of the metal ion can be controlled by the spin conductivity in order to prepare polyfunctional spintronic devices [53].

An importance of interactions at the interface of the molecular layer and ferromagnetic electrodes was also confirmed by the studies of the $F_{16}CuPc$ complex (Pc is phthalocyanine) [55], which revealed high magneto- and photosensitivity of the vertical spin valve with the electrode of permalloy $Ni_{80}Fe_{20}$ at room temperature in an air atmosphere even at low (~10 mV) external voltages [55]. Metal complexes with a possibility of targeted apical functionalization that makes it possible to change the ligand field with the retention of the general structure of the complex are also of particular interest. For instance, the dependence of the magnetoresistance on the apical ligand nature was first demonstrated experimentally for the vertical spin valves with the complexes of the $TPP[M(Pc)L_2]_2$ type (TPP is tetraphenylphosphonium; Pc is phthalocyanine; L = CN, Cl, Br; M = Fe [56, 57], Co [57]). An important role of the ligand field in achieving high conductivities and magnetoresistances was confirmed by the studies of the $[Ni(Qs)_2]$ complexes (Qs is quinoline-8-selenoate) [58], which made it possible to appreciably improve these characteristics compared to the vertical spin valve with the thio analog $[Ni(Qt)_2]$ (Qt is quinoline-8-thiolate) [59].

The listed achievements of molecular spintronics due to the use of organic semiconductors based on coordination compounds allowed one to prepare a series of new spintronic devices within a relatively short time and to advance assumptions about the spin transport mechanisms in molecular materials. For example, the spinterface effect was thus discovered and turned over traditional concepts on the principles of the operation of a vertical spin valve and specific features of the purposeful design of coordination compounds for problems of molecular spintronics.

SINGLE-MOLECULE MAGNETS

Another approach to the preparation of a vertical spin valve is the use of compounds, whose individual molecules manifest the properties of a permanent magnet. This allow these single-molecule magnets (SMMs) [60, 61] to act as analogs of ferromagnetic electrodes due to a very slow spin relaxation [24]. These peculiarities of coordination compounds of this type bearing some rare-earth elements and metal ions of the transition row make them promising candidates for the preparation of efficient spin transistors or logical devices of quantum computers [24, 62, 63].

Since SMMs can retain magnetization of an individual molecule even in the absence of a magnetic field, they resemble ferromagnetic materials from which electrodes in spintronic devices are made. This allows one to produce so-called single-molecule spin valves capable of changing the strength of current passed through one molecule of the complex depending on the molecular magnetization of the SMM [62]. The theoretical calculations showed an efficiency of these devices of various architecture, including variants with the ferromagnetic electrode, nonmagnetic electrode, and SMM (Figs. 2a and 2b) [64, 65] and with two nonmagnetic electrodes and SMM containing two magnetic centers (Figs. 2c and 2d) [66, 67]. Although the sizes of similar devices can potentially be decreased to the scale of one molecule, their preparation is a technological problem to be solved further.

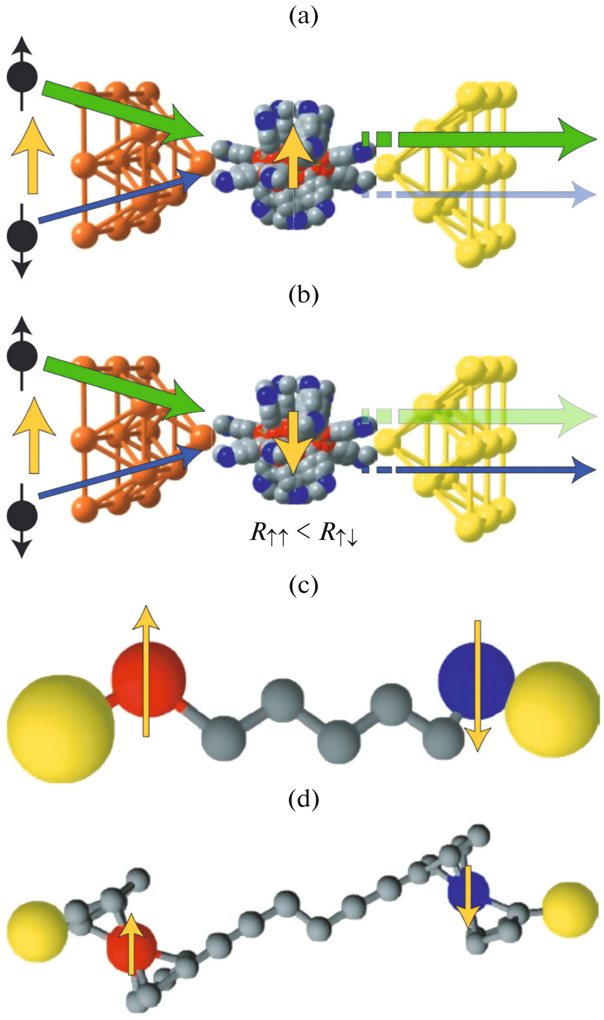

Fig. 2. Devices based on SMMs with one ferromagnetic electrode, nonmagnetic electrode, and SMM in the (a) codirectional and (b) contradirectional configurations, (c) with two nonmagnetic electrodes and SMM with two magnetic centers, and (d) device based on cobaltocene (red) and ferrocene (blue) [62]. Yellow arrows show the magnetization direction.

At the same time, the ability of some lanthanide complexes (e.g., sandwich phthalocyanine complex [$LnPc_2$] (Ln = Tb, Y; Pc is phthalocyanine) [66–68]) to retain magnetic properties in the form of a monomolecular layer on the metallic support [69, 70] allows their use as a transport layer in nanosized spin valves of more traditional architecture. For instance, the $TbPc_2$ complex was a component of the highly efficient spin valves with the ferromagnetic electrodes and monolayer of the chosen SMM supported on graphene (Fig. 3) [71] or carbon nanotubes [72]. This demonstrated a possibility of developing newest logical devices, the conductance of which can be controlled by both the external magnetic field and voltage on the prepared device.

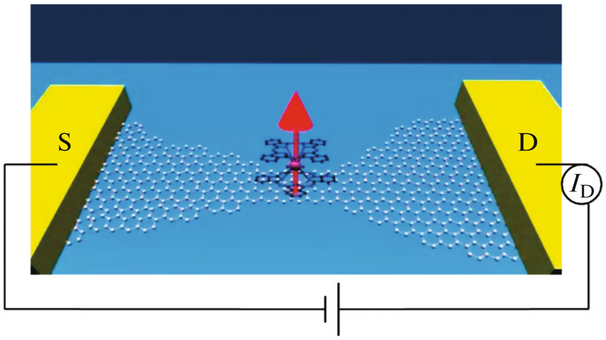

Fig. 3. Scheme of the device based on the $TbPc_2$ complex supported on graphene [71].

For a long time, an obvious drawback of these devices was the necessity to maintain very low temperatures (e.g., about 40 mK) during operation, which allows SMMs to manifest a slow magnetic relaxation necessary for these purposes. However, the compounds for which this temperature reaches 80 K [73] have already been synthesized to date, which shifted the main focus of research to the comprehensive study of the behavior of individual molecules on a metallic support and to search for methods of formation of uniform monolayers of SMMs [40, 62]. Similar studies predicted a high efficiency of vertical spin valves containing as a monolayer such popular SMMs as [$Fe_4(L)_2(Dpm)_6$] (HDpm is dipivaloylmethane; H_3L is 11-(acetylthio)-2,2-bis(hydroxymethyl)undecan-1-ol [74] or 7-(acetylthio)-2,2-bis(hydroxymethyl)heptan-1-ol [75]) and [$Mn_9O_4(Me\text{-}sao)_6(L)_3(MeO)_3(MeOH)_3$]Cl (Me-sao$H_2$ is methylsalicylaldoxime; HL is lipoic acid) [76]). The monolayer of the SMM supported on the ferromagnetic electrode can also be combined with organic semiconductors for the targeted modification of the spinterface in vertical spin valves of the traditional architecture. This approach made it possible to increase the magnetoresistance of the device with the monolayer of the $Tb[Pc(PO_3Et_2)]_2$ complex (Pc is phthalocyanine) placed between the ferromagnetic electrode prepared from lanthanum–strontium manganate ($La_{0.33}Sr_{0.67}MnO_3$, LSMO) and the layer of gallium(III) hydroxyquinolate Gaq_3 [77].

An alternative approach to the formation of a molecular layer on the electrode surface is the deposition of macroscopic (thickness ~10 nm) layers of the SMM, whose thermal stability allows one to use thermal sputtering as, e.g., 5,7-dichloro-8-hydroxyquinolate $Na[Ln(5,7Cl_2q)_4]$ (Ln = Y(III), Tb(III) [78], Dy(III) [34, 78]). In these layers, the SMMs can retain a slow magnetic relaxation. This is attributed to the exchange interaction with the surface of the ferromagnetic electrode made of permalloy due to which this class of compounds can be used as an active layer in traditional vertical spin valves.

The study of conducting and magnetic properties of films and individual molecules of SMMs made it possible to propose the design of single-molecule spintronic devices, which are yet at the stage of development, and approaches to the integration of SMMs in the traditional architecture of vertical spin valves. However, the latter implies the further search for stable SMMs retaining their magnetic properties as thin films on ferromagnetic supports and exhibiting a slow magnetic relaxation at temperatures close to room temperature for the everywhere propagation of molecular spintronic devices.

METAL COMPLEXES EXPERIENCED SPIN TRANSITION

Another class of compounds that also favored the development of molecular spintronics is presented by the transition metal complexes capable of existing in two spin states and reversibly switching over them under an external action (e.g., temperature, pressure, or irradiation). A similar spin transition makes them ideal candidates for the preparation of switchable vertical spin valves in storage devices [79]. Similarly to SMMs, the magnetic properties of spintronic devices containing complexes with spin transitions depend strongly on the method of film formation and film thickness, which often requires a detailed analysis of the surface by scanning tunneling microscopy [80]. For this reason, special attention is given to compounds from which thin films can be obtained using immobilization methods accepted in microelectronics (e.g., thermal sublimation) [81, 82]. Examples of such compounds that experience spin transitions are the iron(II) complexes $[Fe(HB(Pz)_3)_2]$ and $[Fe(H_2BPz)_2(L)]$ (Pz is pyrazolyl; L is phenanthroline or 2,2'-bipyridine) [83]. For example, the $[Fe(HB(Pz)_3)_2]$ film 200 nm thick in the device composition made it possible to provide a random-access memory effect [84], and the $[Fe(H_2BPz)_2(L)]$ layers 400–500 nm thick provided the spin transition induced by the temperature ($T = 10$ K) and irradiation ($h\nu = 525$ nm) [85]. Another promising class is formed by cell complexes (clathrochelates) of transition metals with a high thermal stability due to the encapsulation of the metal ion by the three-dimensional cell ligand, whose substituents in the edge and apical positions control its spin state. For some such complexes of the general formula $M(GmX_2)_3(BR)_2$ (M = Co, Fe; X = Cl, Br; R is *n*-butyl, *n*-hexadecyl), not only thin films that experience temperature-induced spin transition were prepared (including by thermal sublimation), but also a series of vertical spin valves was produced from them [82, 86]. Unfortunately, similarly to the reference devices containing no clathrochelate layer, these valves exhibited no magnetoresistance, which was explained by a very fast relaxation of spin carriers in the tunneling barrier layer of vanadium oxide.

As in the case of SMMs, attempts to produce single-molecule spin valves were made for the complexes with spin transitions. For instance, one molecule of the $[Fe(Tzpy)_2(NCS)_2]$ complex (Tzpy is 3-(2-pyridyl)[1,2,3]triazolo[1,5-*a*]pyridine) [87] allowed one to evaluate prospects of this device with gold electrodes [88], whose electron-transport properties changed depending on the spin state of the chosen compound [88]. The theoretical calculations of the magnetoresistance [89] in the single-molecule device with another known iron(II) complex $[FeL_2]^{+2}$ (L = 2,2':6,2''-terpyridine) [79, 90] that undergoes the spin transition exhibited the dependence of this parameter on the spin state of the metal ion. Owing to this effect, the magnetoresistance changed from 200 to 3000% depending on the external voltage.

In spite of a high potential of similar devices containing layers or even individual molecules of the complexes with spin transitions as polyfunctional spin valves, their practical accomplishment is yet restricted. The main obstacles for achieving this purpose are both a necessity of search for compounds retaining wholeness upon immobilization on the surface by thermal sublimation and the absence of an optimum architecture of the corresponding single-molecule devices.

METAL-ORGANIC FRAMEWORKS

Metal-organic frameworks keep apart the classes of coordination compounds listed above [91]. Although they are crystalline materials with the *n*-meric ($n = 1$–3) periodical structure built of metal ions and organic ligands, specialists in molecular spintronics traditionally assign them to molecular materials. In spite of the existence of one- and three-dimensional MOFs with ferromagnetism, the most part of these compounds is dielectric, which substantially diminishes their allurement for the production of microelectronic devices [91]. On the contrary, 2D MOFs are often characterized by a good conductance, a relatively high Curie temperature [92, 93], a slow spin relaxation, and uniformity of the formed thin films [94, 95] owing to which they are interesting for molecular spintronics [96]. For instance, the recent theoretical study of $Re_3C_{12}N_{12}H_{12}$ ($T_c = 180$ K) (Fig. 4a) revealed the high spin selectivity of this MOF, which allows its use as an active layer in spintronic devices [97] (see caption to Fig. 4a). Similar properties can be manifested by the 2D MOFs of the MBHT composition (M = Cr, Mn, Fe, Co; BHT is hexamercaprobenzene) (Fig. 2b) [98] (see caption to Fig. 4b) and by the MOFs in which the transition metal ions of the first row are coordinated by the aminosubstituted naphthalene derivatives (Fig. 2c) [99].

The properties of thin films of MOFs are significant for the preparation of future vertical spin valves. In particular, an extremely high Curie temperature

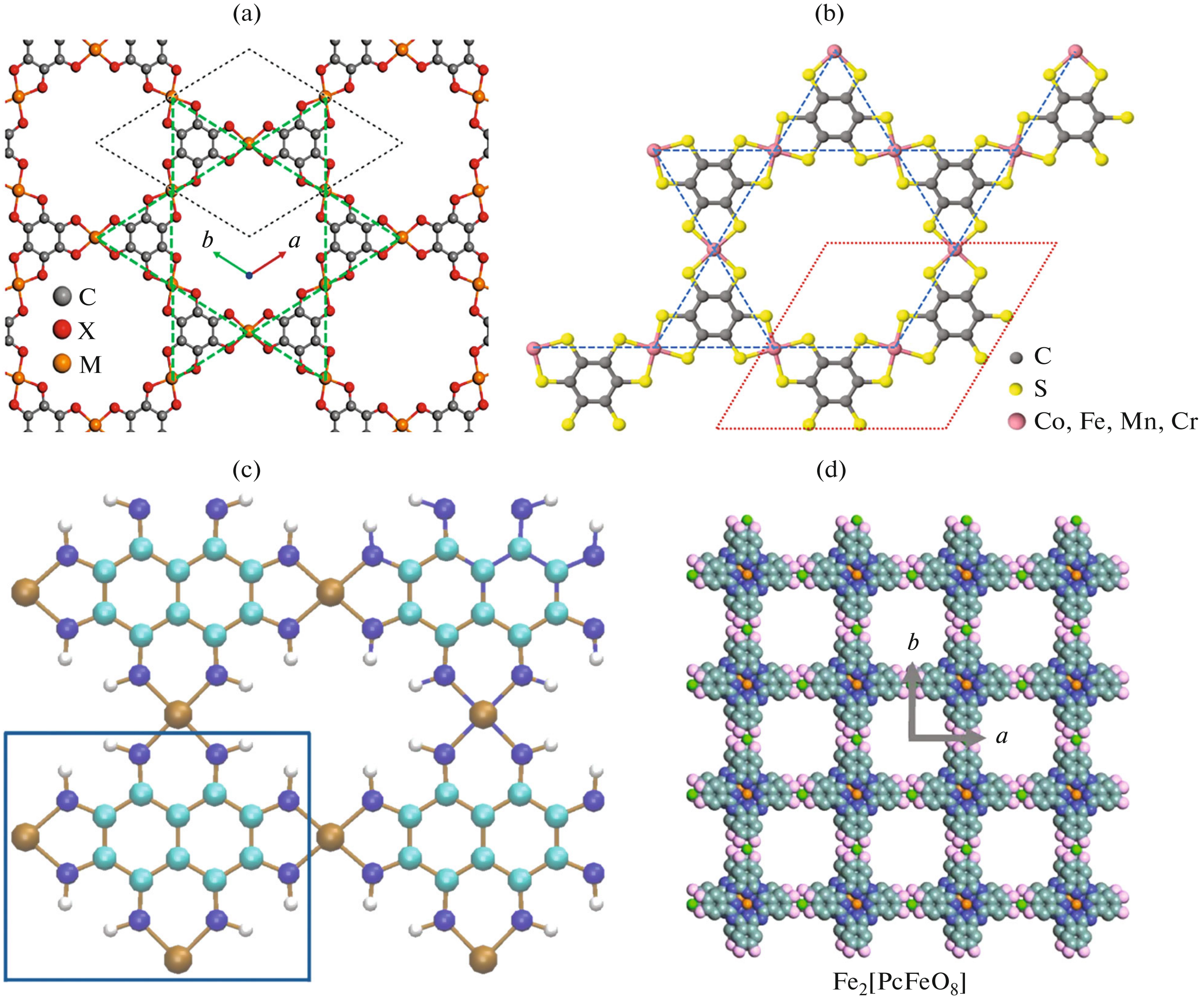

Fig. 4. Fragments of the crystal structures of (a) MOF $Re_3C_{12}N_{12}H_{12}O$ (see text) [97], (b) MBHT MOF [98], (c) MOF with transition metal ions of the first row and naphthalene amino derivatives (white, blue, dark blue, and brown spheres designate atoms of hydrogen, carbon, nitrogen and transition metal, respectively) [99], and (d) $K_3Fe_2[PcFeO_8]$ (blue, dark blue, pink, orange, and green spheres designate carbon atoms, nitrogen atoms, oxygen atoms, Fe^{3+} ions, and Fe^{2+} ions, respectively; hydrogen atoms and K^+ counterions are omitted for clarity) [93].

exceeding 350 K and semiconductor conductivity [93] of the $K_3Fe_2[PcFeO_8]$ films ($PcFe(OH)_8$ is iron 2,3,9,10,16,17,23,24-octahydroxyphthalocyanate) (Fig. 4d) 10–100 nm thick made it possible to observe the magnetoresistance effect already at room temperature. Unfortunately, the preparation of vertical spin valves with the molecular layer formed by 2D MOF is usually associated with difficulties of thin film formation by their deposition from a solution on the ferromagnetic electrode, which often requires to develop special methods of deposition or another architecture of the spintronic device. For instance, for the MOF $Cu_3(HHTP)_2$ (HHTP is 2,3,6,7,10,11-hexahydroxytriphenylene), the bottom electrode made of lanthanum–strontium manganate (LSMO) was functionalized by 3-aminopropyltrimethoxysilane: the required MOF was layer-by-layer deposited from the solution on 3-aminopropyltrimethoxysilane [100]. This approach made it possible to produce vertical spin valves containing uniform $Cu_3(HHTP)_2$ films with a thickness of 30–100 nm demonstrating a significant magnetoresistance at 10 K.

One of advantages of the compounds of this class, which was absent from their molecular analogs in molecular spintronics, is a high porosity of 3D MOFs. The predicted [101, 102] ability of MOFs to act as a porous matrix for magnetic guest molecules (e.g., SMMs) initiated active experiments on the development of strategies of production and characterization of similar systems. For instance, the use of high reso-

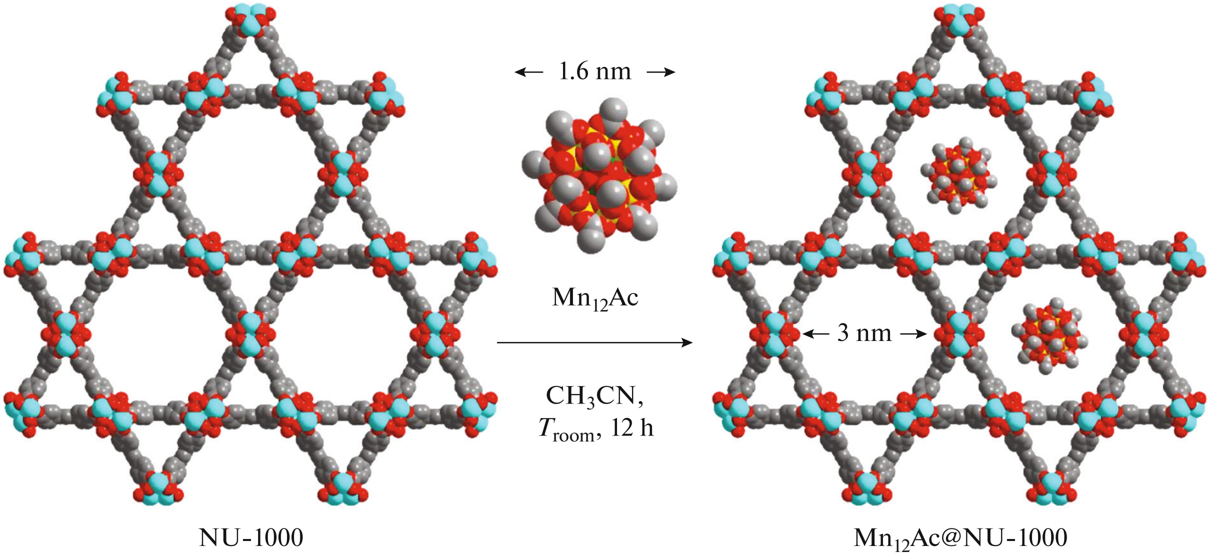

Fig. 5. Fragment of the crystal structure of MOF NU-1000 with the guest molecules of SMM $Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4$ [103].

lution transmission electron microscopy confirmed that the SMM molecules incorporated into pores of the MOF NU-1000 $[Zr_6(\mu_3\text{-}OH)_8(OH)_8(Tbapy)_2]$ (Tbapy is 1,3,6,8-tetra(4-carboxyphenyl)pyrene) (Fig. 5) from the solution [103]. A similar approach allows the properties of isolated SMMs to be retained in macroscopic films, which can be fruitful for manufacturing MRAM cells and other devices, whose operation is based on using spins of individual molecules.

The theoretical calculations show that MOFs provide broad possibilities of developing spintronic devices with characteristics tunable to researcher's needs by the choice of the metal ion, organic ligands, and guest molecules. However, these devices have not been accomplished yet, because there are no published experimental results for diverse MOFs that could allow one to choose the optimum method for the preparation of their thin films and an optimum architecture of the corresponding devices of molecular spintronics.

CONCLUSIONS

At the moment, molecular spintronics is a rapidly developed field of science at the nexus of physics and chemistry where special attention is given to molecular compounds acting as a transport layer in devices of various types (vertical spin valves, etc.), its possible interaction with ferromagnetic electrodes at the interface, and related spinterface effects. In addition to a high thermal stability and a possibility of preparing uniform films with the thickness from 10 to 200 nm, suitable compounds should have magnetism and conductance that can be controlled by molecular design methods. The majority of them are coordination compounds, such as organic semiconductors, single-molecule magnets, complexes with spin transitions, and metal-organic frameworks. The use of some representatives from the listed classes of substances in vertical spin valves and other molecular spintronic devices turned over traditional concepts in spintronics based on the behavior of inorganic materials. For example, the molecular compounds to which MOFs are disputably referred made it possible to discover the earlier unobserved effects of spinterface and negative magnetoresistance. In addition, the possibility of controlling the magnetic properties of the complexes that undergo spin transition or single-molecule magnets under the external action formed a basis for the new generation of nanosized polyfunctional devices.

It is important that many coordination compounds with a necessary set of chemical and physical properties were never tested inside molecular spintronic devices. However, this gap can easily be filled by specialists in the field of coordination chemistry, who possess resources of substances that are appropriate for these purposes but are kept on the shelves of chemical laboratories, know methods of their targeted functionalization, and wish to extend the range of possible practical applications of these compounds.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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