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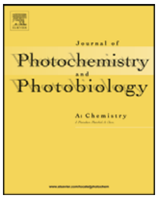

Heading to photoswitchable magnets

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ABSTRACT

In the review, available strategic approaches to the photomodulation of magnetic properties in molecular hybrid substances combining magnetic and optical properties have been considered. The developed approaches have been divided in two groups, namely, photocontrol of intra- and inter-molecular magnetic coupling and the effect of a photochromic sub-lattice on bulk behavior of a molecular magnet. In the frame of the first approach, the following has been considered: photoinduced phase transitions with the charge transfer and the change of a spin state of magnetic centers; photoswitching of intra-molecular exchange interactions between magnetic centers linked by a photochromic bridge; generation of high-spin organic molecules forming high-spin groups due to inter-molecular exchange interactions. In the frame of the second approach, hybrid polyfunctional compounds combining magnetic and photochromic sub-lattices in the same crystalline lattice, as well as intercalation of organic photochromes in cavities or inter-layer space of an organic magnetic (or vice versa) have been discussed. Creation of such materials allows not only unification of several functions in one lattice (this being important for reducing the size of the element base in devices), but also control and modification of these properties through synergetic effects. Fundamental results suggest that new materials for various practical applications can be created using crystal chemical design.

To control various physical–chemical properties, such as phase state of liquid crystals, refraction index, electronic conductivity, redox potential, electron transfer, non-linear optical properties, Faraday effect, etc., reversible photochromic transformations between two isomers with different absorption spectra and different geometric and electronic structure can be successfully used [1–8]. The influence of photochromic transformations on magnetic properties has been studied much less [9,10]. However, the development of bifunctional molecular materials with reversible modification of their magnetic properties due to photochromic transformations opens possibilities for synthesis of photochromic magnetic materials for different applications, for example, in displays, devices for storing and transformation of information and energy, sensors, etc. [11].

At present, there are several strategic approaches to photomodulation of magnetic properties in molecular compounds combining magnetic and optical properties. They can be tentatively divided into two groups: photocontrol of intra- and inter-molecular magnetic coupling (Fig. 1a and b) and influence of a photochromic sub-lattice on bulk behavior of molecule-based magnets (Fig. 1c and d). The first approach deals with the creation of molecules containing fragments or centers with unpaired spins and photochromic fragments. The second one is based on the combination of different types of light-sensitive and magnetic units in the same crystalline structure.

1. Photomodulation of intra- and inter-molecular magnetic coupling

1.1. *Photoinduced phase transitions with the charge transfer and change of the spin state of magnetic centers*

1.1.1. *Photoinduced magnetization of cobalt–iron cyanides*

Photoinduced magnetization was discovered in $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot 6.9H_2O$ (**1**), the analog of Prussian blue, by Fujishima and co-workers [12]. Irradiation of (**1**) by red light leads to the increase of critical temperature T_c from 16 to 19 K. In addition, after irradiation, magnetization grows essentially below 26 K in the ferromagnetic region, and after the further thermal treatment, it comes back to the initial state (Fig. 2). These photoinduced changes of magnetic properties are due to the increase of the contribution of paramagnetic chains $Fe^{III}(S = 1/2)$–CN–$Co^{II}(S = 3/2)$ to the structure of the salt, as compared to that of diamagnetic ones, $Fe^{II}(S = 0)$–CN–$Co^{III}(S = 0)$. A new magnetic phenomenon – "photoinduced magnetic pole inversion" – has been discovered, which arises even without external magnetic field [13]. The authors have

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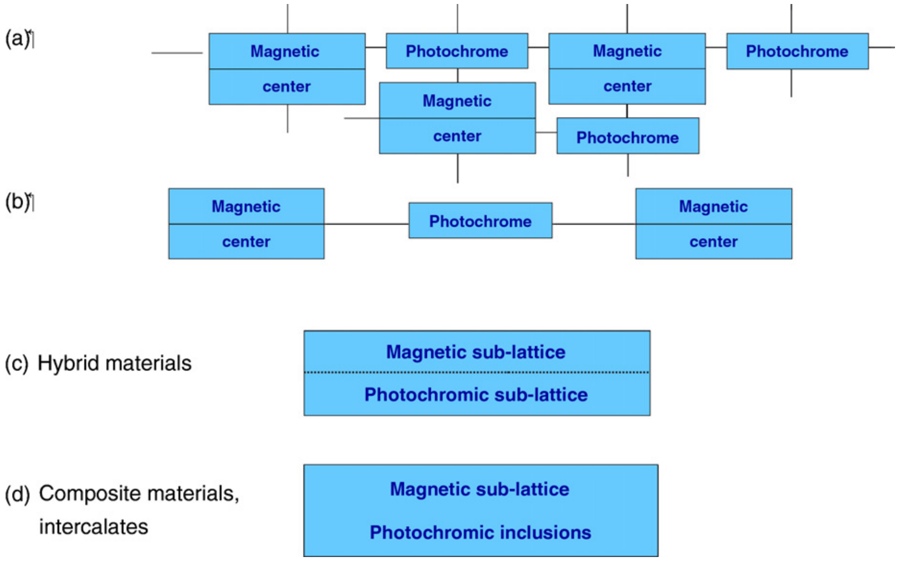

Fig. 1. Photoswitching of physical–chemical properties via photochromic transformations.

synthesized a new class of triple metallic salts (analogs of Prussian blue) $[Fe^{II}{}_xMn^{II}{}_{1-x}]_{1.5}[Cr^{III}(CN)_6]\cdot zH_2O$, which involves a photosensitive fragment Fe^{III}–Cr^{II}. Upon photoirradiation, a reversible photoinduced magnetization, and sometimes variation of the magnetization sign, arises due to superexchange coupling between neighboring fragments Fe^{II}–Cr^{III} and Mn^{II}–Cr^{III}.

The photomagnetic effect should have been more efficient in the case of the nanoparticles as compared to the bulk. This effect is related to better light penetration due to film processing. Indeed, in ref. [14], the preparation of anisotropically shaped nanoparticles of $Mo(CN)_6Cu_2$ and their photomagnetic behavior when processed as films have been reported. Upon irradiation, an electron transfers from one diamagnetic Mo^{IV} center to a Cu^{II} site creating ferromagnetically coupled Mo^{V}–CN–Cu^{II} units within the compound.

1.1.2. Photoinduced phase transition with the charge transfer in mixed-valence iron complexes $[R_4N]$ $[Fe^{II}Fe^{III}(dto)_3]$ $(dto = C_2O_2S_2)$.

In complexes of transition metals with d^4–d^7 configuration, spin transitions between low-spin and high-spin states are possible. For mixed-valence complexes, with spin states being in a spin-crossover region, various types of spin-crossover complexes have been discovered, which are characterized by variation of the spin state and charge between neighboring metal ions due to the phase transitions [15,16]. In spin-crossover systems, Gibbs energy $(G = H - TS)$ is characterized by a dominating enthalpy member H for a low-spin phase, and a dominating entropy member $(-TS)$ for a high-spin state.

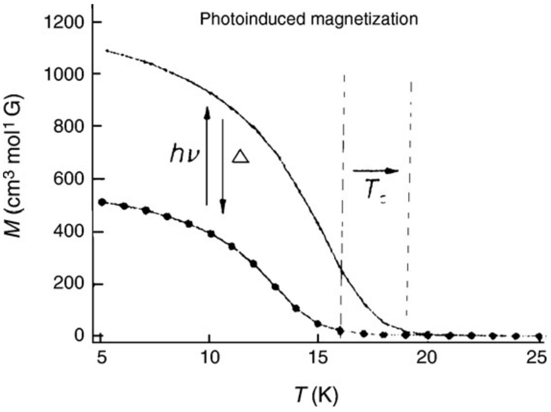

Fig. 2. Photoinduced magnetization of cobalt–iron cyanides.

In $Fe^{II,III}$ mixed-valence complexes, spin states Fe^{II} and Fe^{III} convert simultaneously with the charge transfer to minimize free energy of Fe^{II} and Fe^{III} sites.

From this standpoint, Kojima et al. have synthesized and studied mixed-valence Fe complexes $(n\text{–}C_nH_{2n+1})_4N[Fe^{II}Fe^{III}(dto)_3]$ $(dto = C_2O_2S_2)$ [17–20]. Thermoinduced phase transitions have been discovered, which are accompanied by spin transitions (Fig. 3). In a high-temperature phase, Fe^{III} $(S = 1/2)$ and Fe^{II} $(S = 2)$ are coordinated by six S atoms and six O atoms, respectively. In a low-temperature phase Fe^{III} $(S = 5/2)$ and Fe^{II} $(S = 0)$ ions, on the contrary, are coordinated by six O atoms and six S atoms, respectively. Phase transitions in the investigated salts depend on the size of intercalated cation, thus providing a possibility to control magnetic properties of $[Fe^{II}Fe^{III}(dto)_3]^-$ with a two-dimensional honeycomb network structure through isomerization of the intercalated cation.

However, photoinduced spin transitions for Fe complexes have been observed for the first time for $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-tetrazole) [21]. Later, Gutlich et al. showed [22] that green light could switch a low-spin state into a high-spin one, which does not have any lifetime limits at low temperature. Red light resets a metastable high-spin state to a low-spin one. This phenomenon was called light-induced excited spin state trapping—LIESST. LIESST can be used in optical information technology.

For spin-crossover Fe^{III} complexes, a long-living high-spin photoinduced state due to a strong π–π-inter-molecular interaction has been first observed by Fujishima and co-workers in complex $[Fe^{III}(pap)_2]ClO_4$ [23]. In ref. [24], LIESST effect has been discovered for Fe(II) complex with ligands containing 1,3-dithiolate ring. The authors succeeded in X-ray investigation of this complex in high- and low-spin states and in determining its specific structural features.

In ref. [25], complexes of iron(II) (and, rarely, other metal ions) are described, which can be switched between their high- and low-spin states by different physical stimuli. At low temperatures, it is possible to trap a compound in a metastable excited spin-state which, in favorable cases, may be stable to thermal relaxation below temperatures as high as 130 K.

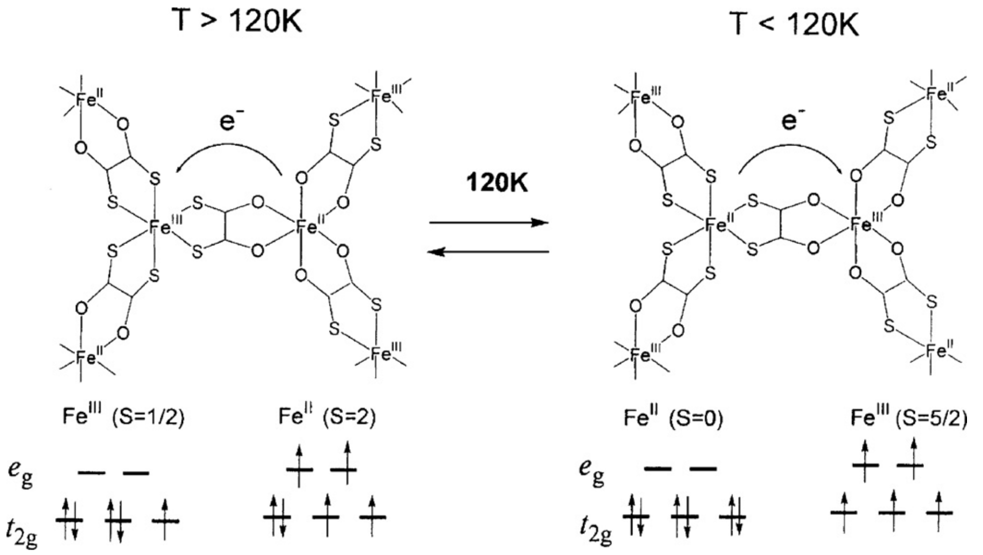

Fig. 3. Photoinduced phase transitions with the charge transfer in mixed-valence iron complexes $[R_4N][Fe^{II}Fe^{III}(dto)_3]$ ($dto = C_2O_2S_2$).

1.2. Photomodulation of intra-molecular magnetic coupling

Magnetic interactions between different magnetic centers in the same molecule depend mainly on a binding structural bridge and mutual symmetry of the orbitals [26]. If the binding bridge contains a photochromic fragment, a photochemical transformation in it will cause the change of interactions between the magnetic centers. Thus, it is possible to control magnetic properties of the molecule photochemically.

Hamachi et al. have for the first time studied a biradical molecule with two stable nitronyl nitroxide [S = 1/2] radicals bound covalently by a photochromic azobenzene fragment [27]. Photomodulation of magnetic coupling in the molecule due to trans–cis isomerization was studied by EPR spectroscopy and magnetic susceptibility measurements. Ferromagnetic exchange between the centers was discovered, and the influence of photoisomerization on the energy of exchange interactions ($2J/k_B$) and Weiss constant (θ) was studied.

Later, Matsuda and Irie [28] have studied thoroughly a two-spin molecular system with two nitronyl nitroxide radicals joined by a photochromic diarylethene bridge (Fig. 4). Diarylethenes have good photochromic characteristics, namely, thermal stability of both isomers up to 100 °C, high fatigue strength (~10^4 cycles of phototransformations) and a very fast photo-response (~1 ps), this being promising for their application in optoelectronics.

Two radical centers in the molecule interact magnetically through a π-conjugated photochromic coupler, with the energy of exchange interaction being J. The sign of exchange interaction depends on topology of the π-system.

In fact, in the studied compound, the open blue form with disjointed π-system is an “off” state, while the closed red-violet form with a flat π-system is an “on” state. Upon photoirradiation, the photochromic system changes reversibly intra-molecular magnetic interactions. Antiferromagnetic interaction between two nitronyl-nitroxide radicals increase from $2J/k_B = -2.2$ K in the “off” state to $2J/k_B = -11.6$ K in the “on” state.

In ref. [29], Nakatsuji describes organic radical compounds that exhibit photo-responsive properties by illumination. They consist of a variety of photo-responsive π-electron moieties, such as azobenzene, diarylethene, biindenylidene, terphenoquinone, anthracene, naphthopyran, arylimine or hexaarylbiimidazoles bearing stable organic radicals or generating organic radicals as spin centers for magnetic properties. The author is focusing mainly on the structural variation of the organic radical compounds. However, these organic spin systems are still in their infancy from the viewpoint of magnetic switching systems and there are some limitations in organic photo-responsive systems (e.g., relative instability of organic radicals on exposure to light and heat, etc.), but the structural versatility of organic radicals and photochromic systems provides a wide range of possible candidates of organic photo-responsive spin systems.

1.3. Photomodulation of intra- and inter-molecular magnetic coupling

1.3.1. Generation of high-spin nitrene molecules by low-temperature photolysis and γ-radiolysis of aromatic azides

Recently, much attention has been paid to studying high-spin nitrenes, promising organic magnetic substances for molecular electronics [30–33]. These substances are usually obtained by low-temperature solid-phase photolysis and γ-radiolysis of aromatic azides, whose aromatic ring is protected from undesired photochemical intra-molecular reactions with nitrene centers by appropriate substituents [34–37]. Photolysis and γ-radiolysis of

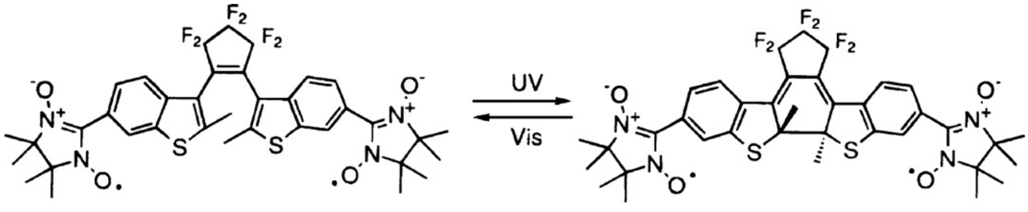

Fig. 4. Photoswitching of intra-molecular magnetic interactions in nitronyl nitroxide diarylethene molecules.

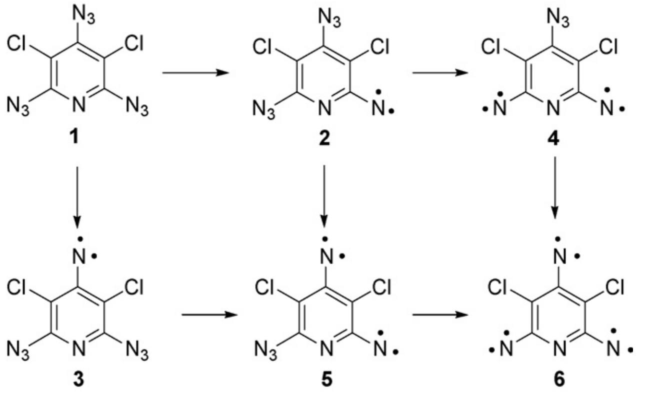

Fig. 5. Generation of high-spin nitrenes by low-temperature photolysis and γ-radiolysis of the pyridine azide-derivative.

2,4,6-triazido-3,5-substituted pyridine **1** involves a consecutive formation of triplet (two-electron, S = 1) nitrenes **2**, **3**; quintet (four-electron, S = 2) dinitrenes **4** and **5**; and six-electron septet trinitrene **6** (S = 3) (Fig. 5). A singlet form of EPR spectra without SFS suggests a strong exchange interaction between the electrons in the molecule, while different resonance values of the magnetic field for each individual nitrene provide a reliable registration and identification of nitrenes by EPR method [38–40].

In the crystals of initial azides, the forming nitrene molecules are not able to re-arrange into azacyclo-products and to capture hydrogen atoms from the environment, while the only possible way of triplet arylnitrenes destruction due to their dimerization into azo-compounds can be blocked by the crystalline structure. Furthermore, with a certain arrangement of the initial azides molecules, triplet arylnitrenes generated in their crystals are able to interact magnetically with each other to yield assemblies of paramagnetic molecules with S > 1. In the literature, the only example of such interaction type is available [41], i.e., triplet pairs generated by UV-photolysis of phenylazides crystals form excited quintet states due to the exchange interaction of antiferromagnetic type.

Photolysis of crystalline diazides **1** (Fig. 6a) by the light with $\lambda = 355$ at 77 K results in arising the signals of X_2- and Y_2-transitions of triplet nitrenes **2** in the region of 670 nm. In addition, in EPR spectra rather weak and widened signals with maxima at 163 and 294 mT are observed. Triplet–triplet inter-molecular pairs of nitrenes forming a quintet spin state are the most probable source of these signals. The formation of such state is possible if the distance between nitrenes is <4.8 Å and the C–N bonds are located at 120–140 °. In the studied structure (Fig. 6b), the angle between the C–N bonds in the neighboring molecules is 136°, and the $N_\alpha \cdots N'_\alpha$ distance is 3.35 Å.

Thus, such transformation of initially diamagnetic crystalline substances into organic materials with a high concentration of paramagnetic centers is of a big practical interest.

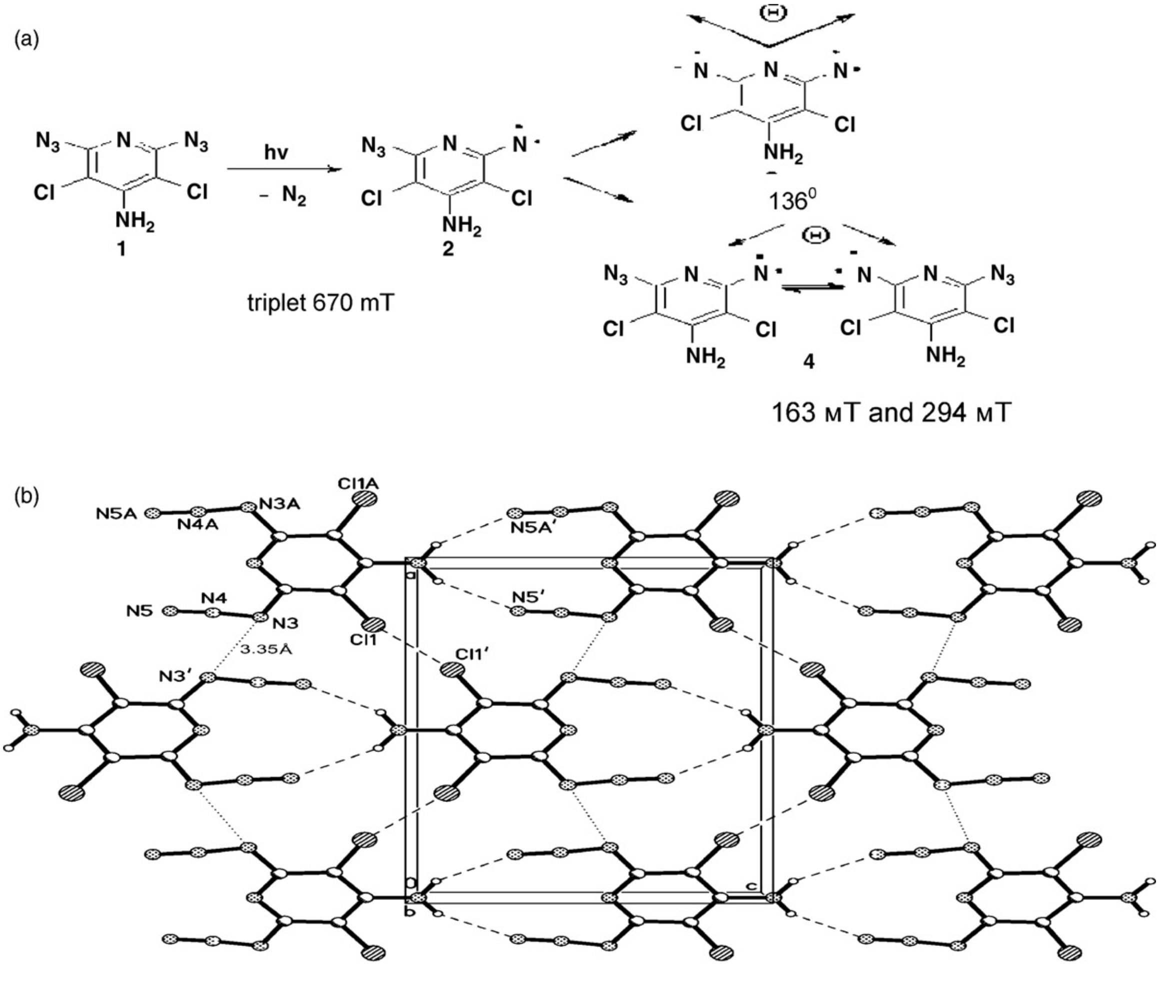

Fig. 6. Photomodulation of high-spin nitrenes in the crystals of aromatic diazides (a) and the structure of the initial nitrene 2,6-diazo-4-amino-3,5-dichloro-pyridine (**1**) (b).

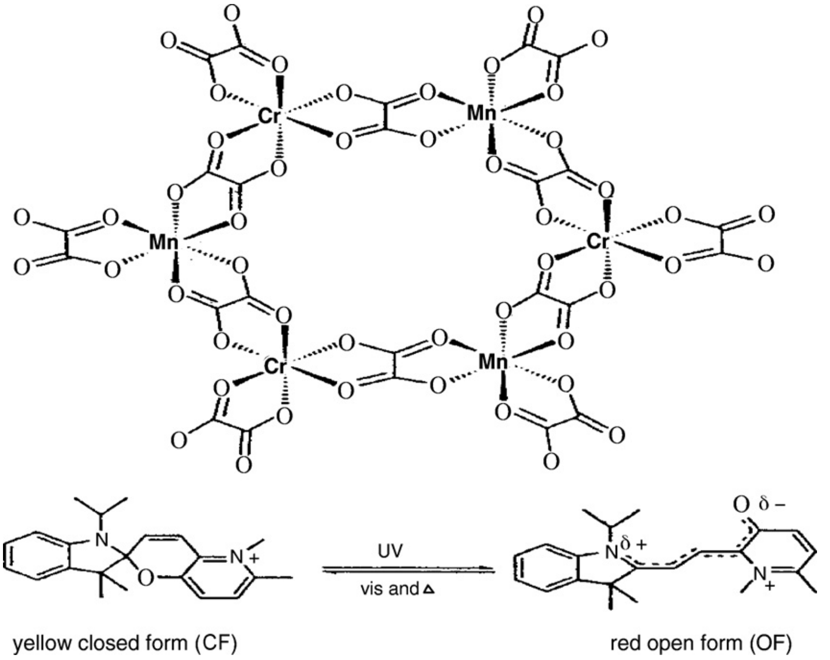

Fig. 7. Photochromic magnets based on magnetic anions of tris(oxalate)metals and photochromic cations of spiropyrans—SP$^+$[M^{II}M^{III}(ox)$_3$]$^-$.

2. Photochromic molecular-based magnets

Bulk magnetic properties of materials depend both on the crystalline structure and on microstructural changes. At present, two approaches to photocontrol of magnetic properties of such materials are being developed, namely, intercalation of organic photochromes into the cavities or inter-layer space of an organic magnetic (or vice versa), and development of hybrid crystalline materials combining a magnetic and a photochromic sub-lattices in the same crystalline lattice. From the basic point of view, the first direction can be considered as a particular case of the second direction, so we will start from the second approach.

2.1. Hybrid photochromic magnets

To create polyfunctional compounds containing different functional sub-lattices, approaches based on the principles of crystal

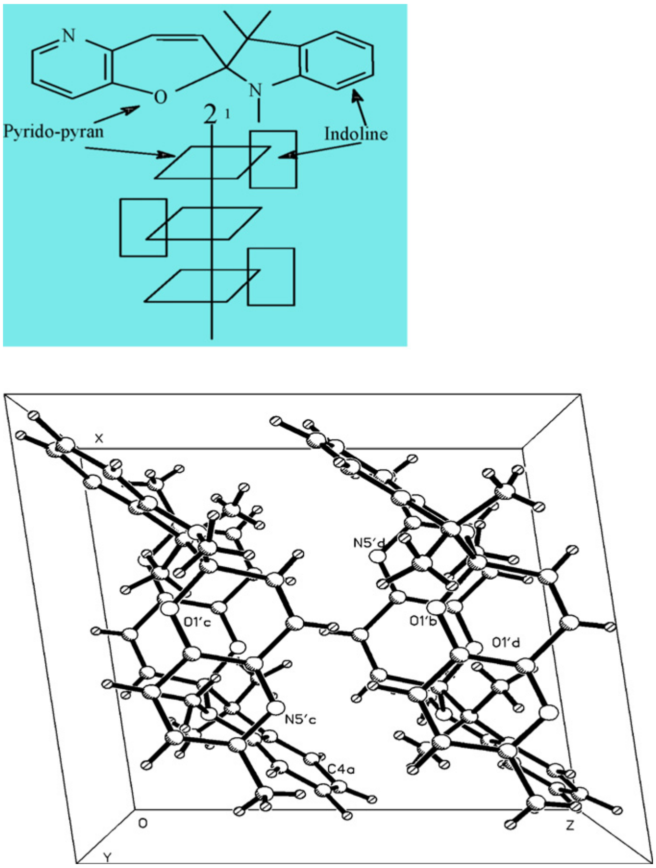

Fig. 8. The molecules arrangement in the crystals of neutral SP (a) and schematic view of the molecules arrangement (b).

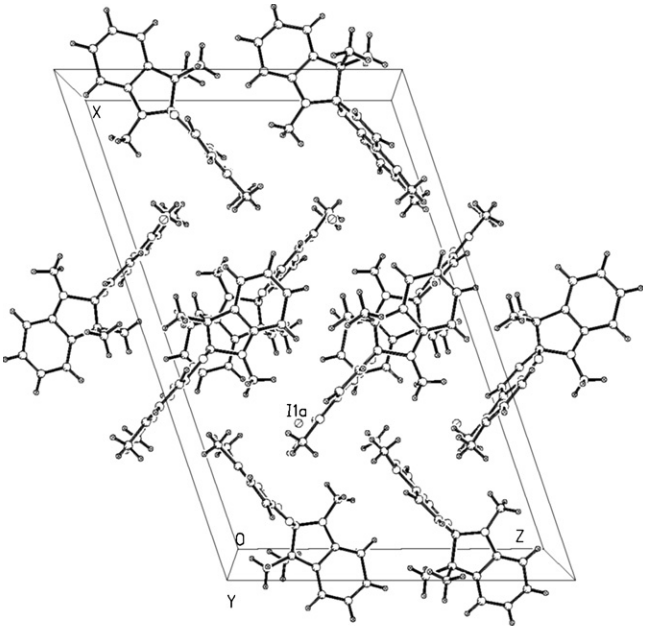

Fig. 9. Specific features of SP$^+$ arrangement in photochromic crystals of SP$^+$X$^-$ salts.

$$SP^{+}I^{-} \xrightarrow{AgCl} SP^{+}Cl^{-} \xrightarrow{K_3Cr(ox)_3 \cdot 3H_2O} SP_3Cr(ox)_3 \cdot 4H_2O \xrightarrow{MnCl_2 \cdot H_2O} SPMnCr(ox)_3 \cdot H_2O$$

Scheme 1.

chemical engineering have been developed during latest years. Such approaches provide a possibility not only to select necessary functional construction blocks, but also to find crystal chemical conditions of their compatibility in the same crystalline lattice, and to develop synthetic methods. Creation of such materials allows not only unification of several functions in one lattice (this being important for reducing the size of the element base in devices), but also control and modification of these properties through synergetic effects.

2.1.1. Photochromic magnets based on magnetic tris(oxalate)metals and photochromic spiropyrans

Salts of bimetallic oxalates $Cat^{+}[M^{II}M^{III}(ox)_3]^{-}$ with the anion having a layered honeycomb arrangement favorable for exchange interactions between metallic magnetic centers are promising for the creation of molecular-based magnetics [42] (Fig. 7). Non-functional low-symmetry bulky cations (8–14 Å), mainly alkylammonium ones, are located between anionic layers.

Photochromic spiropyrans (SP) and spirooxazines (SO) are perspective photochromic substances for the creation of systems for recording, storing and processing of information, as well as for optical switches of properties of functional materials [1]. However, in crystals, photochromic transformations of SP and SO, which are due to the rupture of C_{spiro}–O bond and further isomerization of molecules (Fig. 7), are impeded because of a dense arrangement of the molecules in the lattice.

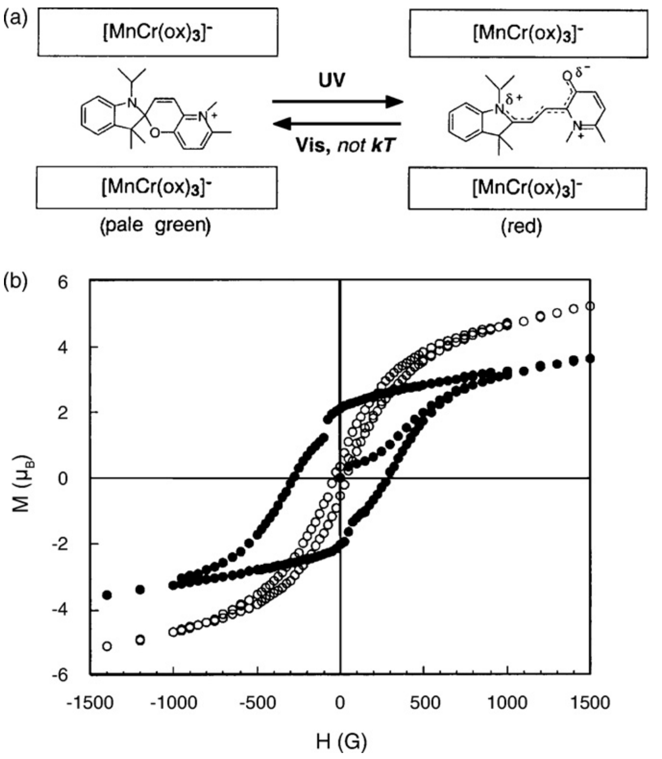

Fig. 10. Schematic structure of hybrid SP(I) $[Mn^{II}Cr^{III}(ox)_3]$ with alternating ferromagnetic and photochromic layers (a) and hysteresis loop at 2 K of the SP(I) $[Mn^{II}Cr^{III}(ox)_3]$ (○, before; ●, after UV-irradiation) (b).

However, recently Benard and Yu [43–45] and then Aldoshin et al. [46–48] have synthesized and studied SP salts ($SP^{+}X^{-}$) having photochromic properties in the crystalline state independently on the anion. Aldoshin et al. have thoroughly studied specific features of the crystalline structure of $SP^{+}X^{-}$, which are responsible for photochromic transformations of SP^{+} in the solid phase ($X^{-} = Cl^{-}$, I^{-}).

A principally new type of arrangement as compared to neutral SP was shown to be realized in the studied $SP^{+}X^{-}$ containing quaternary positive N^{+} in the pyridine rings annelated to the pyran fragments. In the crystals of neutral SP, the pyridopyran moieties responsible for photochromic transformations are densely arranged in the stacks. Such arrangement prevents photochromic transformations in crystals (Fig. 8). In $SP^{+}X^{-}$ crystals electrostatic interaction of X^{-} with quaternary N^{+} prevents the stack arrangement of the pyridopyran fragments. The indoline fragments are stacked, while the pyridopyran ones, together with X^{-} anions, are located in a loose inter-stack space, such packing being favorable for reversible photochromic transformations in crystals (Fig. 9). The arrangement of $SP^{+}X^{-}$ salts does not depend on the anion size, but it is very sensitive to substituents in the indoline fragment of SP^{+} [48].

Therefore, photochromic cationic construction unit SP^{+} can easily replace non-functional cations between magnetic anionic 2 D-layers of bimetallic oxalates.

Such photochromic magnet with alternating ferromagnetic and photochromic layers (Fig. 10a), with $T_c = 5.5$ K, was obtained for the first time by Benard et al. [45] who used a cationic pyridopyran SP^{+} as a counter-ion to anion $[Mn^{II}Cr^{III}(ox)_3]^{-}$ with a layered honeycomb arrangement. SP^{+} in such a system has a unique feature, namely, both a closed form and photoinduced open merocyanine (MC) form are thermally stable, as distinct from neutral SP. The latter ones are non-photochromic in the crystalline state with only one form being thermally stable. Upon UV-irradiation, irreversible changes of magnetic properties of the anionic sublattice occur: initially a very soft magnet transforms into a more rigid one, this being evident from the widened hysteresis loop (Fig. 10b).

This substance has been obtained according to Scheme 1, with the intermediate chromo(tris)oxalate salt of the corresponding SP^{+}, $(SP)_3[Cr(ox)_3]$.

This salt has been isolated and studied by Aldoshin et al.[1] The crystalline structure is formed by structural units $3SP^{+}.[Cr(ox)_3]^{3-}$, with SP^{+} being directed to the oxalate-groups by their charged pyridopyran fragments. The indoline fragments of SP^{+} are directed to the cavities between the structural units (Fig. 11a).

In the photochromic crystalline structure of salts $SP^{+}X^{-}$ [46–48], the indoline fragments are arranged in stacks, while the pyran fragments are located in the loose inter-stack space. The indoline part, not the pyran one, appeared to be the most "loose" in the cation. However, due to loose packing of the whole structure ($\rho = 1.302$ g/cm^3), enough free space is available for isomerization of the cation into merocyanine open form.

Similar to $SP^{+}X^{-}$ salts, in crystals of $SP_3[(Cr(ox)_3]$ fast reversible photochromic transformations occur, namely, formation of MC form ($\lambda_{max} = 574$ and 603 nm) under UV-irradiation, and the reverse

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[1] Unpublished data.

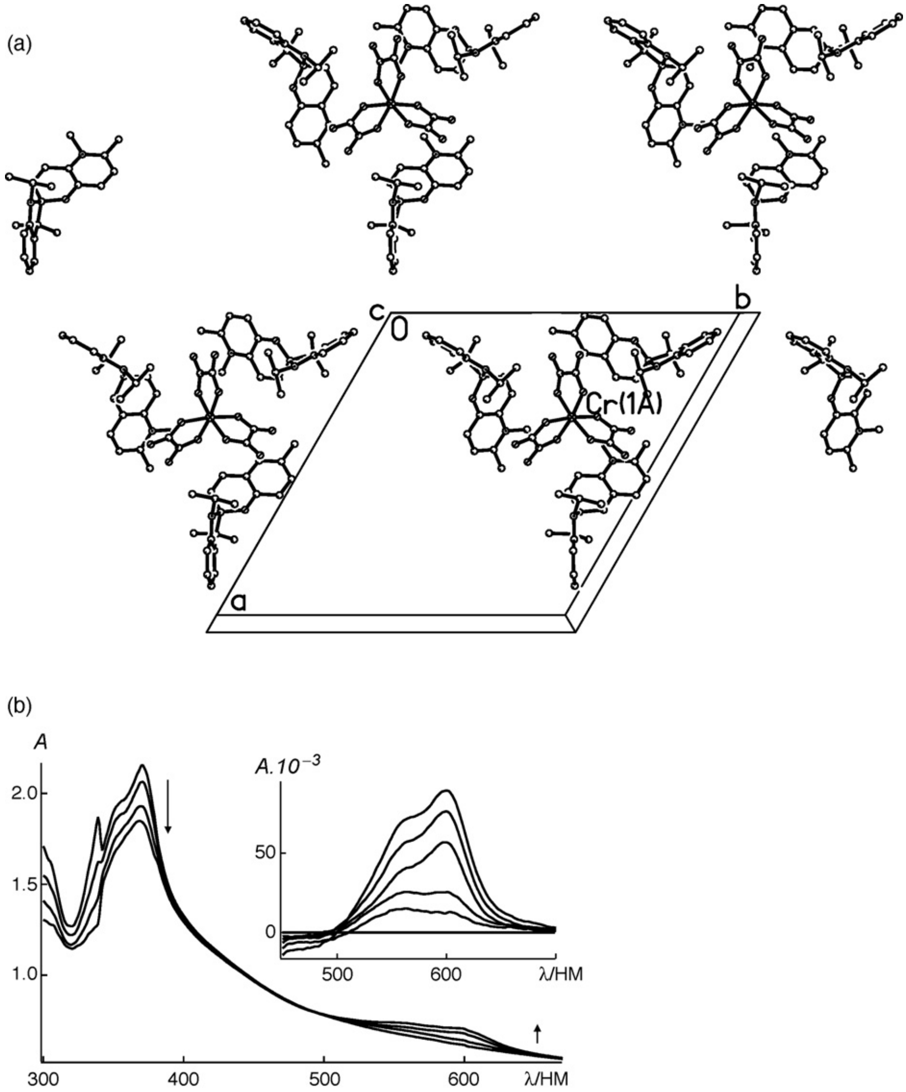
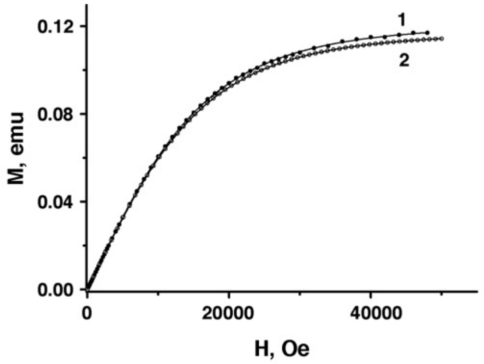


Fig. 11. The structure of paramagnetic salt $(SP)_3[Cr(ox)_3]$, the intermediate in the synthesis of photochromic molecular magnetics (a) and its photochemical properties (b).

reaction of cyclization under the visible light action. The irradiated crystals bleach slowly in the dark (Fig. 11b).

The samples are paramagnetic. Below 14 K, UV-irradiation results in a reversible reduction of an average spin and almost four-fold increase of exchange interactions of ferromagnetic type (Fig. 12). The discovered photomagnetic effects are due to the influence of SP^+ photoisomerization on the magnetic centers.

Basing on SP^+ containing the pyridine ring annelated not to the pyran but to the benzopyran fragment, the paramagnetic salt has been obtained, with SP^+ being in the open MC^+ form ($MC^+[Cr(ox)_3]^-$) (Fig. 13a). $[Cr(ox)_3]^-$ anions are located in the triclinic P1 unit cell along plane “obc”, while MC^+ are stacked between these planes approximately perpendicular to axis “c”, and, by overlapping mutually along axis “b”, they form blocks. In the blocks, the nearest molecules are packed in dimeric associates in “head to tail, tail to head” mode, while the dimeric associates are located with the shift along axis “b” in “head to head”, “tail to tail” mode (Fig. 13b). In spite of a stack arrangement of MC^+, packing density is low ($\rho = 1.371\ g/cm^3$). Nevertheless, crystalline samples of $(MC)_3[Cr(ox)_3]$ are not photochromic.



	Before irradiation	After irradiation
Average spin, s	1.42±0.02	1.37± 0.02
Exchange interaction, T	0.04 K	0.51 K

Fig. 12. Magnetic moment M of $(SP)_3[Cr(ox)_3]$ vs. the magnetic field at $T = 2$ K before irradiation (1) and after UV-irradiation (2) at room temperature.

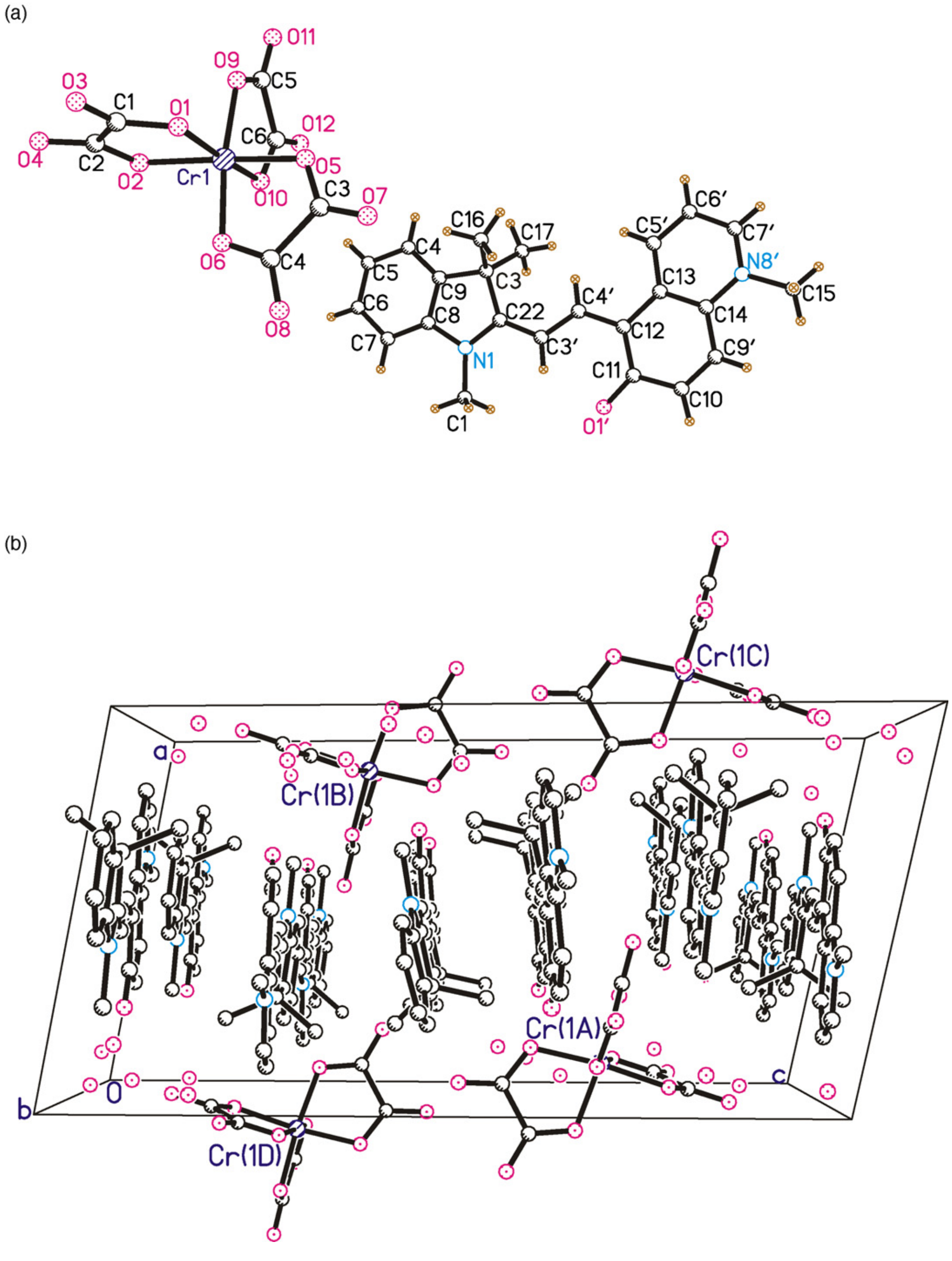


Fig. 13. The molecular structure of MC^+ and $[Cr(ox)_3]^-$ (a) and the crystalline structure of paramagnetic salt $(MC)_3[Cr(ox)_3]$ (b).

In the temperature range 300–230 K, $MC_3[Cr(ox)_3]$ sample has a constant effective magnetic moment $\mu_{eff} = 4\,\mu_B$, this being close to a theoretical one, 3. 87 μ_B, calculated for $S = 3/2$ and $g = 2$ (Fig. 14).

Magnetic moment *M* vs. magnetic field before and after irradiation at 2 K has been obtained (Fig. 15). UV-irradiation was shown to lead to M growth. Approximation of field dependencies by Brillouin function with exchange parameter T_0 [49] provided the value of this parameter and of an average spin of the particles in the sample before and after irradiation. The obtained values of spins coincide with the calculated values and those obtained experimentally at high temperatures. The parameters of exchange interaction confirm the conclusion about the change of exchange interactions character under irradiation.

Aldoshin et al. [50] have for the first time obtained salts of benzopyran SP^+X^- with quaternary N^+ in the pyridine ring, which is not annelated to the π-conjugated pyran fragment, but is located in the side aliphatic chain.

Polycrystalline gray-green powder of a photochromic ferromagnetic based on this SP (SP^+(II) $[Cr^{III}Mn^{II}(ox)_3]^-$) was synthesized by a four-step method (Fig. 16). The reaction mixture was constantly irradiated by light with $\lambda > 500$ nm in order to shift the equilibrium between two SP(II) forms in polar solvents to the closed form [50].

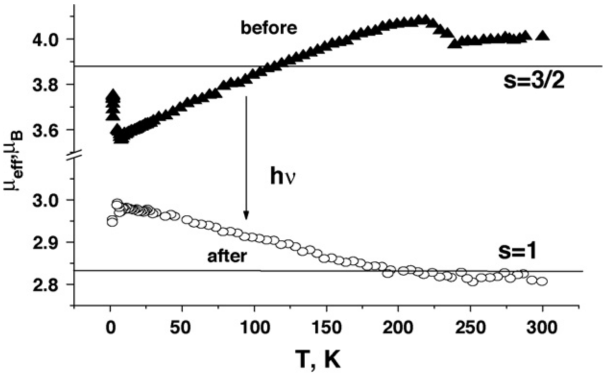


Fig. 14. Temperature dependence of effective magnetic moment of complex $(MC)_3[Cr(ox)_3]$ before (▲) and after (○) UV-irradiation.

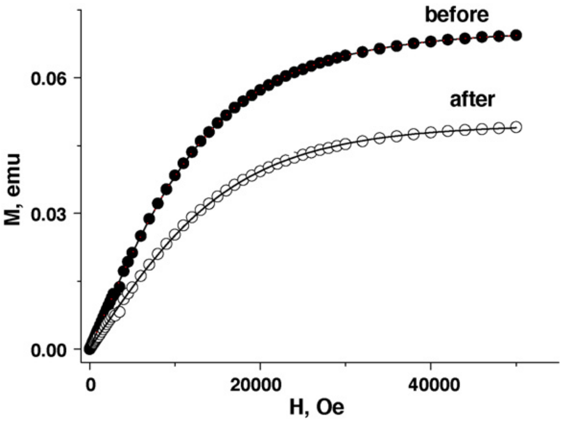


Fig. 15. Magnetic moment of sample $(MC)_3[Cr(ox)_3]$ vs. the magnetic field at 4 K before and after UV-irradiation. Approximation of the experimental data by modified Brillouin function with exchange parameter To is marked with solid lines.

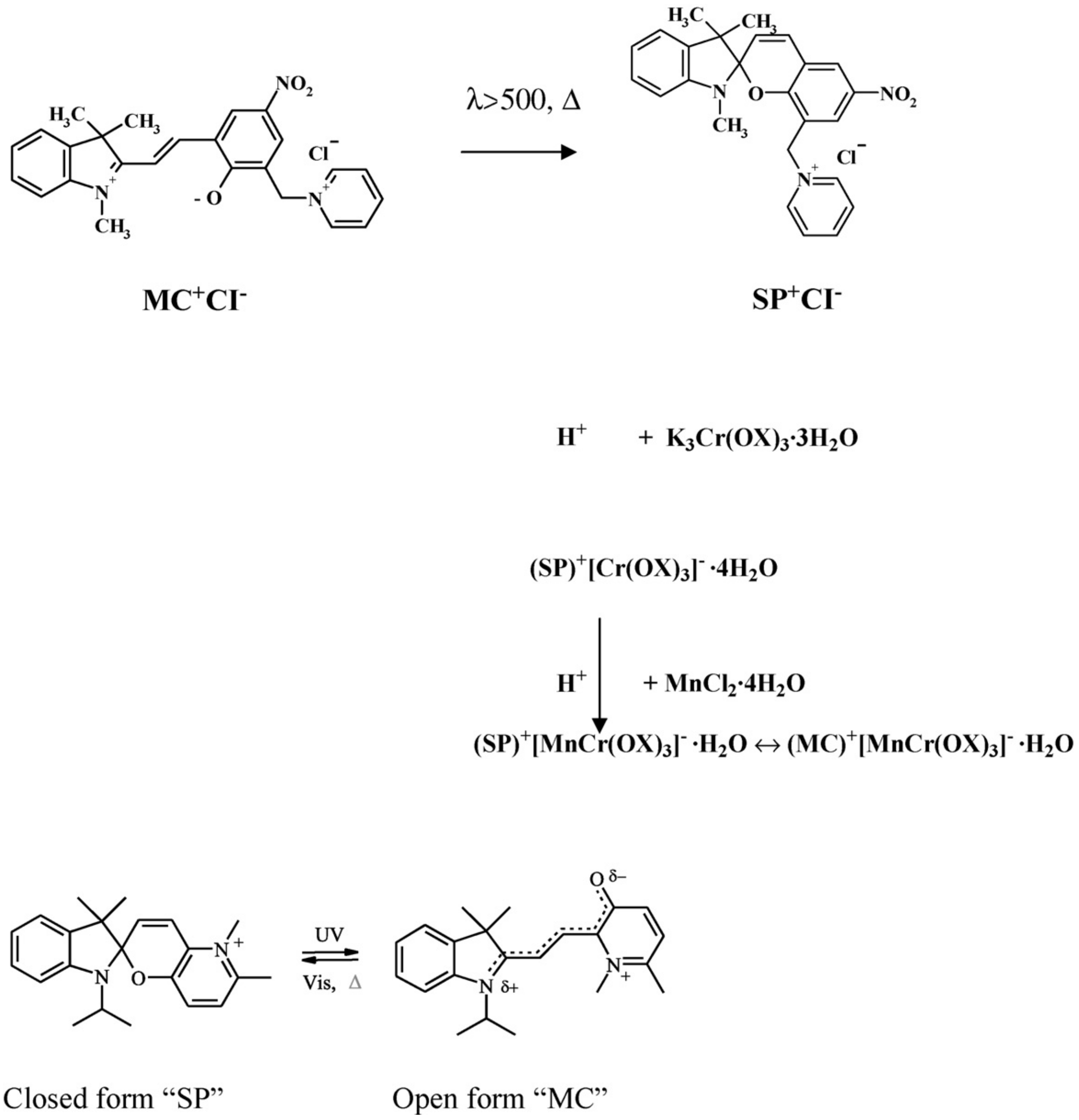


Fig. 16. Synthesis of hybrid photochromic magnetics $SP(II)[MnCr(ox)_3]$ based on SP with quaternary N^+ atom in the pyridine ring, which is located in the side aliphatic chain.

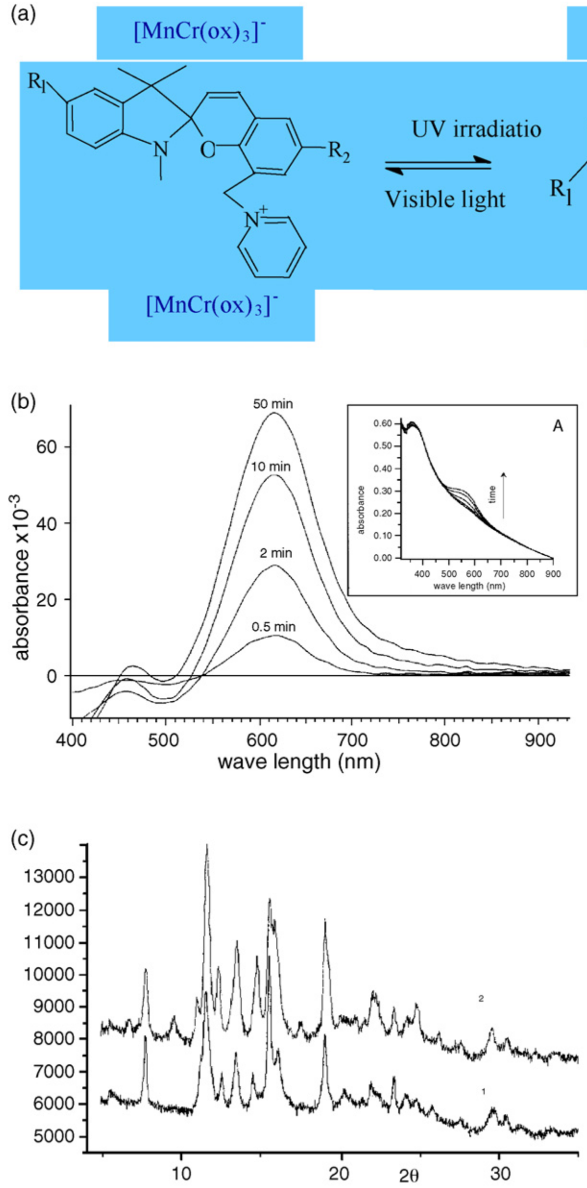


Fig. 17. Hybrid system SP(II)[CrMn(ox)$_3$] (a); reversible photochromic transformations of SP(II)[CrMn(ox)$_3$] (b); reversible structural transformations of hybrid system SP(II)[CrMn(ox)$_3$] (1, before; 2, after UV-irradiation) (c).

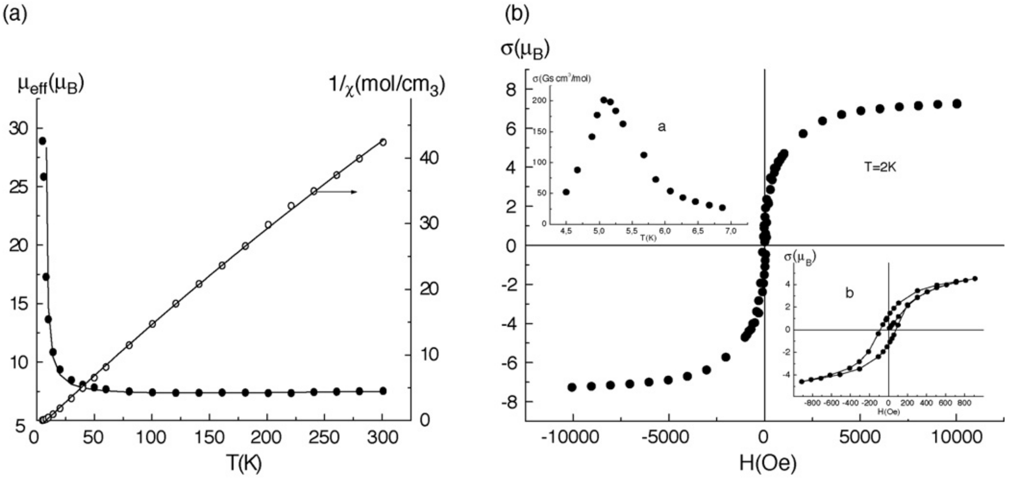


Fig. 18. Effective magnetic moment (●) and reverse magnetic susceptibility (○) vs. temperature for SP(II)[CrMn(ox)$_3$] in the range of 5–300 K (a); field dependence of magnetization for SP(II)[CrMn(ox)$_3$] at 2 K. Insert (a): $\sigma(T)$ in a small magnetic field. Insert (b): Hysteresis loop (b).

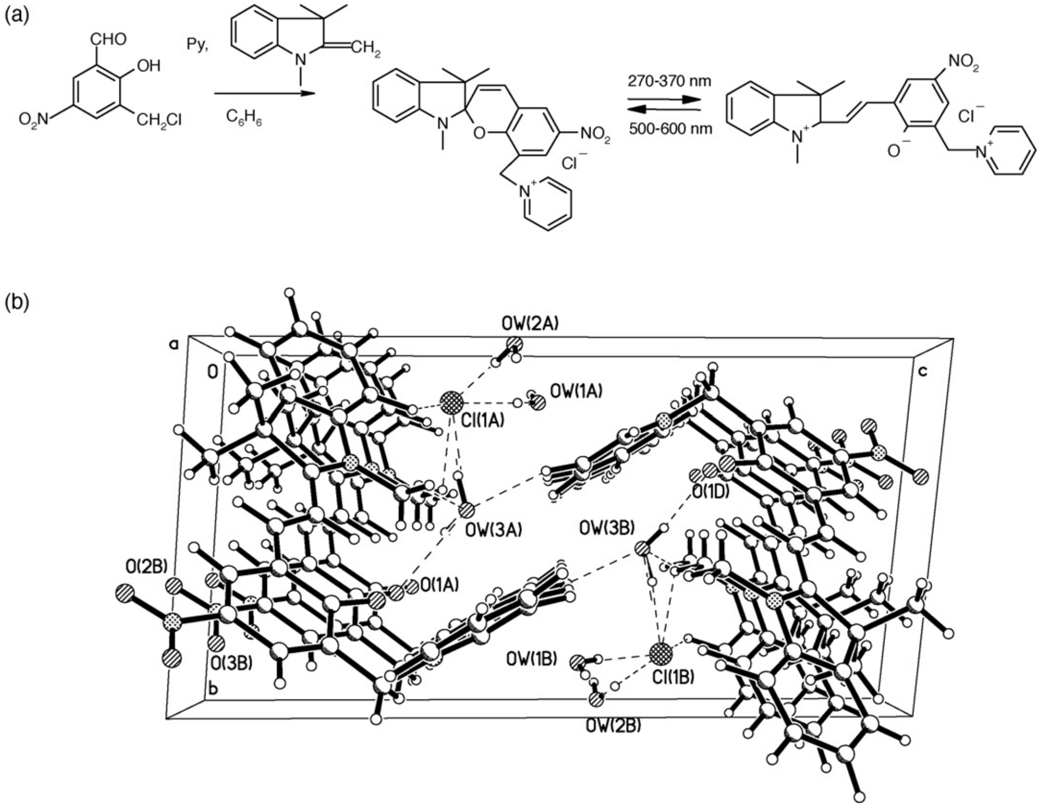


Fig. 19. The scheme for synthesis of MC (a) and the structure of $(MC)_3Cr(ox)_3$ crystals (b).

The obtained salts $SP^+[CrMn(ox)_3]^-$ [50,51], similar to the initial salts SP^+X^-, exhibit reversible photochromic properties in the crystalline state (Fig. 17a). Both forms are available in the samples before irradiation, and they transform into each other upon UV-irradiation (Fig. 17b). The rate of balancing in the dark is negligible ($k = 10^{-6}$ to $10^{-7}\,s^{-1}$).

UV-irradiation of the samples is accompanied by noticeable changes in the powders diffraction patterns, thus suggesting considerable structural rearrangements with the crystalline unit cell being preserved (Fig. 17c).

The studied hybrid substances are the ferromagnetics with Curie temperature about 5 K (the latter was determined from the temperature dependence of magnetization $\sigma = \chi H$ at 2 K).

μ_{eff} value at 300 K equal to ~7 M.B. is in a good agreement with the calculated 7.07 M.B. ($g = 2$) for weakly interacting ions Mn(II) and Cr(III). The field dependence of magnetization at 2 K has a hysteresis (Fig. 18). Saturation of magnetization is achieved at about 10,000 Oe and is 6.8–7.0 M.B. Such saturation is lower than can be expected for configuration Cr(III) and Mn(II) with 3 + 5 = 8 spins. Coercitivity in various substances is in a range of 30–80 Oe and depends, apparently, on specific crystalline features. However, unlike photochromic magnetics SP^+(I) $[CrMn(ox)_3]$ [45], obtained by Benard et al., in the studied hybrid substances no noticeable influence of SP^+ photochromic transformations on rigidity of the magnetic sub-lattice was observed. This can be due to the fact that in pyrido-pyran SP(I) quaternary N^+ is in the π-conjugated part of SP, which is responsible for photochromic transformations, while in benzopyran SP(II), N^+ is located in the side chain of the substituent.

As it was mentioned, hybrid photochromic magnetics could be only obtained upon irradiation of the reaction mixture and shifting the equilibrium $SP^+(II) \leftrightarrow M^+(II)$ to the closed SP^+ form. Aldoshin and co-workers succeeded in isolating and studying both $SP(II)^+Cl^-$ and $MC(II)^+Cl^-$ forms in the crystalline state [52] (Fig. 19a).

In crystals of $SP^+(II)Cl^-$, reversible photochromic transformations are observed under the light action. Cation $SP(II)^+$ obtained in the closed form transforms to the open $MC(II)^+$ form under UV-irradiation (270–370 nm), and upon irradiation with visible light (500–600 nm) the crystals bleach (Fig. 19a). Salt $SP(II)^+Cl^-$ could not be studied by X-ray analysis. Apparently, the structure similar to $SP(II)^+$, which is favorable for photochemical transformations, is preserved in photochromic magnetics, too.

In crystals of salt $MC(II)^+Cl^-$, no photochromic transformations were found upon stationary irradiation. In the crystalline structure of $MC(II)^+Cl^-\cdot 3H_2O$, $MC(II)^+$ cations are planar, and they form dense translational stacks, with Cl^- and water molecules forming a network of hydrogen bonds located in the channels (Fig. 19b). The structure is additionally stabilized by electrostatic interactions between the indoline N^+ and the phenolate O^- (3.293 Å), and quaternary N^+ of the pyridine ring and Cl^- (3.872 Å). Such a structure prevents isomerization of the open MC^+ form into the closed SP form.

No hybrid photochromic magnetics have been obtained basing on benzopyran $SP(II)^+$ without substituents in the indoline and benzopyran parts of the molecule (SP(III)). The crystals of the initial salt $SP(III)^+Br^-\cdot H_2O$ appeared to be non-photochromic either. Unlike previously studied salts SP^+X^-, cations $SP(III)^+$ do not form a crystalline structure favorable for photochromic transformations, with benzopyran fragments responsible for photochromic transformations being located in a loosely arranged part. $SP(III)^+$ cations are densely packed in blocks. Br^- and water molecules are located in inter-stack space and form a system of hydrogen bonds. The pyridine fragments are also located in the inter-stack space. $N^+ \cdots Br^-$ distance is 3.57 Å (Fig. 20) [53].

Nevertheless, the authors have managed to obtain paramagnetic complexes $SP(III)^+$ $[M(ox)_3 \cdot 4H_2O]$, ($M = Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}$) [53]. In all samples, no change of the magnetic moment *M* upon UV-irradiation was detected. However, a long (during 5 h) irradiation of the complex with $M = Fe^{3+}$ resulted in a small change of the magnetic moment. Using approximation of magnetic moment dependence of the sample on magnetic field by Brillouin function, the value of an average spin was determined (5/2), and the reduction of the number of magnetic particles upon irradiation was found to be by 2%. Hysteresis M before and after irradiation was absent. Apparently, decrease of M upon UV-irradiation for the sample with Fe^{3+} is due to a side process of Fe^{3+} reduction to Fe^{2+}.

Paramagnetic complexes of Mn^{3+} have configuration d^4 with S = 2, and are characterized by a non-symmetric single line in EPR spectra with *g*-factor 2.0046. A double integration of EPR spectra yielded a value of magnetic susceptibility χ. As follows from χT vs. *T*, the sample is characterized by significant antiferromagnetic correlations.

By developing combinatorial approach, Kashima et al. [54] have obtained photochromic ferromagnetic hybrid system [SP(I)-R] $[Fe^{II}Fe^{III}(dto)_3]$ based on magnetic dithiooxalate ($dto = C_2O_2S_2$) network and SP(I) containing different N-substituents in the indoline fragment (Me, Et, Pr) (Fig. 21a), and studied photoinduced influence of SP(I) isomerization on magnetic properties. Two phases have been detected in the studied systems: a high-temperature one with Fe^{III} (S = 1/2) and Fe^{II} (S = 2) and a low-temperature one with Fe^{III} (S = 5/2) and Fe^{II} (S = 0). Photochromism of SP^+ induces the change of ferromagnetic transition temperature for high- and low-temperature phases T_{c_1} and T_{c_2} (SP-Et: T_{c_2} from 8 to 12 K, SP-Me: $T_{c_1} = 22$ K and $T_{c_2} = 5$ K to $T_c = 17$ K) and the change of coercitivity from 3800 to 8400 G for SP-Et (Fig. 21b).

2.1.2. *Bifunctional materials based on the ions of photochromic mononitrosyl complexes of transition metals and paramagnetic metal complexes*

Combination of anions of photochromic mononitrosyl complexes of transition metals as light sensitive units, and paramagnetic metal cations is one of approaches to the development of hybrid photochromic-magnetic materials. Nitroprusside anion $[Fe(NO)(CN)_5]^{2-}$ is diamagnetic, but under irradiation in the region 350–380 nm below 180 K it undergoes photoinduced transitions into long-living metastable states MSI and MSII. In complex $Ni[Fe(NO)(CN)_5]$, randomly oriented neighboring spins Ni^{II}(S = 1) order after excitation into MSI state due to two antiferromagnetically paired spins formed at the expense of the charge transfer from the Fe atom to the NO ligand [55,56]. These spins cause magnetic coupling between neighboring Ni^{2+} cations, thus forming magnetic clusters with S = 5.

Recently, cations of mononitrosyl Ru complexes were shown to exhibit photochromic properties, forming two long-living metastable states [57–59]. Photochromic cations of Ru mononitrosyl ($[Ru(NO)(NH_3)_5]^{3+}$) were used by Yagubskii and co-workers [60,61] as the construction blocks for synthesis of hybrid bimetallic compounds with paramagnetic anions $[M(CN)_6]^{3-}$, (M = Cr(**1**), Fe(**2**)), $[M(ox)_3]^{3-}$ with M = Cr(**3**), Fe(**4**) and $[Cr(NO)(CN)_5]^{3-}$ (**5**). Substances **1**, **3** exhibit reversible photochromic properties; irradiation of **2** and **4** results in irreversible photochemical reactions, substance **5** does not possess photochemical properties. Paramagnetism of **1** and **3** is due to Cr^{3+} spins. Magnetic moment $\mu_{\rm eff}$ of both complexes changes slightly in the temperature range 300–5 K. Below 5 K, $\mu_{\rm eff}$ of **1** reduces considerably from 3.83 to 2.91 $\mu_{\rm B}$, while $\mu_{\rm eff}$ of **3** does not change. Field dependence of magnetization for **3** corresponds to the model of non-reacting spins, while behavior of **1** cannot be explained in the frame of Brillouin function. Abnormal behavior of **1** below 5 K is due to splitting of Cr^{3+} (S = 3/2) ground state in the zero field and weak exchange interactions between $[Cr(CN)_6]^{3-}$ anions. For **1**, a weak reversible increase of $\chi_M T$ was discovered upon UV-irradiation at low temperatures (Fig. 22).

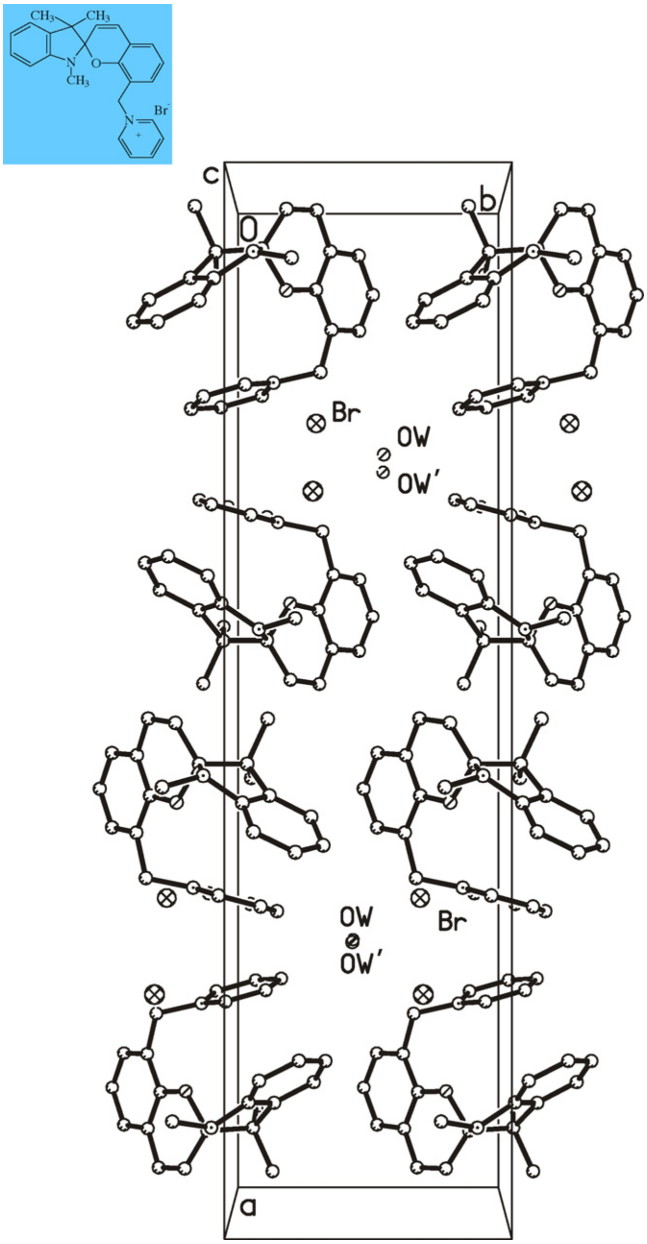


Fig. 20. Crystal structure of non-photochromic salt $SP(III)^+Br^-$.

2.2. *Photomodulation of magnetic properties due to intercalation of photochromic molecules into the magnetic structure*

Creation of photofunctional/magnetic composite materials due to intercalation of a functional component into a layered structure or cavities of the host's structure (the latter one having

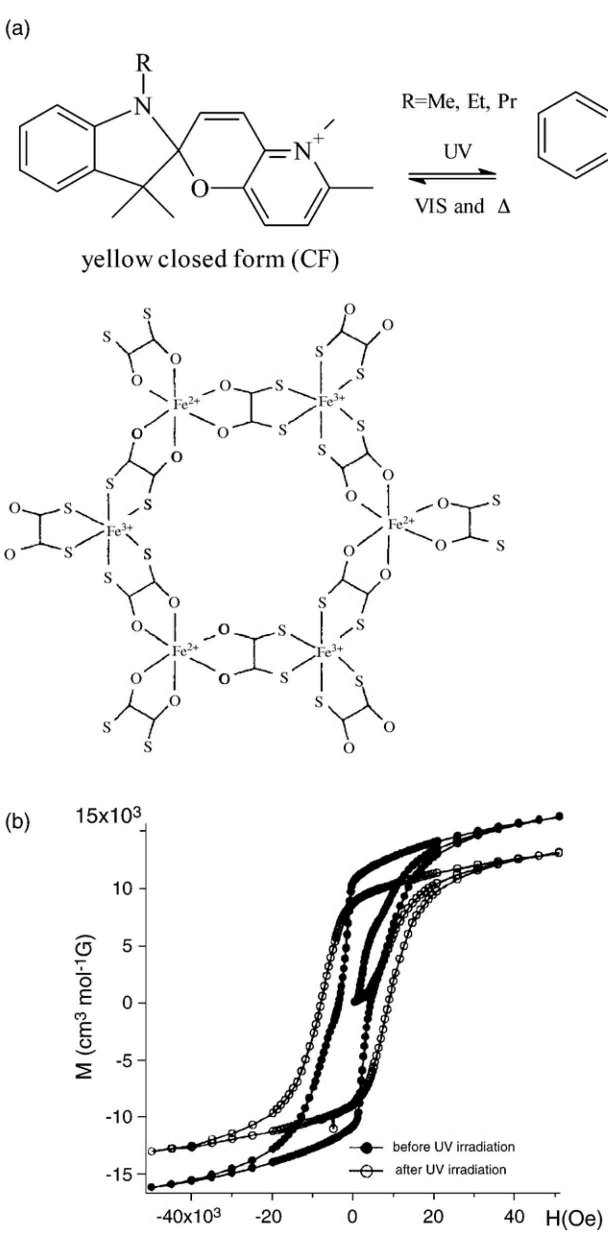


Fig. 21. Schematic view of complex [SP(I)-R][$Fe^{II}Fe^{III}(dto)_3$] (dto = dithioxalate $C_2O_2S_2$) (a) and influence of photochromic transformations of SP(I) on the magnetic properties of the complex (b).

the other function) seems promising for mutual control of these functions.

Photochromic molecules of azobenzene have been intercalated between magnetic layers of $[Cu_2(OH)_3]^-$ [62] by Fujita and Awaga. Einaga et al. have obtained the composite material involving nano-sized magnetic particles of Prussian blue intercalated in photosensitive organic medium containing azobenzene molecules [63].

Recently, Benard et al. [64] have synthesized intercalation substances $MnPS_3$ by including guest SP molecules. Semiconductors MPS_3 with a layered structure are characterized by unique intercalation chemistry (Fig. 23). Various organic and inorganic cations with a wide range of physical properties, such as ferrimagnetism, ferroelectricity, generation of the second harmonics, optical properties, can be intercalated into inter-layer space of MPS_3 by replacing M^{2+} ions [65–66]. Compounds MPS_3 (M = Mn, Cd), which can be the base for intercalated thin optically transparent films suitable for light irradiation and UV–visible spectroscopy studies, are of a particular interest [67].

In ref. [64], two composites $Mn_{0.89}PS_3[SP(I)\text{-}Me]_{0.22}$ and $Mn_{0.925}PS_3[SP(I)\text{-}Ph]_{0.15}$ have been studied. Reversible photochromic transformations SP ↔ MC occurring in the inter-layer space are strongly impeded by the host's lattice. In particular, reverse dark reaction MC → SP is very slow, and for SP(I)-Me intercalate it is practically impossible. Upon visible light irradiation it is not completed either. This can be due to restrictions from the host lattice and to the formation of stable aggregates of MC molecules, as we have shown in [52]. Spontaneous bulk magnetization of SP(I)-Me intercalate at $T_c \sim 45$ K (Fig. 24a) and the influence of photochromic transformations on the magnetic properties at low temperatures ($<T_c$) (Fig. 24b) are of a particular interest. The

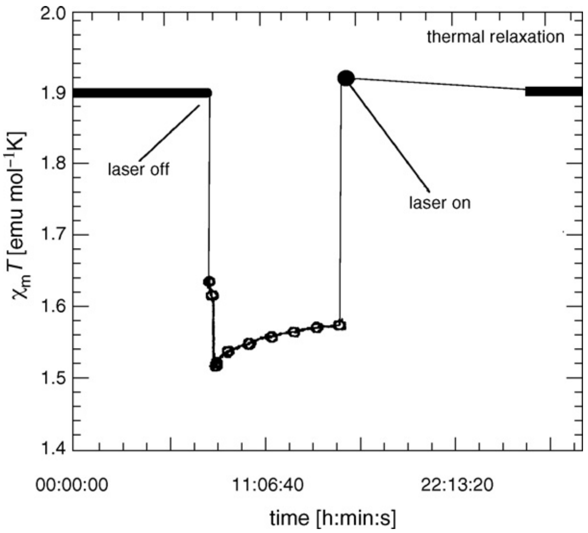


Fig. 22. Time dependence of $\chi_M T$ before, during and after irradiation at 406–415 nm.

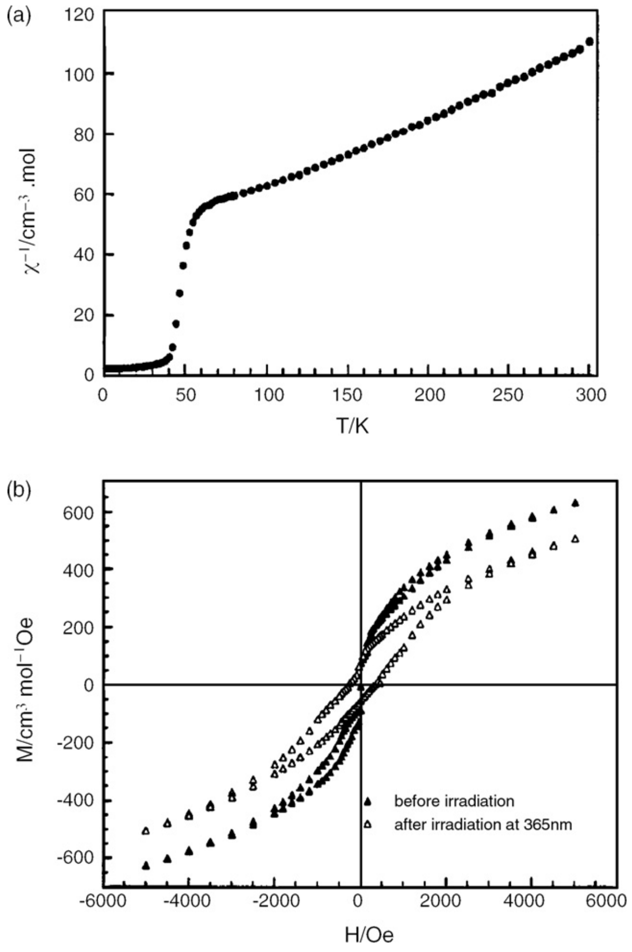


Fig. 24. Spontaneous bulk magnetization of composite $Mn_{0.89}PS_3$[SP(I)-Me] (a) and influence of photochromic transformations on the magnetic properties at low temperature (b).

following explanation of a spontaneous magnetization in the composites was suggested: though interaction between neighboring magnetic centers Mn^{2+} ($S = 5/2$) located in the angles of honeycomb lattice is antiferromagnetic, loss of some Mn^{2+}-ions during intercalation gives rise to the vacancies in the layer. Sometimes these vacancies spontaneously form ordered superstructures in one of two sub-lattices with anti-parallel spins, thus resulting in a spin misbalance.

Upon UV-irradiation at $T = 10$ K, hysteresis loop of the magnetization is noticeably widened and flattened (Fig. 24b). Unlike irreversible widening of hysteresis loop in (SP(I)-Me)[CrMn(ox)$_3$] due to the defects formation, in the studied intercalated samples this effect is at least partially reversible upon irradiation with visible light.

New results on intercalation of inorganic magnetic materials into organic photosensitive matrix have been classified in Einaga's review [68]. Photofunctional magnetic materials have been obtained by intercalation of magnetic anionic salt Prussian blue or magnetic nano-particles γ-Fe_2O_3 into a matrix containing photochromic molecules of azobenzene or spiropyran derivatives and having a bilayer vesicles assembly. The photochromic transformation in the matrix changes the structure of the vesicle where a magnetic particle is located, and its magnetization. The higher is the arrangement of the hybrid structure of multi-layers, the higher is the effect of photoinduced magnetization. The origin and structure of the matrix containing photochromic molecules and magnetic particles appear to be very important. By using magnetic nanoparticles γ-Fe_2O_3 characterized by a big contacting surface with a photosensitive medium, photoswitching of magnetic properties at room temperature has been realized.

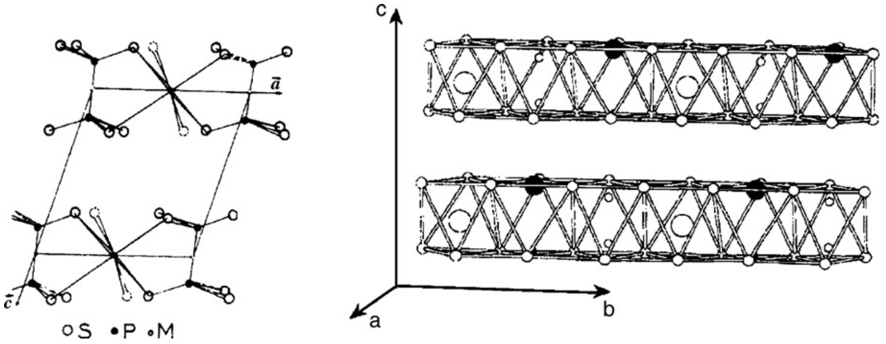


Fig. 23. The layered structure of MPS_3.

3. Conclusion

Although, as follows from the above examples, possibilities of photocontrolling of magnetic properties are of a fundamental interest so far, this direction is certainly very promising for the creation of hybrid polyfunctional compounds. The obtained results show that basing on fundamental research and using crystal chemical principles of design, such materials can be developed for practical application.

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