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Light-controlled molecular switches based on bistable spirocyclic organic and coordination compounds †

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Contents

I.	Introduction	1
II.	Mechanism of thermal and photochemical rearrangements of spiropyrans and spirooxazines	3
III.	Photochromic rearrangements of spiropyrans and spirooxazines for switching of physical and biological properties	6
IV.	Spiropyrans and spirooxazines as photodynamic sensors of metal ions	14
V.	Spiropyrans in molecular logic systems	18
VI.	Spiroperimidines	19
VII.	Metal bis(chelate) complexes	20
VIII.	Conclusion	22

Abstract. Modern concepts of mechanisms of thermal and photochemical rearrangements responsible for the photochromic properties of spiropyrans, spirooxazines, spiroperimidines and metal bis(chelate) complexes have been considered. The most important applications of spiropyrans and spirooxazines as light-controlled molecular switches of physical and biological properties of hybrid molecular and supramolecular structures and macroscopic materials have been discussed. The bibliography includes 185 references.

I. Introduction

Molecular switches — compounds or supramolecular associates capable of bistability, *i.e.*, able to exist in two (or more) thermodynamically stable isomeric forms — are essential structural components of devices of molecular electronics, photonics and spintronics. The switching between stable forms **A** and **B** of bistable structures is triggered by different external stimuli [reaction (1), where i is an applied electrical potential], and the transition from one isomeric state to the other is accompanied by reversible changes in physical properties, which creates conditions for recording and reading information encoded by these properties (Fig. 1).

$$\mathbf{A} \underset{}{\overset{\Delta,\, h\nu,\, H^+,\, i}{\rightleftharpoons}} \mathbf{B} \qquad (1)$$

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An active interest in studying molecular switches has been initiated by the creation of a prototype of three-dimensional rewritable molecular memory on the basis of photochromic spiropyran system **1a** (Scheme 1).[1] Inasmuch as the capacity of such devices can be as high as $\sim 10^{14}$ bit cm^{-3} when hard UV radiation is used for writing information, the phenomenon of photochromism ‡ came to be regarded as one of the most efficient molecular switching mechanisms, which has rapidly stimulated the search for new photochromic structures and thus has rapidly extended

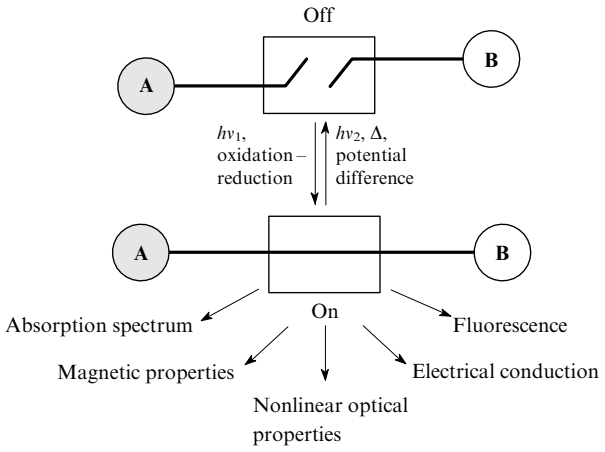
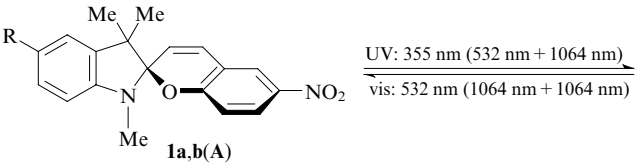


Figure 1. Switchable properties of bistable structures.

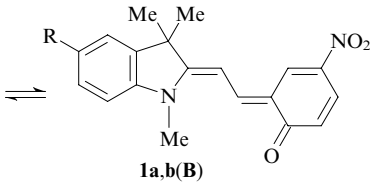
† Based on the materials of the lecture delivered at the XIXth Mendeleev Congress, Volgograd, 2011.
‡ Photochromism is 'reversible transformation of a molecular entity between two forms **A** and **B**, having different absorption spectra, induced in one or both directions by absorption of electromagnetic radiation'.[2]

the range of known photochromic structures.[3–5] Light is an external source of energy that should be applied to a bistable photochromic molecular system in order to initiate its transition to the isomeric state with different physical properties. Among the important advantages of the environmentally clean light energy as the external stimulus for triggering rearrangements of type (1) are the quickest response of the system (at the femtosecond level), the availability of well-adapted optical equipment (lasers, radiation sensors), the possibility of converting light signal into electrical output signals and the lack of interference with extraneous electromagnetic fields.

Scheme 1



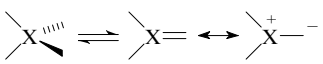
1a,**b**(**A**)



1a,**b**(**B**)

R = Cl (**a**), H (**b**)

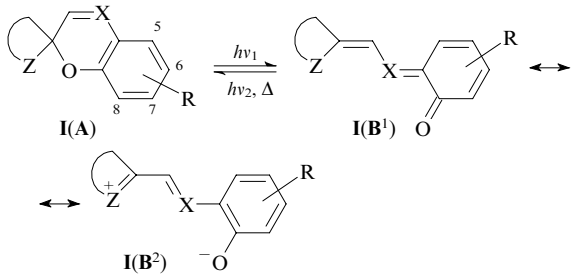
Nowadays, the range of applications of bistable molecular structures with switchable physical and chemical properties has been considerably extended to include their use for tailoring the dynamic properties of materials, targeted delivery of biochemical information and signal transduction across biological membranes and design of photochemically and electrochemically switchable catalytic, enzymatic and bio- and chemosensory systems. The two-volume collective monograph *Molecular Switches*,[6] released last year in the second edition, contains detailed reviews of these and other uses of molecular switches for the design of molecular machines and logic devices and targeted drug delivery. The present review examines the structure, properties and promising technological applications of spirocyclic compounds, constituting one of the most important classes of light-controlled bistable structures. Common mechanism (2) of reversible rearrangements of these compounds is determined by the transformation of the spirocyclic carbon atom or metal centre X contained in the molecule.



(2)

The best-studied bistable compounds for which this mechanism is realized through thermally and photochemically initiated rearrangements are spiropyrans and spirooxazines.[7–13] The photochromic behaviour of spiropyrans discovered in 1952 [14] (Scheme 2) was a prelude to the search for new types of photochromic compounds that have properties of molecular switches crucial for optical information recording and storage. For many technical applications and for use in a variety of molecular machines, an especially important quality of a molecular switch is the high thermal stability of both forms **A** and **B**, *i.e.*, the high activation barrier of reverse dark reaction (1). Most spiropyrans and spirooxazines of general structure **I** (see Scheme 2) do not have such properties and are inferior in this respect to the photochromic systems for which the mechanism of transformations is based on the electrocyclic $[2_\pi + 2_\pi + 2_\pi]$ rearrangement.

Scheme 2

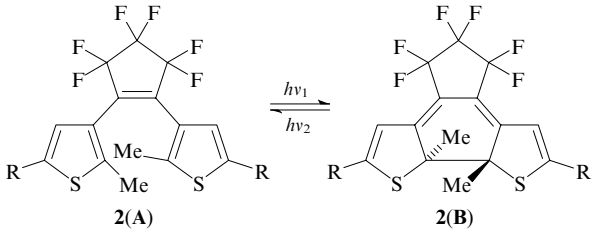


I(**A**) **I**(**B**^{1}) **I**(**B**^{2})

X = CH, CR′ are spiropyrans; X = N are spirooxazines;
Z is heteroatom

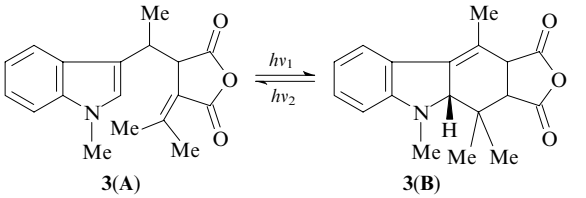
The main representatives of such systems are diaryl(hetaryl)ethenes and fulgides (for example, compounds **2** and **3**, respectively) [5–8] for which the rearrangements of the isomers in both directions are photochemical reactions (Schemes 3, 4).

Scheme 3



2(**A**) **2**(**B**)

Scheme 4



3(**A**) **3**(**B**)

This common disadvantage of spiropyrans and spirooxazines is counterbalanced by a number of positive features of these photochromic systems, such as preparative accessibility and structural variability of these compounds, which affords a convenient opportunity for tailoring the thermodynamic, kinetic, spectral and photochemical properties to the requirements of specific technical applications. Photoinduced isomerizations of spiropyrans and spirooxazines are characterized by high quantum yields of the forward and reverse reactions and have the highest two-photon absorption coefficients of both isomeric forms among the known photochromic systems. The latter factor is of crucial importance for the formation of three-dimensional molecular optical memory media. Table 1 summarizes the most important spectral and photochemical characteristics of the above photochromic systems.

The methods of synthesis, reactions and photochemistry of spiropyrans [7, 8, 23] and spirooxazines [11, 15] have been comprehensively covered in a number of reviews. The present review has focused on analysis of mechanisms of thermal and photoinduced rearrangements of spirocyclic photochro-

Table 1. Spectral and photochemical characteristics of compounds from major classes of photochromic systems.

Characteristics	Photochromes			
	spiropyrans (Refs 7–10, 12, 13, 15)	spirooxazines (Refs 10–12, 15, 16)	fulgides [17]	diarylethenes [18, 19]
Cyclic isomers: λ_{max} /nm	320–380	330–435	270–390	230–300
Open-chain isomers:				
λ_{max} /nm	440–660	540–670	470–825	530–820
ε /litre mol^{-1} cm^{-1}	$(40–45)\times10^3$	$(39–80)\times10^3$	$(4.8–26)\times10^3$	$(5–18)\times10^3$
Quantum yield of photocolouration	0.1–0.9	0.1–0.6	0.02–0.7	0.2–0.5
Quantum yield of the reverse photoreaction	0.001–0.05	0.001–0.05	0.0005–0.9	0.003–0.13
Photoisomer lifetime /s	$1\times10^{-3}–6\times10^5$	$3\times10^{-1}–5\times10^3$	$7\times10^3–25\times10^4$	$45–>3\times10^5$
Two-photon absorption cross section /cm^4 s photon^{-1}	$>10^{-48}$ (Ref. 20)	—	10.3×10^{-48} (Ref. 21)	$\sim10^{-50}$ (Ref. 22)

mic compounds and on the most interesting aspects of technical application of these systems.

II. Mechanism of thermal and photochemical rearrangements of spiropyrans and spirooxazines

Photophysical and molecular mechanisms of photoinduced rearrangements of spiropyrans and spirooxazines have been the subject of much experimental and theoretical research, and results of these studies have been surveyed in reviews [12, 13]. The primary stage of the photochromic rearrangement is dissociation of the $C_{spiro}-O$ bond followed by the establishment of thermal equilibrium of the initial cyclic spiropyran species (**Sp**) with a mixture of coloured merocyanine isomers. These transformations, involving the formation of two types of stacked aggregates of polar merocyanines,[10, 24] are described by the scheme shown in Fig. 2. The position of the resulting complex equilibrium and the composition of the equilibrium mixture depend on many factors, first of all, on the nature of substituents R, solvent polarity and solution temperature and concentration. Of the eight possible merocyanine stereoisomers with different configurations with respect to the three exocyclic bonds, the structures with the *trans* configuration (**T**) with respect to the central bond are the most energetically favourable according to quantum chemical calculations at different levels,[25–29] as well as to the data of time-resolved emission spectroscopy [30] and 2D NMR spectroscopy (NOESY, ROESY).[27, 31] The formation of the merocyanine isomeric *cis-s-trans-cis* form (**CTC**) of 1,3,3-trimethyl-6′-nitrospiro[indoline-2,2′-[2*H*]benzopyran] (6-nitro-BIPS, **1b**) as the major product that appears upon irradiation with UV light (λ = 266 nm) has been revealed by laser desorption–electron diffraction.[32]

The main challenge in studying the mechanism of photoinduced rearrangement of spiropyrans and spirooxazines is determining the nature of the excited state responsible for the first stage of the reaction and revealing the presence (or absence) of an intermediate *cis-s-cis-cis* structure (**CCC**) in the ground or electronically excited state. Irradiation of spiropyran and spirooxazine solutions or vapour at the wavelength of the long-wavelength absorption band of the cyclic form ($\sim$270–400 nm) generates a singlet excited state ($^1\pi\pi^*$) localized on the chromene (azachromene) moiety of the molecule, which undergoes further transformation in a matter of femtoseconds (< 100 fs).[33–40] For unsubstituted spiropyrans and spirooxazines, secondary, slower, processes mainly proceeding on a picosecond time scale [37, 38, 41] occur exclusively on singlet potential energy surfaces (PESs), whereas for the compounds containing a nitro group in the

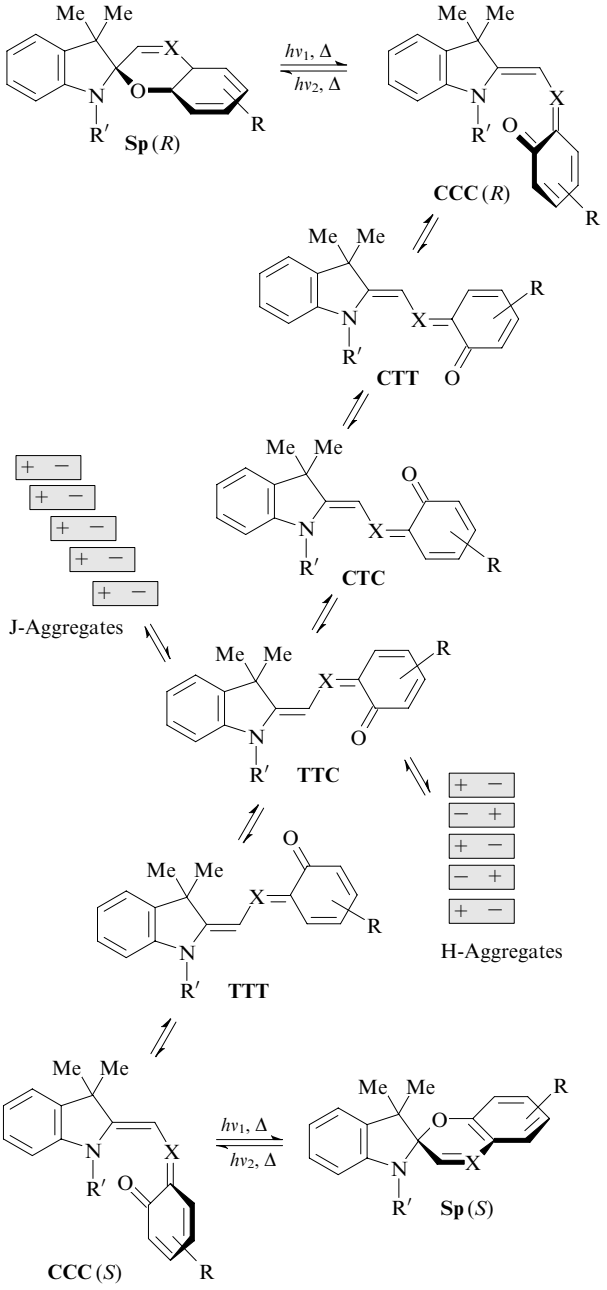
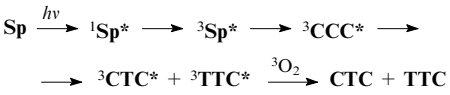


Figure 2. Generalized scheme of thermal equilibria established in solutions of spiropyrans (X = CH) and spirooxazines (X = N) after exposure to UV light.[12, 13]
Symbols **C** and **T** denote, respectively, *cis* and *trans* configurations with respect to double bonds.

chromene ring, the major channel of the photochemical reaction is the triplet mechanism.[32, 34, 41–44] The nanosecond laser flash photolysis method detects the formation of the transient triplet form ^{3}**Sp*** of the cyclic isomer of 6-nitro-BIPS (**1b**), its intersystem crossing to the ^{3}**CCC** merocyanine form and the subsequent transformation into the ^{3}**CTC** and ^{3}**TTC** forms (see Fig. 2). The lifetime of the latter is estimated at about 10 ms. This mechanism, supported by the extremely high sensitivity of the dynamics of the above transformations to the presence of oxygen traces in solutions, is described by generalized Scheme 5.[43, 44]

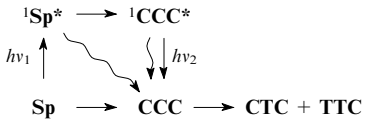
Scheme 5



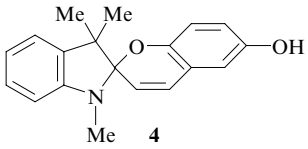
The appearance of the transient *cis-s-cis-cis*-6-nitro-BIPS isomer upon the femtosecond two-photon excitation of this spiropyran in solution is suggested to be an essential stage preceding the isomerization into the merocyanine form.[45] At the same time, the mechanism of photoinitiated opening of the 2*H*-pyran ring of 6-nitro-BIPS shown in Scheme 5 has not been confirmed by femtosecond time-resolved UV/visible and UV/mid-IR pump-probe spectroscopy.[46] The transient features observed in these experiments have been assigned to spiropyran $S_1 \rightarrow S_n$ absorption and the merocyanine triplet T_2 state.

For the spiropyrans and spirooxazines that do not contain nitro groups or other substituents with low-lying π* and/or n orbitals in the chromene (azachromene) ring, the triplet mechanisms play a subordinate role, and the mechanism of the photochemical rearrangement is described most generally by Scheme 6,[43, 44] in which wavy arrows show nonradiative transitions.

Scheme 6



Formation of the intermediate of the spiropyran photochromic rearrangement with the geometry close to the initial spirocyclic form but with the broken $C_{spiro}-O$ bond has been suggested even in early studies of the photochemistry of spiropyrans[47, 48] and has been subsequently proved by nano- and femtosecond transient UV spectroscopy.[33, 35] It has been demonstrated that such an intermediate, usually referred to as X intermediate (corresponding to the **CCC** structure in Fig. 2), is a primary product that appears in 100 fs following excitation with UV light of spiropyran **4** containing the hydroxy substituent in the 6′-position and undergoes ring transformation with the characteristic time 200 fs, as well as isomerization to form a open merocyanine product in ~100 ps.[33]



4

The lifetime of the **CCC** isomer that forms upon photolysis of spiropyran **5** (R = Bu^t) is considerably longer.[49] The presence of the bulky *tert*-butyl group in the molecule of this compound substantially hinders the relaxation into the stable flattened merocyanine structure (Scheme 7), which makes it possible to record the absorption and fluorescence spectra of species **5**(**CCC**) even at room temperature upon continuous irradiation. The structure of this intermediate has been determined by means of quantum

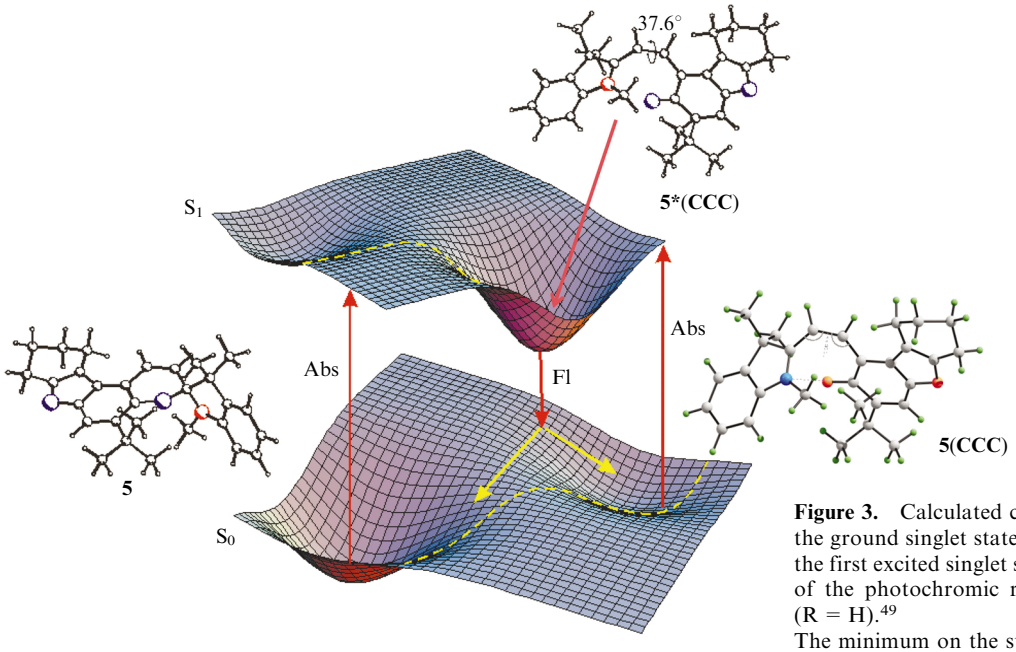
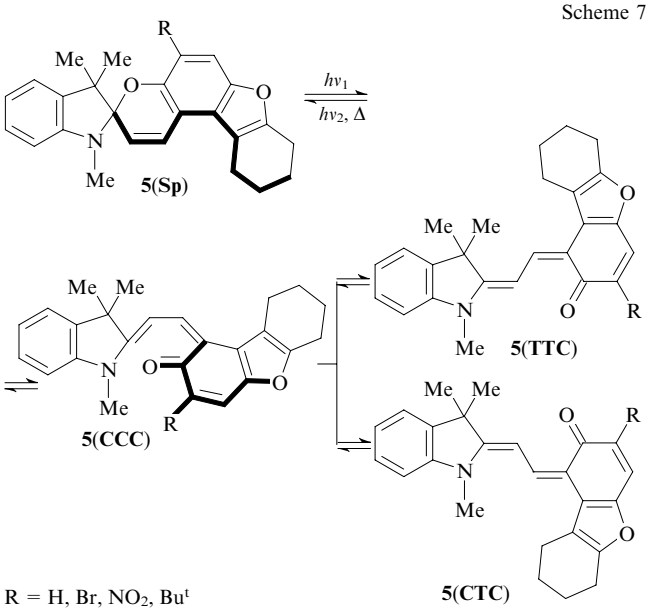


Figure 3. Calculated critical fragments of the PES of the ground singlet state (HF/6-31G** calculation) and the first excited singlet state (CIS/6-31G** calculation) of the photochromic rearrangement of spiropyran **5** (R = H).[49]
The minimum on the surface of S_1 corresponds to the structure responsible for fluorescence. Abs is absorption, Fl is fluorescence.

chemical calculations, and its presence is fixed on the PESs of the ground and first singlet excited states (Fig. 3).

Scheme 7

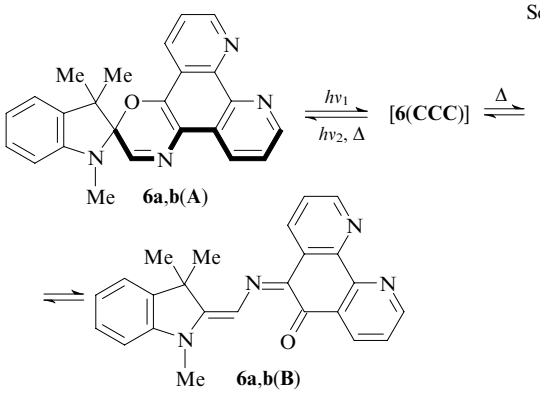


R = H, Br, NO_2, Bu^t

The primary photochemical processes that determine the mechanism of the photochromic behaviour of spirooxazines **I** (X = N, see Scheme 2), studied by stationary [37, 50, 51] and laser [34, 35, 52–55] (nano-, pico- and femtosecond) flash photolysis, are very close in nature to the major processes realized for spiropyrans. The primary photoproduct with a lifetime of 100–300 fs is the *cis-s-cis-cis* intermediate (**CCC**), which is rearranged in a few tens of picoseconds into the more stable merocyanine species. The existence of a transient species with a tentative **CCC** structure has been revealed upon irradiation of polystyrene films of spirooxazines **6a**,**b**.[37] The rearrangement of isomer **6**(**CCC**) into the merocyanine species (Scheme 8) proceeds rapidly even at 25 K, and its energy barrier is estimated at only 8 kJ mol^{-1}.

Formation of coloured merocyanine isomers of indoline spirooxazines (see Fig. 2) and other spirooxazines is a result of photoinitiated rearrangements that occur exclusively in

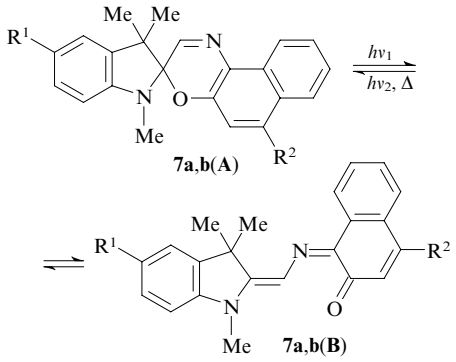
Scheme 8



R = Me (**a**), n-$C_{16}H_{33}$ (**b**)

excited singlet electronic states. The introduction of electron-withdrawing substituents into the oxazine moiety and/or electron-releasing groups into the indoline moiety of spirooxazines leads to a considerable decrease in the photocolouration quantum yields of these compounds.[39, 51, 55] This effect has been explained when studying the dynamics of photoinitiated processes in the molecules of spironaph-

Scheme 9



$R^1 = R^2 = H$ (**a**); R^1 = OMe, R^2 = CN (**b**)

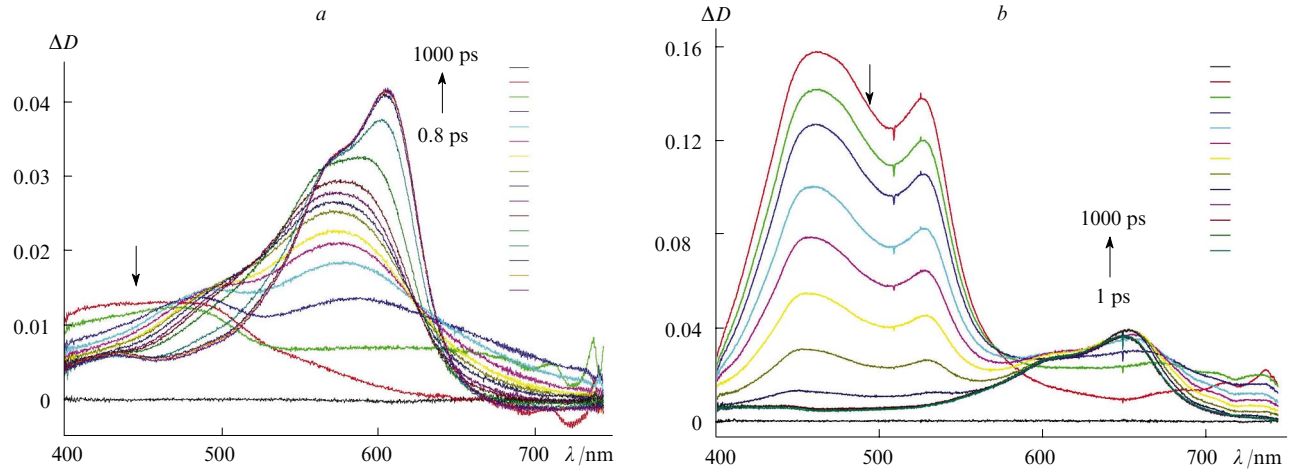


Figure 4. Dynamics of photoinduced spectral changes observed in butanol solutions of spirooxazine **7a** in the time interval from 800 fs to 1000 ps (*a*) and spirooxazine **7b** in the time interval from 1 to 1000 ps (*b*) upon the excitation by a 100-fs pulse at 375 nm.[40]
D is optical density.

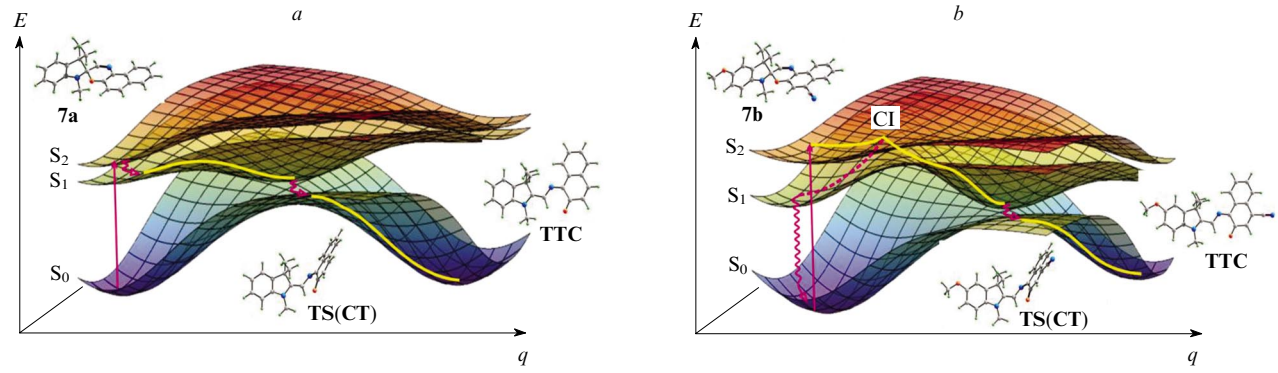


Figure 5. Topology of the PES of the ground state and lowest excited singlet states (S_1 and S_2) of the ring opening reactions of spirooxazines **7a** (*a*) and **7b** (*b*) as calculated with the use of the stationary (DFT) and time-dependent density functional theory (TDDFT) by the PBE0/6-311+G** method with inclusion of the solvent (acetonitrile) effects in the framework of the conductor-like polarizable continuum model approximation (CPCM).[40]
The elongation and rupture of the $C_{spiro}-O$ bond are used as the reaction coordinate (*q*). Symbols **TS(CT)** and **TTC** denote transition states of the *cis–trans* isomerization stage and the most *trans-trans-cis* forms of the merocyanine isomers, respectively. CI denotes the conical intersection of the PESs of the electronically excited and ground states.

thoxazines **7** on the femto- and picosecond time scale (Scheme 9).[40] As follows from Fig. 4, upon excitation with a 100-fs pulse (λ = 375 nm) of solutions of spirooxazine **7b**, containing the electron-withdrawing cyano group in the naphthoxazine ring, the absorption band that emerges in the range 450–550 nm is much stronger than the absorption in the same range of unsubstituted spirooxazine **7a.** The process determining the relaxation of this band is not involved in the sequence of transformations leading to the establishment of equilibrium with the open merocyanine species; rather, it occurs concurrently with the time constant in the range 2–60 ps.

Figure 5 shows the results of calculations of the minimum-energy path for the isomerization reaction of spirooxazines **7a**,**b** in the ground electronic state. To estimate its position with respect to the PESs of the nearest excited states according to the reported procedure,[56] the vertical projections onto the S_1 and S_2 PESs have been calculated. The calculations show that irradiation of initial spirooxazine (both substituted and unsubstituted) at the wavelength of the long-wavelength absorption band of cyclic form **A** excites the $S_0 \rightarrow S_2$ transition localized on the chromene moiety, whereas the $S_0 \rightarrow S_1$ transition accompanied by charge transfer from the indoline moiety to the orthogonal chromene fragment has a nearly zero probability. In the case of spirooxazine **7a**, the energy levels of the S_1 and S_2 states near the vertical transition from the minimum of the cyclic structure are close to each other, and after excitation of the S_2 level, internal conversion to the PES of S_1 occurs with the characteristic time 0.3–0.4 ps, and the sequential cleavage of the $C_{spiro}-O$ bond is a quasi-adiabatic process. For substituted spirooxazines, in particular, for compound **7b**, the PESs of S_1 and S_2 are noticeably separated and come closer together in the course of the $C_{spiro}-O$ bond cleavage, nearly coinciding in energy at R_{C-O} = 1.726 Å. This is evidence of the presence of the S_2/S_1 conical intersection in the vicinity of this point, which accounts for the existence of two electronic excitation channels. While passing through this region, some molecules of the evolving system go on the PES of S_1, and precisely these molecules are responsible for the emergence of the strong absorption band in the range 450–550 nm observed immediately after irradiation. Thus, the major channel of deactivation of the electronic excitation energy, competing with the $C_{spiro}-O$ bond cleavage, is population of the charge transfer excitation state S_1 and its sequential conversion into the ground state of the cyclic species. Electron-withdrawing substituents R^2 in the oxazine moiety and/or electron-releasing substituents R^1 in the indoline moiety of spirooxazines **7** increase the probability of the charge transfer state being populated and deteriorate the efficiency of the photocolouration reaction.

III. Photochromic rearrangements of spiropyrans and spirooxazines for switching of physical and biological properties

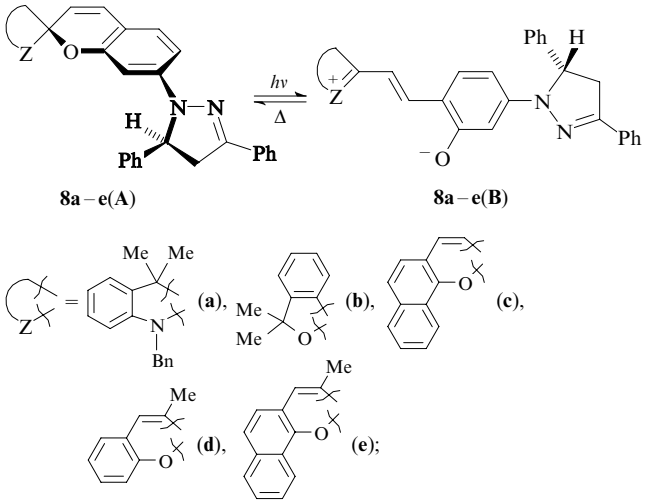
Photoinduced rearrangements (1) of cyclic structures of spiropyrans and spirooxazines into their isomeric π-conjugated merocyanine forms lead to significant changes in their physical properties — dipole moments, polarizabilities, nonlinear optical properties and emission spectra — and to sharp changes in the macroscopic properties of materials based on these compounds. These rearrangements are associated with considerable changes in the molecular geometry and chemical reactivity of isomers and can be used for targeted design of photocontrolled biologically active compounds, membranes and light-sensitive surfaces.

1. Photoinduced fluorescence modulation: application to molecular optical memories and subdiffraction microscopy

Because of the exclusively high sensitivity of the fluorescence detection methods and quick response to the activating signal, the possibility of reversible modulation of fluorescence characteristics of spiropyrans and spirooxazines by means of initiation of their photochromic rearrangements is of special interest for creating 3D optical memory devices with non-destructive readout of stored optical information. This approach has been applied to creating a prototype of 3D optical memory based on rearrangement (1) of 5-chloro-6-nitro-BIPS (**1a**).[1] Information recording is achieved by means of two-photon spectroscopy,[57,58] when the energy required for the rearrangement to occur is synchronously delivered to a definite domain of a bulk material by two

quanta, their total energy corresponding to the excitation energy. Information reading is based on detecting fluorescence emitted by at least one of the isomers. In the above system, as in the vast majority of other spiropyran and spirooxazine systems, only the merocyanine isomer has fluorescent properties. The merocyanine fluorescence is characterized by low quantum yields (Φ_{fl}). A better approach to create bistable molecular systems with photoswitchable fluorescent properties is based on functionalization of a photochromic system with an efficient fluorophore, its emission being modulated as a result of the change in molecule polarity or due to resonance energy transfer in the forming isomer species. Similar photochrome–fluorophore conjugates are exemplified by spiropyrans **8a–e**, which contain the fluorophore 3,5-diphenylpyrazoline group in the benzopyran ring; upon excitation of solutions and polymer films of cyclic isomers **8(A)** at 420–430 nm, this group emits green fluorescence (Scheme 10).[59, 60]

Scheme 10



Φ_{fl}(**A**) (PMMA, 298 K): 0.43 (**a**), 0.86 (**b**), 0.58 (**c**), 0.47 (**d**), 0.51 (**e**) [PMMA is poly(methyl methacrylate)]

Being irradiated, spiropyrans **8(A)** are rearranged to form polar merocyanine isomers **8(B)**, which do not exhibit fluorescence. Fluorescence quenching in compounds **8(B)** is caused by fluorescence resonance energy transfer (FRET), which is realized when the fluorescence spectrum of emitting (donor) species **8(A)** is overlapped with the absorption spectrum of acceptor species **8(B)** and at rather small distances (usually < 10 nm) between the donor and acceptor moieties. The **8(A)** ⇌ **8(B)** system is of interest for recording and nondestructive fluorescent readout of optical information. As shown in Fig. 6, the fluorescence excitation spectrum is bathochromically shifted from the maximum absorption wavelength of the cyclic species ($\lambda_{max} \approx 360$ nm), and the irradiation with light in the long-wavelength region of the fluorescence excitation spectrum

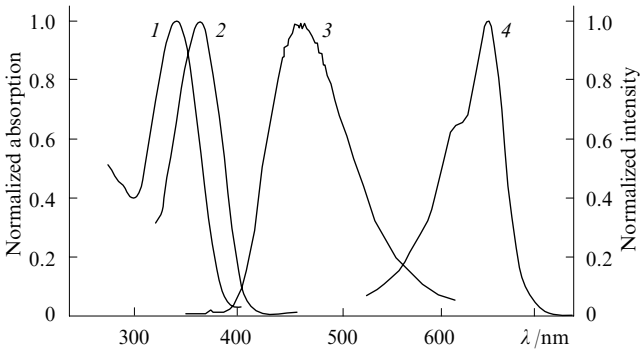
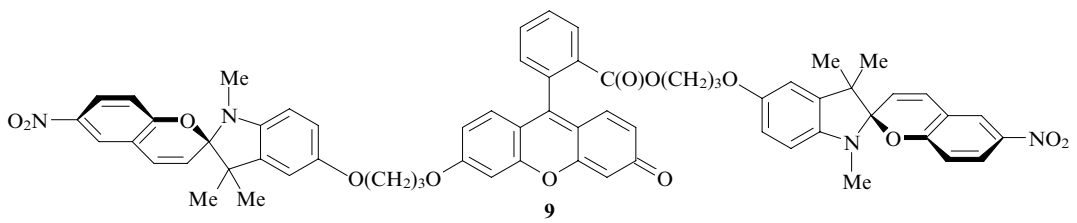


Figure 6. Absorption (*1*), fluorescence excitation (*2*) and fluorescence (*3*) spectra of the cyclic isomer of spiropyran **8c(A)** and the absorption spectrum of its merocyanine isomer **8c(B)** (*4*) in poly(methyl methacrylate) film.[59, 60]

hardly initiates the rearrangement into the merocyanine species. The FRET mechanism also underlies modulation of fluorescence of photochromic dyad **9** composed of spiropyran **1b** and fluorescein as a conventional fluorophore.[61] The spiropyran units attached to the fluorescein unit do not reduce its strong fluorescence (λ_{max} = 550 nm), but UV irradiation of solutions of compound **9** leads to opening of spiro rings and complete fluorescence quenching.

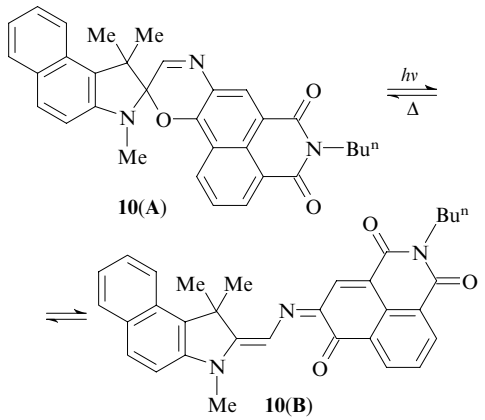
Photochromic systems **8** and **9** are distinguished by excellent spectral characteristics, the high rate of photoinitiated rearrangements and high quantum yields of photochemical reactions and fluorescence; however, they share the disadvantage common to most spiropyran systems: the photocoloured merocyanine species has a relatively low thermal stability. This parameter, crucially important for the creation of efficient media of three-dimensional molecular memory with fluorescent readout of stored information, is significantly improved in spironaphthoxazine system **10**, containing the fluorescent 1,8-naphthylimide label. The photoinduced rearrangement of spirocyclic form **10(A)** leads to nonfluorescent polar merocyanine isomer **10(B)** (Scheme 11), which has a rather long lifetime ($\sim 10^4$ s at room temperature in isopropyl alcohol).[62]

New approaches to the creation of photoswitchable photochromic systems with fluorescence response have been recently developed. These approaches are based on encapsulation of spiropyran derivatives into polymeric nanoparticles. In particular, compound **11**, a derivative of spiropyran **1b**, incorporated into polymeric particles obtained by emulsion copolymerization of *N*-isopropylacrylamide and styrene, exhibits strong red fluorescence (Φ_{fl} = 0.24) of the photocoloured merocyanine forms.[63] The basic principles of designing nanostructured systems containing photochromic and fluorescent components have been considered in review [64]. The most promising strategy is integration of separate fluorescent and photochromic sub-

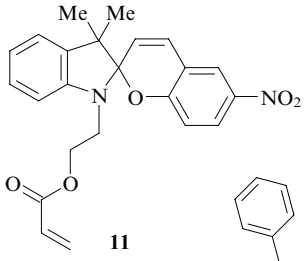


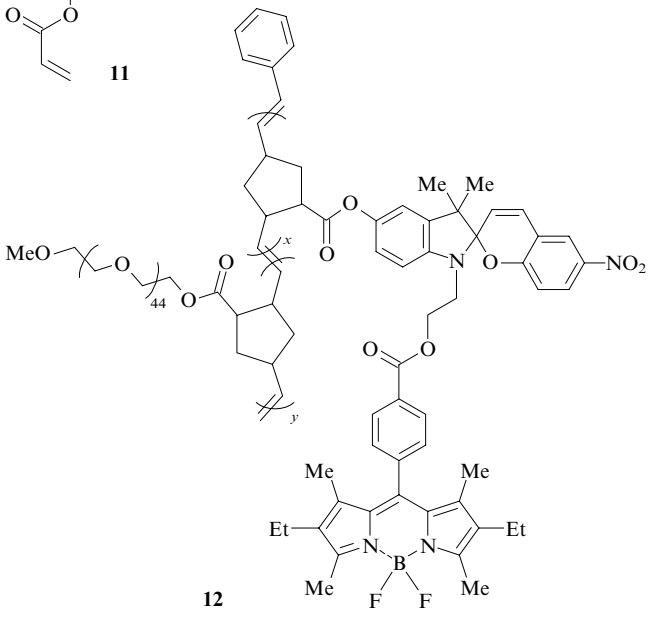
9

Scheme 11



units or photochrome–fluorophore dyads into a common polymer chain. An example of such a macromolecular system is copolymer **12**, in which the photochemical transformation of the spiropyran unit controls the emission intensity (λ_{fl} = 545 nm) of the conjugated fluorophore 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY).[65] In compound **12**, there are, on average, 15 poly(ethylene glycol) chains per photochromic unit, which makes it readily soluble in aqueous solutions and, thus, determines the possibility to use this compound in biological fluids.



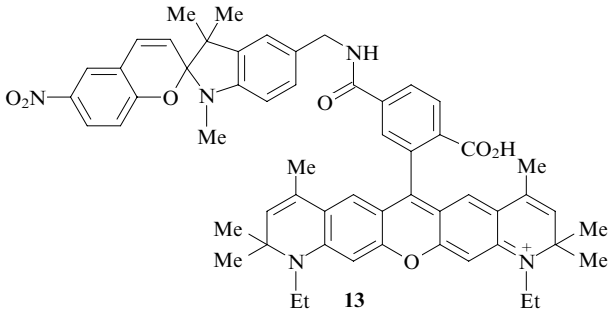


A new way of application of photochromic spiropyrans in biology and medicine is associated with the prospect of using these compounds for three-dimensional imaging of intracellular structures and tissues by means of fluorescence microscopy. The novel methods developed in this field made it possible to overcome the conventional physical limit of resolution ($r > \lambda/2$), restricting the possibilities of common optical microscopy to studying objects more than 200–250 nm in size. At present, the diffraction limit of fluorescence microscopy is decreased to almost molecular size.[66–68] Photochromic compounds with fluorescent properties enable the reversible switching between the fluorescent (on) and nonfluorescent (off) states. In such a way, time resolution of the observed fluorescence is achieved, which is a necessary condition for identification of separate fluorophores and their location with an accuracy of a few tens of nanometres. To obtain full image at the subdiffraction level, different strategies are used which are based on the time-resolved stochastic activation and high-precision localization of the positions of individual fluorophores.[66,69] The developed techniques are able to localize the positions of inserted fluorophores with one nanometre accuracy and make it possible to study the dynamics of living structures, for example, to observe, in real time, migration of a fluorophore conjugated with myosin proteins in actin filaments.[70] An important advantage of the method with photoswitchable fluorophores that have two thermally stable states (stimulated emission depletion, STED) over conventional fluorescence microscopy methods is a considerably lower excitation energy (< 1 kW cm^{-2}) required for switching between two states. For successful application in subdiffraction fluorescence microscopy, photochromic compounds with modulated fluorescence should have a set of properties, such as high quantum yields of fluorescence and photoinitiated rearrangement, the stability of the 'on' and 'off' states against photodegradation and quick response to photoirradiation. Especially important characteristics of a photoswitchable system are its solubility in water and the fulfillment of the condition $\tau_{off} > \tau_{on}$, which means that for the fluorescent state to be correctly read out, the rate of the reverse reaction should be considerably smaller than the rate of the forward reaction.

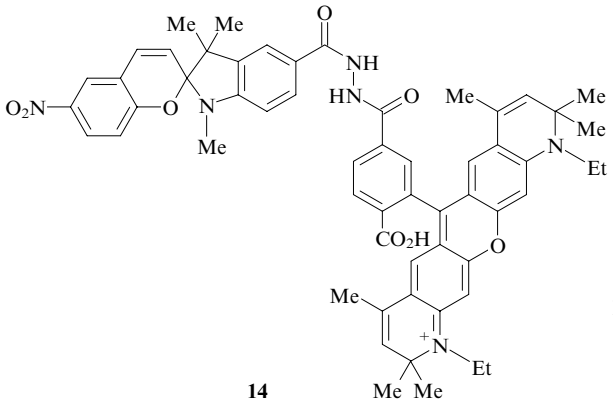
It is expected that these conditions will be best met by functionalized photochrome–fluorophore conjugates. An example of the latter are dyads based on spiropyran **1b** and common fluorescent dyes ATTO, for which the fluorescence modulation mechanism is based on resonance energy transfer.[71] The sufficiently high solubility in water (10^{-4}–10^{-5} mol litre^{-1}) is achieved owing to the presence of hydrophilic carboxyl and amide groups in molecules **13** and **14**. When the photochromic moiety is in the most stable cyclic form, the compounds exhibit strong fluorescence at 600–640 nm. The UV-initiated rearrangement into the polar merocyanine form is favourable for resonance energy transfer and leads to fluorescence quenching. An analogous behaviour is shown by dyads **15** and **16**, based on the indolinenaphthoxazine photochromic component and the tetramethylrhodamine fluorescent dye.[72] Advantages of these systems are rather high solubility in water, high quantum yields of fluorescence of the cyclic species and long lifetimes of the merocyanine 'off' forms. Testing compounds **13**–**16** demonstrates that they are good candidates to be used for obtaining high-visibility and well-resolved images of specific proteins of living cells by means of subdiffraction microscopy methods.

2. Photocontrolled magnetic properties

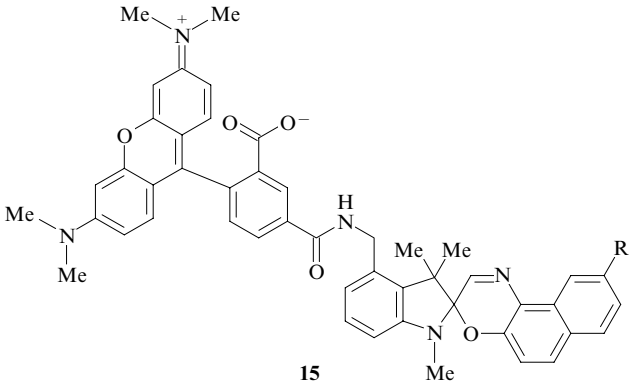
The fabrication and study of compounds and materials with optically controlled magnetic properties required for creation of high-density magnetic storage media and fast-response switches of magnetic properties currently constitute one of the most actively developed fields of structural magnetochemistry.[73–76] For light-driven switching of mag-



13

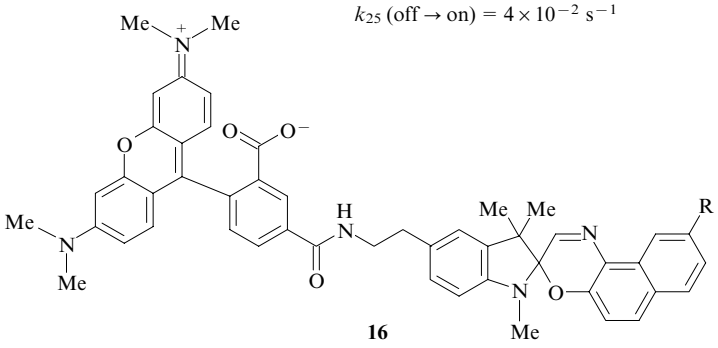


14



15

R = H, OH, OMe; for R = H: Φ_{fl} (water, 25 °C) = 0.38;
k_{25} (off → on) = 4×10^{-2} s^{-1}



16

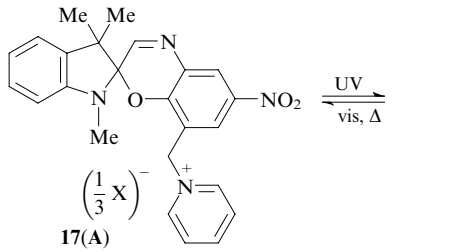
R = H, OH, OMe; for R = H: Φ_{fl} (water, 25 °C) = 0.25;
k_{25} (off → on) = 2.2×10^{-2} s^{-1}

netic characteristics with the use of photochromic compounds, the most important approaches are based on intercalation of these compounds into paramagnetic or ferromagnetic inorganic structures or on design of hybrid structures involving photochromes and transition metal complexes in which the multiplicity of electronic states is controlled by spin crossover effects.

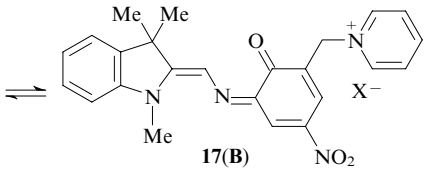
Modulation of properties of a magnetic material by means of photoinduced structural transformations of photochromic moieties contained in it has been achieved for cationic spiropyrans in salts with paramagnetic complex anions (trioxalates[77–81] and dithiooxalates[82]), as well as upon the intercalation of photochromes into layered semiconductor $MnPS_3$.[83,84] An example of such systems is shown in Scheme 12.[85] Being UV-irradiated in the crystalline phase, spiropyran **17**, which exists in cyclic form **A**, reversibly converts into coloured merocyanine form **17(B)**. X-Ray powder diffraction reveals considerable changes in the layered honeycomb structure of the anion in the coloured form, which are responsible for the change in magnetic properties. At temperatures below 5 K, photospecies **17(B)** exhibits ferromagnetic properties. The effective magnetic moment increases from 7.5 μ_B (corresponds to eight electrons: d^3-Cr^{III} and d^5-Mn^{II}) to 29 μ_B, which is evidence of the transition from the paramagnetic state to a structure with ferromagnetic exchange coupling of unpaired electrons of Cr^{III} and Mn^{II}.

Another proof of the ferromagnetic behaviour and formation of a magnetically ordered phase is the observed dependence of magnetic susceptibility on the magnetic field strength at temperatures below 10 K. The magnetization isotherm at 2 K has a hysteresis loop.[85] The ability of hybrid structures formed by photochromic spiropyrans

Scheme 12

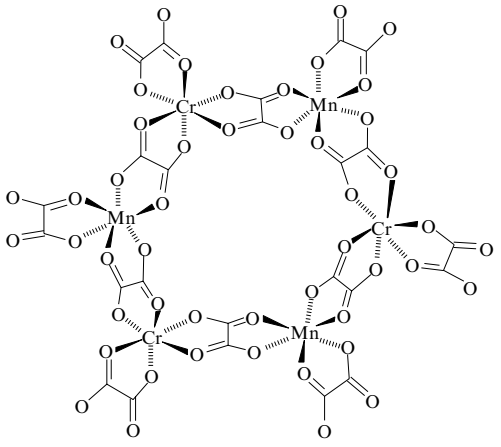


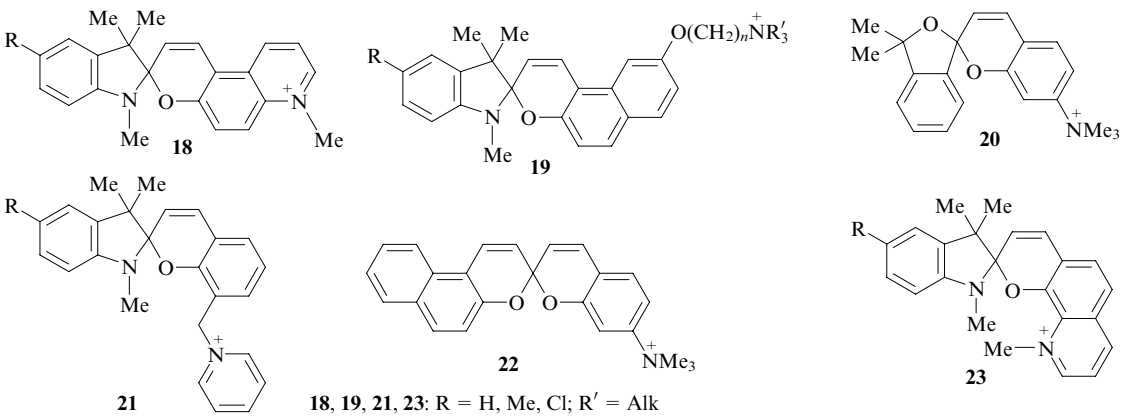
17(A)



17(B)

X =



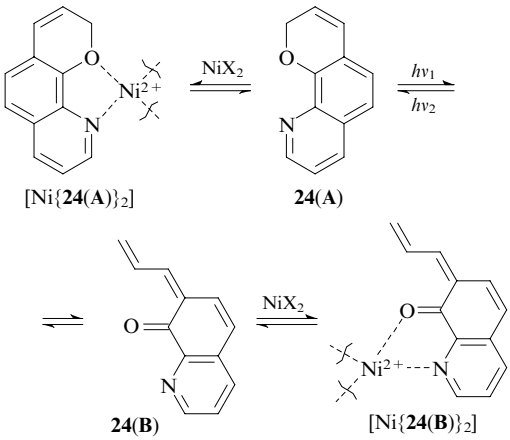


with layered paramagnetic heteronuclear complex anions to reversibly change magnetic properties under UV irradiation, in particular, to transform to the ferromagnetic state, strongly depends on specific features of the structure of the photochromic component. In this context, a wide range of salts of cationic spiropyrans **18**–**23** has been studied.[77–81, 85]

A promising use of photochromic structures for controlled switching of magnetic properties is based on formation of their conjugates with transition d^4–d^7metal complexes. The light-induced isomerization of the photoactive ligand is reflected in the character of the structural environment of the central ion, leading to such changes in the ligand field strength for this ion that result in spin crossover. The possibility of such an approach, referred to as ligand-driven light-induced spin change (LD-LISC), was first demonstrated for the $Fe^{II}L_4(NCS)_2$ complex (L is 4-styrylpyridine). UV irradiation initiates the *trans*–*cis* isomerization of the ligand accompanied by a sharp transition (at 160 K) between the high-spin paramagnetic and low-spin diamagnetic electronic states of the complex.[86] The LD-LISC systems known to date are based on photoinduced rearrangements determined by *cis*–*trans* isomerization with respect to double bonds C=C or N=N.[75, 87–89]

As distinct from the transformations of d^4–d^7-metal complexes caused by the spin crossover effect, the mechanism of LD-LISC rearrangements is of molecular nature, which eliminates the necessity of the cooperative effects and enables the observation of such rearrangements not only in the solid state but also in solution and thin films. This substantially extends the possibilities and increases the reliability of theoretical modelling of new LD-LISC systems. Recently, a new type of such systems has been predicted. The systems are based on photochromic spirocyclic ligands for which the transformations are determined by an electrocyclic rearrangement rather than by *cis*–*trans* isomerization and spin exchange is caused by configurational isomerism of the coordination core rather than by the

Scheme 13



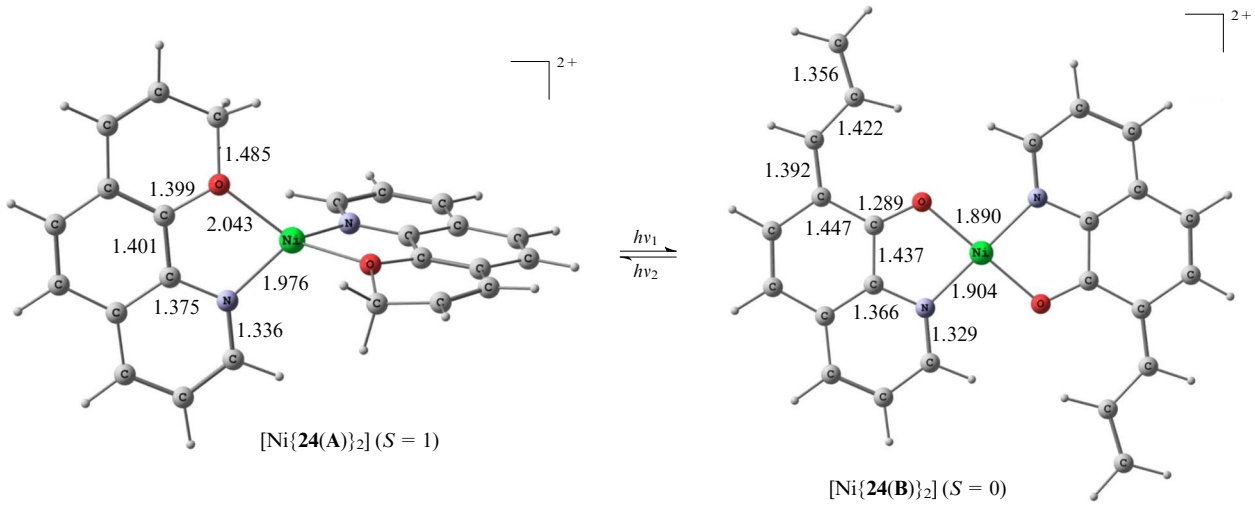


Figure 7. Geometric parameters of Ni^{II} complexes with isomers of ligand **24** calculated by the DFT B3LYP/6-311++G(d,p) method.[90] The distances between atoms are in Ångströms.

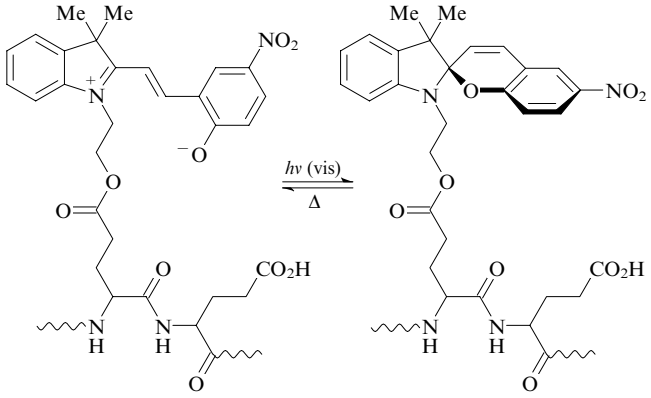
spin crossover effects.[90] The principle of the new mechanism is illustrated by the reactions in Scheme 13 and Fig. 7. The rearrangement of 2*H*-chromene **24**, which models a spiropyran, in the presence of nickel salts yields complexes of two types, the [Ni{**24**(**B**)}$_2$] complex with an open-ring form of the ligand and a flat diamagnetic configuration of the central ion being energetically preferred. Conversely, the isomeric [Ni{**24**(**A**)}$_2$] complex with the cyclic form of the ligand has a tetrahedral configuration of the central ion and is paramagnetic. Thus, the necessary condition for the manifestation of the LD-LISC effect is fulfilled: the Ni^{II} complex with the closed 2*H*-chromene form has a high-spin ground state ($S = 1$), whereas the ground state of the complex with the open-ring ligand form is low-spin ($S = 0$). The calculated difference between the energies of the isomeric [Ni(**24**)] complexes is 14.5 kcal mol^{-1}. An advantage of the configurational modulation of the spin state is an exclusively high rate of the realized spin-forbidden rearrangement, which is as high as or even higher than the rates of electronic transitions.[91]

3. Light-controlled modulation of biological properties

In recent years, a new branch of physicochemical biology has been significantly developed dealing with the use of light stimulus to control the efficiency and selectivity of function of various biologically important structures.[92–95] In addition to compounds that undergo irreversible transformations,§ considerable attention is paid to the use of photochromic compounds, in particular, spiropyrans and spirooxazines, able to reversibly change properties on exposure to light. Special interest focuses on the ability to artificially control the structures and properties of proteins and protein channels, which is achieved by means of doping, functionalization or bioconjugation of biological structures with appropriate photochromic compounds. This field of investigation, pioneered by researchers engaged in studying nonspecific insertion of photoswitchable spiropyrans into the surface sections of different enzymes (α- and β-amylase, urease, α-chymotrypsin) (see, *e.g.*, [96]), was termed 'chemical genetics'.[95]

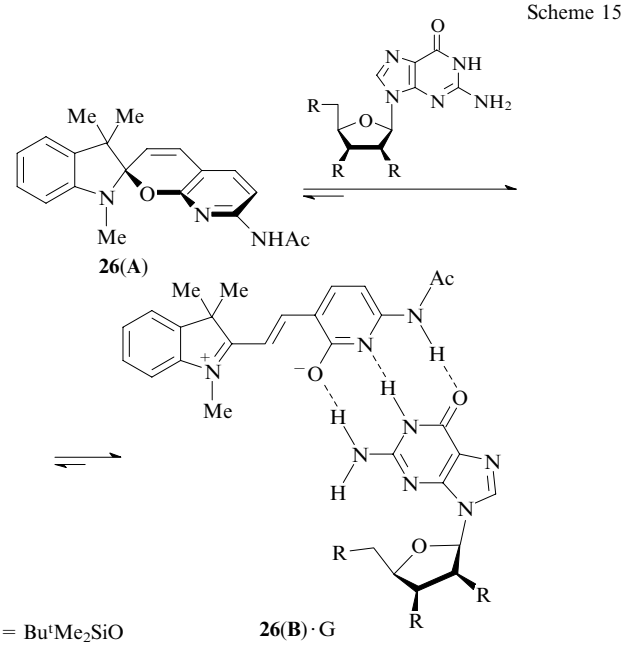
The random coil/α-helix transition of poly(L-glutamic) acid caused by photochromic rearrangements of the spiropyran (6-nitro-BIPS) moiety is one of the most comprehensively studied examples of light-controlled reversible modulation of protein structure.[93] In a hexafluoropropan-2-ol solution, spiropyran **25** exists as a polar merocyanine species, which accounts for dimerization processes leading to a disordered random coil structure of the macromolecules. UV irradiation initiates the transition to the nonpolar cyclic form of spiropyran, destroys the initial dimers and stabilizes the α-helix conformation. The transformations shown in Scheme 14 underlie the mechanism of photoinduced inhibition of the catalytic activity of α-amylase and cytochrome P450 3A4.[94,97] As distinct from polyglutamate, polymeric micelles and vesicles of the amphiphilic block copolymer obtained by functionalization of poly(2-hydroxypropyl methacrylamide) with 6-bromoindolinespiropyran incorporate the spiropyran units in their nonpolar cyclic form. The light-induced formation of the polar merocyanine unit leads to sharp destabilization of polymeric micelles and vesicles. Thus, the incorporation of drugs into micelles and vesicles enables their use for delivering drugs released upon exposure to light.[98]

Scheme 14



An important aspect of application of light-controlled reversible spiropyran systems is their use as artificial receptors of biologically important compounds. Once the functionality is correctly selected, one of the isomeric species (as a rule, this is the polar merocyanine species) can be rather precisely structurally adapted to selectively bind to such a compound to give a corresponding complex. An illustrative example of this approach is the design of spiropyridopyrans **26**: their merocyanine isomers are structurally strictly complementary to guanine nucleosides (G) and their oligonucleotide derivatives (Scheme 15).[99] Because of formation of three bridging intermolecular hydrogen bonds in structure **26**(**B**)·G, the equilibrium **26**(**A**) ⇌ **26**(**B**) is almost completely shifted to the right, which is detected by the appearance of a strong long-wavelength absorption band (λ_{max} = 550 nm, CH_2Cl_2). Spiropyran receptor **26** excellently distinguishes guanosine derivatives from other nucleosides unable to form triple bridges of hydrogen bonds. An analogous idea of molecular recognition based on the creation of optimal steric condi-

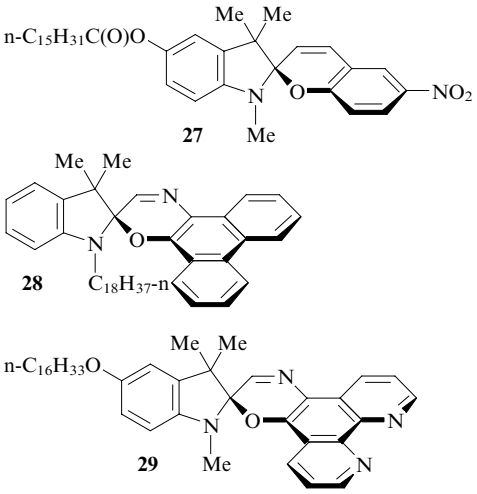
Scheme 15



§ Referred to as 'caged compounds'.[94]

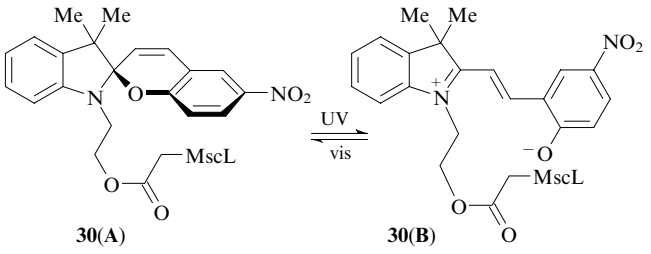
tions for analyte binding not through hydrogen bonds but through multipoint electrostatic interactions has been recently implemented for quantifying glutathione.[100] The polar merocyanine form of the tailor-designed bis(spiropyran) appearing upon irradiation of aqueous solutions of amino acids selectively binds glutathione to give a stable adduct emitting strong fluorescence.

The photoinduced rearrangement of spiropyrans and spirooxazines doped into biological membranes have been successfully used to control the concentration gradients across the membranes, since maintaining the gradients within required limits is of crucial importance for the functioning of living cells. The ability to control the structural features of the surfaces of biological and synthetic membranes is of interest for the design of systems of targeted drug delivery and selection of conditions for the application of protein solutions.[95, 101] Photoinduced rearrangements of amphiphilic spiropyran **27** and spirooxazines **28** and **29**[102, 103] inserted into the bilayer of dihexadecyl phosphate and phosphatidylcholine liposomes make it possible to reversibly vary the permeability and membrane-penetration rate of potassium and $Co(bipy)_3^{2+}$ ions (bipy is 2,2′-bipyridine).



By means of covalent binding of the 6-nitro-BIPS derivative to the cysteine fragment of the mechanosensitive channel of large conductance (MscL), which is a mobile homopentameric pore opened upon the stretching of the membrane, Feringa and coworkers[104, 105] have designed a photoswitchable model of MscL (**30**), which functions as a nanosized valve (Scheme 16). The size of the merocyanine moiety that forms upon UV irradiation exactly matches the largest diameters of the open pore (30–40 Å) of the mechanosensitive channel, which is opened upon UV illumination

Scheme 16



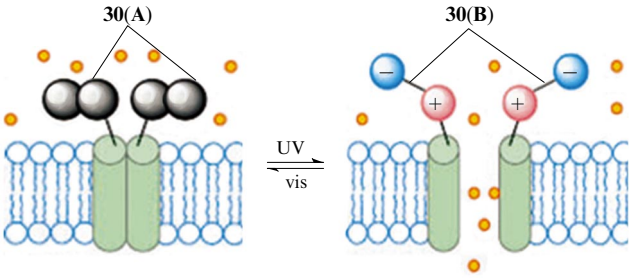


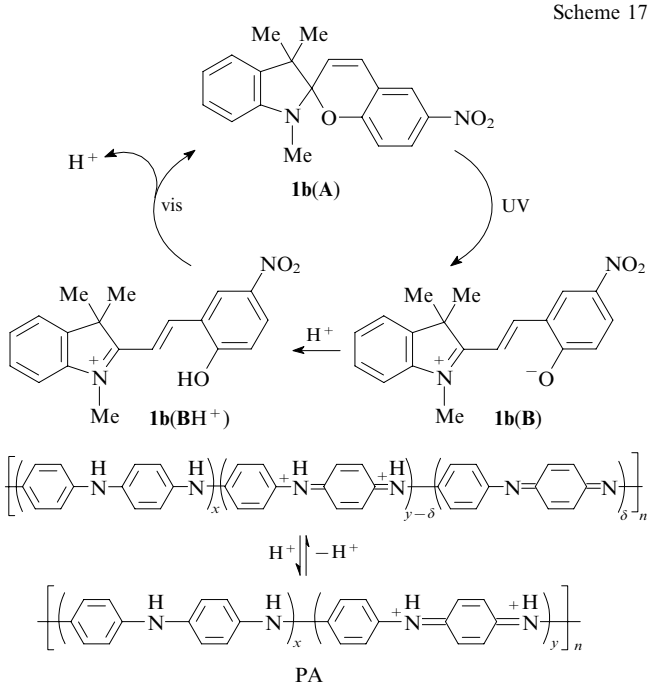
Figure 8. Light-controlled transport through the mechanosensitive channel of large conductance (MscL).[105]
Upon irradiation with UV light of a membrane with incorporated spiropyran **30**, the protein channel is opened owing to electrostatic repulsion of bipolar merocyanine structures **30**(**B**).

(365 nm) and is closed upon illumination with visible light (Fig. 8). The designed nanovalve can serve as a prototype of photocontrolled systems for targeted drug delivery.

4. Reversible control of electrical conductivity

The ionization potentials of isomeric forms **A** and **B** of spiropyrans and spirooxazines have considerably different magnitudes; therefore, photoinduced rearrangements (1) are inevitably associated with reversible changes in the electrical properties of photochromic structures. The irradiation-induced changes in the electrical conductivity of the photochromic layers of diarylethene and fulgides (for example, compounds **2** and **3**, respectively), as well as the ability to initiate their rearrangements by electric current, have been rather comprehensively studied, and various technical applications of these effects have been covered in review[106]. The application of spiropyrans and spirooxazines in this field is limited to a few examples, of which reversible control of electrical conductivity of thin polyaniline films doped with spiropyran **1b** is of special interest.[107] The electrical

Scheme 17

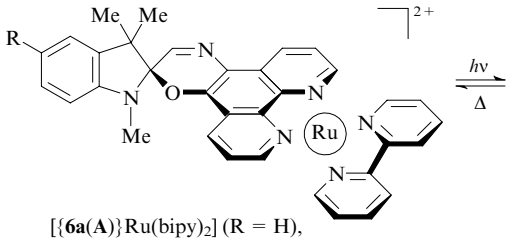


conductivity of polyaniline (PA) depends not only on the degree of its oxidation but also on the degree of its protonation. Photochromic spiropyran acts as a proton donor (photoacid) since its protonated form **1b**(**B**H$^+$) loses the proton upon irradiation with visible light. This gives rise to fast reversible equilibrium between the basic and salt (emeraldine) forms of polyaniline. Thus, the electrical conductivity of thin polymer films deposited on quartz substrates can be efficiently varied. The corresponding transformations are illustrated by Scheme 17.

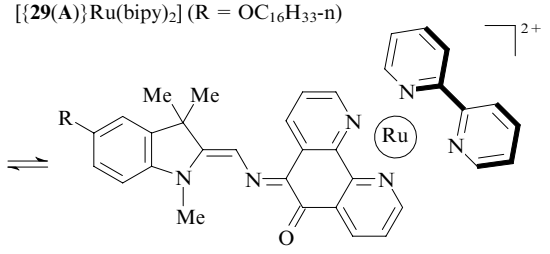
5. Modulation of intramolecular charge and energy transfer in transition metal complexes

The introduction of photochromic spiropyrans and spirooxazines functionalized with extra donor sites into the ligand environment of transition metal ions produces efficient systems with photocontrolled charge and energy transfers.[108–110] The mechanisms and dynamics of these processes, in particular, of metal-to-ligand charge transfer (MLCT), can be modified in the electronically excited states of such complexes,[110–113] which is of special interest. A typical molecular switch realizing charge transfer is a donor–photochrome–acceptor triad. The photochromic rearrangement leads to the change in the geometry of the composite system that enhances the interaction between the donor and acceptor components, which is favourable for donor-to-acceptor charge transfer. The MLCT effect coupled with electron density transfer from the *d* orbitals of Ru^{II} to the molecular π*-orbital of spirooxazine **6a** or **29** coordinated to Ru(bipy)$_2^{2+}$ leads to a sharp increase in the dark ring closing reaction rate (Scheme 18, one of the bipy ligand is omitted for clarity).[103]

Scheme 18

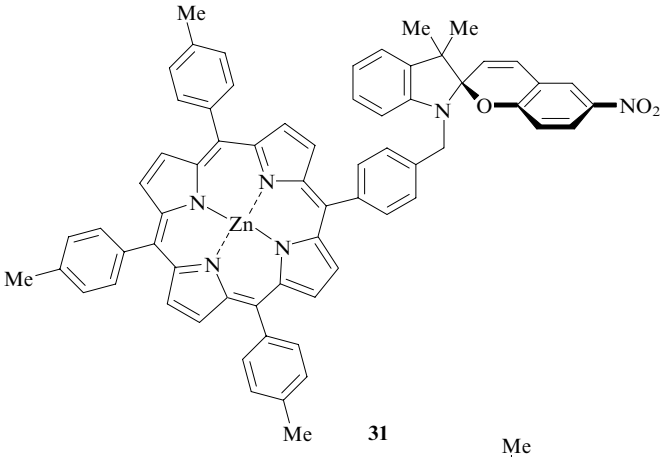


[{**6a**(**A**)}Ru(bipy)$_2$] (R = H),
[{**29**(**A**)}Ru(bipy)$_2$] (R = $OC_{16}H_{33}$-n)

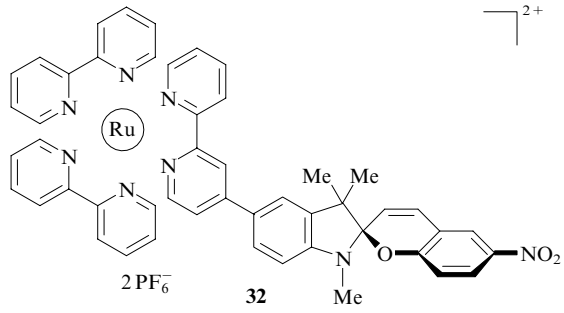


[{**6a**(**B**)}Ru(bipy)$_2$], [{**29**(**B**)}Ru(bipy)$_2$]

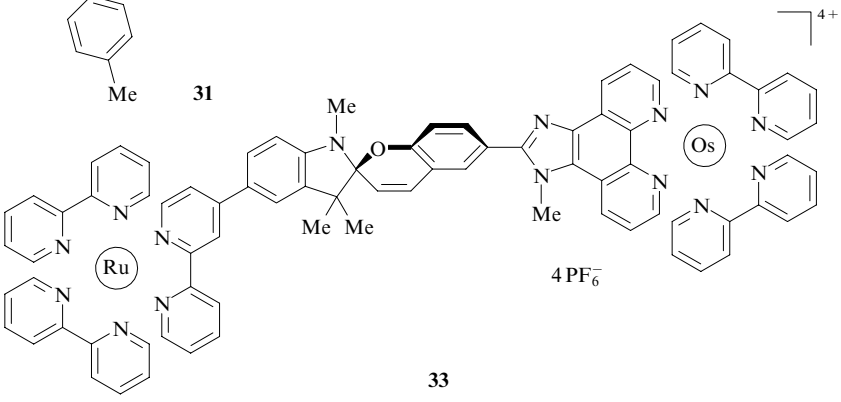
The rearrangement initiated by UV irradiation of solutions of spiropyran–porphyrin dyad **31** leads to formation of the corresponding merocyanine form of this complex, which absorbs at 600 nm, and to singlet–singlet energy transfer responsible for quenching of strong fluorescence of the porphyrin moiety.[30] As distinct from dyad **31**, the photoisomerization of spiropyran in dyad **32** has little effect on the dynamics of charge transfer (^{1}MLCT) from the metal ion to the bipyridine ligands. However, this process can be activated by using a more sophisticated system, namely, triad **33**, in which the Os^{II} centre functions as a more powerful acceptor.[114, 115] Upon the irradiation in the range of the ^{1}MLCT absorption band, energy transfer occurs from the higher-lying orbitals of the Ru^{II} centre through the bridging photochromic ligand to the orbitals of the Os^{II} centre. Varying the properties of the bridging photochromic ligand makes it possible to control the intensity and wavelength of the light emitted by the excited states of both metal centres of complex **33**.



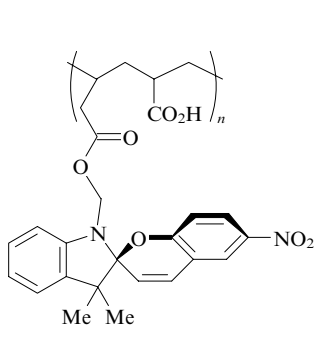
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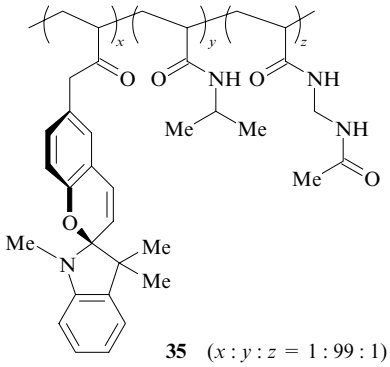
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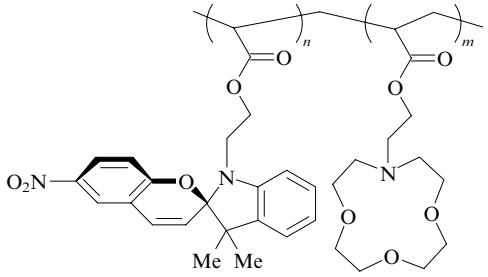
33



34



35 ($x : y : z$ = 1 : 99 : 1)



36

6. Reversible control of properties of macroscopic materials

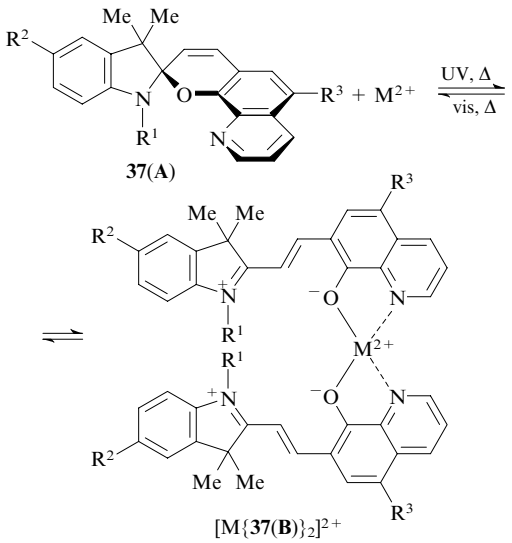
The above examples of modulation of magnetic properties of crystal structures and electrical conductivity of thin films belong to the rapidly developing field of application of photochromic compounds to control the properties of macroscopic materials. The light-initiated rearrangements of photochromic compounds bring about considerable structural changes at the molecular level. Upon the intercalation or covalent impregnation of such compounds into different materials, these changes have an impact on the macroscopic properties of materials, for example, on refraction index, hydrophobicity and hydrophilicity, electrical conductivity, crystal structure, surface morphology and others. Numerous and diverse examples of this kind have been presented in reviews.[76, 106, 116–119] Much recent attention has been paid to formation of photoactive surfaces with controllable wettability,[119–121] which are required for antifog and self-cleaning glass for car and building windows. Spiropyrans and spirooxazines represent an especially valuable doping material for formation and fabrication of such surfaces since the light-initiated rearrangement leads to a sharp change in the polarity of their photoinduced form and to a sharp increase in hydrophilicity. Spiropyrans are successfully used for reversibly imparting the superhydrophilic properties to titania-based hydrophobic surfaces, as well as for analogous transformation of the properties of surfaces of silicone nanowires and protein and polymeric membranes,[101, 122, 123] for control of the supramolecular organization of liquid-crystalline materials[124, 125] and aggregates of metal nanoparticles.[119]

For many technical applications of photochromic materials, they should be introduced into polymer matrices necessary for the formation of films, fibres, plates and other constructions used in practice. Such materials can be fabricated by doping a polymer with appropriate photochromic compounds or by means of covalent binding of the photochromic species to the macromolecule. Polymeric matrices have a significant effect on the kinetics, photophysical mechanism of a photochromic reaction and, in the case of spiropyrans, on the processes of aggregation of photoinduced species.[10] The photochromic rearrangements that occur in polymeric systems make it possible to control, by means of irradiation, the conformation of the polymer chain and the viscosity of polymer solutions and gels as, for example, in the case of polyelectrolytes **34**[126] and **35**.[127] The photoinduced formation of the polar merocyanine form of polymer **36** with pendant crown ether groups and other analogous polyvinyl systems in the presence of metal ions is accompanied by intense aggregation of the polymer chains. This process leads to considerable changes in the rheological properties of the polymers and is used for fabricating materials for photochemical valves that control solvent infiltration processes.[128]

IV. Spiropyrans and spirooxazines as photodynamic sensors of metal ions

The cleavage of the $C_{spiro}-O$ bond upon the rearrangement of the cyclic spiropyran structures leads to the formation of the isomeric polar merocyanine species. The phenolate oxygen atom that appeared in the merocyanine structure has powerful donor properties for coordination to metal ions. This fact enables the creation of efficient spiropyran- and spirooxazine-based thermo- and photoactivated chemical sensors with the chromogenic and fluorescent response. The first investigations into the area of application of photochromic spiropyrans as chemosensors were initiated about half a century ago.[129, 130] Remarkable progress in this field is associated with the works by Winkler and coworkers[131–133] who proposed to use derivatives of 6′-nitrospiro[indoline-2,2′-pyrido[3,2-*h*]chromene] **37** ($R^3 = NO_2$) as a metal-complexation ligand. The merocyanine isomeric form obtained upon irradiation of solutions or polymeric films of these spiropyrans contains two closely spaced donor centres, which coordinate the metal ions to give stable chelates (Scheme 19). Such complexes emit rather strong fluorescence, which makes it possible to detect

Scheme 19



37(A)

$[M\{\mathbf{37(B)}\}_2]^{2+}$

R^1 = Me, $(CH_2)_2OH$, $(CH_2)_2CO_2H$; R^2 = H, $OC_{16}H_{33}$-n; R^3 = H, NO_2, Cl

divalent metal ions (Zn^{2+}, Co^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+}) at solution concentrations of ~1 mg litre^{-1}.

In a subsequent work,[134] the set of spiro[indoline-2,2′-pyrido[3,2-*h*]chromenes] **37** has been expanded and the stability constants of complexes have been determined. It has been shown that, along with the M{**37**(**B**)}$_2$X$_2$ complexes, solutions also contain considerable amounts of the M{**37**(**B**)}X$_2$ complexes. The Mg^{2+} and Zn^2 complexes exhibit the strongest fluorescence with emission maxima at 610–625 nm, which provides for good selectivity of their determination. The ionophoric effect observed on addition of zinc salts to solutions of spiropyran **37** (R^1 = Me, R^2 = H, R^3 = Cl) is shown in Fig. 9.

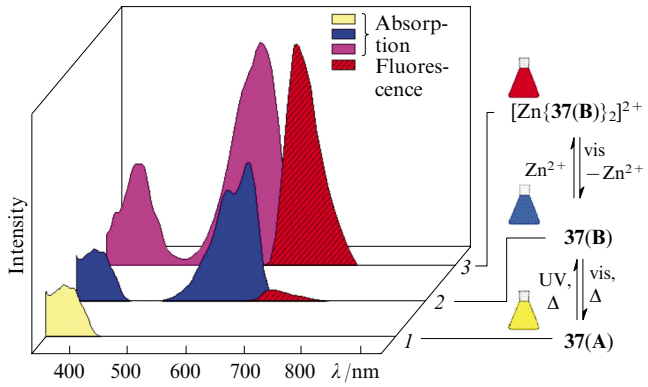
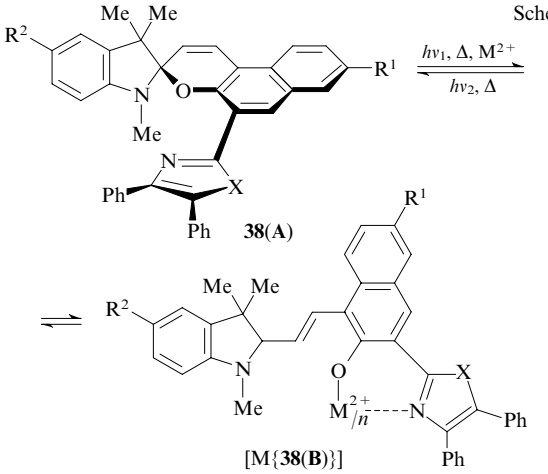


Figure 9. Spectral changes observed in a solution of spiropyran **37** (R^1 = Me, R^2 = H, R^3 = Cl) in acetonitrile.[13, 134]
(*1*) The spectrum before irradiation with UV light, (*2*) after irradiation (weak fluorescence of the merocyanine form is observed), (*3*) after irradiation in the presence of $Zn(ClO_4)_2$ (fluorescence rise).

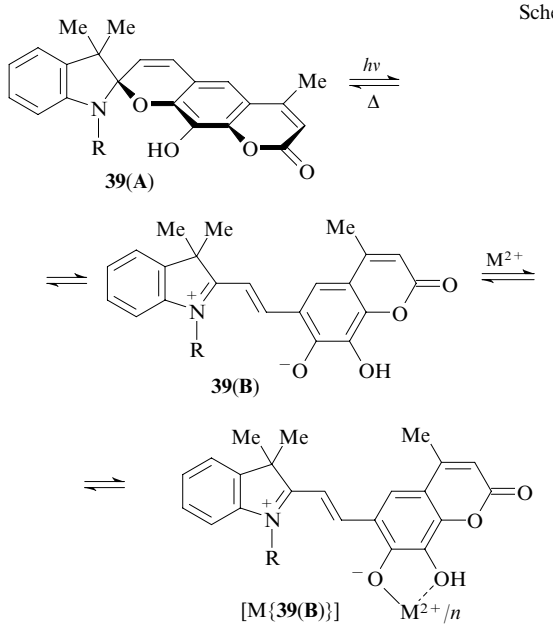
The general principle of designing high-sensitivity and selective photodynamic chemosensory spiropyran compounds — functionalization of spiropyrans with extra donor sites sterically and complementarily adapted to the phenolate oxygen atom for coordination to metal ions — has been applied to obtain new series of photo- and

Scheme 20



X = O, S; R^1 = H, OMe; R^2 = H, OMe, OAll, Cl;
M = Mg, Zn, Cd, Ni, Co, Cu, Mn; *n* = 1, 2

Scheme 21



R = Me, Pr^i, Bn, n-C_6H_{13}; M = Mg, Zn, Ni, Cu, Pb, Hg; *n* = 1, 2

ionochromic spiro[indoline-2,3′-benzo[*f*]chromenes] **38** (Scheme 20)[134–139] and spiro[pyrano[3,2-*g*]chromene-2,2′-indolin]-8-ones **39** (Scheme 21).[140] On addition of metal salts (Cu^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) to almost colourless solutions of equivalent amounts of spironaphthopyrans, the solutions become strongly coloured because of the formation of merocyanine complexes (see. Schemes 20, 21). The absorption spectra of solutions of 5′-(4,5-diphenyl-1,3-oxazol-2-yl)spiro[indoline-2,3′-benzo[*f*]chromene] **38** (X = O, R^1 = R^2 = H) in acetone in the presence of metal cations are shown in Fig. 10. The kinetic and thermodynamic analysis of complexation of metal ions with photo-

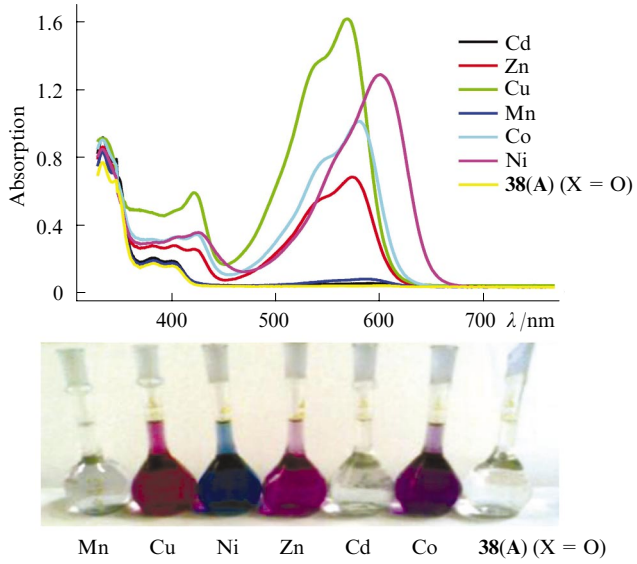
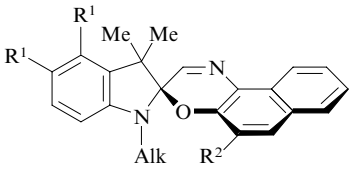


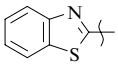
Figure 10. Absorption spectra of acetone solutions ($c = 4 \times 10^{-5}$ mol litre^{-1}) 5′-(4,5-diphenyl-1,3-oxazol-2-yl)spiro[indoline-2,3′-benzo[*f*]chromene] **38**(**A**) (X = O, R^1 = R^2 = H) in the presence of metal cations M^{2+} (Ref. 135).

chromic spiropyran ligands has been considered in detail in reviews.[141, 142]

Spirooxazines **40**–**42** containing, like spiropyrans **38**, chelating groups in the *ortho* position to the oxazine oxygen atom readily form stable complexes of their merocyanine species on addition of Ni^{2+}, Co^{2+}, Zn^{2+}, Fe^{2+} and Al^{3+} salts to solutions in acetone or an acetone–hexane mixture.[143, 144] The absorption spectra of the complexes show strong long-wavelength bands; however, as distinct from the complexes of the merocyanine forms of spiropyrans [M{**38**(**B**)}], analogous complexes of spirooxazines do not exhibit fluorescent properties.



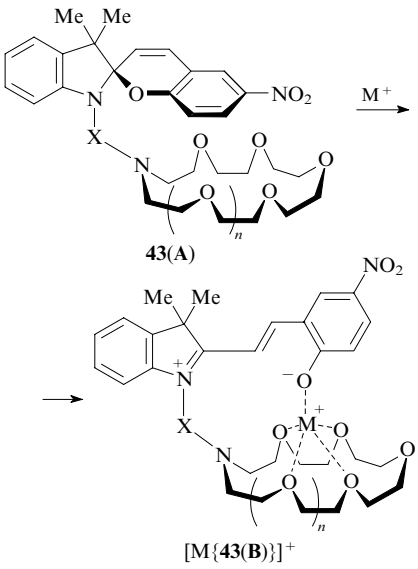
40–**42**

R^2 =  : R^1 = H (**40**), R^1–R^1 is benzo (**41**);

R^1 = H, R^2 = OH (**42**)

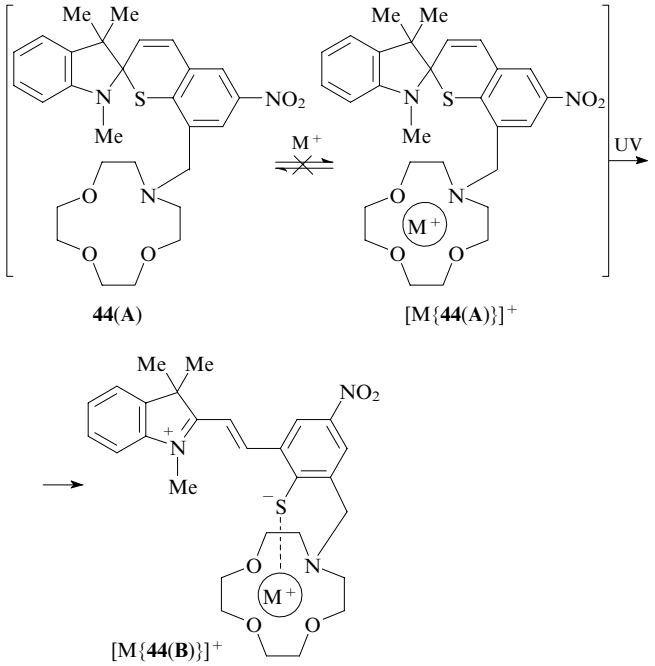
A new type of efficient photodynamic chemosensors for metal ions is represented by hybrid structures obtained by functionalization of spiropyran and spirooxazine molecules with crown ether fragments. The photochromic moiety is responsible for considerable photoinduced changes in the complexation properties of the crown ether receptor of ions used for selective recognition of alkali metal, alkaline earth and transition metal ions. Investigations in this field have been covered in reviews.[145–149] The basic principle of the design of photodynamic sensors containing photochromic spiropyran or spirooxazine moieties and ionophoric fragments is to adjust the phenolate donor centre of the merocyanine form appearing upon the photoinduced rearrangement to the geometry of the rigid crown ether cage in order to achieve additional stabilization of the complex with a metal ion. An example of successful realization of this principle is spiropyran **43**.[150] The selectivity of the spiropyran receptor of ions can be tuned by varying the size of the crown ether cavity and the distance between the phenolate oxygen atom and the metal ion. Spiropyrans **43** (X = CH_2, n = 1) readily capture Li^+ ions, which is indicated by intense colouration of their solutions caused by complexation with the merocyanine form of spiropyran **43**. Larger ions (Na^+ and K^+) do not fit into the cavity of this spiropyran and are not detected by such a chemosensor, but they form stable and coloured complexes with spiropyran **43** (X = CH_2, n = 2). For complexation of the even bulkier Cs^+ ion, the distance between the metal ion and the phenolate oxygen atom turns out to be too short so that an extra bridging group X = $(CH_2)_2O(CH_2)_2$ is introduced to meet the steric requirements for formation of a stable complex. The transformations of spiropyrans **43** shown in Scheme 22 do not require photoactivation and proceed as dark reactions. As distinct from compounds **43**, the merocyanine form of spirobenzothiopyran **44** does not form complexes with metal ions without illumination of solutions (Scheme 23). This spirothiopyran is a true photodynamic sensor for the Li^+, Ag^+ and Tl^+ ions. The high affinity of the 'soft' thiolate sulfur atom for the 'soft' metal ions Ag^+

Scheme 22



43(**A**) [M{**43**(**B**)}]$^+$

Scheme 23



44(**A**) [M{**44**(**A**)}]$^+$ [M{**44**(**B**)}]$^+$

and Tl^+ is an additional factor that stabilizes the [M{**44**(**B**)}] complexes and increases the selectivity and sensitivity of compound **44** with respect to these ions.[148] The structure of the complex with the Ag^+ ion is shown in Fig. 11.

Spiropyrans **43** and spirothiopyran **44**, whose merocyanine species form stable 1 : 1 complexes with M^+ ions, are efficient sensors for univalent metal ions, in particular, alkali metal ions. To provide for strong and selective binding to polyvalent metal ions in such a way, the receptor molecule should be structurally modified by introducing additional donor centres for coordination to the ion. Bis(spiropyran)s whose merocyanine isomers are excellent polydentate ligands for the ions of divalent (Mg^{2+}, Ca^{2+}, Zn^{2+}, Ni^{2+}, Sr^{2+}, Ba^{2+}) and trivalent (Fe^{3+}, Eu^{3+}, Ce^{3+}, La^{3+}) metals fit well to this purpose.[135, 136, 139] Bis(spiropyran) **45** is an example of such a system containing 6-nitro-

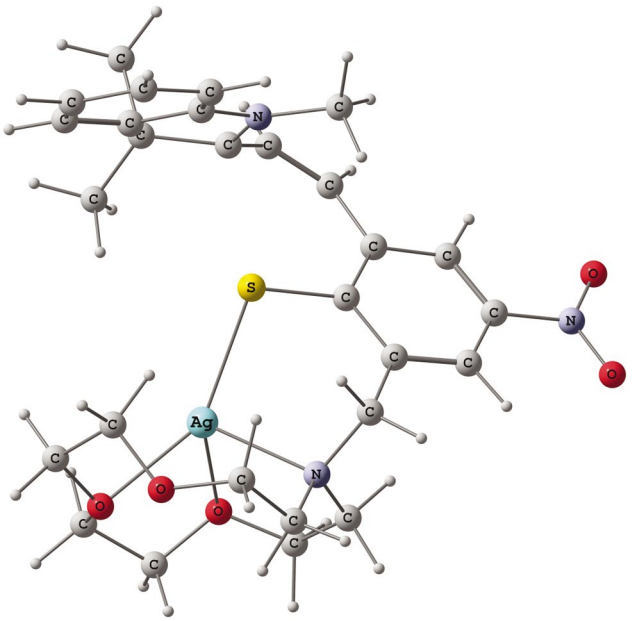
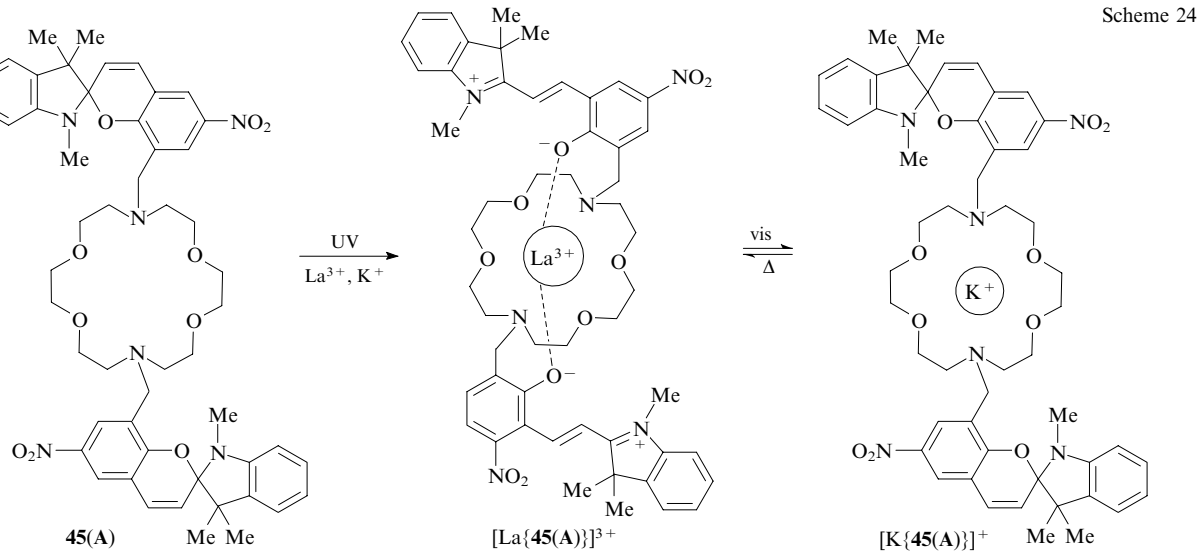


Figure 11. Structure of the $[Ag\{\mathbf{44(B)}\}]^+$ complex as calculated by the B3LYP/Lanl2dz method (unpublished data).

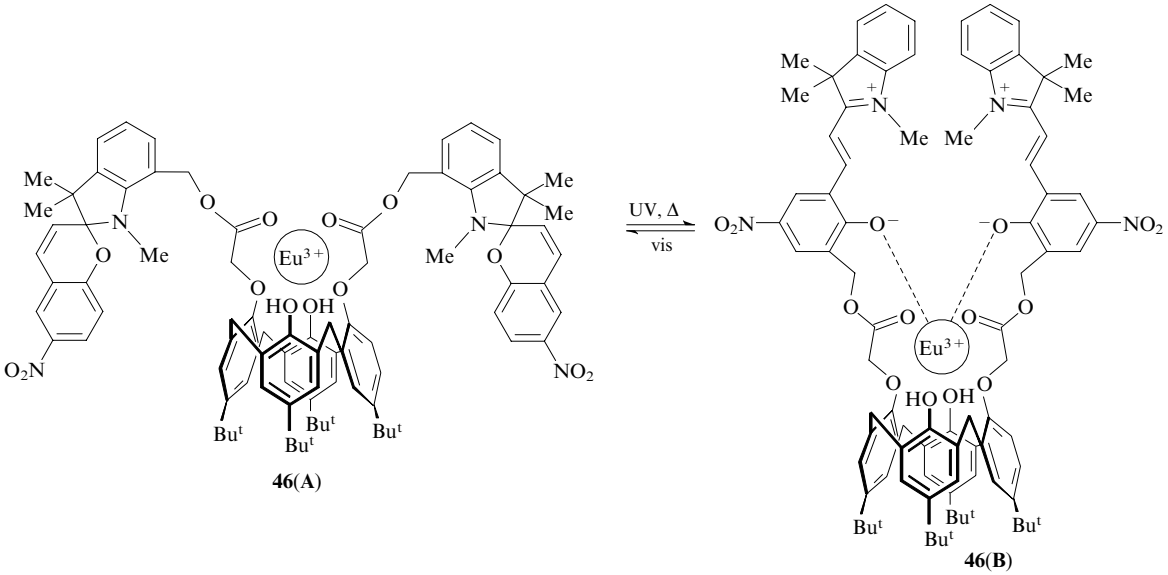
BIPS and diaza-18-crown-6 moieties and exhibiting high affinity for the La^{3+} ion. The transformations shown in Scheme 24 demonstrate exclusively high affinity of this bis(spiropyran) for the La^{3+} ion, which is indicated by the photoinduced ion-selective switchings $\mathbf{45}-[La(\mathbf{45})]^{3+}-[K(\mathbf{45})]^+$. UV irradiation of a methanol solution of compound **45** containing potassium and lanthanum chlorides leads to selective complexation of the merocyanine isomeric form with the La^{3+} ion. Subsequent irradiation with visible light recovers initial cyclic form **45(A)**, which is selective to the K^+ ion.[151] Liquid membranes based on bis(spiropyran) **45** are characterized by the high selectivity of light-controlled transport of alkali metal ions.[152, 153]

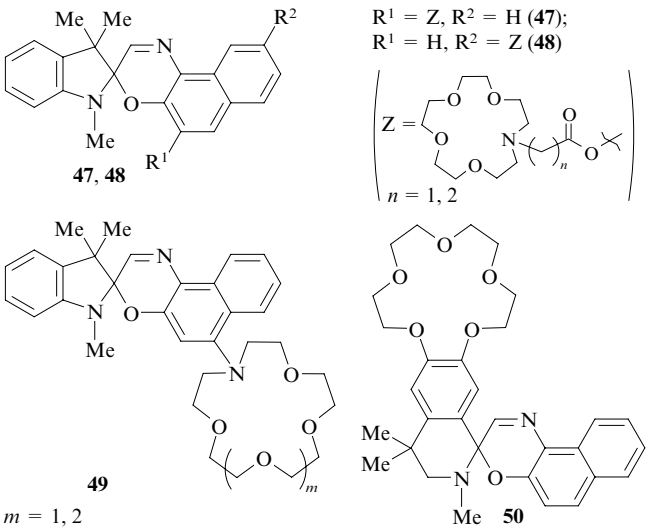
In addition to the crown ether moiety, the calixarene moiety, for example, in compound **46**, is a good acceptor of polyvalent metal ions, in particular, rare earth metal ions.[154] Alternate irradiation with UV and visible light makes it possible to control energy transfer between the ligand and Eu^{3+} ion and to switch the system between the fluorescent isomeric form of complex [**46(A)**] and the non-fluorescent form [**46(B)**] (Scheme 25). The photochromic behaviour of spirooxazines **47**–**50**, containing (aza)-15(18)-crown-5(6) substituents, has been addressed in a series of

Scheme 24



Scheme 25





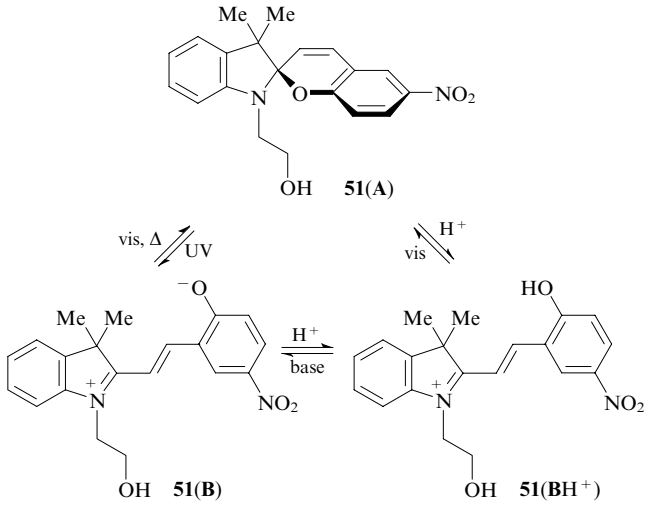
joint works by Russian and French researchers.[155–158] The addition of Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} salts to solutions of spirooxazines causes a hypsochromic shift of the long-wavelength absorption band of the cyclic form and a bathochromic shift of the long-wavelength absorption band of the merocyanine form.

V. Spiropyrans in molecular logic systems

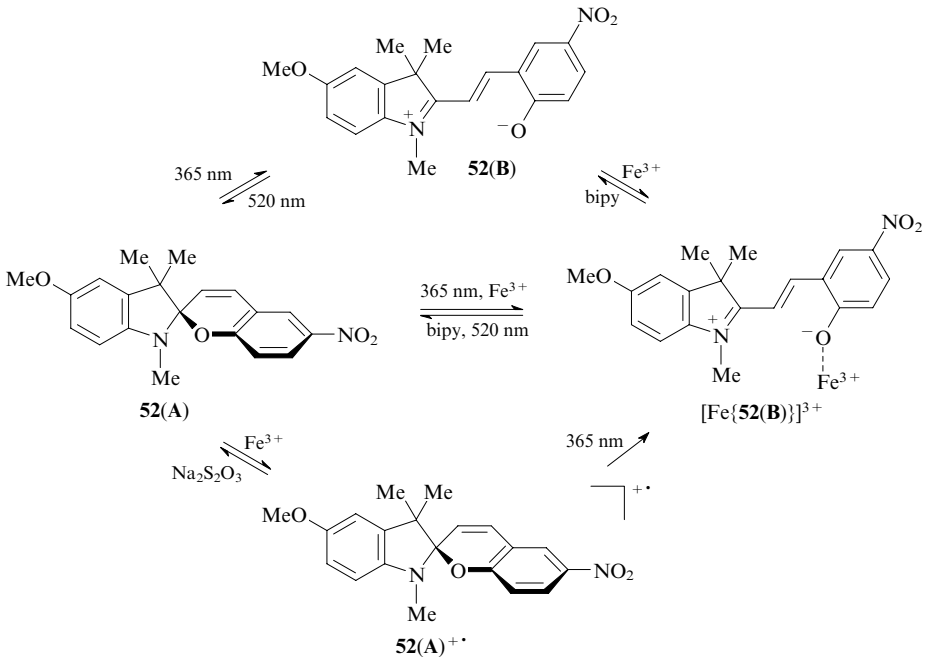
In bistable photochromic systems, switching between two isomers, in informatics terms, corresponds to switching between symbols '0' and '1' of the digital binary code. Such systems can serve as components for various devices of molecular photonics and, in prospect, molecular computer with the performance far exceeding the possibilities of modern computational devices.[159–164] The light-controlled molecular switch receives the input signal (light pulse) and converts it into the output signal, which is read either from the modified spectrum and luminescence rise or quenching or from any physical property of the isomer obtained by photorearrangement (see Fig. 1). Using such signal conversions implemented by molecules, one can construct molecular logic gates corresponding to the basic functions of the binary Boolean logic: YES, NOT, AND, NAND, OR, NOR, XOR, XNOR and INH, as well as different nanosized logic devices, such as adders and half-adders, subtractors, multiplexers and demultiplexers.[164–167]

Scheme 26 shows an example of a photochromic spiropyran system with three stable states, which provides formation of molecular gates NOT (no) and NOR (no/or).[168–170] Information input is accomplished by means of irradiation of a solution of spiropyran **51**(**A**) with UV light, which leads to formation of photoisomer **51**(**B**), and its long-wavelength absorption is read as the output. A simple construction made of two series connected cells containing a solution of compound **51** allows one to compose sets of inputs (UV irradiation) and outputs (detection of the spectrum of the merocyanine form) corresponding to the truth tables of the above logic gates. The inclusion into the process of the protonated acidochromic form of

Scheme 26



Scheme 27



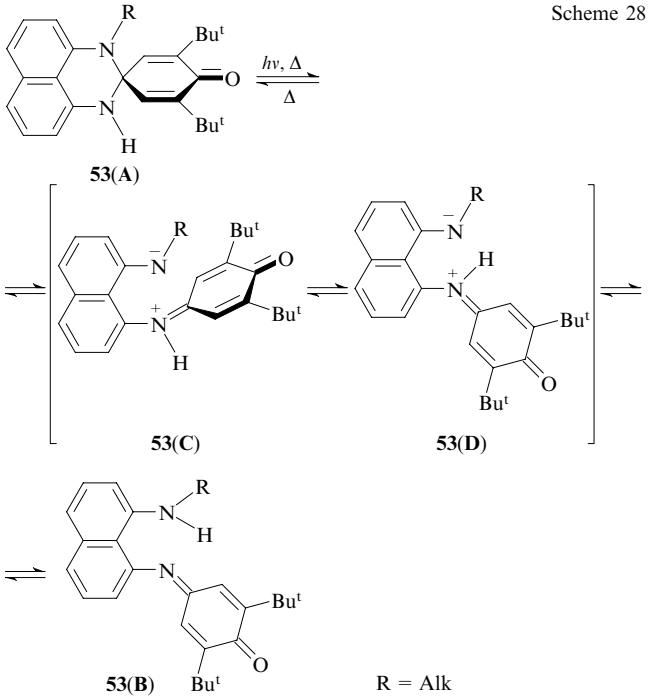
spiropyran **51**(**B**H$^+$) leads to the design of an optical system comprising three light sources. One of the cells of the system contains solutions of three fluorophores (naphthalene, anthracene and tetracene) emitting light upon excitation in different spectral ranges (λ_{ex} = 275, 357, 441 nm, respectively). The emitted light is absorbed by a solution of spiropyran **51** in another cell, and its state changes according to the irradiation conditions and acidity of a medium indicated in Scheme 26.

Scheme 27 demonstrates the use of the photochromic system of spiropyran **52** implementing the functions of a half-adder in which the inputs are Fe^{3+} ions and UV light with a wavelength of 365 nm.[171] Merocyanine isomer **52**(**B**) and radical cation **52**(**A**)$^{+\bullet}$ absorb at 520 nm. In the absence or upon simultaneous action of both factors, the absorption at 520 nm is almost absent. Such a behaviour corresponds to the XOR (exclude/or) logic. The short-wavelength output signal (λ = 420 nm) caused by the absorption of the [Fe{**52**(**B**)}]$^{3+}$ complex of the merocyanine isomer that forms only upon irradiation of a solution of spiropyran with UV light (365 nm) in the presence of iron ions serves for formation of the AND logic gate.

VI. Spiroperimidines

The photo- and thermochromic behaviour of a new spirocyclic system — spiro derivatives of perimidine [172–176] — is based on the ring opening mechanism coupled with concerted proton transfer as shown in Scheme 28 for 2′,6′-di-*tert*-butylspiro[2,3-dihydroperimidine-2,4′-cyclohexa-2′,5′-dienes] **53**. Upon UV irradiation, the yellowish colour of solutions of compounds **53**(**A**) rapidly changes to dark blue due to the appearance of a long-wavelength band (λ_{max} = 590–630 nm) arisen from isomer **53**(**B**). The initial spectrum is slowly restored at room temperature ($k_{25} \approx 10^{-4}$ s^{-1}). The absence of the concentration dependence of the dark reaction rate is evidence of its intramolecular character. Evolution of the spectrum of spiroperimidine **53** (R = Bn) upon irradiation of its solution is shown in Fig. 12. The reversible process **53**(**A**) ⇌ **53**(**B**) is characterized by a very large number of cycles and can be repeated more than a hundred times without noticeable loss in intensity of the long-wavelength absorption band of species **53**(**B**). Upon irradiation of polystyrene films of compounds **53** (R = Alk) with light of intensity 10^{15} photons s^{-1}, the period of time required for the twofold decrease in the intensity of the long-wavelength absorption band of photocoloured isomers **53**(**B**) with respect to the initial value is ~130 h. The slow process of bleaching is caused by the occurrence of the high-barrier stage of *cis*–*trans* isomerization **53**(**D**) → **53**(**C**). The quantum yields of the photochromic rearrangement of spiro [2,3-dihydroperimidine-2,4′-cyclohexadienones] in nonpolar solvents are close to the values characteristic of most spiropyrans and diarylethenes (Table 2). The introduction of triplet quenchers has no significant effect on the photocolouration rate and efficiency, and according to calculations,[176] this fact is evidence in favour that the rearrangement occurs through population of exclusively singlet electronically excited states of compounds **53**. The evolution of the photochromic rearrangement after excitation to the first excited singlet state S_1 and its movement along the PES of S_1 to the region of the conical intersection returning the excited molecule on the PES of the ground electronic state is shown in Fig. 13.

Scheme 28



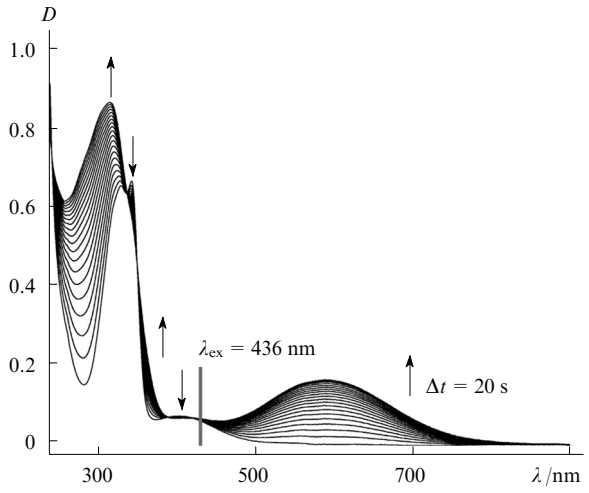


Figure 12. Photoinduced changes in the electronic absorption spectra of a solution of spiroperimidine **53** (R = Bn) in acetonitrile ($c = 5.9 \times 10^{-5}$ mol litre^{-1}) upon irradiation with light at 436 nm recorded at intervals Δt = 20 s.[175]

Table 2. Quantum yields (mol einstein^{-1}) of photoinduced rearrangements **53**(**A**) → **53**(**B**) in different solvents measured on exposure to light with λ = 365 nm of intensity 1.02×10^{16} photon s^{-1} (Ref. 175).

R	Solvents		
	octane	MeCN	polystyrene
Me	0.24	0.06	0.12
Et	0.42	0.06	0.19
Pr^n	0.38	0.05	0.13
Bn	0.26	0.06	0.08

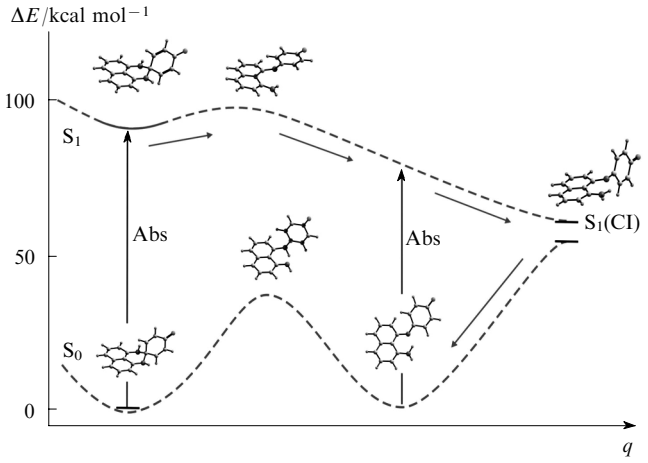
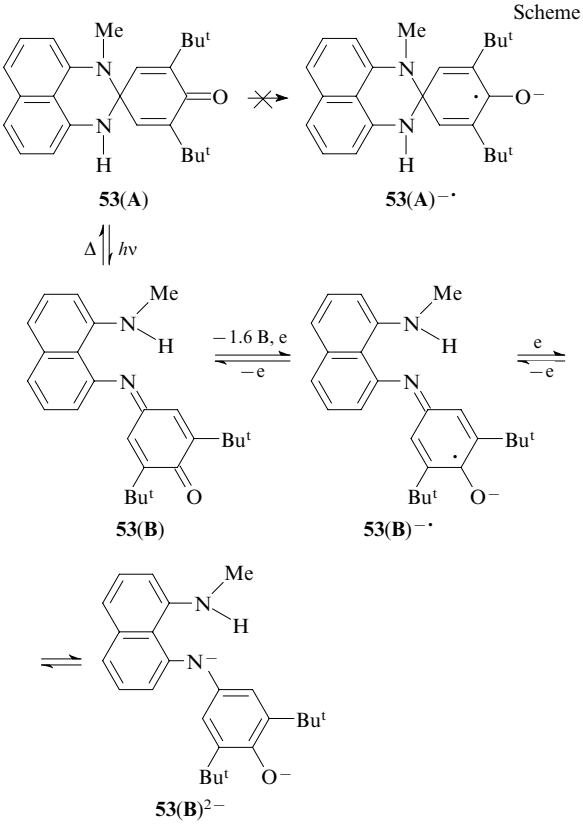


Figure 13. Energy profile of the photochromic rearrangement of model spiro[2,3-dihydroperimidine-2,4′-cyclohexadienone] **53** (R = H, without Bu^t groups) calculated by the DFT B3LYP and UB3LYP/6-31G** methods when system moves along the reaction coordinate (q) corresponding to the elongation and rupture of the $C_{spiro}-N$ bond synchronized with intramolecular proton transfer.[176]
S_1(CI) denotes the point of conical intersection of the S_0 and S_1 PESs.

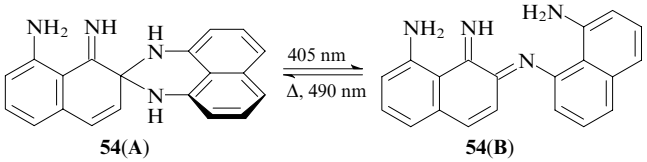
As distinct from species **53(A)**, isomer **53(B)** has an extended chain of conjugated bonds so that the isomers have significantly different electrochemical properties. Spirocyclic form **53(A)** (R = Me) is characterized by a rather low reduction potential ($E^r_p = -2.150$ V *vs.* ferrocene), whereas the reduction potential for form **53(B)** is only −1.230 V. Thus, it is possible to switch the electronic conductance and redox characteristics of compound **53** under the action of light. Scheme 29 describes the stages of the reversible process that occurs when an intermediate potential (∼ −1.600 V) is applied. This potential is sufficient for the reduction of isomer **53(B)** to radical anion **53(B)**$^{-\bullet}$. Under these conditions, generation of form **53(B)** in a spectroelectrochemical cell upon irradiation with UV light enables the observation of formation of radical anion **53(B)**$^{-\bullet}$ and dianion **53(B)**$^{2-}$, which is detected as the switching on of the cathode current, which is switched off when the irradiation is removed.[177]

Scheme 29

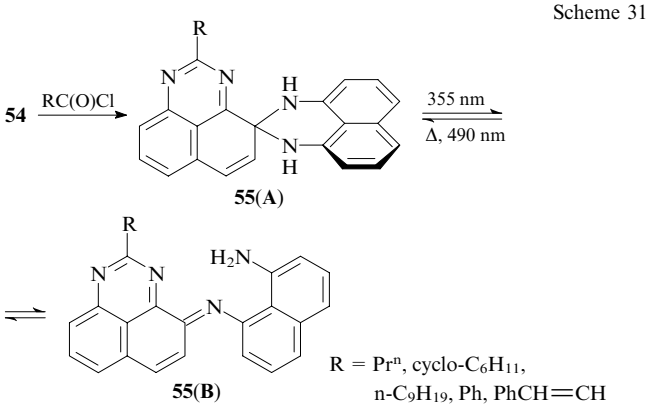


New interesting perimidine-containing photochromic systems **54** and **55** (Schemes 30, 31) have been developed by Japanese researchers.[178–180]

Scheme 30



Scheme 31



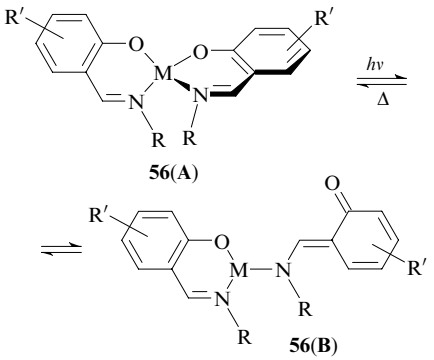
Compounds **55** are synthesized from **54** by the reaction with carboxylic acid halides. UV irradiation of solutions or polymeric films of spirodimer **55(A)** (R = Pr^n) generates a coloured conjugated isomeric form of this compound **55(B)** absorbing in the long-wavelength region of the spectrum (λ_{max} = 650 nm), which undergoes slow thermal relaxation into isomer **55(A)**. A unique feature of this system is that irradiation of cyclic form **55(A)** gives rise to fluorescence with the emission maximum in the region of the long-wavelength absorption of isomer **55(B)**. This effect is completely reversible, isomers **55(A)** and **55(B)** per se exhibiting no fluorescent properties. The nature of the fluorescing form that appears upon initiation of the photochromic rearrangement is still unknown. According to Davis and Tamaoki,[178] its appearance is associated with the *cis–trans* isomerization of the open form with respect to the C=N double bond.

VII. Metal bis(chelate) complexes

By molecular topology, metal bis(chelate) complexes with Schiff bases **56** are full analogues of spiropyrans, and in the case of main-group metal complexes, their structures are even isolobal and isoelectronic. It has been shown[181, 182] that, like spiropyrans and spirooxazines, complexes **56** reversibly rearrange upon UV irradiation of their solutions, polymeric films or thin amorphous and fine-crystalline films

to give deeply coloured isomers, which rapidly relax into the initial forms. The reversible thermal rearrangements of chiral tetrahedral complexes **56** (M = Be, Zn, Cd, Hg) have been comprehensively studied.[91] These rearrangements proceed either *via* the mechanism of bond inversion of the central metal ion or *via* the cleavage–formation of $M_{spiro}-N$ bonds. These low-barrier rearrangements are not accompanied by colouration of solutions of bis(chelate) complexes. As distinct from thermal rearrangements, the initial stage of reversible photoinduced rearrangements of bis(chelate) complexes involves the $M_{spiro}-O$ bond cleavage, as predicted by quantum chemical TDDFT calculations,[40, 183] and the photocoloured isomer should have structure **56(B)** (Scheme 32).

Scheme 32



M = Be, Zn, Co, Cd, Ni, Cu, Pd; R = Alk, Ar;
R′ = H, Hal, NO_2, benzo

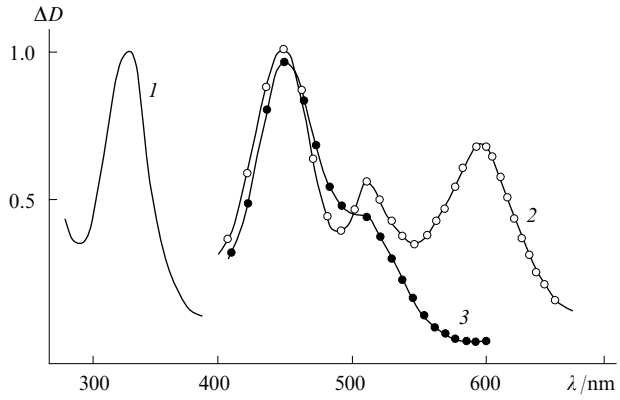
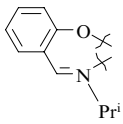
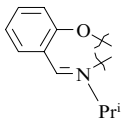
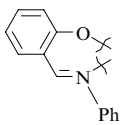
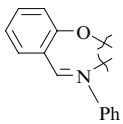
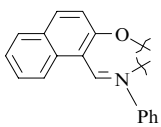


Figure 14. Absorption spectra of bis(chelate) complex **56** (M = Be, R = Pr^i, R′ = H) (toluene, 293 K).[181]
(*1*) Before irradiation, (*2*) after irradiation with a pulse of light from a xenon lamp (500 J, 2×10^{-4} s), (*3*) 20 ms after irradiation.

Irradiation of toluene and methanol solutions of complexes **56** with the light of the photolytic lamp leads to the appearance of new long-wavelength absorption bands with maxima in the range 440–660 nm. These transformations are illustrated by the data in Table 3 and Fig. 14. After the irradiation has been switched off, the induced long-wavelength absorption bands completely disappear in 80–250 ms.

The dynamics of photoinduced transformations of complexes **56** has been studied by femto- and picosecond time-resolved spectroscopy.[184] Figure 15 shows the time evolu-

Table 3. Spectral characteristics of photochromic bis(chelate) complexes **56** (293 K).[182, 184]

M	Ligand	Toluene			Acetonitrile		
		λ_{abs}	λ_{ex}	λ_{fl}	λ_{abs}	λ_{ex}	λ_{fl}
Zn		–	–	–	366 (9500)	366	439
Be		368 [a]	365	425	357 (11 600)	357	428
Zn		402 (17 400)	391	480	395 (18 700)	393	483
Be		–	–	–	383 (19 900)	385	478
Zn		422 (25 400)	425	477	414 (25 300)	418	478

Note. The λ_{max} (nm) are presented for absorption (abs), fluorescence excitation (ex) and fluorescence (fl); for the absorption, the ε_{max} (litre mol^{-1} cm^{-1}) values are parenthesized. [a] Hexane.

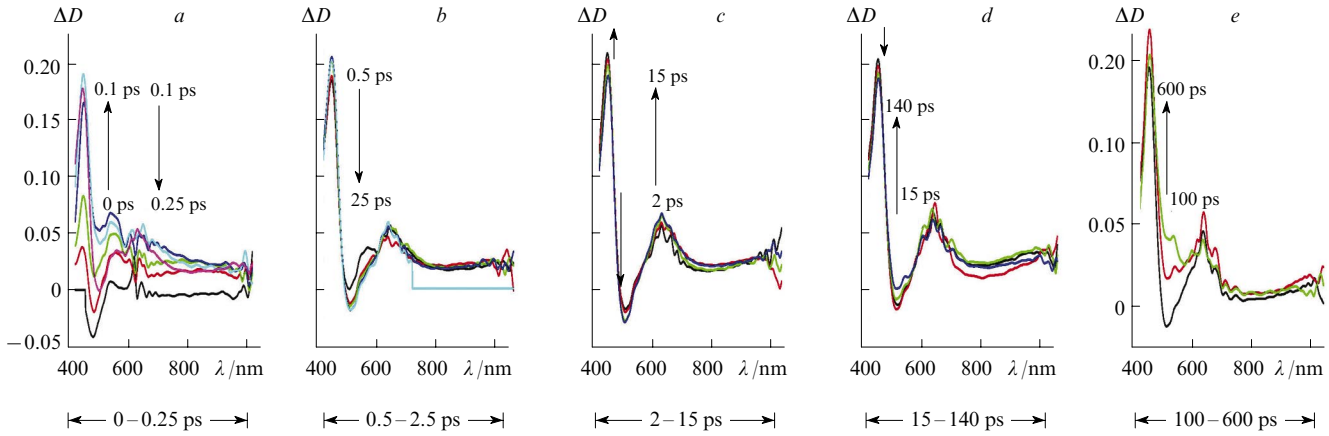


Figure 15. Dynamics of photoinduced spectral changes for a solution of bis(chelate) complex **56** (M = Be, R = Ph, R′ = H) in dioxane in successive time intervals (ps): 0–0.25 (*a*), 0.5–2.5 (*b*), 2–15 (*c*), 15–140 (*d*), 100–600 (*e*) after irradiation with a 100-fs pulse at a wavelength of 308 nm.[185]

tion of the spectrum of beryllium complex **56** (M = Be, R = Ph, R′ = H) in the range 500–1000 nm after excitation with a 100-fs pulse.[185] In the time interval 100–10 000 fs, there is some increase in the absorption with the time constant 0.6 ps (see Fig. 15 *b*,c). The spectral changes with the characteristic time 10 ps in the time interval 10–100 ps are manifested in the narrowing of the absorption band with λ_{max} = 635 nm (see Fig. 15 *d*). In the time interval 100–600 ps, the absorption band at 635 nm becomes stronger and the bands at 496 and 616 nm build up with the time constant τ_2 = 135 ps. These absorption bands arise from photoproduct **56(B)** in the ground electronic state (see Fig. 15 *e*). Quantum chemical modelling of the photochromic rearrangement of complex **56** (M = Be, R = Me, R′ = H)[183] provides insight into the detailed mechanism of the concomitant transformations. As follows from the computational data, the PES of the ground state of complex **56** (M = Be, R = Me, R′ = H) has two local minima in addition to the global minimum of the initial structure of type **56(A)** (**I** in Fig. 16). The former stationary points correspond to the structures with one broken Be–O bond, *i.e.*, to nonplanar intermediate **III** and its conformer **V** (see Fig. 16). After excitation of the complex to the S_1 state, the excited molecule returns to the PES of the ground state S_0 by passing through conical intersection point **VI** into the region of transition state **II**. The resulting open-ring product **III** is at equilibrium with isomer **V**, which corresponds to the only photoproduct experimentally observed 600 ps after femtosecond excitation. The subsequent structural modifications of open-ring intermediates occur within the nano- and microsecond time interval and are associated with the appearance of longer wavelength absorption bands in the range 600–700 nm.

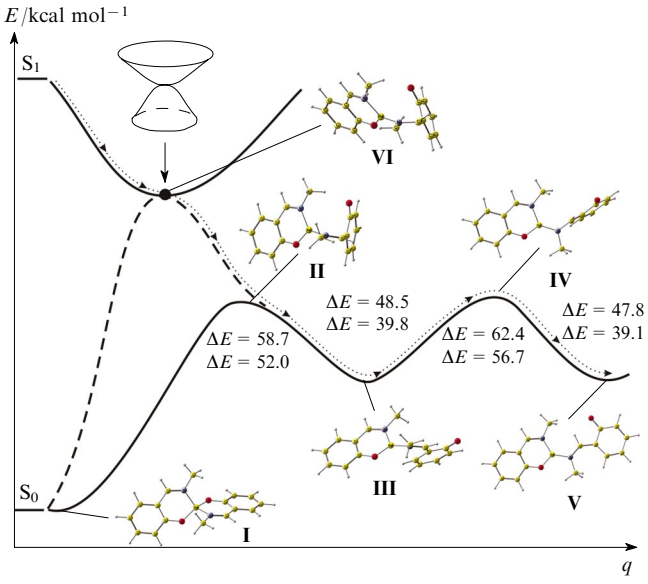


Figure 16. Energy profile of the photochromic rearrangement of complex **56** (M = Be, R = Me, R′ = H) calculated by the RHF/4-31G (higher values) and B3LYP/6-311++G** (lower values) methods.[183]
The full profile is obtained by the mirror doubling of the calculated curve.

Valuable photochromic properties of metal complex analogues of spiropyrans and spirooxazines **56** are the high cyclicity and complete reversibility of the rearrangements described by Scheme 32, the very fast response to irradiation initiating the process and the high rate of the initiated thermal reactions.

VIII. Conclusion

Spiropyrans and after them spirooxazines became the first organic compounds with photoswitchable properties that have found useful technical application. First, their use was limited to fabrication on their basis of optical filters and light-sensitive optical lenses for sunglasses. Although this sector continues to be the main focus of commercial use of spiropyrans and, especially, spirooxazines, active studies of the spectral characteristics and photophysical and photochemical mechanisms of photoinduced rearrangements of spiropyrans and spirooxazines have revealed new potentialities of these compounds as efficient molecular switches of various molecular and macroscopic properties of high-tech materials. Spiropyrans and spirooxazines are at the heart of high-sensitivity and selective chemosensors, hybrid organo-inorganic structures with photocontrolled magnetic charac-

teristics and photocontrolled surfaces with variable hydrophobic and hydrophilic properties. Functionalization with spirocyclic photochromes makes it possible to use light to control the permeability of biological and artificial membranes, the rheological properties of polymers and liquid crystals and the activity of enzymes and to impart additional physical properties, for example, fluorescent properties, to these structures. The efficiency of these applications of spiropyrans and spirooxazines as molecular switches is ensured by the high quantum yields of their photoinduced rearrangements and the sharp difference between the spectral and geometrical parameters of the interconvertible isomeric forms, as well as by available convenient synthetic methods for introducing these compounds into molecules, macromolecules and bulk structures to be studied. At the same time, the major disadvantage of spiropyran and spirooxazine photochromic systems is relatively low thermal stability of their photogenerated isomeric forms, which considerably limits the possibility of their use for creation of rewritable optical memory. This disadvantage can be overcome through targeted structural modifications and by using stabilizing media; however, in this respect, spirocyclic systems are inferior to the photochromic systems for which the mechanism of rearrangement is based on *cis–trans* isomerization or cyclization of hexatriene structures. Possible applications of spiropyrans and spirooxazines, as well as of other photochromic spirocyclic compounds, briefly considered in Sections VI and VII of this review, to the design of new photocontrolled molecular devices and biological materials, logic gates and sensors are still far from being exhausted. It can be expected that new efficient systems of light-controlled molecular switches will continue to be created with taking into account the growing understanding of specific features of the photophysical and photochemical mechanisms of reactions of spirocyclic photochromic compounds and the structure–property correlations revealed for these compounds.

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