DOI: 10.1070/RCR4685

Light-controlled molecular switches based on carbon clusters. Synthesis, properties and application prospects

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The review integrates and analyzes the experimental and theoretical studies published in the last 15 years dealing with the synthesis and physicochemical and photochromic properties of the hybrid molecules based on carbon clusters (fullerenes, nanotubes and graphene) and photochromic molecules (diarylethenes, spiropyrans, spirooxazines and azobenzene). The state-of-the-art trends of the application of photochromic compounds as light-controlled electronic devices, sensors and optical memory elements are considered. The main types of optical molecular switches derived from carbon clusters are described. The synthetic approaches to these hybrid molecules and the relationships between their structure and photochromic properties are discussed.
The bibliography includes 199 references.

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I. Introduction

Molecular switches are molecules able to exist in two or more stable isomeric states that can be reversibly interconverted in response to an external action, such as irradiation, heating and electrical or chemical impact. Depending on the nature of action, molecular switches are classified into optical, electrical and chemical ones.

The enhanced interest in molecular switches is caused by the possibility of using them for the design of fundamentally new devices not only for molecular electronics and photonics, but also for controlling the dynamic properties of materials, targeted transport of biochemical information and signal transmission through biological membranes and also for the development of photochemically and electrochemically switchable catalytic, enzymatic and bio- and chemosensory systems.[1–16] Nanoelectronics is an especially interesting and promising area of application of molecular switches, since nowadays the technological potential for the manufacture of traditional materials for modern computers has virtually reached its maximum.

Photochromic molecules (dihetarylethenes, spiropyrans, spirooxazines, fulgides and azobenzene), which undergo *cis–trans* isomerization, pericyclic transformations or proton phototransfer upon transitions to higher electronically excited states, can be considered as the most studied and popular types of molecular switches.[6,7,17–25] The topological isomers of supramolecules or supramolecular associates are also quite promising as switches.[26–32] Despite the fact that supramolecular associates are thermodynamically less stable than single molecules due to van der Waals forces or hydrogen bonds between molecules, they are kinetically more labile and dynamically more flexible. Quite a number of review articles[2,3,5–9,18–27,29–39] and monographs[1,4,17,28] covering various aspects of synthesis, properties and applications of classical molecular switches have been published to date.

The discovery of fullerenes in 1985[40] and later the discovery of carbon nanotubes and graphene markedly extended the range of existing molecular switches of various types and made it possible to improve them.[41–43] For example, components of organic solar cells,[44,45] nanomachines[46] and holographic recording media[47,48] have been

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Received 1 August 2016
Translation: Z.P.Svitanko

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developed on the basis of fullerene-containing molecular switches and the possibility of using them as memory devices for molecular computers of the future has been studied.[48] Despite numerous publications and the achievements made in the synthesis and investigations of molecular switches based on carbon clusters and their derivatives, unfortunately, the investigation results have not been systematically described, only scattered papers and patents being available.

The authors of this review have attempted to integrate and analyze the available published data on the synthesis, structure and properties of molecular photoswitches based on carbon clusters such as fullerenes, nanotubes and graphene. Particular attention is paid to the prospects of their application.

The following abbreviations are used:

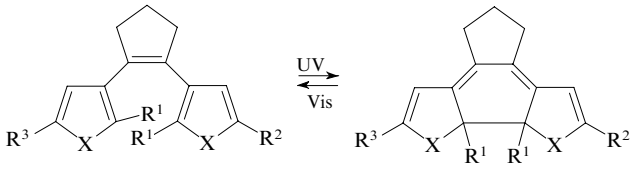
acac — acetylacetonate,
AZO — azobenzene,
AzoM — azobenzene monomer,
β-Ala — 3-aminopropionic acid,
BPhen — 4,7-diphenyl-1,10-phenanthroline,
Boc — *tert*-butyloxycarbonyl,
CLSM — confocal laser scanning microscope,
DAE — diarylethene,
DAE-F — fluorinated diarylethene,
DAE-FN — fluorinated dihetarylethene containing a nitrogen atom in the heterocycle,
DBU — 1,8-diazabicyclo[5,4.0]undec-7-ene,
DHI — dihydroindolizine,
DMAP — 4-dimethylaminopyridine,
DOX — doxorubicin,
DTEo —dithienylethene open-ring form,
DTEc —dithienylethene closed-ring form,
EDC — 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochoride,
FE-SEM — field emission scanning electron microscopy,
FF — fill factor,
FWCNT and MWNT — few/multiwalled carbon nanotube,
GO —graphene oxide,
HDI — hexane-1,6-diisocyanate,
HOMO — highest occupied molecular orbital,
ICBA — indole C_{60} bisadduct,
ITO —indium – tin oxide,
J_{sc} — short circuit current,
LUMO — lowest unoccupied molecular orbital,
LbL — layer-by-layer,
OPE — oligo(phenylene-ethynylene),
PC — photochromic compound,
PCBM — phenyl-C_{61}-butyric acid methyl ester,
PC-FSNP — photochrome-conjugated fullerene silicon nanoparticles,
PEDOT — poly(3,4-ethylenedioxythiophene),
PSS — poly(styrene sulfonate),
P3HT — poly(3-hexylthiophene),
rGO — reduced graphene oxide,
SWNT — single-walled carbon nanotube,
TD-DFT — time-dependent density functional theory,
TDI — toluylene-2,4-diisocyanate,
TEOS — tetraethyl orthosilicate,
UV — ultraviolet radiation,
Vis — visible radiation,
V_g — gate voltage,
V_{oc} — open-circuit voltage,
V_{sd} — source-to-drain voltage.

II. Dihetarylethene-based carbon hybrids

Optical molecular switches are subject to electronic recombinations under photochemical reaction conditions. The interest in optical molecular switches was initiated in 1989 by the fabrication of a high-capacity 3D molecular data storage prototype based on photochromic compounds, which induced vigorous development of the research in this area [23] and consequently extended not only the range of known photochromic structures, but also the scope of their possible applications.

A highly promising class of photochromic bi-stable compounds (owing to their high thermal stability) are diaryl- and dihetarylethenes, which implement the electrocyclic $[2\pi + 2\pi + 2\pi]$-rearrangement mechanism (Scheme 1).

Scheme 1



Colourless (open-ring) form Coloured (closed-ring) form

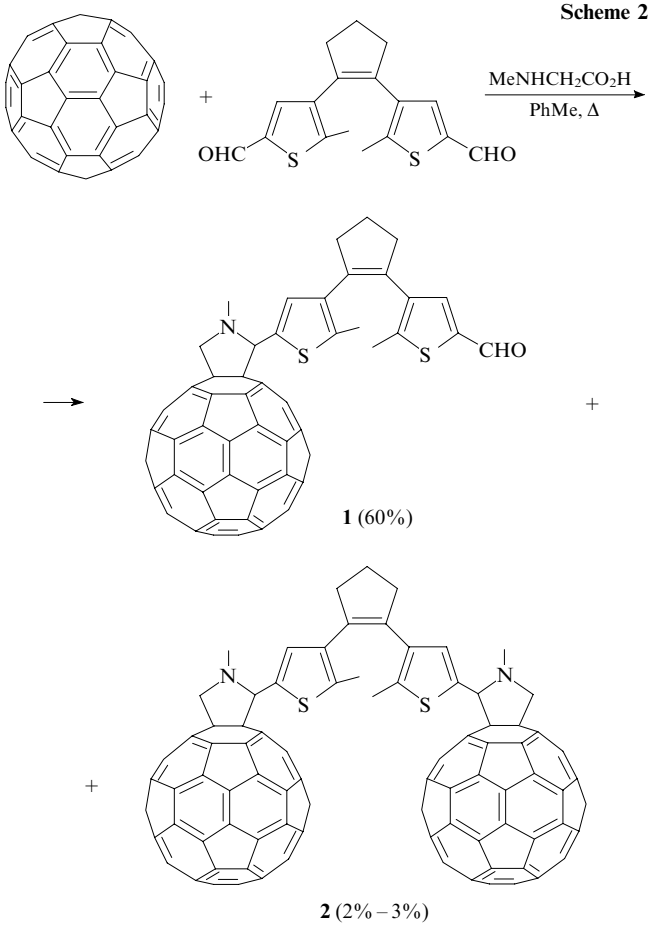
X = S, O, NH or NMe

Currently, a number of 1,2-di(het)arylethene derivatives have been synthesized,[18, 22, 24] which differ in the nature of the ethene moiety,[49 – 55] the presence of electron-donating or electron-withdrawing groups in the aryl or hetaryl moiety [56 – 59] or in the length of the alkyl chain at the active carbon atom of the aryl substituent.[60, 61] This variety was used to determine the effect of the nature and structure of these substituents in a photochromic molecule on the spectral and luminescence properties and thermal stability of the two isomeric forms that undergo reversible photoisomerization, the quantum yields of the reversible photoisomerization, phototransformation cyclability and photodegradation efficiency.

Despite the progress in the synthesis of photochromic diarylethenes, there is still no large-scale production of molecular optical memory systems and optical switches for various purposes based on them. Therefore, in recent years vigorous research has been in progress for investigation and practical implementation of nano-sized photochromic molecules [9] such as fullerenes, nanotubes, graphene and its derivatives. This area is relatively new and has not been adequately explored; therefore, works aimed at chemical modification of these classes of carbon clusters to endow them with specified properties and operating characteristics are of high practical value.

The first examples of spacerless linking of carbon clusters to dihetarylethenes are monomeric (**1**) and dumbbell-type dimeric (**2**) C_{60} adducts synthesized by 1,3-dipolar cycloaddition reaction of fullerene C_{60} with the appropriate azomethine ylide that are generated *in situ* from dithienylethene dialdehyde (Prato reaction,[62] Scheme 2).[63] The *ab initio* HF-3/21G and PBE/3z calculations of the geometric parameters of adducts **1** and **2** have shown [63, 64] that

Scheme 2



the thiophene rings strongly deviate from the plane of the photochromic cyclopentene moiety (Fig. 1). The dihedral angles between the two thiophene rings in compound **1** are 67.12(7) and 61.84(9)° for the antiparallel and parallel conformers, respectively.

In a study of the fluorescence of dyads **1** and **2**, the fullerene core in the singlet excited state has been found to undergo a fast intramolecular electron transfer to give the short-lived radical ion pair $[C_{60}]^{\bullet -}$–$[DTE]^{\bullet +}$; this has been attributed [63] to the short distance between the carbon molecule and the photochromic moiety.

Later [65, 66] it has been shown that linking carbon clusters to dithienylethenes without a spacer leads to almost complete loss of photochromism of the new hybrid molecule. This is consistent with published data [67] for dithienylethene – porphyrin dyads without a fullerene.

For obtaining new photochromic molecules based on C_{60}, a number of fulleropyrrolidines **1** and **3** – **7** with various substituents in the second thiophene ring have been prepared (Scheme 3).[66] Considering the variation of the differential absorption spectra on exposure to UV and visible light, it has been found that these hybrid compounds have poor photochromic properties. Furthermore, the positions of absorption bands of the ring-closed forms of the dithienylethene moieties incorporated in fulleropyrrolidines **1** and **3** – **7** and the efficiency of their photochromic transformations depend on the nature of substituent in the second thiophene ring. However, no persistent structure – property relationships have been established for this series of compounds.

Analogous results have been obtained for a cyclopropane fullerene derivative **8** (Scheme 4), which also shows lower photochromic properties than the initial dithienylethene.[68]

Despite the decrease in the photochromism of the dithienylethene moiety after binding to fullerene, the hybrid compounds thus formed are of certain interest, as they are thermally stable [66] and also stable against photodegradation.[66, 68] This suggests good prospects for further research aimed at the synthesis of new dithienylethene – fullerene C_{60} derivatives in which the photochromic moiety is remote from the fullerene core.

This hypothesis is supported by a publication [65] in which the covalent binding of electron-donating tetrathiafulvalenes with electron-withdrawing pyrrolidine C_{60} derivatives occurs *via* a dithienylethene spacer (Scheme 5). Triads **9** – **12**, in which the pyrrolidine moiety is linked to dithienylethene *via* a phenylethynyl spacer, exhibit photochromic properties, whereas the absence of such a spacer in compound **13** leads to complete loss of photochromism. The presence of electron-withdrawing fluorine atoms in the cyclopentene ring of triads **9** and **11** affects the absorption spectra of only closed-ring forms, which show a pronounced bathochromic shift of the absorption peaks with respect to those of analogues **10** and **12**. Meanwhile, the latter are characterized by higher quantum yields of phototransformations of open forms to closed ones (95% and 91%,

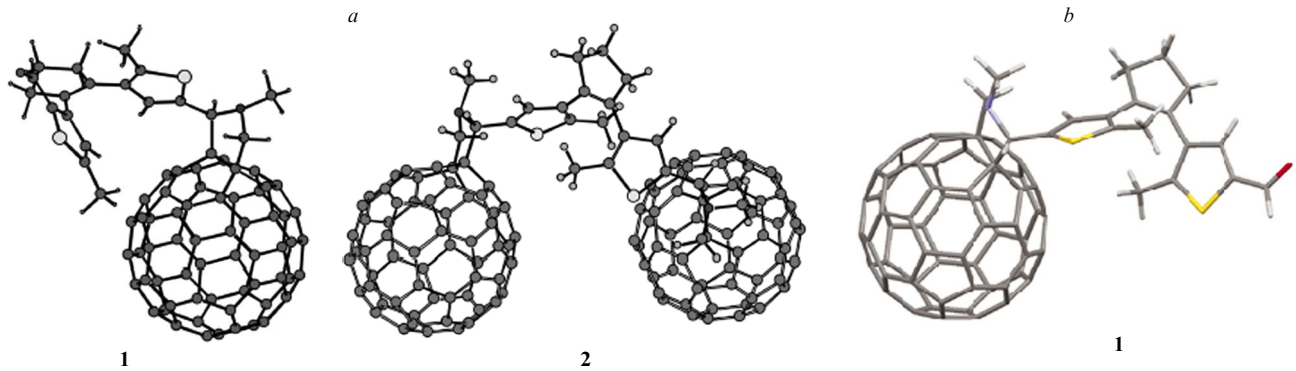
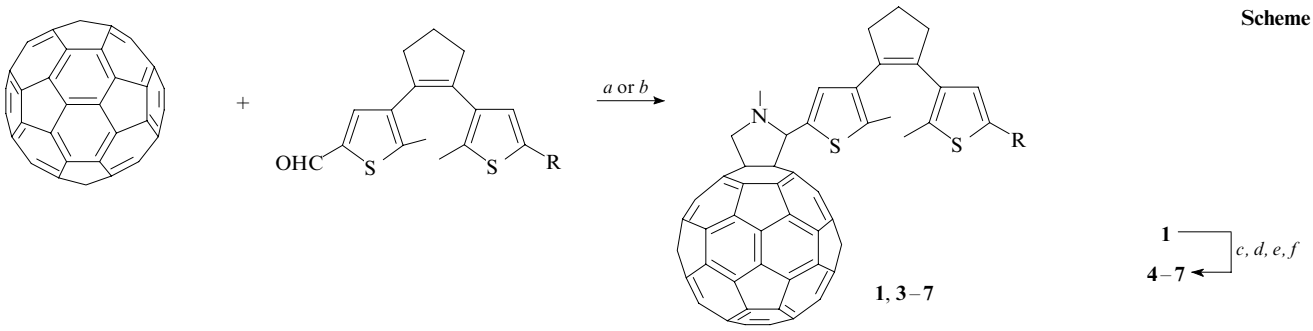


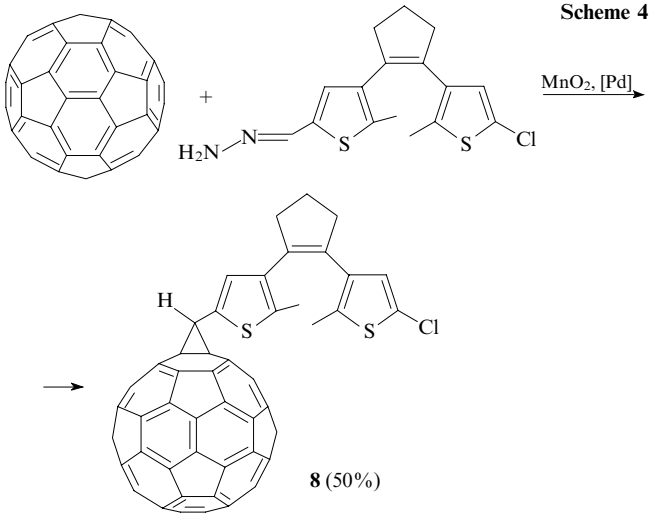
Figure 1. Structures of compounds **1** and **2** optimized by the HF-3/21G method (*a*) [63] and the PBE/3z method implemented in the PRIRODA program (*b*).[64]

Scheme 3



Product	R	Preparation conditions	Yield (%)
1	CHO	*a*: $MeNHCH_2CO_2H$, PhCl, Δ	~60
3	Cl	*b*: $MeNHCH_2CO_2H$, PhCl, Δ	~62
4	CN	*c*: $NH_2OH \cdot HCl$, $FeCl_3$, DMF, Δ, 5 h	~95
5	CH=C(CN)$_2$	*d*: $CH_2(CN)_2$, β-Ala, PhMe, Δ, 2 h	~88
6	CH=NPh	*e*: $PhNH_2$, Na_2SO_4, PhH, Δ, 10 h	~95
7	CH=NPhNH$_2$	*f*: 4-NH_2PhNH_2, Na_2SO_4, PhH, Δ, 10 h	~97

Scheme 4

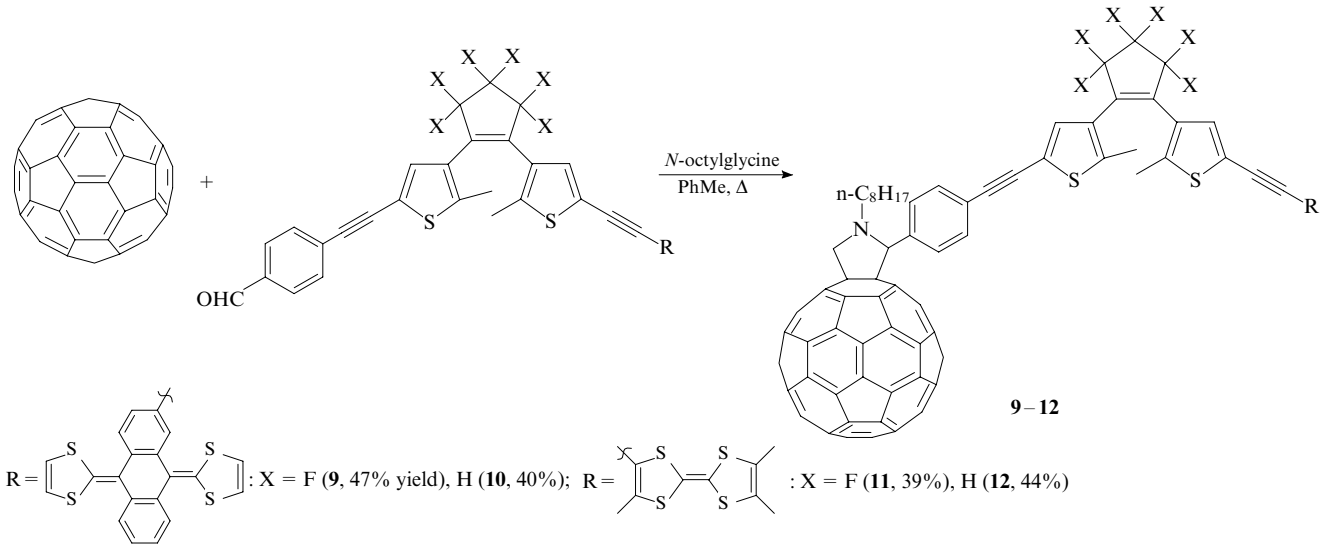


[Pd] = $Pd(acac)_2 - 2\,PPh_3 - 4\,Et_3Al$

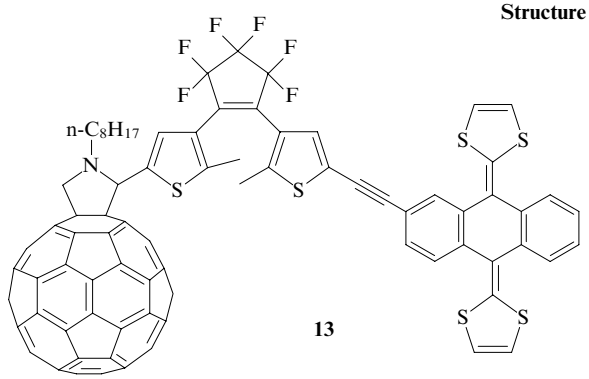
respectively) than fluorine-containing triads **9** and **11** (37% and 43%, respectively). The efficient charge separation in triads **9**–**12** and the possibility to change the lifetime of these states by two orders of magnitude by varying the irradiation wavelength make the approach proposed by Castellanos *et al.*[65] promising for the development of improved solar energy conversion systems.

One more example of the synthesis of hybrid molecules based on fullerenes and hetarylethenes is the formation of photoswitchable photoluminescent nanoparticles from C_{60}, tetraethyl orthosilicate and a dithienylethene amino derivative using the reverse microemulsion method (Scheme 6, Fig. 2).[69] It has been shown that photoluminescence of the resulting PC-FSNP nanoparticles can be reversibly and repeatedly switched by exposure to UV (λ = 365 nm) and visible (λ = 512 nm) light as a result of energy transfer in the intermolecular photoinduced transformations of PC and $C_{60}-O-Si$. The nanosystem thus obtained, which comprises a photochrome molecule and a rigid biocompatible and photostable photoluminescent moiety, can be used to

Scheme 5



Structure 13



13

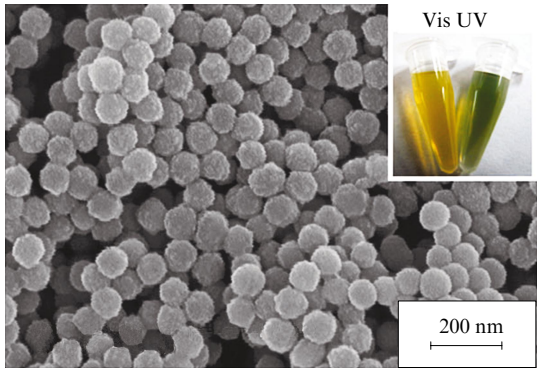


Figure 2. FE-SEM image of nanoparticles.[69]
The inset shows the images of solutions of PC-FSNP before and after UV irradiation.

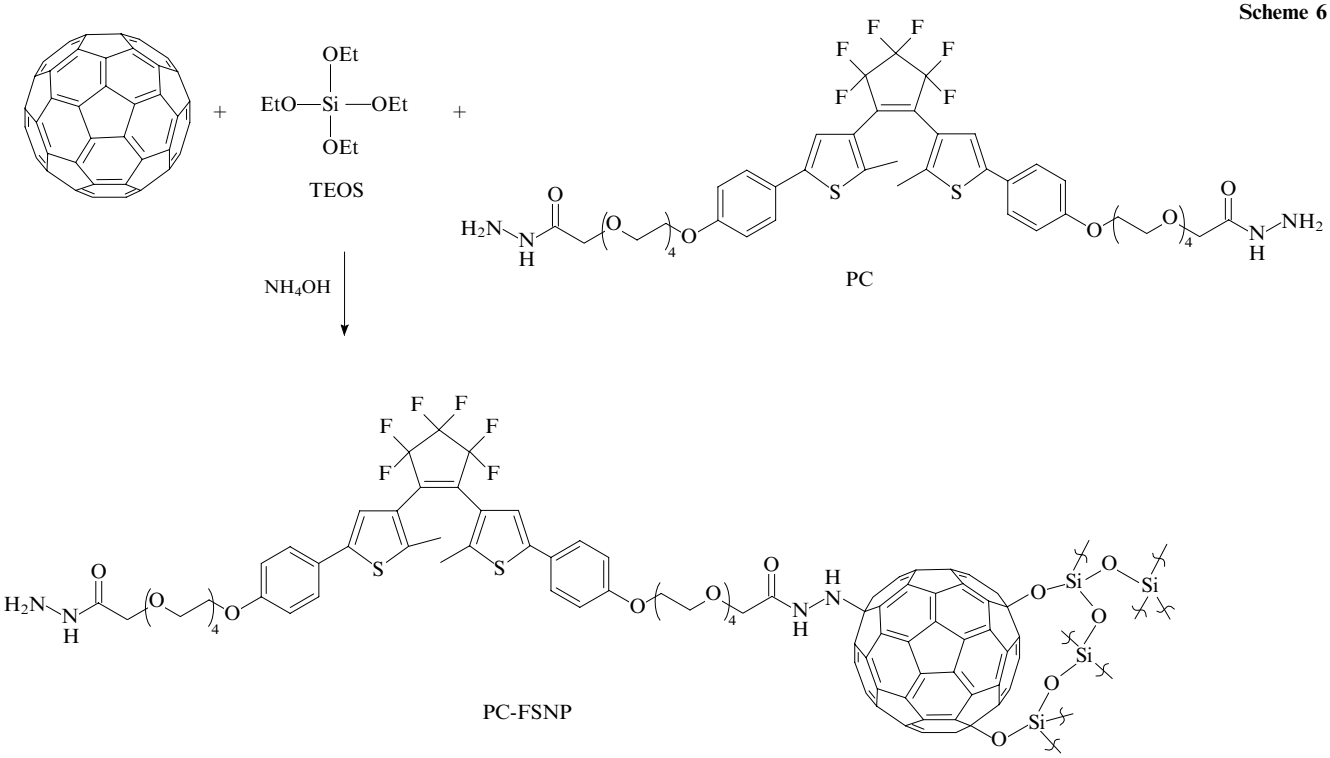
analyze photoswitching processes and to detect the target molecules in a complex biological system with a high signal-to-noise ratio.

The use of dithienylethenes in the switchable supramolecular systems not only considerably extends the range of possible chemical transformations of photochromic molecules, but may also lead to the development of new thermally stable systems. Indeed, as a continuation of studies [70, 71] aimed at the design of electron transfer switches by linking porphyrin or anthracene to photochromic molecules (spiropyran and dithienylethenepyridinium, respectively), Liddell *et al.*[72] synthesized dithienylethene – porphyrin – fullerene triad **14** in 79% yield by the Prato reaction (Scheme 7).

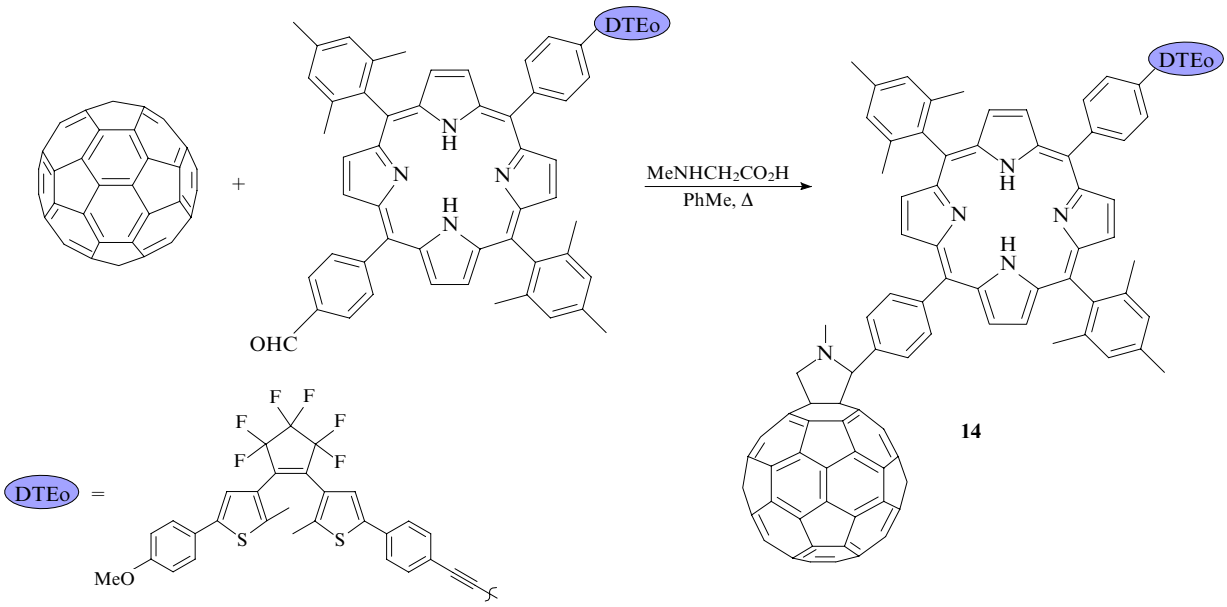
This research demonstrated that in triad **14** with the open-ring photochrome, the porphyrin moiety (P) in the excited state transfers one electron to the fullerene core on exposure to visible light ($\lambda \approx 600$ nm); this gives rise to the radical ion pair $[DTEo\text{-}P]^{\cdot+}[C_{60}]^{\bullet-}$ with a charge separation quantum yield close to unity, as evidenced by the absorption band appearing at about 1000 nm. Ultraviolet irradiation ($\lambda \approx 360$ nm) of triad **14** gives rise to the closed form of the photochrome without generation of the fullerene radical ion. The absence of electron transfer from the porphyrin addend to the fullerene core means that the first excited singlet state of porphyrin in the DTEc-^{1}P – C_{60} system is quenched *via* energy transfer to dithienylethene. The photonic switching of the photoinduced single-electron transfer in triad **14** can be repeated many times; this makes the system suitable for the design of optoelectronic components for digital logic and memory storage nano-devices.

Currently, along with the chemical binding of photochromic molecules to various organic semiconductors, methods based on combining photochromic systems and organic semiconductors in either blends or layers are also widely used for the design of organic transistors.[73 – 81] This is done, most often, using p-type semiconductors.[82 – 84] However, Borjesson *et al.*[85] fabricated and characterized

Scheme 6



Scheme 7



the photoswitchable thin-film transistors based on dihetarylethenes **15**, **16** and n-type organic semiconductors, in particular, fullerenes **17** and **18**.[86–89]

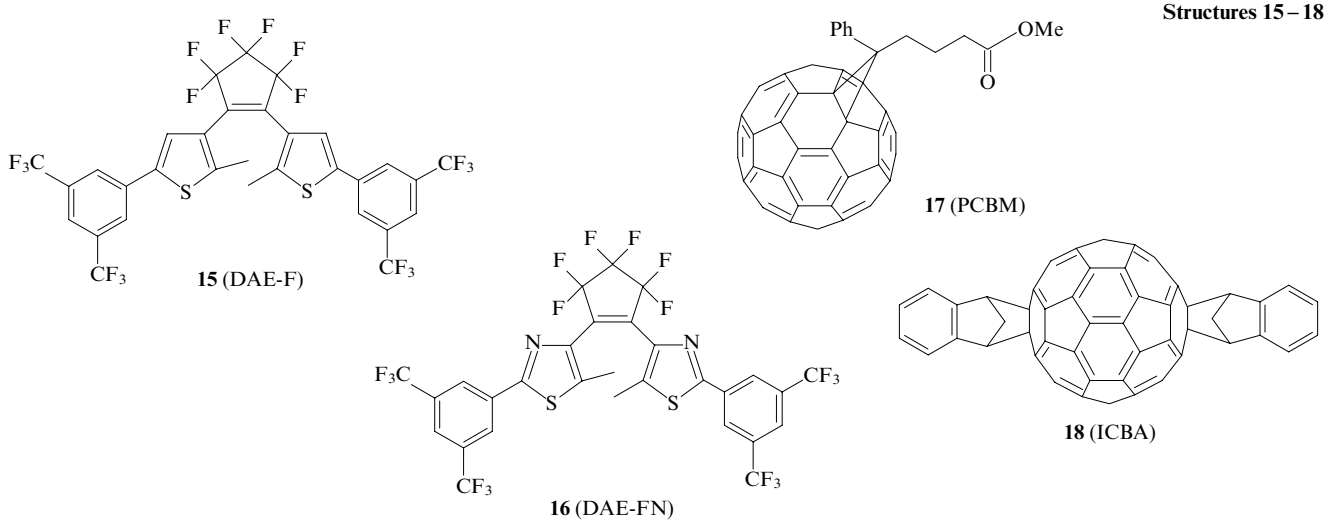
The conduction of the transistor channel was found to be due to the lateral electric field created by the voltage applied to the gate or to photochromic transitions induced by UV light. The best efficiency of switching of the open to closed form (55%) was observed upon UV irradiation (320 nm) of a mixture of compounds **16** and **18**; however, this mixture was more susceptible to fatigue.

In recent years, various types of carbon nanotubes and graphene derivatives have been often employed, apart from fullerenes, to prepare new hybrid photochromic compounds based on nano-sized carbon clusters and diarylethenes.

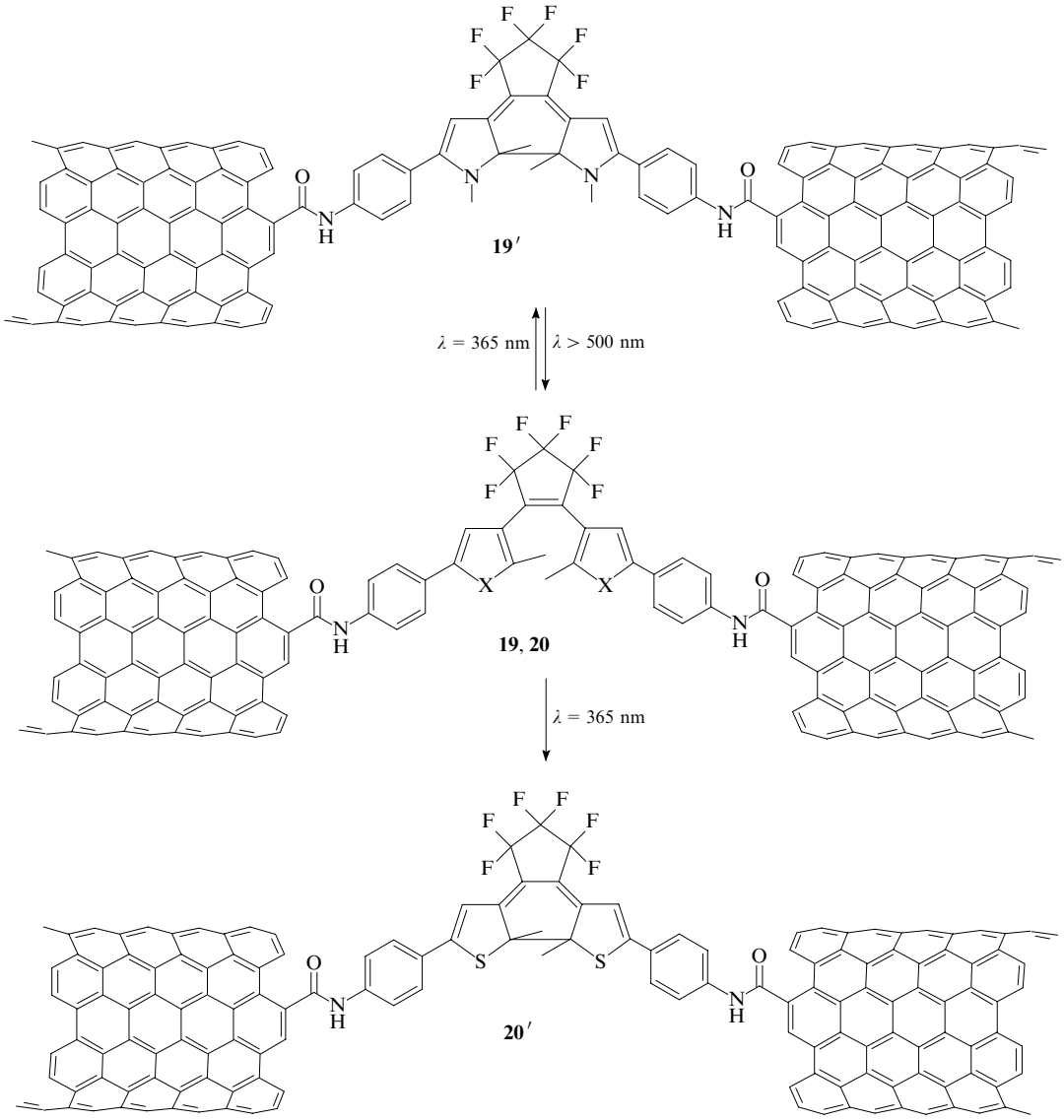
For example, Whalley *et al.*[90] reported the results of conductivity measurements for molecular electronic devices composed of dihetarylethenes and single-walled carbon nanotubes, which act as electrodes. On exposure to light, device **19** with pyrrole groups in the photochromic moiety can be reversibly switched from the insulating (diarylethene open form) to conducting state **19′** (diarylethene closed form). Meanwhile, molecule **20** with thienyl groups undergoes irreversible light-induced rearrangement of the photochrome (Scheme 8). Similar irreversible transformations of dithienylethenes were observed when gold rather than SWNT electrodes were used;[91] this was apparently related to quenching of the first excited state of the photochrome open form by gold. If SWNTs chemically bound to dithienylethene are used as the electrodes, carbon nanotubes dissipate the energy generated in the excited closed form, as has been confirmed by experiments.[18,92] An increase in the π-conjugation length at the ends of these switches leads to a decrease in the quantum yield of phototransformation of the closed to open form.

Additional theoretical and experimental studies have been performed[93] to gain a better understanding of this phenomenon. The lifetime of the photoexcited open isomer **20** was found to be ~ 40 fs. This is quite sufficient for the ring in the dithienylethene moiety to close. The lifetime of the excited state for system **20′** is only 7 – 10 fs; hence, the

Structures 15 – 18



Scheme 8

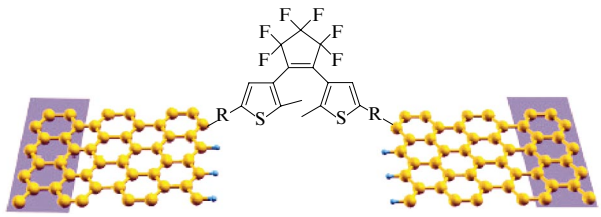


X = NMe (**19**), S (**20**)

reverse photochemical isomerization does not take place. The lack of photoswitching of the closed dithienylethene photochrome in **20′** to the open form is due to strong overlap of the closed-form LUMO with the SWNT conduction band. According to calculations, binding of the nanotube to dithienylethene by an amide bond in the *meta*-position of the phenyl substituent should increase the lifetime of the photoexcited closed form of the dithienylethene moiety from 7 to 130 – 140 fs, which, in turn, would enhance the efficiency of switching on exposure to visible light.

It has been shown[94] that the electrical conductivity of molecular devices composed of nanotubes and diarylethenes can be tuned by choosing chiral SWNTs.

The replacement of carbon nanotubes by graphene electrodes chemically bound to dithienylethenes enables the reversible photoisomerization of the photochromic addend.[95] It has been found that pericyclic transformations in the dithienylethene moiety of such a molecular device (Fig. 3) can be induced by short electric pulses, with a 2 – 4 V voltage bias being sufficient for electrons to rearrange. In the opinion of Motta *et al.*,[95] graphene electrodes differ from gold or SWNT electrodes in less pronounced quenching of the photoexcited closed form of the dithienylethene moiety and in the possibility of tuning the resonance hybridization of the HOMO and LUMO by changing the orientation of the photochromic molecule relative to the graphene plane.



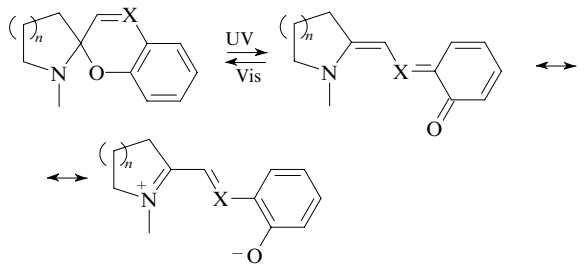
R = CH_2, 4-$PhCH_2$, C(O)NH, 4-C(O)NHPh

Figure 3. New hybrid photochromic molecules based on graphene and dithienylethene.[95]

III. Spiropyran- and spirooxazine-containing carbon clusters

The most popular and extensively studied photochromic spiro compounds are spiropyrans and spirooxazines. These compounds have lower thermal stability than dihetarylethenes; however, the ability to undergo reversible intramolecular transformations (Scheme 9), accompanied by changes in the electronic absorption spectrum, with femto- and picosecond times of photoprocesses, made the photochromic spiro compounds highly promising for the design of information storage and processing devices, in particular, 3D optical memory devices. The phototransformations of spiropyran and spirooxazine molecules have high quantum yields for the forward and reverse reactions and, unlike the photochromic molecules mentioned above, have high two-photon absorption coefficients for both isomers.[23]

Scheme 9



n = 1, 2; X = CH (spiropyrans), N (spirooxazines)

The photochromic properties of spiropyrans with reversible transformations of the spirocyclic moiety were discovered in 1952.[96] This stimulated active search for new types of photochromic molecular switches. The results of these studies formed the grounds for numerous reviews and monographs [1–5, 7, 9, 17–23, 34, 97–100] devoted to targeted synthesis, chemical reactivity and photochemistry of spiropyrans and spirooxazines and mechanisms of thermal and photochemical rearrangements in the photochromic spirocyclic molecules.

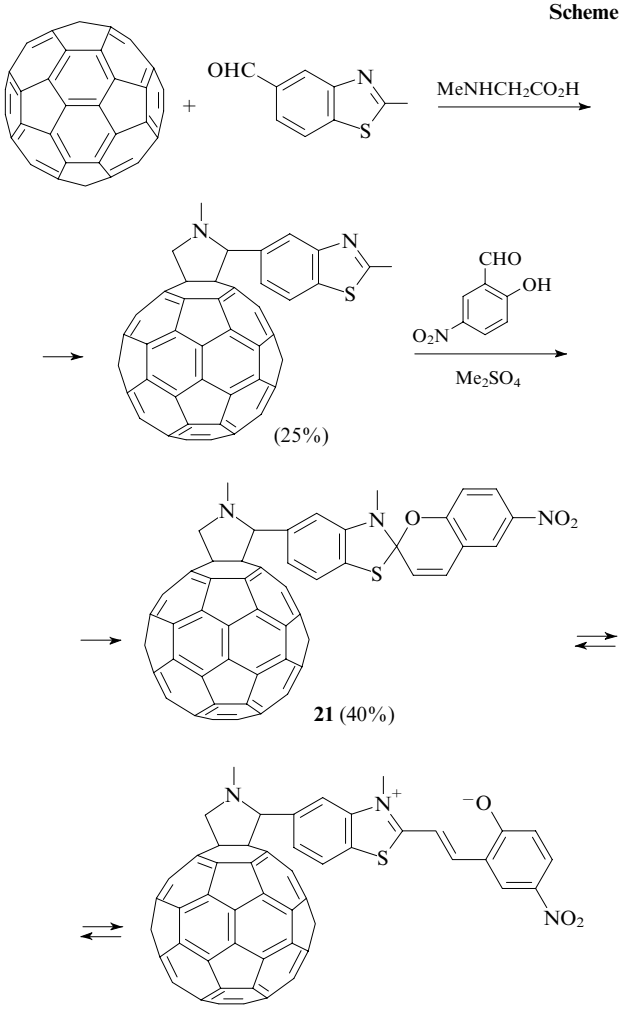
Published data on the modification of photochromic spiro compounds with fullerenes are virtually missing. There are only a few exceptions describing the preparation of a chemically bound C_{60} adduct with spiropyran,[101–103] hybrid C_{60} derivatives containing simultaneously dihydroindolizine and dithienylethene moieties [104] and optical memory elements based on photoswitchable organic field effect transistors in which a layer of photochromic spirooxazine adjoins a fullerene C_{60} layer.[105]

The first example of the synthesis of a photochromic spiro compound covalently bound to a carbon cluster has been reported by Xu *et al.*[101, 102] The authors synthesized fulleropyrrolidine **21** by the Prato reaction (Scheme 10). The proximity of the fullerene core to the spiropyran moiety results in considerable decline of the photochromic properties of compound **21**. The compound has been found to exhibit allochromatic properties in polar solvents (methanol or DMF) (Fig. 4 *a*) and in acidic and alkaline media (Fig. 4 *b*).

An alternative approach to the synthesis of hybrid molecules composed of fullerenes and photochromic spiro compounds is the reaction of C_{60} with spiropyrans containing aldehyde groups. Tuktarov *et al.*[103] prepared a series of pyrrolidinofullerenes **22a**–**c** in ~60% yields (Scheme 11). Photochromic properties were found only for compound **22a**, which has the NO_2 group in the spiropyran moiety. Hybrid compounds **22b**,**c** obtained using chlorine- and fluorine-containing spiropyrans do not undergo photochromic transformations, no matter whether the photoexcitation is continuous or pulsed. A possible cause of this phenomenon is re-absorption of the activating radiation by the fullerene moiety, because the absorption bands of chlorine- and fluorine-substituted spirans considerably overlap with the absorption spectrum of C_{60}. For nitro-substituted spiropyrans, the spectral bands overlap only partly; therefore, photochromic transformations can be observed for hybrid molecule **22a**.

One more approach to the synthesis of hybrid fullerene derivatives with photochromic spiro compounds is to separate the parts by an electron-donating porphyrin moiety.[104] Consecutive transformations of functionally substituted porphyrins, photochromic spiro compounds and dithienylethenes give rise to new C_{60} pyrrolidine derivatives containing two photochromic groups, either simultaneously (compound **23**) or separately (compounds **24** and **25**), that can isomerize independently of each other (Scheme 12, Fig. 5). An unusual photochemical behaviour was found for compound **23**. Initially, the porphyrin moiety of hybrid compound **23** undergoes photoinduced electron transfer to the fullerene core to give the photostationary charge distribution, $P^{\bullet+}-C^{\bullet-}_{60}$. Under these conditions, the quantum yield

Scheme 10



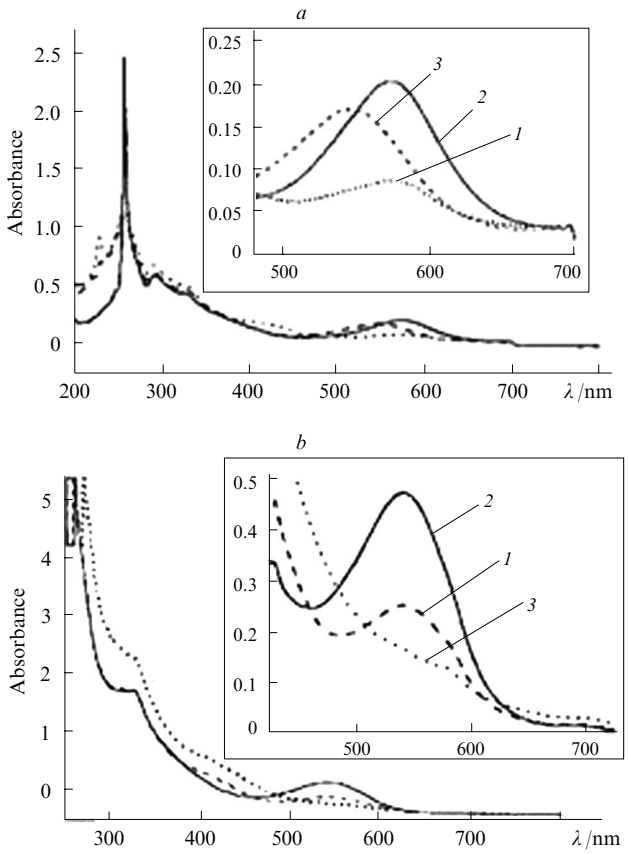
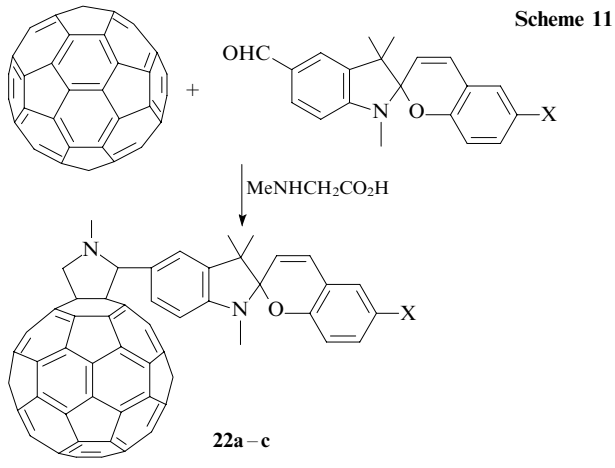


Figure 4. UV spectra of compound **21**.[101, 102]
(*a*) In chloroform (*1*), with DMF added (*2*) or with methanol added (*3*); (*b*) in a chloroform – methanol mixture (5 : 1) (*1*), with acetic acid added (*2*) or with EtONa added (*3*).

of $P^{+\bullet}-C_{60}^{-\bullet}$ is modulated by the two photochromic moieties, each of them independently quenching the porphyrin excited state, thus decreasing the quantum yield of electron transfer almost to zero. On irradiation of molecule **23** with white light ($\lambda > 360$ nm), the quantum yield of electron transfer decreases and white light intensity increases, whereas additional UV irradiation ($\lambda \approx 312$ nm) induces phase reversal, in particular, the quantum yield increases

Scheme 11



X = NO_2 (**a**), Cl (**b**), F (**c**)

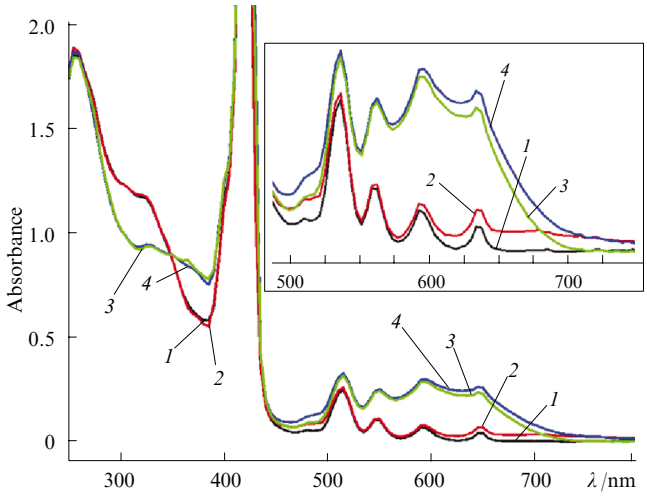
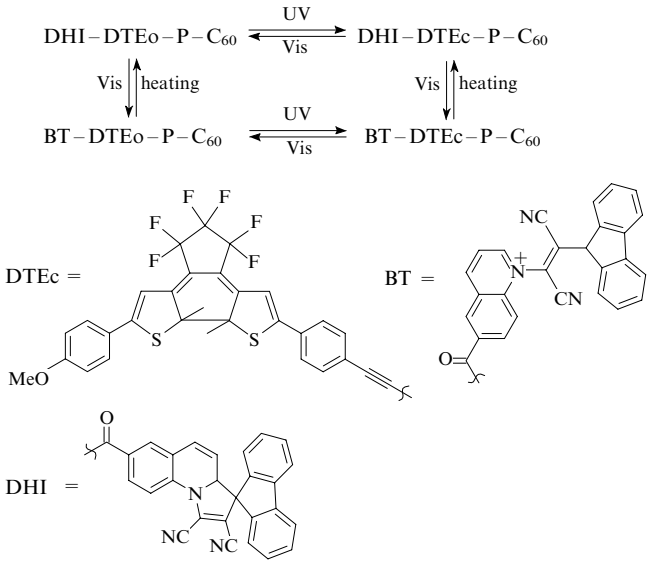


Figure 5. Variation of the absorption spectrum of compound **23** in 2-methyltetrahydrofuran enriched in isomers: DHI – DTEo – P – C_{60} (*1*), BT – DTEo – P – C_{60} (*2*), DHI – DTEc – P – C_{60} (*3*) and BT – DTEc – P – C_{60} (*4*).[104]

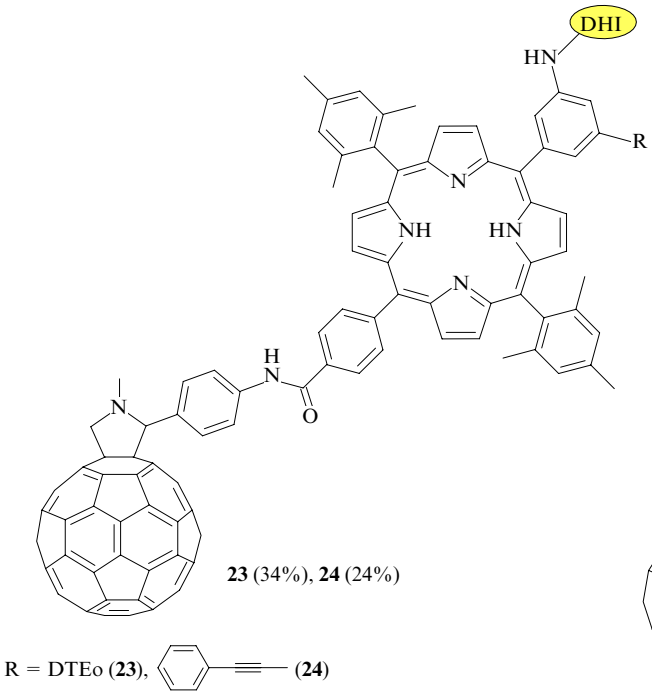
with increasing white light intensity. These effects, which arise in a relatively simple system, attest to similarity of molecule **23** with electronic signal converters. This opens up prospects for using this molecule as molecular memory and also for photochemical labelling and targeted drug delivery.

In compounds **21** – **25** described above,[101 – 104] the photochromic spiro molecule is chemically bound to the fullerene core. Frolova *et al.*[105] have shown that the insertion of a photosensitive spirooxazine film at the interface between semiconductor (fullerene) and dielectric layers may give rise to a low-voltage photoswitchable organic field effect transistor (Fig. 6). The photo- and electroisomerization processes of spirooxazine are depicted in Scheme 13. This transistor has a switching coefficient of > 1000, which is 2 – 3 orders of magnitude higher than the known values of this coefficient for photoswitchable optical field effect transistors containing photochromic compounds.[76 – 79, 106, 107] The results indicate that the proposed

Scheme 12

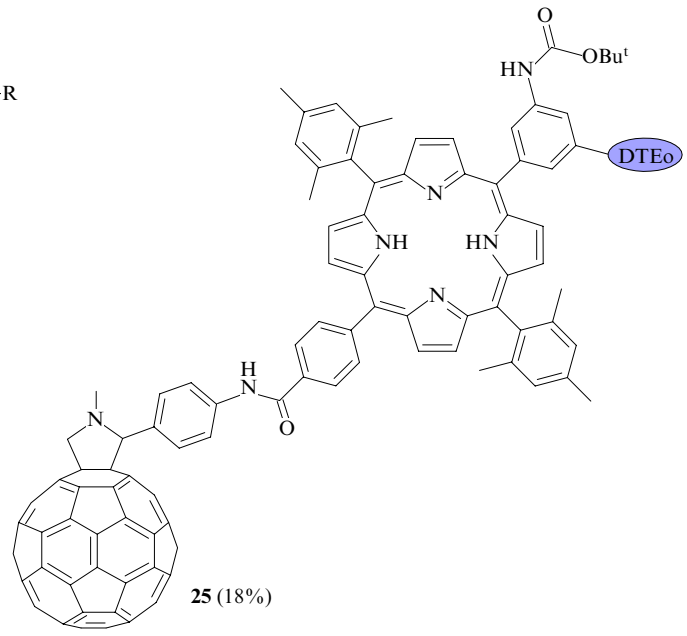


Structures 23 – 25



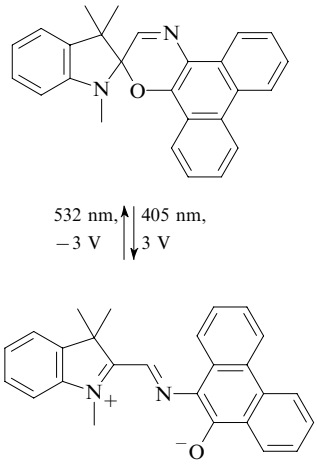
23 (34%), **24** (24%)

R = DTEo (**23**), (**24**)



25 (18%)

Scheme 13



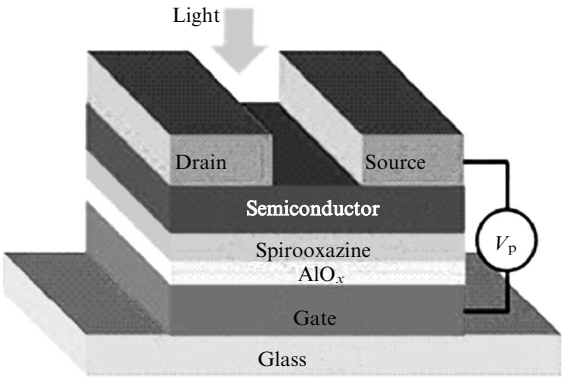
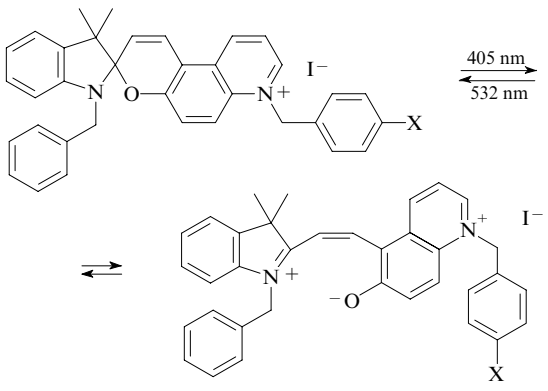


Figure 6. Architecture of a photoswitchable optical field effect transistor.[105]

approach is promising for the design of multi-bit optical memory elements with good stability and reliability and improved electrical characteristics.

A similar method for the fabrication of light-sensitive components was implemented by Frolova *et al.*[108] As photochromes, the authors used quaternary salts of spiropyrans **26** and **27** (Scheme 14). The transistors thus obtained exhibited impressive electrical characteristics — wide memory windows, low operating voltages, switching coefficients exceeding 10^4 and high switching speeds (programming time of 0.5 – 20 ms). It was shown that even minor differences in the structures of spiropyran salts change the behaviour of the transistors. Indeed, the structure containing spiropyran **26** operates like an energy-independent flash memory element owing to the reversible photoelectric switching of the photochrome and shows good electrical performance and also high stability and reproducibility of the write – read cycle. Meanwhile, the device based on spiropyran **27** showed irreversible switching resembling the operation of read only memory elements. Thus, with performance of optical field effect transistors being dependent on the

Scheme 14



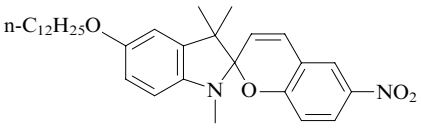
X = H (**26**), NO_2 (**27**)

photochrome structure, it becomes possible to tune the electrical parameters and design stable and reliable multi-bit optical memory elements with enhanced performance characteristics.

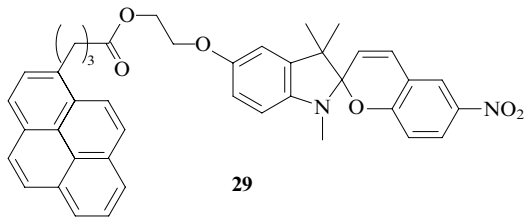
Later, it has been shown [109] that even minor changes in the structure of the photochromic spiro compound have a strong influence on the electrical behavior of photoswitchable optical field effect transistors and programming time of the device.

Apart from fullerenes, carbon nanotubes can also be used as the semiconductor layer in field effect transistors. Guo *et al.*[110] fabricated field effect transistors based on SWCTs and spiropyrans. The associates of photochromes non-covalently bound to the surface of a carbon material were obtained using spiropyrans **28** and **29**, which contain a long alkyl (or pyrenyl) substituent. By chemical transformations, it is possible to change the wavelengths of the forward and reverse photoisomerization, which allows for fabrication of different devices that respond to light of a particular wavelength. At a primitive level, these devices accomplish functions analogous to biological ones such as vision and photosynthesis.

Structures 28, 29



28

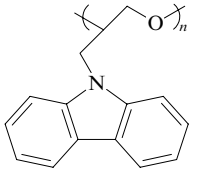


29

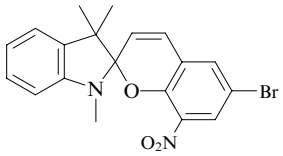
The obtained [105, 108, 110] data on various combinations of photochromic and semiconductor materials based on carbon clusters are of great practical value for the development of potential industrial processes for the manufacture of new types of memory devices and light sensors based on organic materials.

In order to find new photochromic materials that could be considered as negative photochromic data storage media suitable for direct holographic recording in the visible spectral region without preliminary UV irradiation, Ciapurin *et al.*[111, 112] developed a new photochromic polymeric composite consisting of poly(*N*-epoxypropylcarbazole) **30**, 6-bromo-1′,3′,3′-trimethyl-8-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (**31**) and a mixture of fullerenes C_{60} and C_{70} taken in a 10 : 1 : 0.001 ratio. The resulting composite allows for recording holograms with diffraction efficiency of up to 23% at 1600 mm^{-1} under laser irradiation (λ = 532 nm).

Structures 30, 31



30



31

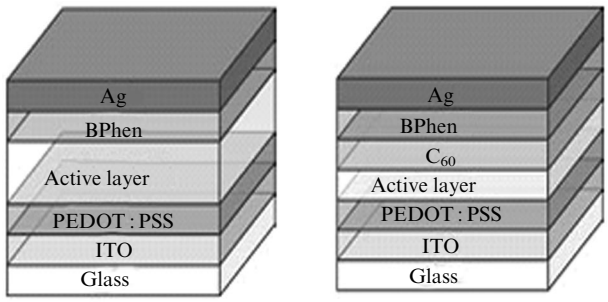


Figure 7. Possible diagrams of the organic solar cells. The active layer contains a spirophotochrome as a donor and PC[60]BM as the acceptor component.[113]

One more possible trend is the use of interfacial films of merocyanine compounds and fullerenes or their derivatives for the design of bulk heterojunction organic solar cell components (Fig. 7). The active layer in these solar cells can be represented by either mixtures or interfacial films of fullerene or fullerene derivatives with a merocyanine compound. The key characteristics of organic solar cells based on fullerenes and merocyanines are summarized in Table 1.

Other analogous studies have also been reported.[118 – 127] Characteristics of some types of solar cells based on merocyanines are comparable with characteristics of devices in which the active layer is represented by poly(3-hexylthiophene), a polymeric p-type semiconductor with good charge carrier mobility. The redox and film-forming properties as well as the packing of merocyanines can be easily tuned by varying the structure of substituents in their

Table 1. Characteristics of solar cells fabricated on the basis of fullerenes and merocyanines.

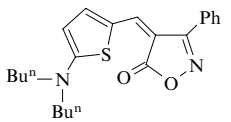
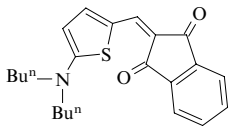
Formulae of active layer compounds	V_{oc}/V	J_{sc}/mA cm^{-2}	FF	PCE (%)	Ref.
 + PCBM	0.57	2.08	0.28	0.44	114
 + PCBM	0.63	2.9	0.27	0.49	114

Table 1 (continued).

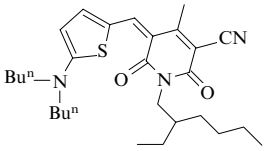
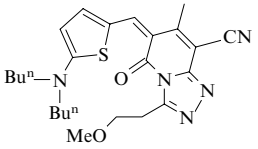
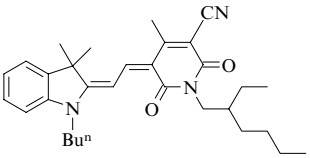
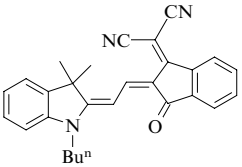
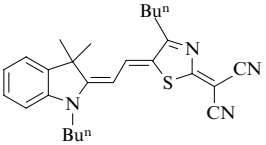
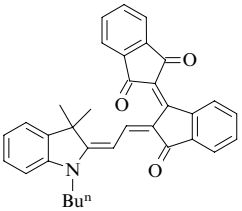
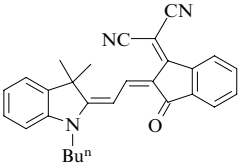
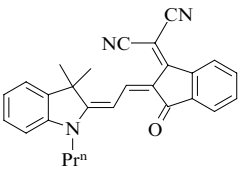
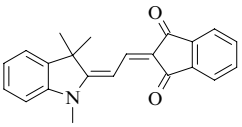
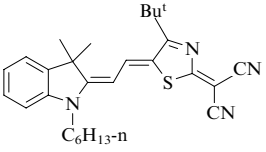
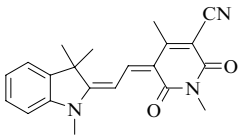
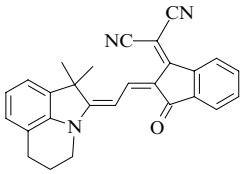
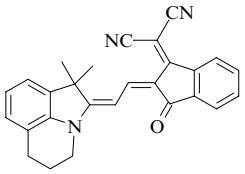
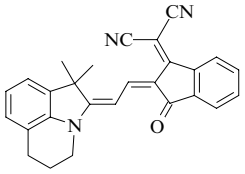
Formulae of active layer compounds	V_{oc}/V	J_{sc}/mA cm^{-2}	FF	PCE (%)	Ref.
 + PCBM	0.73	4.0	0.32	0.91	114
 + PCBM	0.49	3.1	0.29	0.43	114
 + PCBM	0.77	4.0	0.29	0.87	114
 + PCBM	0.90	5.3	0.32	1.54	114
 + PCBM	0.76	6.3	0.36	1.74	114
 + C_{60}	0.52	4.8	0.28	0.8	113
 + C_{60}	0.65	8.9	0.41	2.6	113
 + C_{60}	1.00	7.5	0.55	4.1	115
 + C_{60}	0.83	5.8	0.55	2.6	116
 + C_{60}	0.71	8.8	0.42	2.7	116

Table 1 (continued).

Formulae of active layer compounds	V_{oc}/V	J_{sc}/mA cm^{-2}	FF	PCE (%)	Ref.
 + C_{60}	0.56	6	0.41	1.5	113
 + C_{60}	0.79	10.8	0.46	4.5	113
 + C_{60}	0.96	12.6	0.47	6.1	117
 + C_{70}	0.50	6.8	0.33	1.8	117

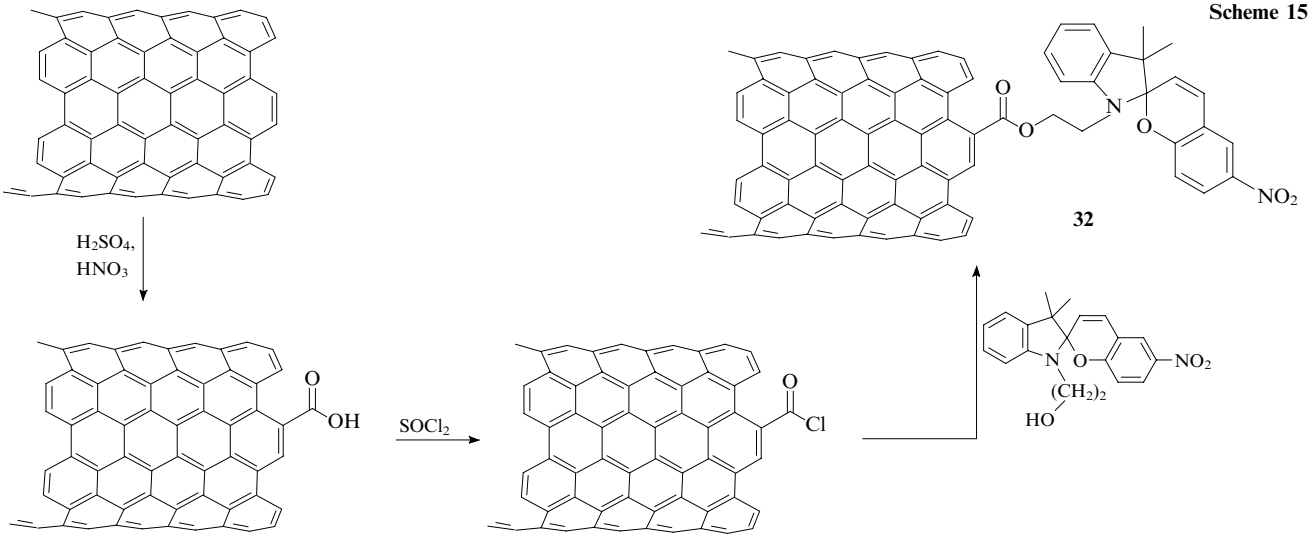
molecules. In the near future, substantial progress can be expected in the design of bulk heterojunction cells and tandem devices.

Unlike fullerenes, carbon nanotubes chemically bound to photochromic spiropyrans and spirooxazines are widely represented in the literature. The first studies along this line were accomplished in 2004.[128] Hybrid compound **32** was synthesized according to Scheme 15. It was found that the intensity of band-to-band electron transitions in superconducting chemically modified SWNTs can be reversibly changed upon light-induced valence band filling/depletion or photoinduced change in the polarity of the spiropyran moiety of hybrid molecule **32** (Fig. 8). This is a rather simple and convenient tool for controlling the conductivity of these semiconductor systems.

A hybrid of a multiwalled carbon nanotube with spirooxazine obtained in a similar way also exhibits a photocontrolled conductivity (Scheme 16).[129]

As a continuation of these studies, spiropyran-containing hybrid compound **33**, in which the photochrome moiety and the nanotube are separated by a triethylene glycol spacer, has been synthesized (Scheme 17).[130] Ultraviolet irradiation (λ = 365 nm) of the initial spiropyran during 30 s leads to increasing intensity of the absorption band of the merocyanine form (λ = 594 nm), which is converted back to spiropyran after a 8 min storage in the dark. In turn, the absorption spectrum of hybrid compound **33** has a

Scheme 15



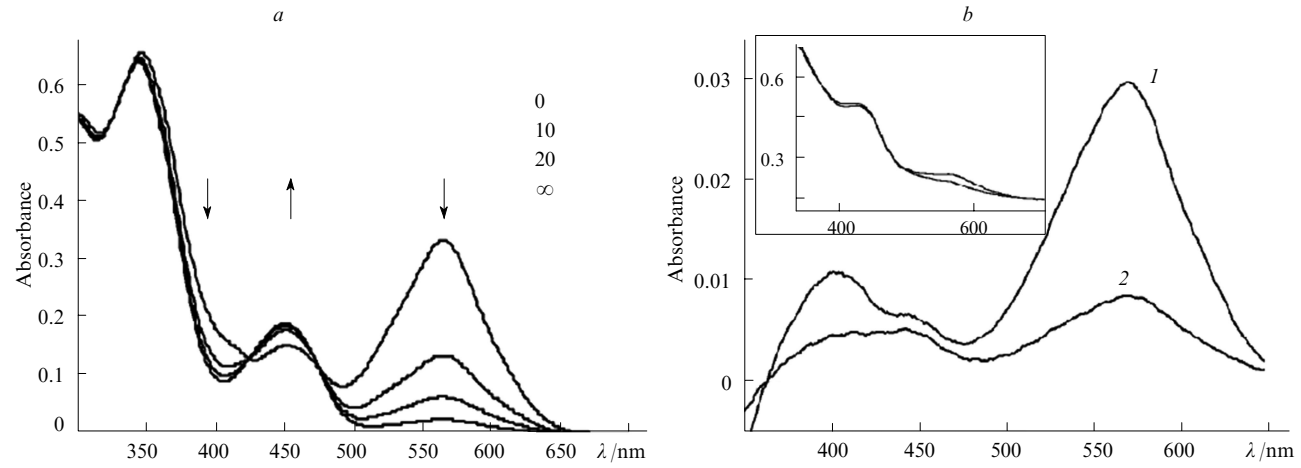
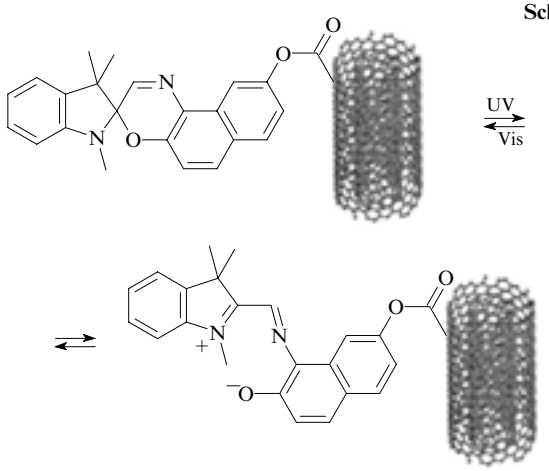


Figure 8. Variation of the absorption spectrum of the initial spiropyran in DMF after UV irradiation for 30 s (*a*)† and differential absorption spectra (*b*) of a solution of compound **32** in DMF after UV irradiation (*1*) and after irradiation at $\lambda > 520$ nm for 30 s (*2*).[128] (*a*) The arrows mark the spectral changes following increase in the spiropyran storage time in the dark from 0 to ∞ (the infinity sign means that no spectral changes were observed after 30 or 40 s, 1 min and so on; the time limit was not indicated by the authors); (*b*) the inset shows the change in the absorption spectrum before (lower curve) and after (upper curve) UV irradiation.

Scheme 16

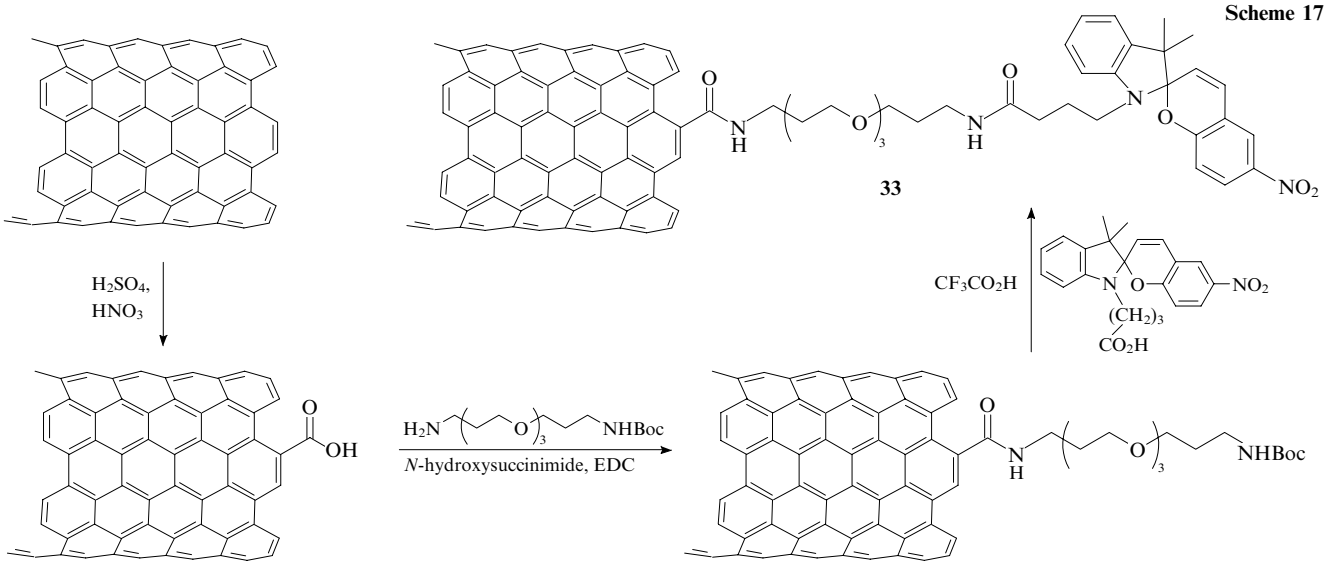


maximum at 417 nm corresponding to the spiropyran moiety. The shift of the absorption band of the photochromic addend in **33** with respect to its position in the spectrum of the initial spiropyran is caused by the π – π-interaction between spiropyran and carbon atoms of the nanotube surface. Exposure of the hybrid molecule to the UV light for 30 s gives rise to the merocyanine form, which has an absorption maximum at 556 nm (Fig. 9).

It is noteworthy that Malic *et al.*[131] predicted a bathochromic shift in the absorption spectra of hybrid materials based on carbon nanotubes and spiropyrans caused by

† Here and in other absorption spectra, the arrows mark the changes that occur upon successive modification of particular conditions (time of irradiation or storage in the dark, concentration and so on). The arrows pointing up and down correspond to an increase and a decrease in the absorption peak intensity, respectively.

Scheme 17



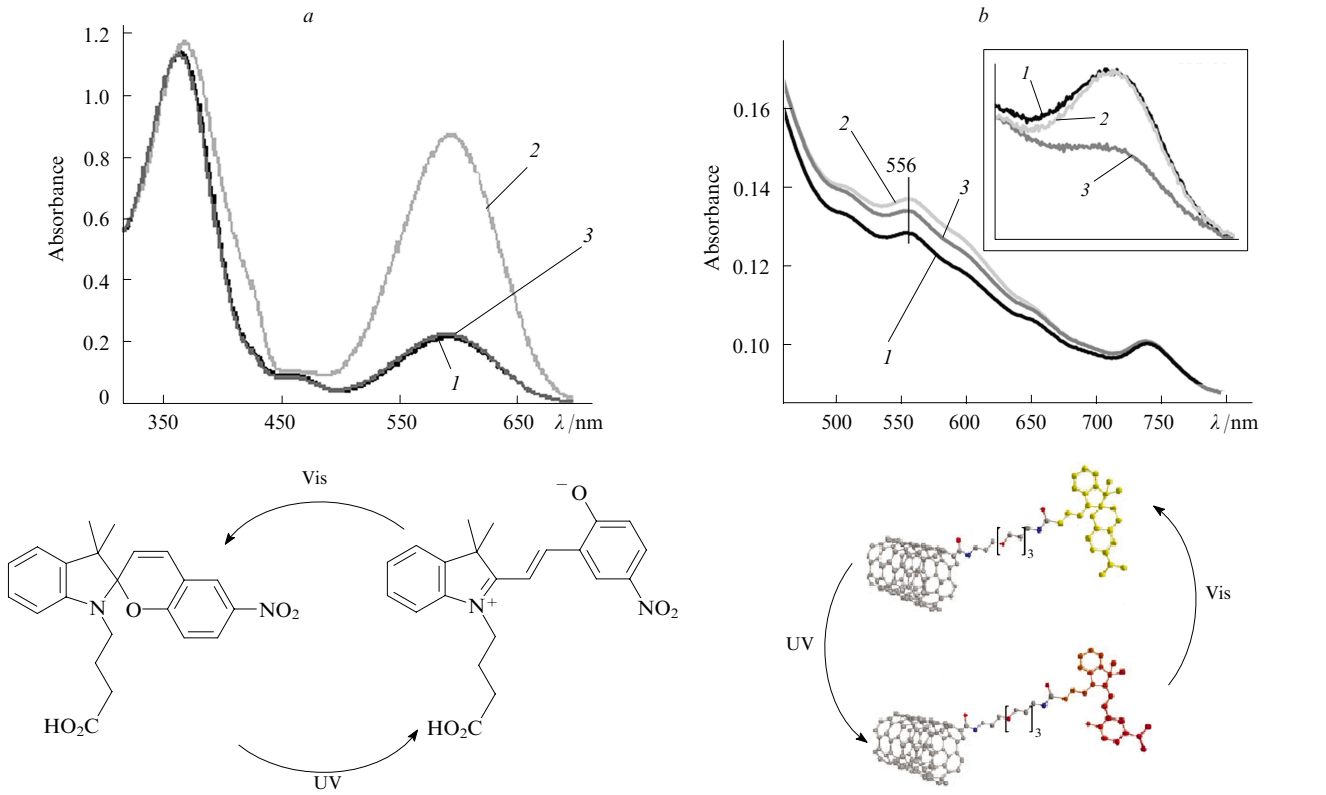


Figure 9. Changes in the absorption spectra of a spiropyran solution in DMF (*a*) and compound **33** (*b*).[130]
(*a*) (*1*) Spiran, (*2*) after UV irradiation (λ = 365 nm) for 30 s, (*3*) after storage of the solution in the dark for 8 min; (*b*) (*1*) compound **33**, (*2*) after UV irradiation (λ = 365 nm), (*3*) after irradiation with visible light (λ = 560 – 900 nm) for 30 s.

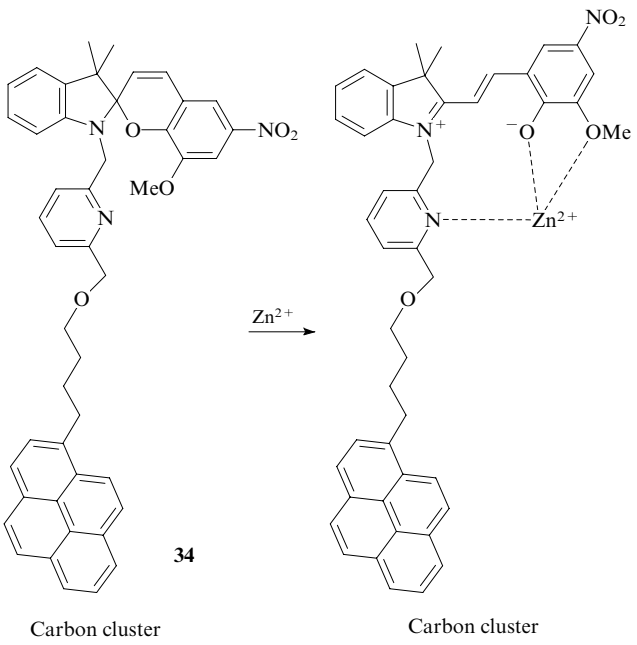
efficient coupling between the charge carrier and the switchable dipole molecule. Depending on the conformation of the attached molecule, the transition energy corresponding to the bathochromic shift can reach 100 meV.

Subsequently, it has been shown in relation to chemically non-bonded carbon nanotubes and spiropyrans [132, 133] that the merocyanine absorption band at 570 nm shifts bathochromically in the case of a shorter spacer separating the photochrome moiety and the SWNT. Also, in hybrid compounds with a short spacer, the merocyanine form is stabilized by a carbon nanotube, which retards the reverse merocyanine → spiropyran switching.

In continuation of research aimed at the synthesis of new hybrid materials composed of various carbon clusters and photochromic compounds, Perry *et al.*[134] developed cationic receptors based on spiropyran **34** non-covalently linked to the surface of carbon materials (nanotubes, graphene) *via* a pyrene anchor (Scheme 18). The receptors showed high selectivity and sensitivity to Zn^{2+} cations, which induce isomerization of spiropyran to highly coloured merocyanine form. Therefore, it is possible to determine the Zn^{2+} concentration by recording the absorption or emission spectra. Studies of the electronic properties of new materials are in progress.

While the hybrid composed of graphene oxide and spiropyran **34** obtained in the study cited above [134] did not respond to Zn^{2+} ions, Li *et al.*[135] succeeded in the preparation of a highly sensitive colorimetric sensor for fluoride anions on the basis of GO and silicon-containing spiropyran **35** (Scheme 19, Fig. 10). As can be seen in Fig. 10,

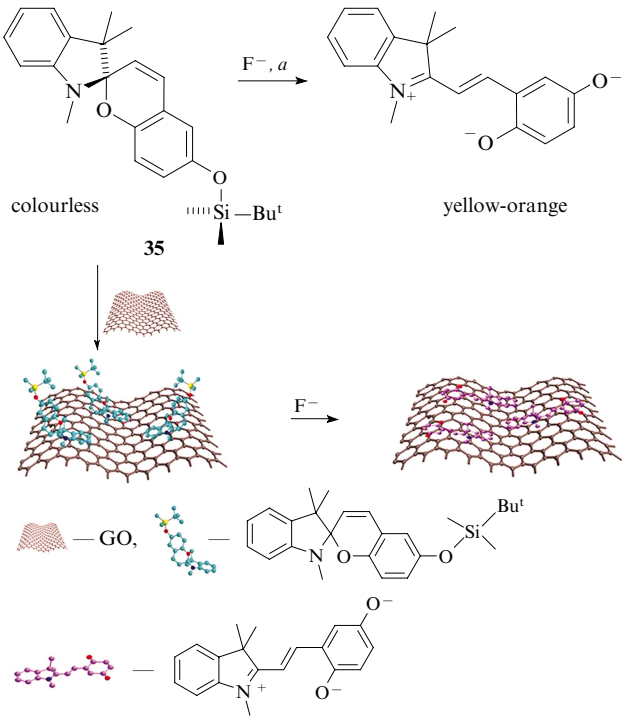
Scheme 18



the sensor based on graphene oxide and spiropyran was much more sensitive to F^- ions than the initial photochrome without a carbon material. The use of graphene oxide markedly reduced the spiropyran response time (from

180 to 30 min) to fluoride anions and decreased the limit of their detection by more than an order of magnitude; this allowed for the successful use of the obtained nanocomposite to monitor F^- ions in biological fluids.

Scheme 19



(*a*) pH > 7.0, polar solvent (acetonitrile)

Unlike researchers cited above, other authors[136, 137] tested the hybrid compound based on graphene oxide and spiropyran **36** as a material for optical field effect transistors. The enormous interest in the application of graphene derivatives as two-dimensional semiconductors for transistors or other electronic devices is due to the possibility to obtain one- or two-atom-thick layers. In such a two-dimensional material, an electron can move within only one layer, that is, much faster than in conventional semiconductors. The currently existing transistors are mainly made of silicon; they comprise several layers, the electrons within the layers are not rigidly fixed and can move in any direction, which leads to substantial energy loss *via* scattering.

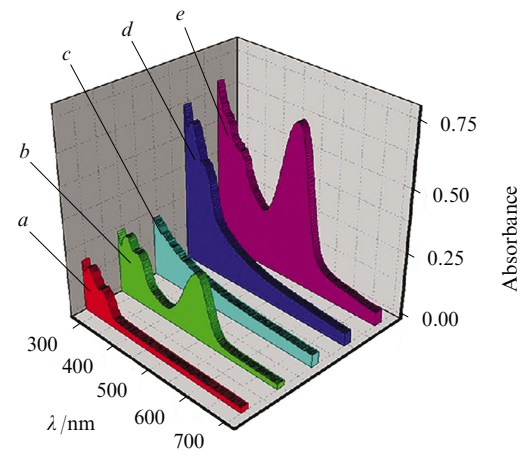
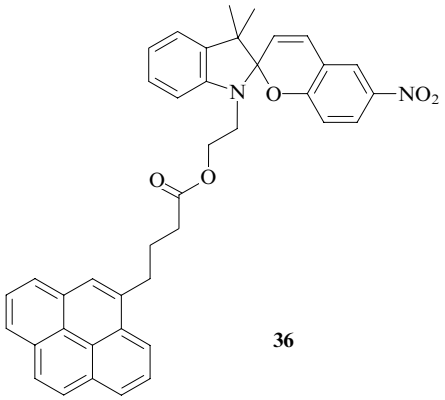


Figure 10. Change in the absorption spectrum of compound **35**.[135] (*a*) 10^{-5} mmol litre^{-1} of compound **35** in a 10% MeCN–tris-HCl solution; (*b*) solution *a* + 10^{-4} mmol litre^{-1} of F^-; (*c*) MeCN–tris-HCl solution containing 40 μg ml^{-1} of GO; (*d*) solution *c* + **35**; (*e*) solution *d* + 5.0×10^{-4} mmol litre^{-1} of F^-.

Structure 36



However, the electronics application of graphene requires solution of a number of problems. In the initial state, graphene has no band gap for free charge carriers. However, by doping or functionalization, graphene can be converted to n- or p-type semiconductors. For example, it has been found that the LbL-assembled graphene field effect transistor (Fig. 11) devoid of the spiropyran moiety behaves as a p-type semiconductor with a Dirac point of 3.6 V.[136, 137] The insertion of molecule **36** into graphene

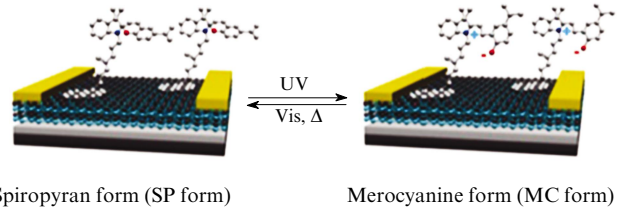


Figure 11. Schematic view of the photoswitchable organic field effect transistor manufactured from a hybrid material based on graphene oxide doped with spiropyran **36**.[136]

gives rise to an n-type semiconductor behaviour with a Dirac point of −1.7 V. This is attributable to the overall negative charge transfer from the attached spiropyran to graphene layers, which is consistent with the data obtained for SWNTs modified with spiropyran **36**.[110] Also, the shift of the Dirac voltage depends on the light irradiation time. Indeed, the initial Dirac voltage of −17 V changed to −4.7 and −10.2 V after UV irradiation for 1 and 5 min, respectively. This shift is fully reversible upon visible light irradiation, which induces the transformation of the transistor merocyanine moiety back to spiropyran with subsequent restoration of the initial Dirac voltage. A control experiment without spiropyrans did not reveal any photoresponsive behaviour. This provided the conclusion that graphene modification with photochromic spiropyrans may serve for

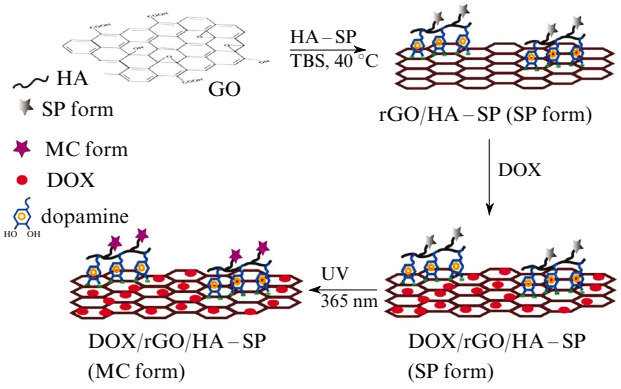


Figure 12. Schematic diagram of fabrication of the rGO/HA – SP carrier able to deliver the hydrophobic DOX drug to cancer cells. The drug is released from the carrier in the lysosome and cell cytoplasm.[140]
TBS is a complex buffer solution.

light-induced fine tuning of the Dirac point of graphene layers.

One more application area of photochromic spiro compounds is medical biology. Spiropyrans are the most popular and well-investigated compounds for cell imaging.[20, 138, 139] Using reduced graphene oxide, hyaluronic acid (HA) and photochromic spiropyran (SP), a fluorescent carrier for the doxorubicin antitumour drug has been developed [140, 141] (Fig. 12).

A *in vivo* fluorescence image of a cancer tumour was obtained for the first time using the merocyanine form of the photochrome-modified graphene (Fig. 13 *a*); this was confirmed by *in vitro* fluorescence data for A549 cells, which were chosen as the CD44 receptor (Fig. 13 *b*).

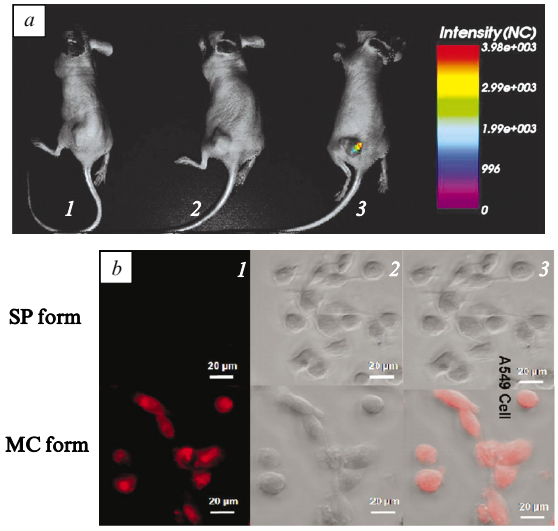


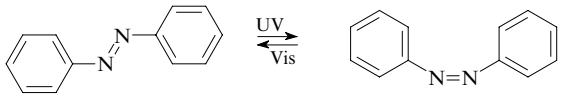
Figure 13. Fluorescence of rGO/HA – SP *in vivo* after injection into the mouse tail vein (*a*); CLSM image of rGO/HA – SP in the A549 cell after 2 h incubation (*b*).[140]
(*1*) Control, (*2*) rGO/HA – SP (SP form), (*3*) rGO/HA – SP (MC form).

IV. Azobenzene-containing hybrid compounds based on carbon clusters

Azobenzene derivatives are typical photochromic compounds promising as optical switches, holographic memory, long-term energy storage devices and non-linear optical materials.[142, 143] The unique photochromic properties of azobenzene derivatives account for their active use as photoswitchable parts that control the structure and function of supramolecular systems.[144 – 147]

The reversible transformations of azobenzene (*cis* – *trans*-isomerism) induced by irradiation or an electric field are reflected in Scheme 20, which shows that the initially coloured, thermodynamically more stable *trans*-isomer is converted to the colourless *cis*-isomer on exposure to UV radiation.

Scheme 20



trans-Isomer *cis*-Isomer

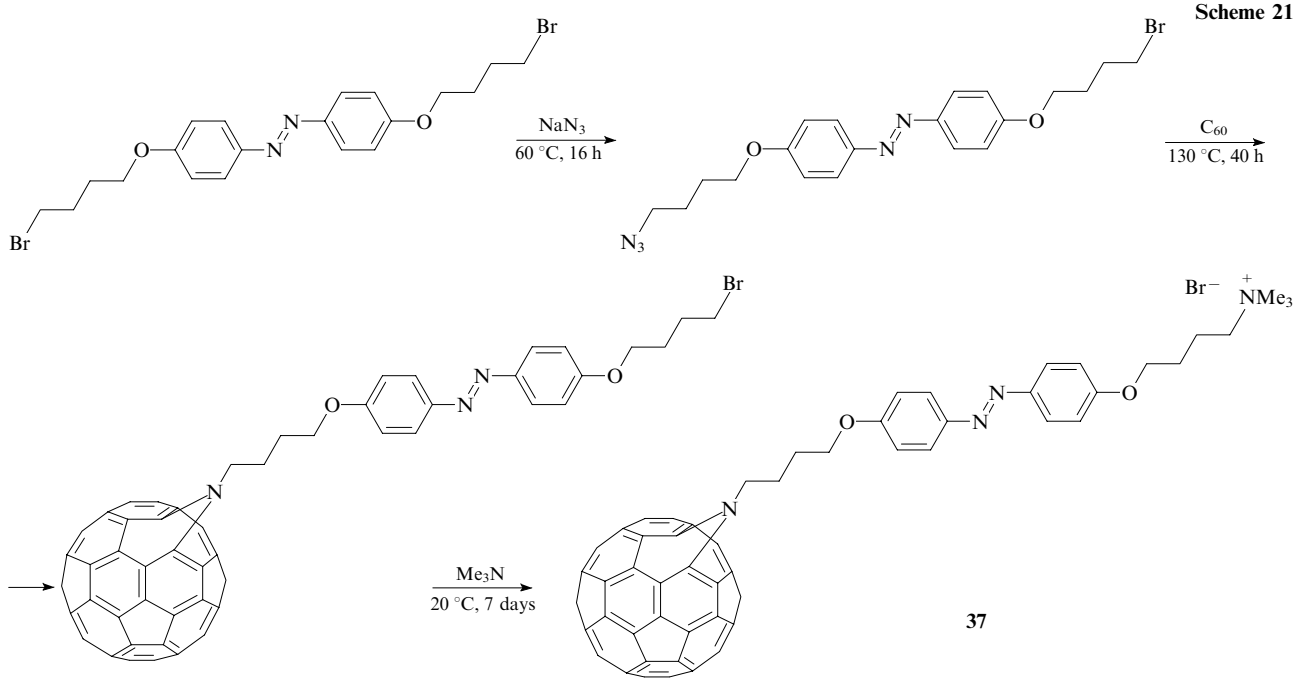
Covalent binding of fullerenes to azobenzene and its derivatives may afford new materials with accessible redox states and low excitation energy, which are required for fabricating optical data storage devices.

The first example of covalent binding of fullerenes to azobenzene is the synthesis of amphiphilic C_{60} derivative **37** (Scheme 21) for the formation of stable monolayers.[148] Unfortunately, the authors did not intend to study the photochromic transformations of the adducts they prepared.

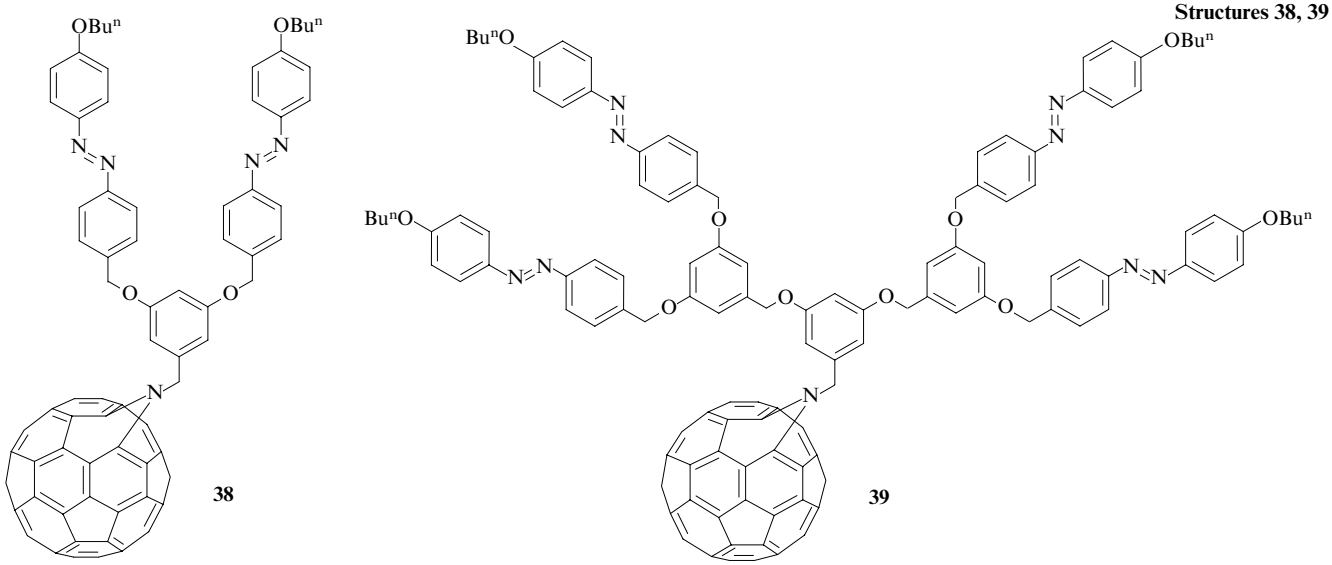
Kay *et al.*[149] have used the azide method to prepare azobenzene- and fullerene-containing dendrimers **38** – **40** with two, four and eight photochromic moieties (in 42%, 67% and 39% yields, respectively); these compounds exhibit photochromic properties. The absorption spectra of compounds **38** – **40** in solutions show a band with a peak at 357 nm characteristic of the *trans*-configuration of the azobenzene chromophore. Irradiation of these solutions for 150 s with UV light (λ = 365 nm) induces isomerization of *trans*-azobenzene to the *cis*-isomer accompanied by a decrease in the peak at 357 nm and an increase in the 437 nm peak (Fig. 14). On storage in the dark, the *cis*-isomer is completely converted to the *trans*-isomer within 6 h, while the reverse isomerization under the action of solar light takes only a few seconds.

It is noteworthy that, as in the case of dihetarylethenes and spiropyrans, azobenzene located close to the fullerene core in the final product leads to the loss of photoisomerization behaviour of the photochrome. Shirai *et al.*[150] studied the photochemical properties of compounds **41** – **43** — acyclic adducts of fullerene C_{60} and azobenzene connected by various spacers. It has been found that fullerenes and oligo(phenylene ethynylenes) strongly affect the photoisomerization of the azobenzene moiety. Direct proximity of the fullerene core to azobenzene markedly reduces the yield of the *cis*-isomer; OPEs attached to azobenzene also have an adverse effect on the photoisomerization of the *trans*-isomer, but this effect is weaker (Table 2). However, the presence of fullerenes on both sides of oligo(phenylene

Scheme 21



Structures 38, 39



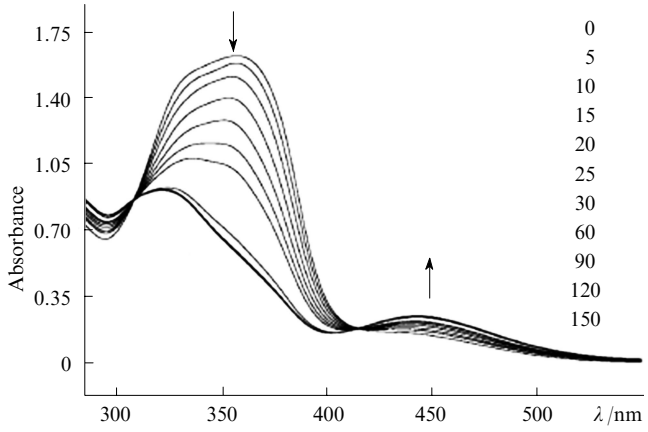


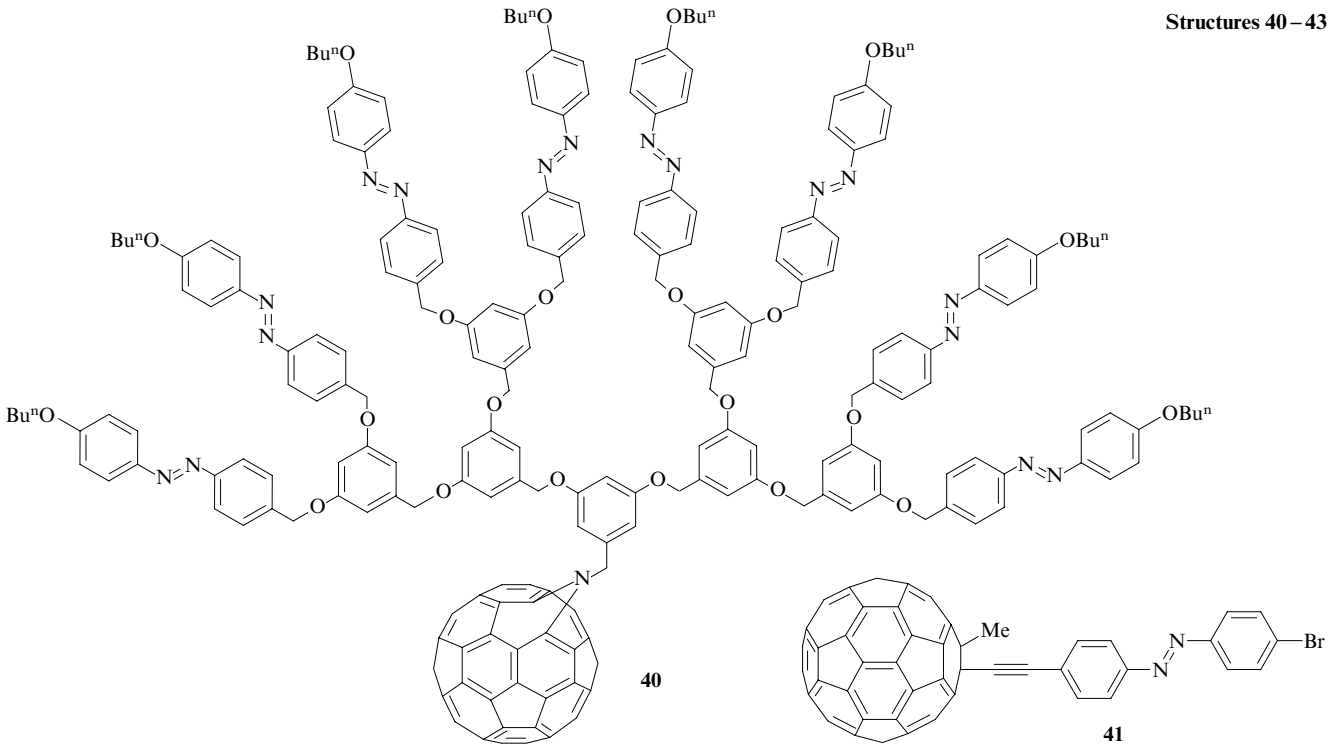
Figure 14. Change in the absorption spectrum of dendrimer **40** with increase in the UV irradiation time from 0 to 150 s.[149]

Table 2. Photoisomerization yields in the photostationary state for compounds **37**, **38**, **41** – **43**.[150]

Compound	Photoisomerization yield (%)	λ /nm
4,4′-Diiodoazobenzene	> 90 [a]	365
Fullerene – azobenzene mixture (1 : 1)	19 [a]	365
Fullerene – azobenzene hybrid		
41	< 10 [b]	365
37 (without fullerene core)	> 90 [a, b]	365
42	~ 35 [b]	334
38 (without fullerene core)	> 90 [a, b]	334
43	~ 0 [a, b]	365

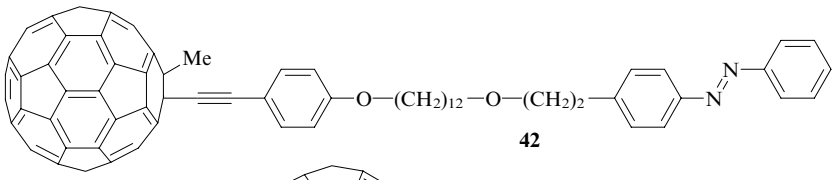
[a] The photoisomerization yield was determined by NMR spectroscopy. [b] The photoisomerization yield was determined from absorption spectra.

Structures 40 – 43

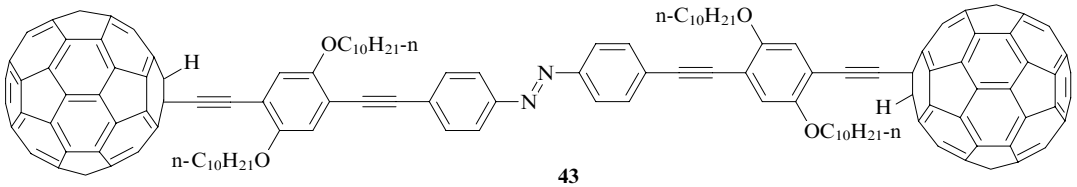


40

41



42



43

ethynylene) chains, as in compound **43**, leads to the complete loss of photochromism of the azobenzene moiety.

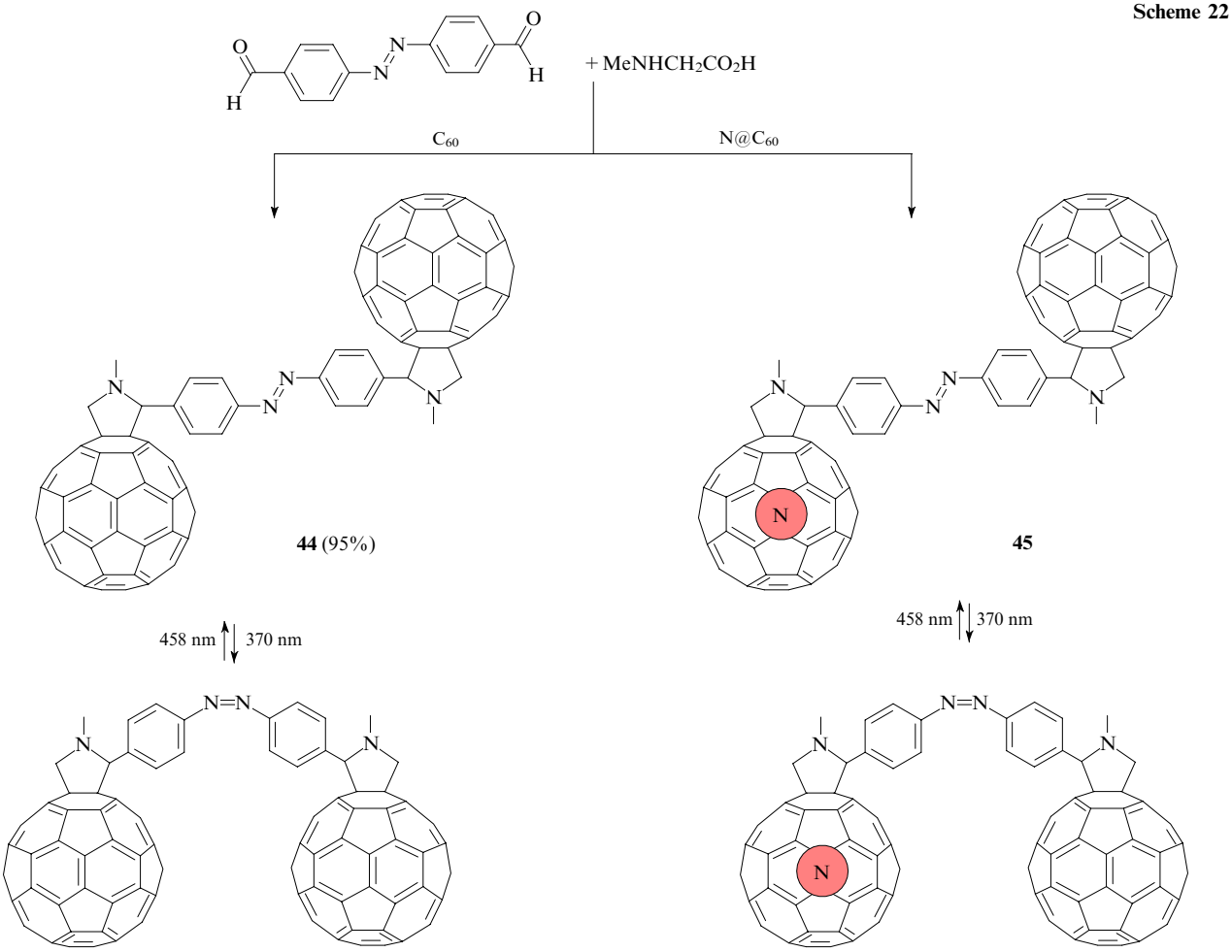
This approach was used for the synthesis of hybrid compounds of fullerene C_{60} and azobenzene, analogous to compound **43**, with the goal to construct nanomachines.[46, 151]

The 1,3-dipolar cycloaddition of azomethine ylides, generated *in situ* from the aldehyde derivatives of a photochrome, to the fullerene carbon cage (Prato reaction) is among the most promising methods for the preparation of hybrid materials based on fullerenes and azobenzene. This method provides the target functionally substituted fullerenes in rather high yields. This procedure was used to prepare dimeric fullerene derivatives **44** and **45**, in which the spherical C_{60} or $N@C_{60}$ molecules are connected by an azobenzene bridge (Scheme 22).[152] The magnetic properties of two isomers of **45** were studied by ESR spectroscopy. The electron spin relaxation times of the two endohedral fullerene isomers, T_1 and T_2, show an exponential decay. Although the zero-field splitting parameter was the same for both isomers in solution (~ 13.0 MHz), the rotational correlation times for the *trans*- and *cis*-isomer molecules were 37.2 ± 1.6 and 34.8 ± 2.7 ps, respectively.

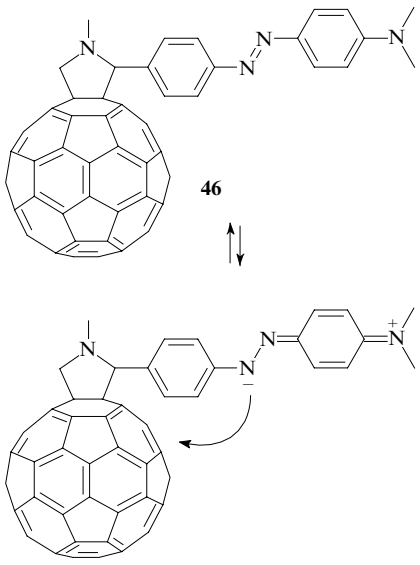
Despite the fact that azobenzene is most often considered as a photo- and electrochromic moiety, it has also been used [151 – 157] as a bridge between electron-donating (*N*,*N*-dimethylaniline) and electron-withdrawing (*N*-methylfulleropyrrolidine) moieties. The character of charge transfer was established for dyad **46** considering the experimental and theoretical data obtained by time-dependent density functional theory.[153 – 156] According to TD-DFT calculations, the charge transfer in compound **46** is induced by irradiation at 750 – 600 nm; this is fully confirmed by experimental data: charge transfer is observed in the UV/Vis spectrum at 721 nm. Kumar and Patnaik [153] have suggested a probable charge transfer pathway in hybrid **46**, starting with the electron transfer from the electron-donating dimethylaniline moiety to the electron-withdrawing phenylazo group in the azobenzene moiety (Scheme 23). The next stage is the charge transfer from the azobenzene (HOMO) to fulleropyrrolidine moiety (LUMO), which is confirmed by the 0.15 V anodic shift of the first reduction potential of the azo group in compound **46**, as opposed to the initial azobenzene.

It has been found [153] that the addition of trifluoroacetic acid to a solution of dyad **46** leads to a sharp colour change from yellow to pink accompanied by the disappearance of

Scheme 22



Scheme 23



the absorption band at 409 nm in the spectrum and the appearance of new bands at 520 and 540 nm attributable to protonated azo-group nitrogen atoms (Fig. 15). The protonation of the azo groups allows for a rational control over the energy and distribution of the frontier molecular orbitals, which affect the photo- and electrochromic properties of hybrid **46**. These results are of great value for the design of molecular devices, in view of the considerable role of the frontier molecular orbitals for the electron transport.

Data on the crystal structure of hybrid molecule **46** and the possibility for its self-assembly in binary solutions, illustrating the donor-acceptor, π – π- and van der Waals interactions during the self-assembly, have been reported.[156, 157]

Dyads **47** and **48** with a similar architecture have been synthesized.[158] In these molecules, porphyrin is linked to fullerene C_{60} *via* an azobenzene spacer (Scheme 24). A study of the photophysical properties of dyads **47** and **48** demonstrated that the azobenzene bridge between porphyrin and fullerene substantially facilitates the forward and back electron transfer, but charge recombination is 3 – 4 orders of magnitude slower than charge separation, which is indicative of the inverted Marcus region for back electron transfer. As was to be expected, no photoinduced *cis*-to-*trans* isomerization takes place in dyads **47** and **48** because of the proximate positions of the azobenzene moiety and the fullerene. Nevertheless, fast energy and electron transfer *via* the azo bridge creates real prerequisites for the preparation of optically controlled hybrids by using this aproach.[159] More comprehensive data about the synthesis and properties of fullerene-based donor-acceptor dyads can be found in the review.[160]

El-Khouly *et al.*[161] further explored this area by synthesizing an original dimeric fullerene adduct **49** (Scheme 25), which is not aggregated in solution even upon irradiation at

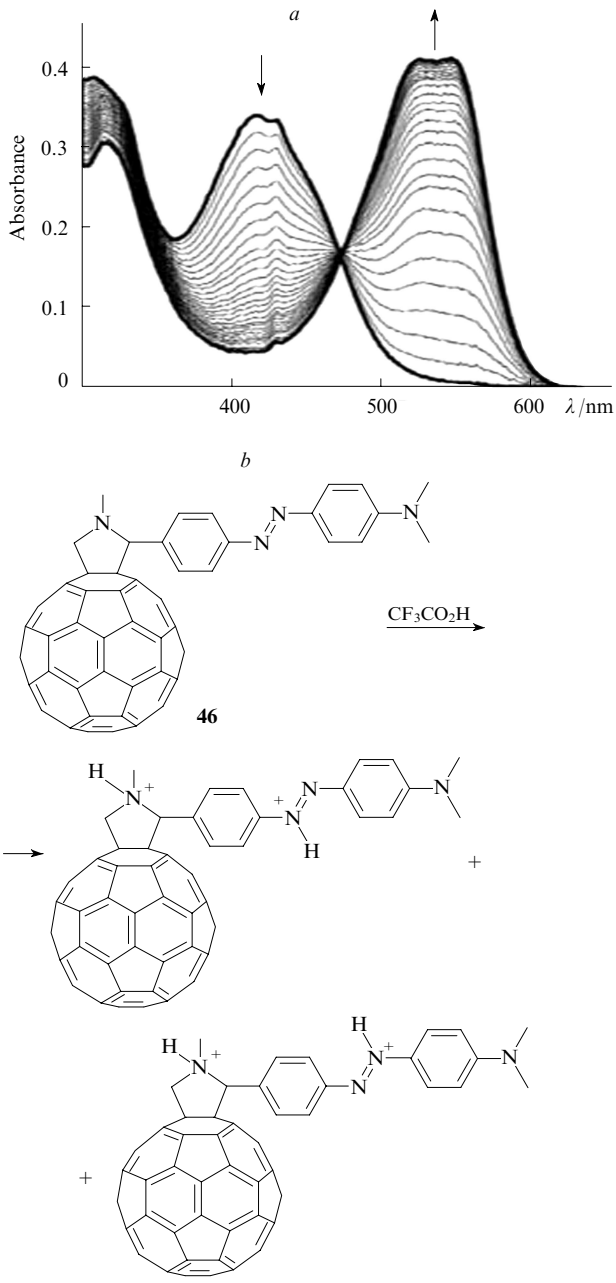
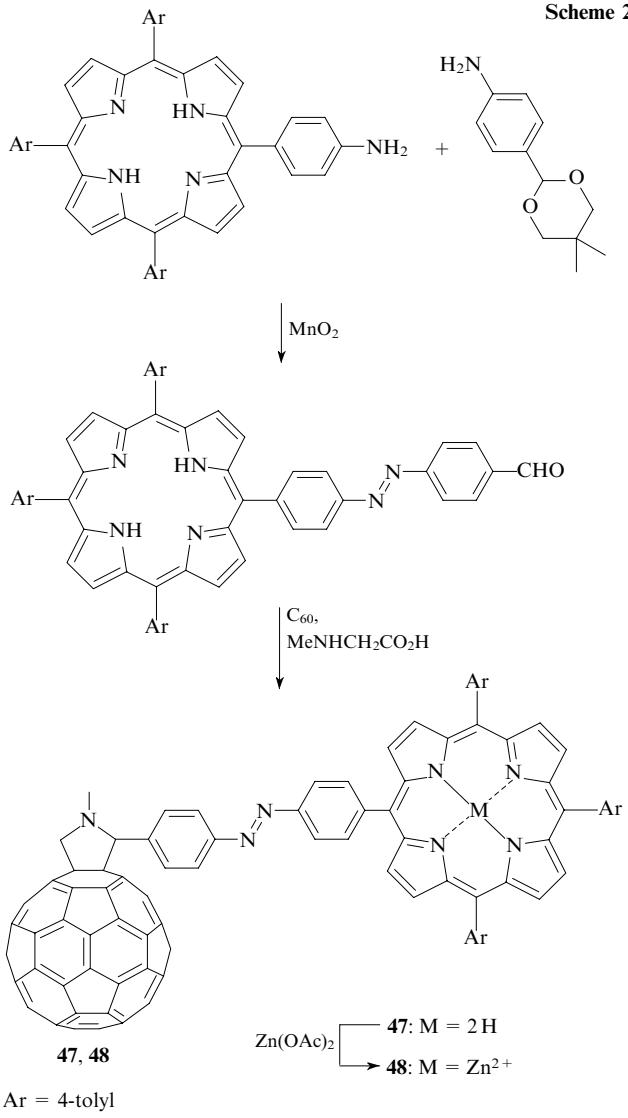


Figure 15. Change in the absorption spectrum of dyad **46** after the addition of trifluoroacetic acid (*a*) and molecular structures of the products (*b*).[155]
Concentration of the acid increased from 10^{-4} to 9×10^{-4} mmol litre^{-1}.

688 nm, but is capable of efficient photoinduced intramolecular electron transfer to give a charge-separated state with a lifetime of ~2.50 ns. Charge separation and recombination inherent in the hybrid molecules such as **49** make them quite promising photoactive materials in the solar energy harvesting system.

Another approach to the chemical linking of fullerenes to azobenzene makes use of nucleophilic cyclopropanation of C_{60} with α-halo carbanions generated *in situ*. This method affords functionally substituted carbon clusters in preparative yields. Han[162] reported a five-step synthesis of phthalocyanine-based fullerene derivative **50** with a light-

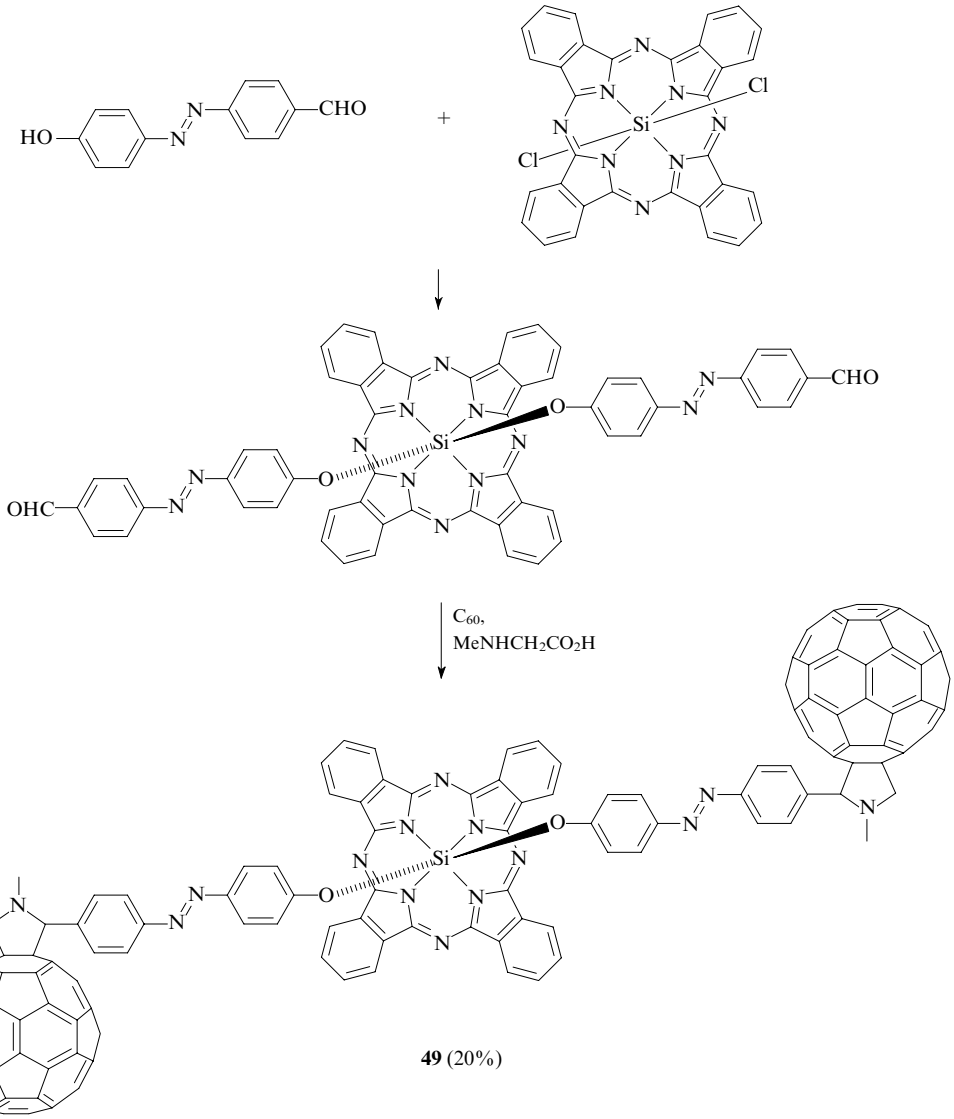
Scheme 24



sensitive azo group (Scheme 26). Like adduct **37**, compound **50** possesses amphiphilic properties and can form stable monolayers. Ultraviolet irradiation (λ = 365 nm) of compound **50** dissolved in chloroform induces *trans*-to-*cis* photoisomerization of the azobenzene moiety, as indicated by decreasing absorption at 351 nm and increasing absorption at 450 nm (Fig. 16). The photostationary state was achieved in ~150 s. The reverse *cis*-to-*trans* isomerization of azobenzene takes place as the sample is stored in the dark at room temperature for 6 h. However, a five-second exposure to a bright solar light induces a more efficient reverse isomerization, indicating the absence of a steric effect on the reversible *trans*-to-*cis* isomerization of compound **50**.

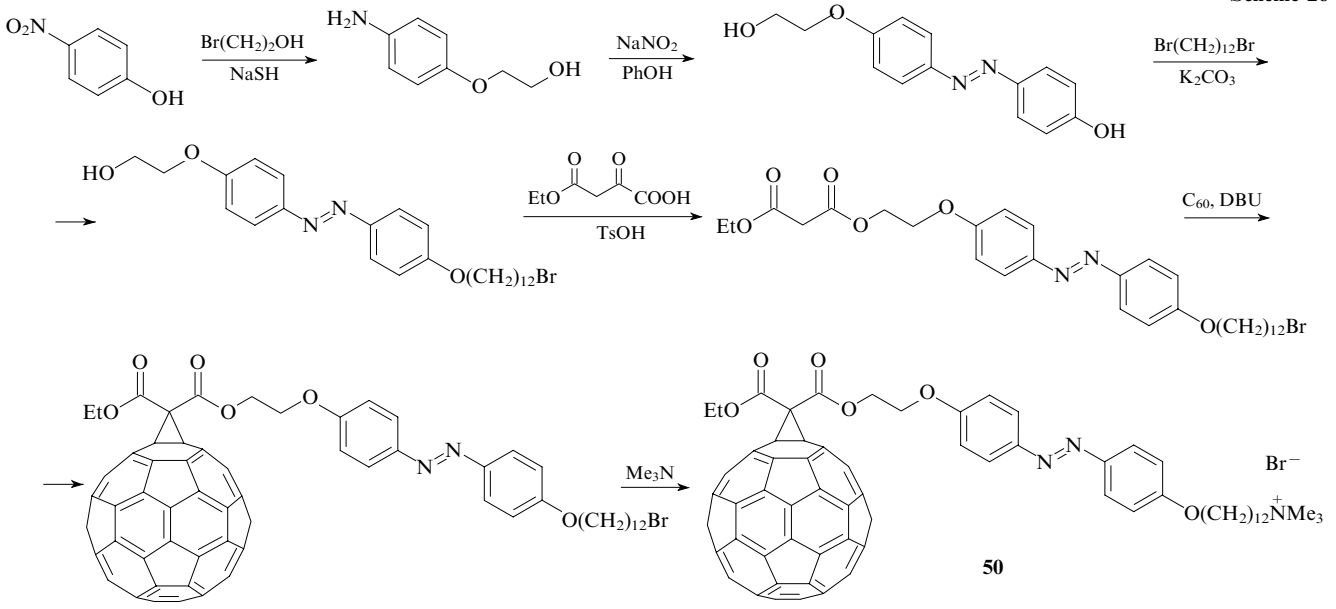
In order to prepare new acceptor materials for polymeric solar cells, Ma *et al.*[163] performed chemical modification of PCBM (widely used for this type of research) with azobenzene (Scheme 27). Mere mixing of methanofullerene **51** and the polymer P3HT (1 : 1) yielded the active layer of a solar cell able to switch between the active and sleep states on exposure to UV and visible light. In the active mode, the device has a power conversion efficiency (PCE) of 2.0%; whereas after UV irradiation it switches to the sleep state with a lower PCE as well as lower J_{sc}, Voc and FF values

Scheme 25



49 (20%)

Scheme 26



50

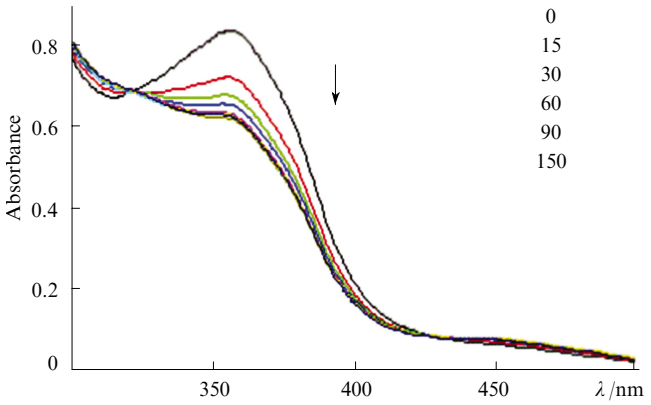
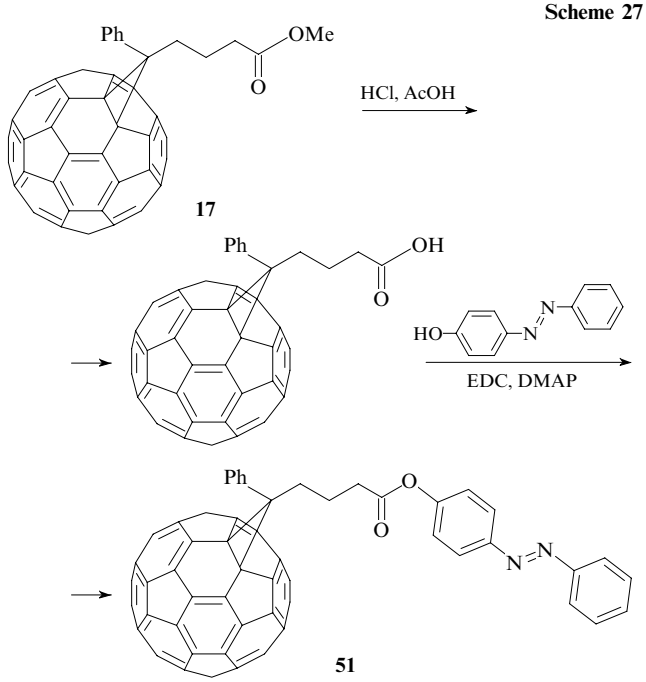


Figure 16. Change in the absorption spectrum of compound **50** with increase in the UV irradiation (λ = 365 nm) time from 0 to 150 s.[162]

Scheme 27



(Table 3). On exposure to visible light, the initial characteristics of the solar cell are partly restored, indicating the system switching to the active state. The switching mechanism implies a difference in the electron mobility of the active layer as a result of *cis*-to-*trans* isomerization of the azobenzene moiety of methanofullerene **51**. The partial restoration of the initial characteristics of the solar cell after irradiation with visible light is apparently caused by changes in the active layer thin film morphology, which deteriorate the electron transport, as evidenced, in particular, by a change in the current density – voltage curve and the fill factor.

An unusual approach to fullerene- and azobenzene-based hybrids has been demonstrated in a theoretical work [164] describing the development of light-sensitive host – guest complexes **52** and **53** (Fig. 17). The proposed host molecule is composed of four azobenzene groups and has a nearly cylindrical shape (1.01 Å height and 13.38 Å

Table 3. Photoelectric characteristics of the device based on methanofullerene **51** after UV and visible light irradiation.[163]

Irradiation time /min	J_{sc} /mA cm^{-2}	V_{oc}/V	PCE (%)	FF
Before irradiation	7.0	0.58	1.99	0.49
UV irradiation				
1	5.6	0.51	1.11	0.39
2	4.8	0.50	0.89	0.37
3	3.9	0.48	0.72	0.38
6	2.3	0.45	0.42	0.40
Visible light irradiation				
1	2.4	0.46	0.44	0.41
2	2.5	0.47	0.48	0.41
6	2.6	0.47	0.50	0.42
Storage in the dark	3.3	0.51	0.72	0.43

inner diameter), which is suited for encapsulation of fullerenes C_{60} and C_{70}. In view of high binding energy, complexes **52** and **53** are expected to be stable, and thermodynamic calculations have shown the possibility of their spontaneous formation. Due to photoisomerization of *trans*-azobenzene to the *cis*-isomer on irradiation at 474 and 506 nm for complexes **52** and **53**, respectively (Fig. 17), the fullerene molecules are easily released.

Carbon nanotubes possess unique electrical and photoconductive properties and represent perfect building blocks for the design of optical nano-devices.[165] Therefore, recent research has been focused on the synthesis of hybrid materials based on carbon nanotubes and azobenzene for modulating their conductivity, electrostatic and non-linear optical properties and quantum effects on exposure to light.

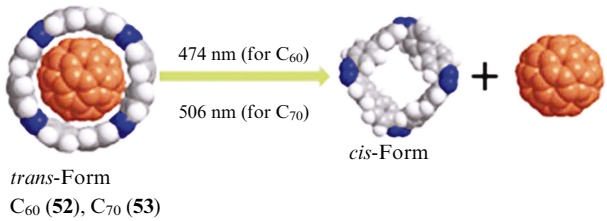
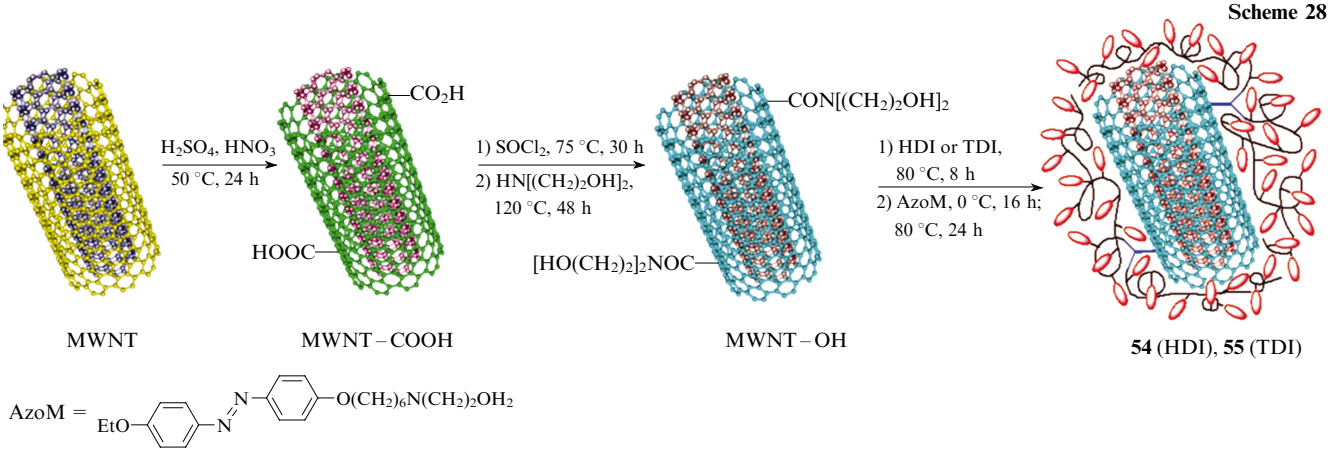


Figure 17. Schematic view of new light-sensitive host – guest complexes **52** and **53**.[164]
The ball is fullerene, the ring are four azobenzene molecules closed to form a circle.

One of the first publications [166] in this area describes the synthesis of two types of photosensitive azobenzene polyurethane multiwalled carbon nanotubes **54** and **55** (Scheme 28). The synthesis was carried out by polycondensation of the azobenzene monomer with diisocyanates [aliphatic diisocyanate (HDI) as a soft monomer or aromatic one (TDI) as a hard monomer] in the presence of hydroxylated MWNTs. Study of the photochemical properties of **54** and **55** has shown that azobenzene binding to the carbon nanotube decreases the rate of photoisomerization of the new hybrid molecules because of steric factors (Fig. 18). Nevertheless, the isomerization rate constant can be effectively controlled by adjusting the flexibility of the backbone of MWNT-grafted polyurethanes. In the opinion of the researchers cited,[166] this could play a key role in the

Scheme 28



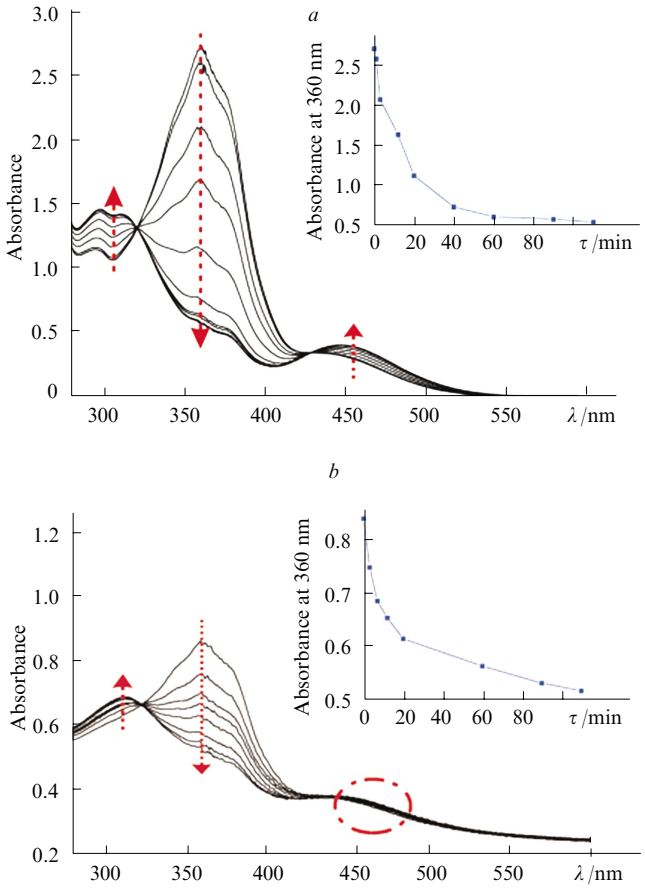


Figure 18. Change in the absorption spectra of the initial azobenzene containing polyurethane (*a*) and hybrid molecules **54** and **55** (*b*) in DMF on exposure to UV light (λ = 365 nm).[166]
τ is irradiation time.

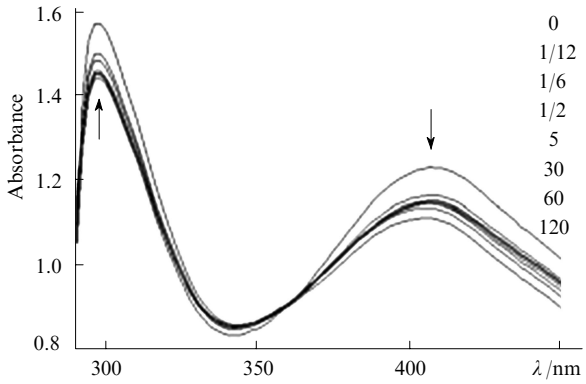
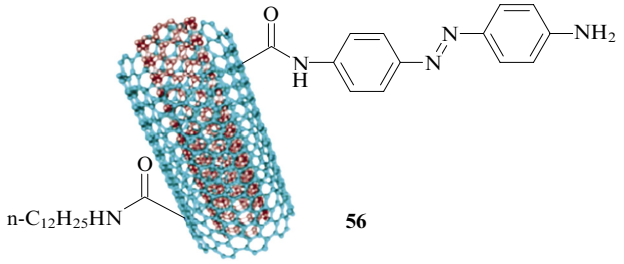


Figure 19. Change in the absorption spectrum of **56** with increase in the UV irradiation (λ = 365 nm) time from 0 s to 120 min (*b*).[167]

development of new high-performance optical and photonic nano-devices.

Virtually at the same time, Feng *et al.*[167] reported the synthesis of photosensitive MWNTs **56** containing azobenzene monomeric units (Fig. 19). Unlike fullerene hybrids **41**, **43**, **47** and **48**, the azo-modified nanotube **56** with a closely located azobenzene group is subject to *cis*-to-*trans* isomerization of the photochromic moiety. As can be seen in Fig. 19, a change in the absorption spectrum of hybrid **56** induced by UV irradiation includes a decrease in the intensity of the absorption peak at 410 nm and an increase in the intensity of the 300 nm peak. The bathochromic shift in the $\pi-\pi^*$ transition region of *trans*-azobenzene is due to overlapping of electron conjugation and enhanced π-plasmon transition along the nanotube.

Structure 56



56

Feng *et al.*[168] have shown that moving the azobenzene moiety farther from the nanotube leads to more efficient *cis*-to-*trans* isomerization and, as a consequence, better electrical conductivity (Fig. 20). Indeed, the rate constant for isomerization of the hybrid with a spacer (6.7×10^{-1} s^{-1}) is fourfold higher than that for the hybrid without a spacer (1.4×10^{-1} s^{-1}).

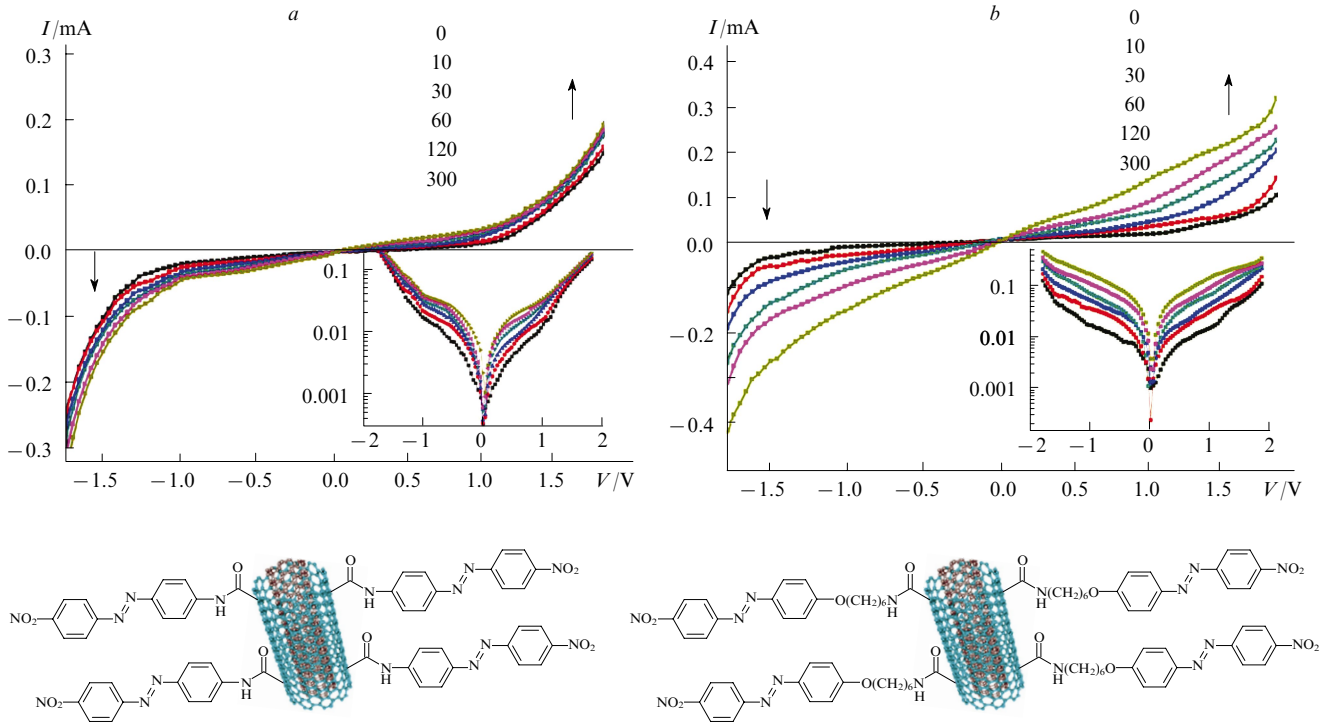


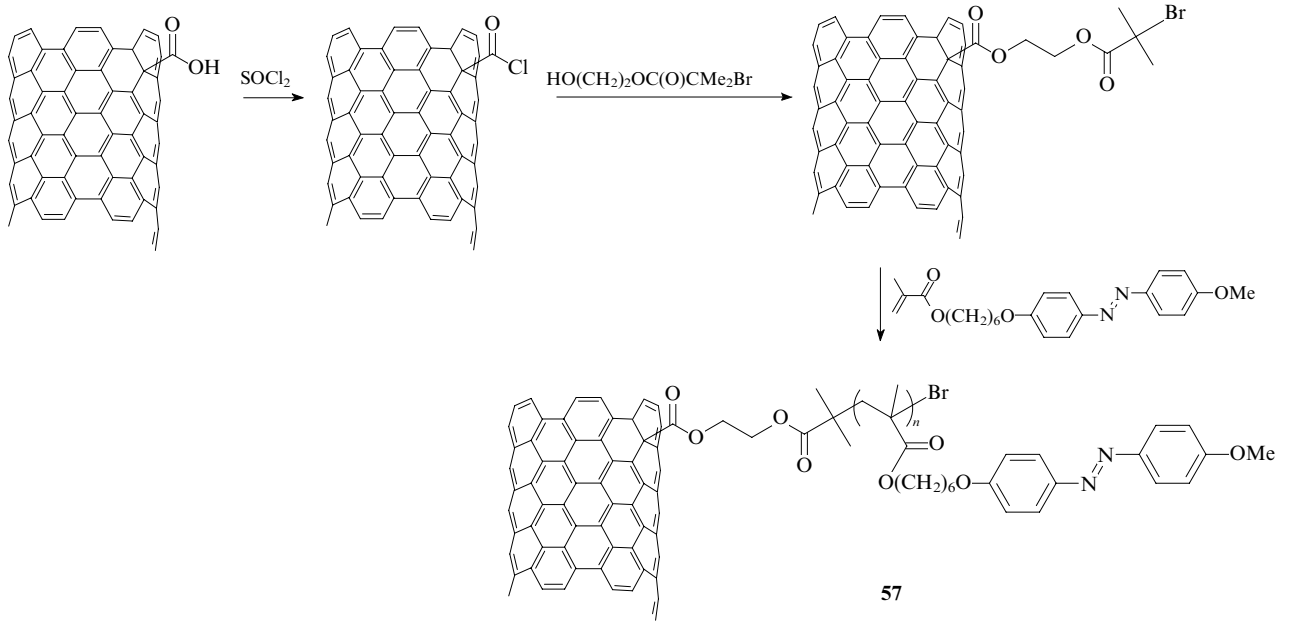
Figure 20. Change in the current – voltage curves for the systems FWCNT – AZO (*a*) and FWCNT – spacer – AZO (*b*) with increase in the UV irradiation time from 0 to 300 s.[168]

Subsequently, Hu *et al.*[169] have prepared hybrid adduct **57** based on an MWNT and azobenzene-functionalized poly(methyl methacrylate) (Scheme 29); the hybrid is of interest for the manufacture of new electrically switchable materials.

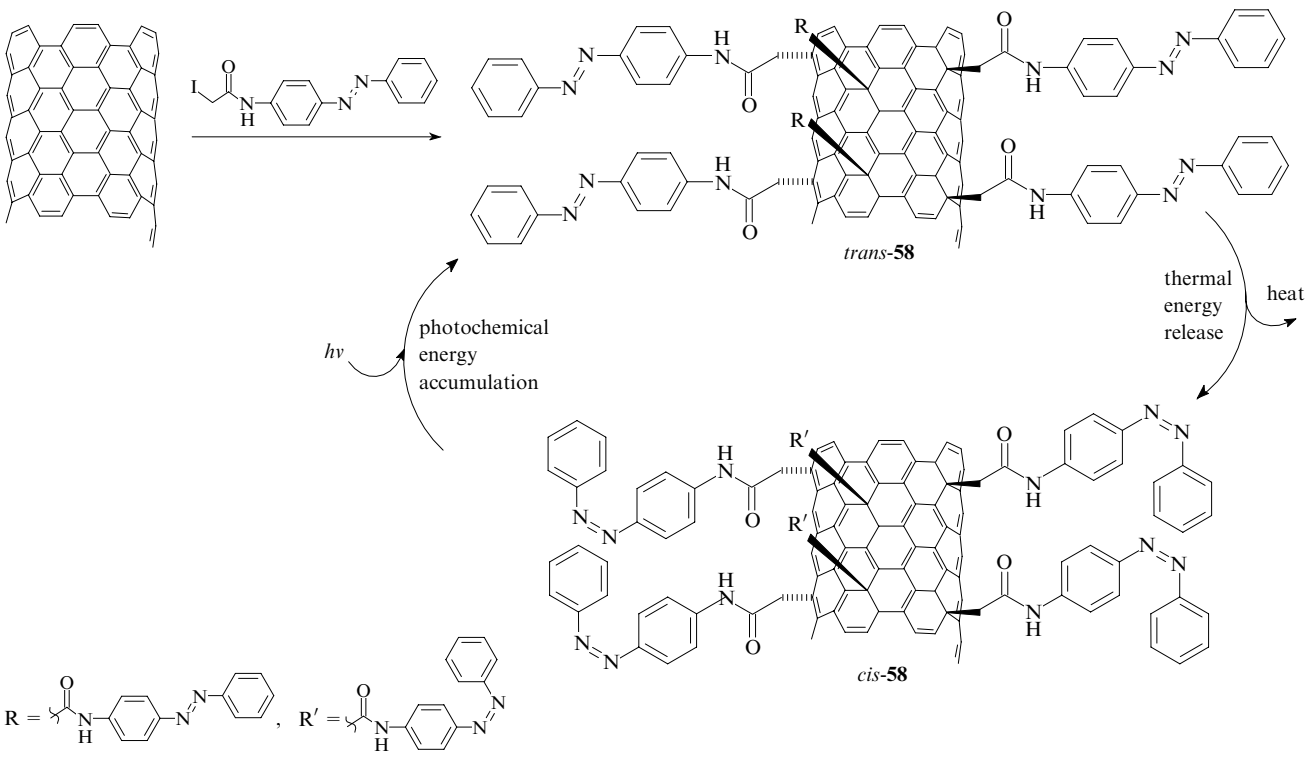
It has been shown[170] that azobenzene-modified SWNT **58** can significantly (by ~200%) increase not only solar energy storage capacity but also the storage time; furthermore, the material retains the degradation stability under repeated cycling. Upon the excitation with UV light, the thermodynamically stable *trans*-isomer **58** is photochemically isomerized into the metastable *cis*-isomer (Scheme 30), which returns to the initial *trans*-configuration and releases the accumulated energy as heat. The half-life period or the reverse *cis*-to-*trans* isomerization time allows for solar energy storage for the peak bias power over a period of a day.

It is noteworthy that the possibility of solar energy storage has also been investigated for graphene[171, 172] modified with azobenzene. The intermolecular hydrogen

Scheme 29



Scheme 30



bonds and the solid-state interplanar packing of the novel materials based on graphene and azobenzene improve the storage capacity and extend the service life of solar energy storage materials. It was shown that new solar heat fuels have an energy storage capacity of up to 138 W h kg^{-1} (Ref. 172). In addition, azobenzene-containing graphene showed an excellent stability in 50 isomerization cycles upon irradiation with visible light, thus indicating a service life of more than 4.5 years.[171]

Not only chemically azobenzene-modified carbon nanotubes, but also their non-covalently bound analogues are of great practical value.[173–176] Ultraviolet irradiation of a hybrid material of this type induces the *cis*-to-*trans* isomerization of the conjugated chromophore, which results in charge redistribution in the vicinity of the nanotube. This changes the local electrostatic field, shifts the threshold voltage and increases the conductivity of a transistor based on this hybrid material.[173,176] The conductivity change is reversible and can be repeated for a long time, indicating that the azobenzene-modified nanotubes could be applicable for the design of integrated nano-photodetectors.[174,175]

In recent years, graphene has received a lot of attention owing to its unique mechanical, optical and electronic properties. The results of studies of new hybrid materials based on fullerenes and carbon nanotubes have stimulated the research aimed at the preparation of similar hybrids using graphene and its derivatives. The encapsulation of azobenzene chromophores into the graphene sheets may lead to optically controlled changes in their electronic properties. Therefore, it is relevant to study the effect of azobenzene photoisomerization on the graphene properties.

Cao *et al.*,[177] who investigated the charge transfer in system **59** in which the azobenzene block is covalently attached to two graphene sheets (Fig. 21), have found that the electrical conductivity of the new hybrid can be varied by exposure to light or by changing the acidity of the medium (Fig. 22, Schemes 31 and 32).

One of the first examples of covalent binding between graphene and azobenzene is the synthesis of adduct **60**, in which the carbon cluster is linked to the chromophore *via* an amide group (Scheme 33).[178] Irradiation with UV light induces the *trans*-to-*cis* isomerization of the azobenzene moiety, as evidenced by changes in the absorption spectrum

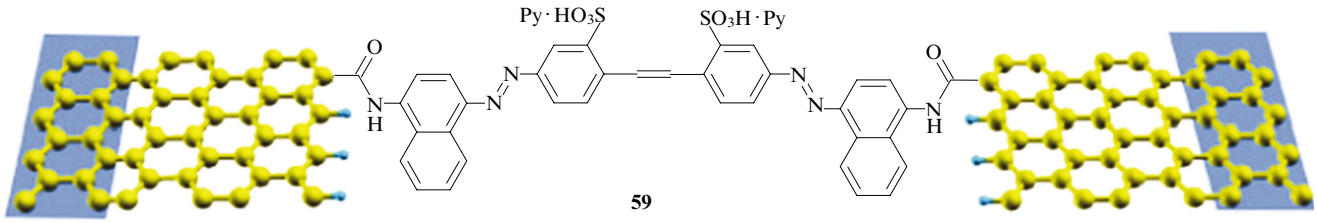


Figure 21. Schematic view of the graphene – azobenzene hybrid **59**.

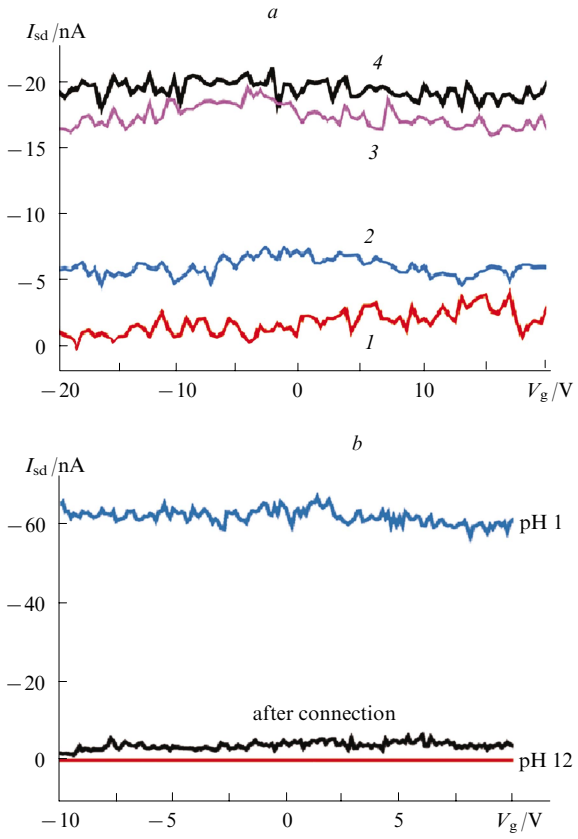
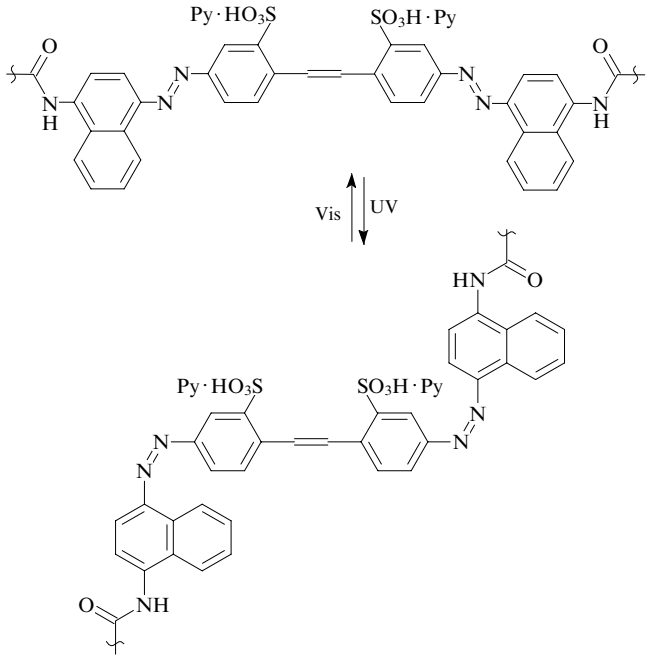


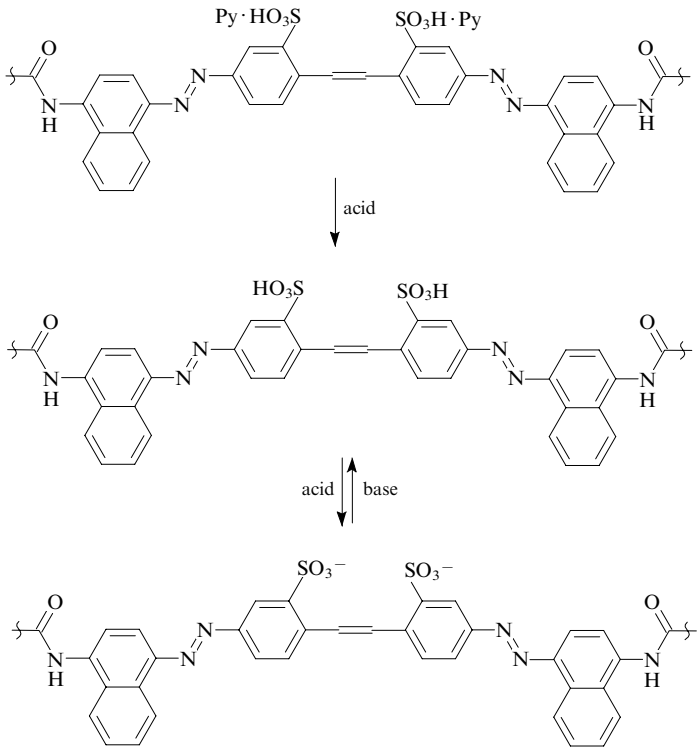
Figure 22. Photoswitching (*a*) and sensing (*b*) properties of hybrid molecule **59**.[177]
(*a*) (*1*) After UV irradiation, (*2*) storage in the dark for 60 h, (*3*) irradiation with visible light, (*4*) after connection (V_{sd} = −50 mV).

Scheme 31

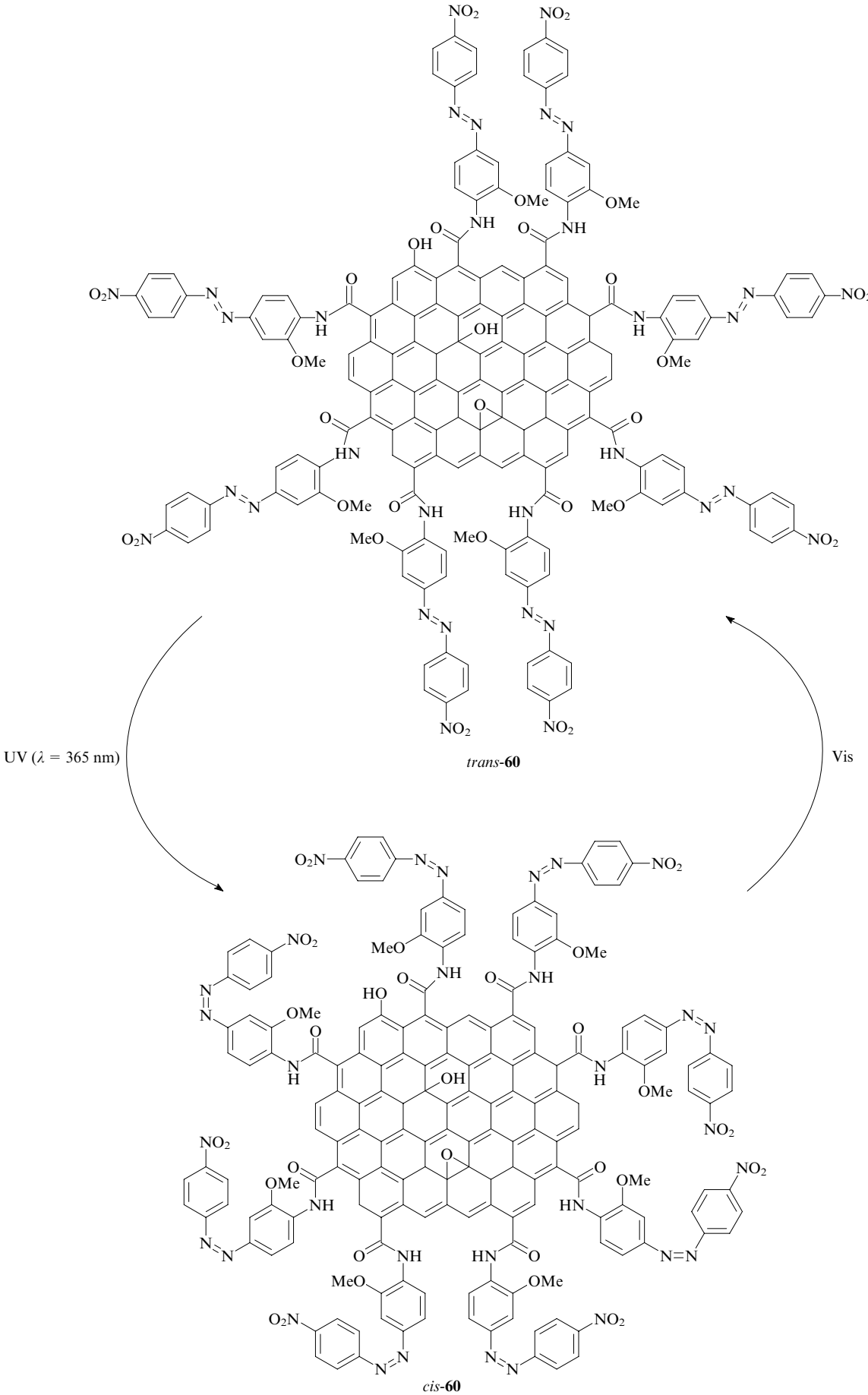


(Fig. 23 *a*), in particular, a decrease in the absorption peak corresponding to the π – π* electron transitions in the *trans*-benzene group. As the hybrid is stored in the dark, the metastable *cis*-form isomerizes back to the thermodynamically stable *trans*-form. The photoinduced conformational changes in hybrid **60** can be used to control the electrical conductivity. The pronounced increase in the current observed after UV irradiation (Fig. 23 *b*) attests to better conductivity of *cis*-isomer **60**. Moreover, slow restoration of the film resistance is also observed.

Scheme 32



Scheme 33



trans-**60**

cis-**60**

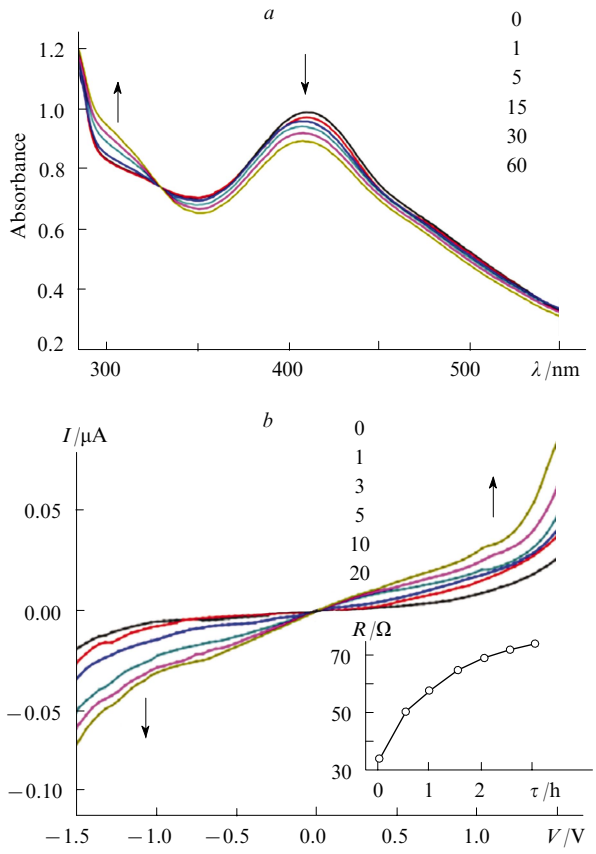
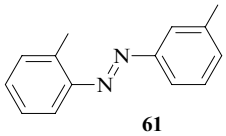


Figure 23. Change in the absorption spectrum of hybrid **60** (*a*) and the current – voltage curve for a device based on **60** (*b*).[178]
(*a*) The UV irradiation time was increased from 0 to 60 min; (*b*) the *I* – *V* characteristics were measured in the 0 – 20 min range; the inset shows the time dependence of the resistance.

Similar results have been obtained by Zhang *et al.*,[179] who used 2,3′-dimethylazobenzene **61** as the azo-chromophore component.

Structure 61



61

The effect of the light-induced *cis*-to-*trans* isomerization of the azobenzene moiety covalently attached to graphene on the electrical conductivity has also been identified in some other studies.[180, 181]

Feng *et al.*[182] synthesized the azobenzene – graphene conjugates **62** and **63**, in which the chromophore was directly attached to the carbon sheet (Scheme 34). The obtained compounds could be useful for the design of solar energy storage batteries. In relation to compounds **62** and **63**, it has been shown that minor changes in the substituent position in the azobenzene moiety may be responsible for crucial differences in the photoisomerization behaviour (Fig. 24).

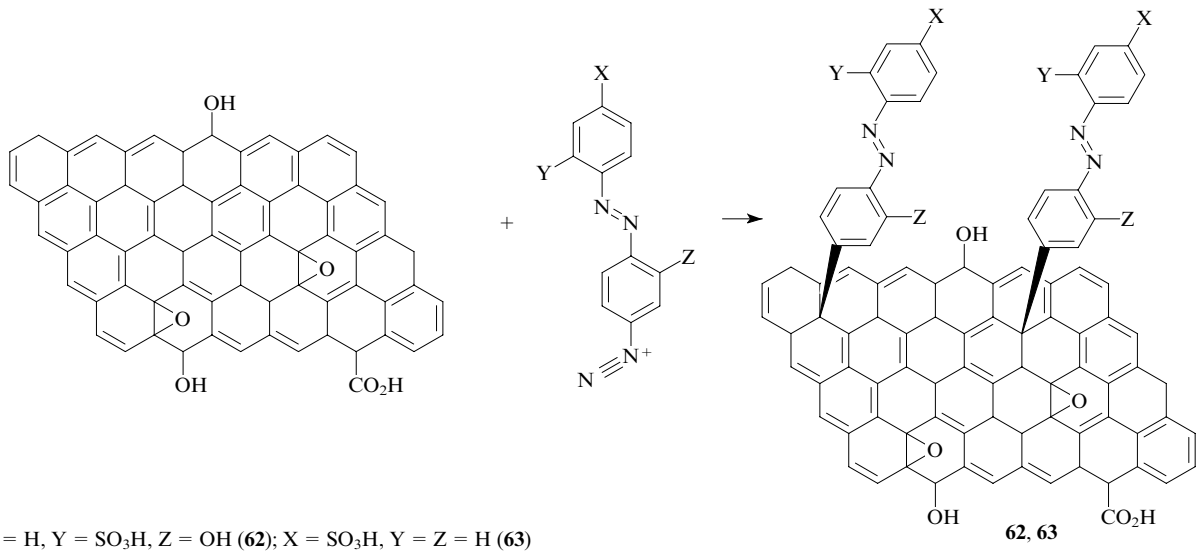
The above-considered chemical binding between graphene and azobenzene has been utilized in a number of studies.[183 – 185] Lee *et al.*[183] obtained nanocomposite **64** of the azobenzene-modified graphene with *trans*-stilbene-4,4′-dicarboxylic acid in the presence of Zn^{2+} ions; the product showed pronounced fluorescence with a rather long lifetime as compared with the initial ligand. In addition, this composite can act as a chemosensor, for example, for the detection of dinitro- and trinitrotoluene molecules.[183] Hybrid **65** served for the fabrication of a flexible rewritable non-volatile memory device (Fig. 25).[185]

Graphene supported on SiO_2 substrate is more reactive towards the azobenzenediazonium salts than graphene supported on octadecyltrichlorosilane.[186]

It has been found theoretically[187] that photoisomerization of azobenzene attached to cobalt atoms encapsulated in the graphene carbon skeleton reversibly changes the magnetic properties of this system. The results open up the prospects for the design of light-controlled molecular-scale spintronic devices.

The electrical conductivity of graphene can be affected by not only chemical attachment of azobenzene, but also by

Scheme 34



X = H, Y = SO_3H, Z = OH (**62**); X = SO_3H, Y = Z = H (**63**)

62, 63

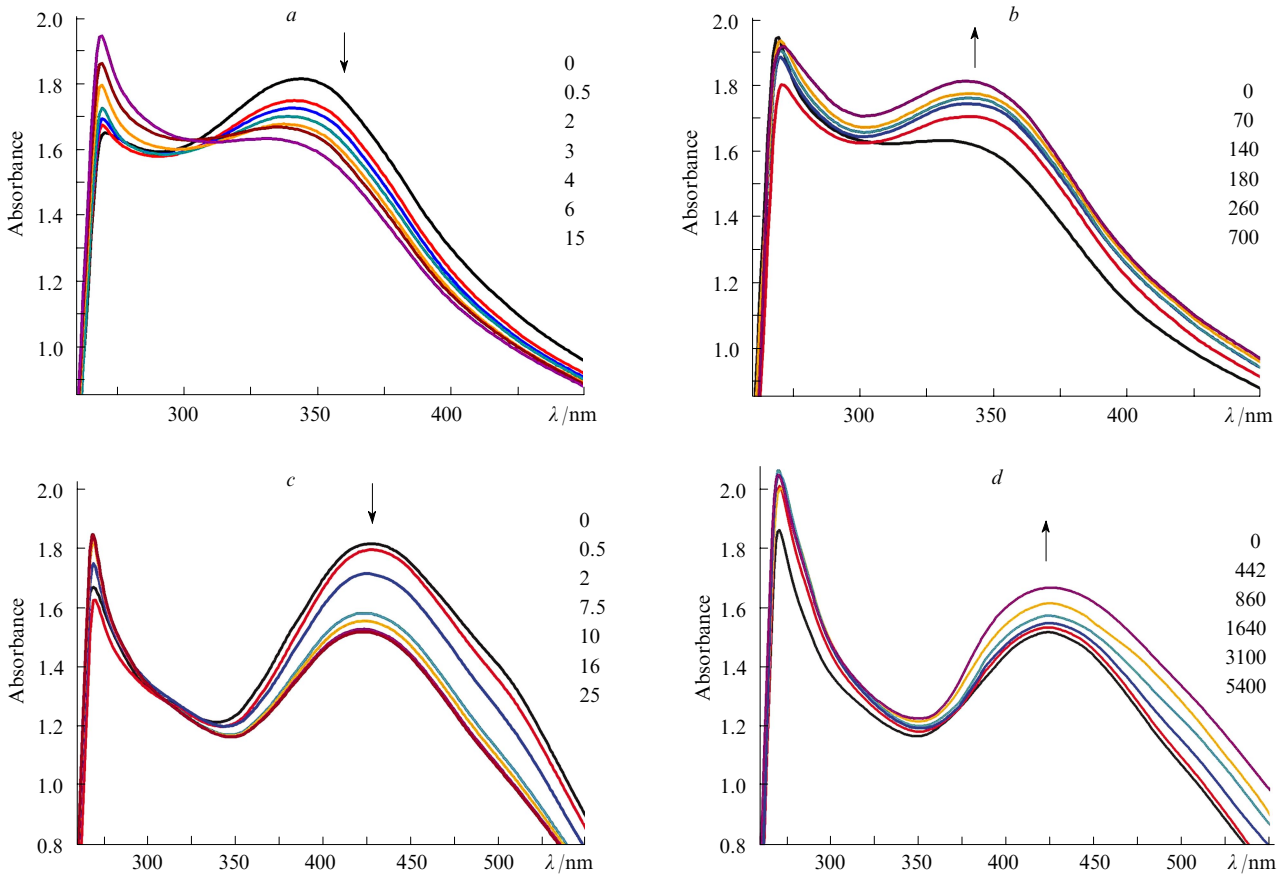
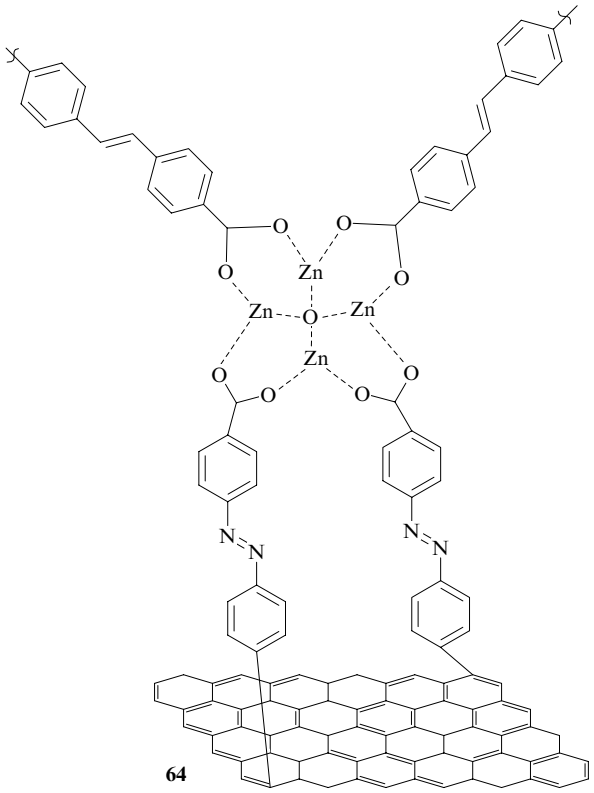
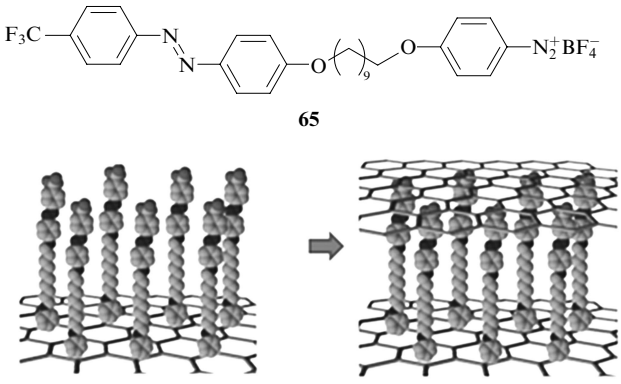


Figure 24. Change in the absorption spectra of compounds **62** (*a*, *b*) and **63** (*c*, *d*) upon UV irradiation (*a*, *c*) and storage in the dark (*b*, *d*) after the irradiation.[182]
The irradiation time was increased from 0 to 15 (*a*) and 25 h (*c*) and the dark storage time increased from 0 to 700 (*b*) and to 5400 h (*d*).

Structure 64



64



65

Figure 25. Sketch view of the flexible non-volatile memory device based on nanocomposite **65**.[185]

doping with azo-chromophore such as methyl orange.[188, 189] The *trans*-azobenzene molecule is adsorbed on the graphene surface *via* π – π interactions (Fig. 26). It has been shown [189] that the surface concentration of azobenzene decreases with increasing number of graphene sheets, the most efficient charge transfer being observed for the transistor fabricated using single-sheet graphene. The calculation results indicate that NO_2 and SO_3 are the best terminal functional groups in azobenzene for p-doping.[190]

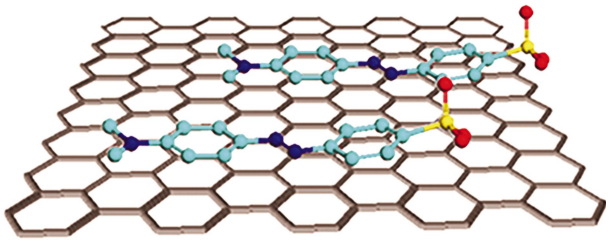


Figure 26. Schematic view of graphene doped with methyl orange.[188]

Unlike the researchers cited above, Kim *et al.*[191] used the pyrene anchor for the adsorption of azobenzene on the graphene surface (Fig. 27). The photoinitiated transformations of the azobenzene moiety in the field effect transistor based on the hybrid material thus obtained make it possible to detect and enhance even relatively small changes in the electrostatic potential. This opens up broad prospects for the use of new hybrid materials as semiconductor graphene analogues, such as graphene nanoribbons[192, 193] or nanoperforated membranes;[194, 195] further increase in the sensitivity and current modulation in these devices may give rise to new bioinspired schemes for photodetection or entirely new classes of light-gated transistors.[191]

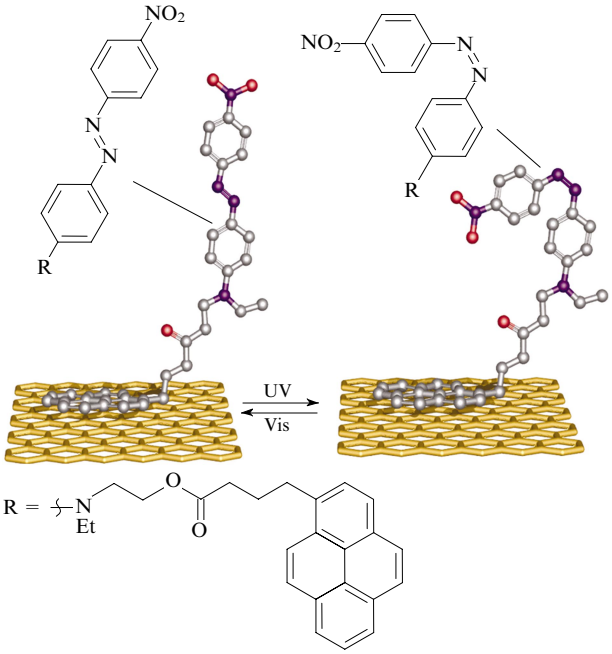


Figure 27. Schematic view of chromophore photoisomerization for azobenzene with pyrene groups adsorbed on the graphene surface.[191]

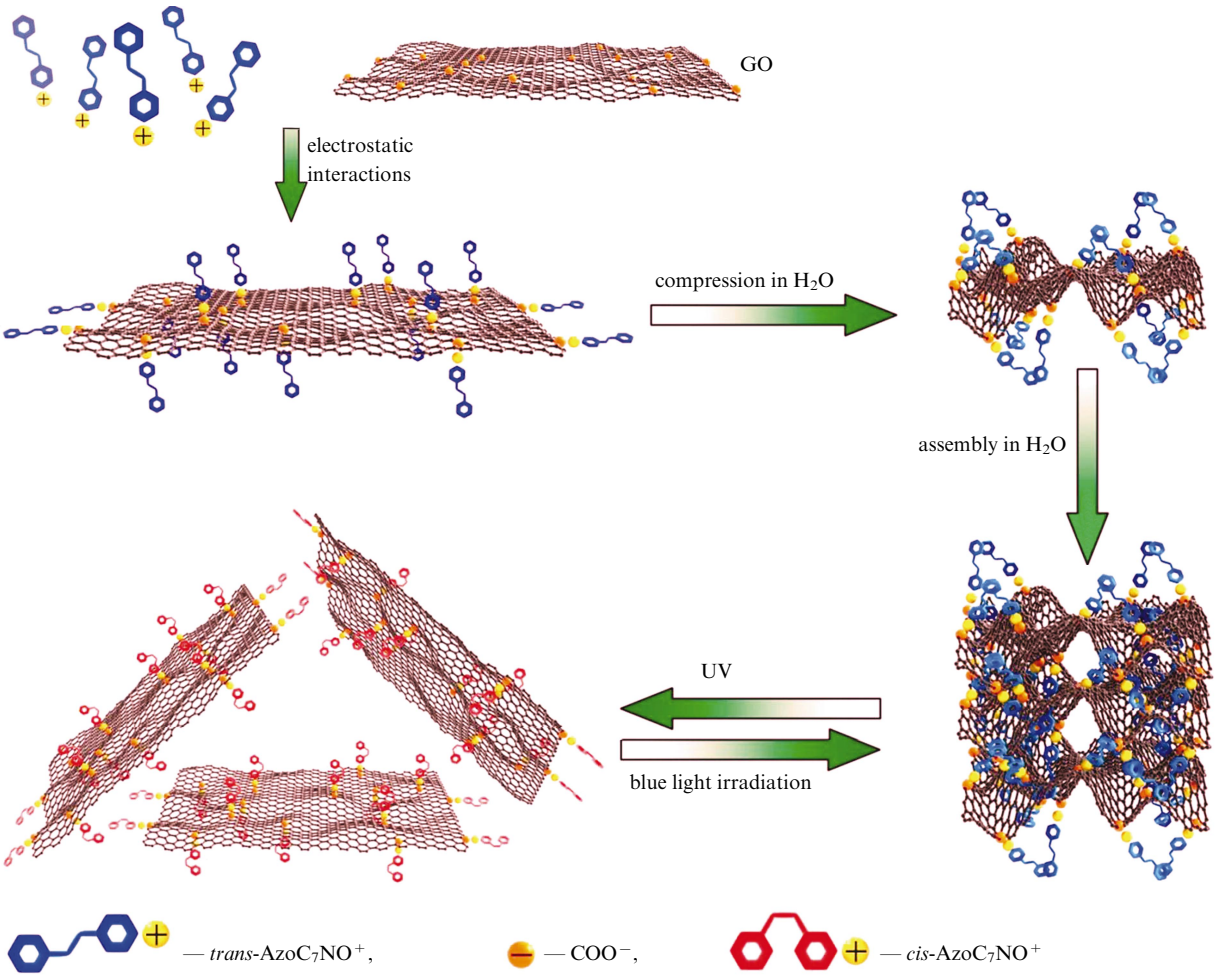


Figure 28. Synthesis of azobenzene-modified graphene and its photocontrolled self-assembly [plus stands for the $O(CH_2)_4N^+Me_3$ group in the *para*-position].[197]

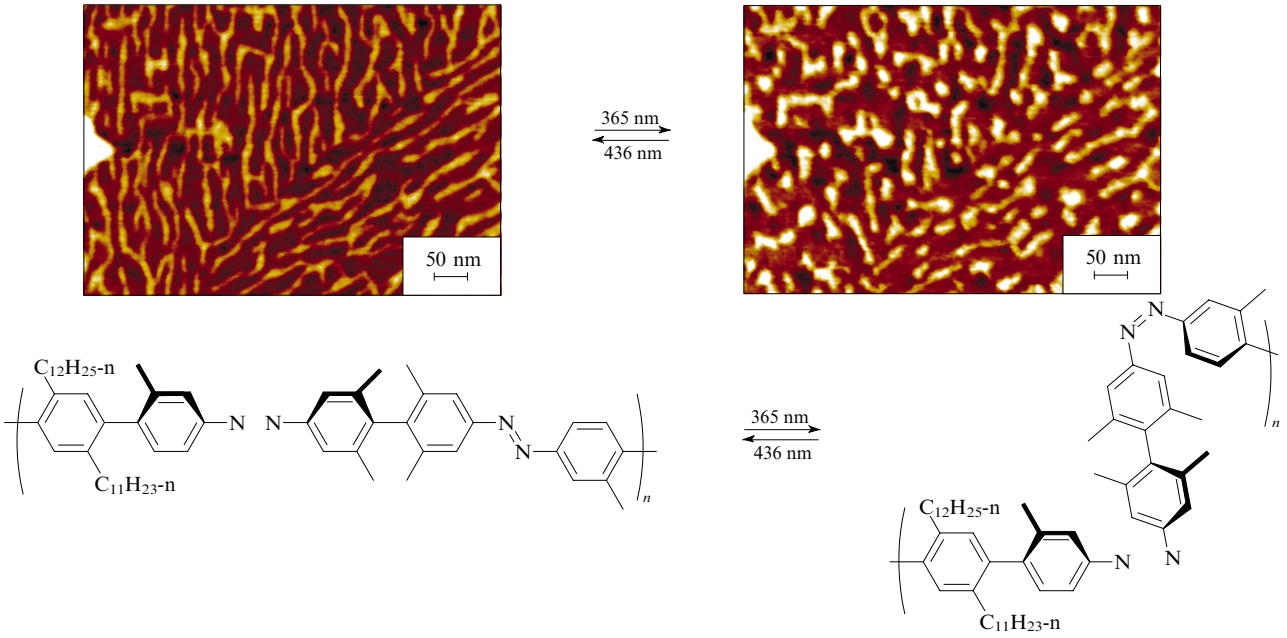


Figure 29. Photomicrographs illustrating the motion of the azobenzene coating on the graphene surface upon light irradiation.[199]

In subsequent studies, it has been shown that the azobenzene moieties are arranged at $\leqslant 34^\circ$ angle to the graphene surface.[196] The terminal functional groups affect only slightly the tilt angle of the chromophores, but have a pronounced influence on the dipole moments of chromophore molecules; this can serve for studying the dipole effect on the charge transfer in graphene and on enhancement of Raman scattering.

Chen *et al.*[197] have demonstrated a new approach to the preparation of graphene modified with azobenzene, namely, the use of electrostatic interactions between the carboxy derivative of graphene oxide and cationic azo-surfactant (Fig. 28). This resulted in the development of a smart reversible self-assembled system of graphene well controllable by irradiation.

Whereas encapsulation of azobenzene into graphene can be used to control graphene electromagnetic properties, graphene in turn catalyzes the *cis*-to-*trans* isomerization of the chromophore. In particular, Shin *et al.*[198] have reported fast isomerization of amino-substituted azobenzene catalyzed by graphene oxide. The amino group markedly facilitates the charge transfer from azobenzene to graphene with respect to that in the unsubstituted chromophore.

Interesting results on graphene doping with azobenzene have been reported by Lee *et al.*[199] A polymer containing azobenzene molecules was deposited on the graphene surface. The irradiation of the coating resulted in chromophore isomerization, which induced motion of the layer (Fig. 29). In the researchers' opinion,[199] this effect may inspire the development of optomechanical systems.

V. Conclusion

As follows from the presented review, the chemistry of photochromic carbon clusters based on fullerenes, carbon nanotubes and graphene with various photochromic compounds has been vigorously developed in the last decade. This is caused by the possibility of designing fundamentally new and efficiently photoswitchable field effect transistors, information and solar energy storage systems, molecular computers and other useful devices for various branches of industry.

An important place in the review is allocated to modern methods for functionalization of carbon clusters with photochromic molecules based on the use of well-known and popular processes such as the Prato reaction as well as the catalytic cycloaddition of diazo compounds and organic azides. High yields of the target hybrid compounds composed of carbon clusters and photochromic molecules, the possibility of preparing single hybrids with high selectivity and the ready accessibility of the initial monomers and reagents make these methods exceptionally promising for the practical use.

Along with the covalently linked hybrid molecules, attention is paid to the synthesis of molecular assemblies *via* $\pi-\pi$ or electrostatic interactions of the initial carbon clusters with photochromes. With this approach, it is possible to preserve as fully as possible the unique electronic structure of the initial carbon cluster in the resulting hybrid system. Meanwhile, the chemical binding of carbon clusters to photochromic compounds provides the target hybrid molecules possessing high thermal stability of photoinduced isomers and photochemical stability against irreversible phototransformations, which are important characteristics for such materials. These properties largely determine the prospective application areas for the hybrid photochromic molecules and the durability of molecular switches without the loss of efficiency.

The properties of the new hybrid molecules are affected by not only the structure and nature of the initial photochromes and carbon clusters, but also by intramolecular interactions in the latter. The efficiency of the photoswitching of hybrid molecules considerably depends on the distance between the carbon cluster and the photochrome. The

short distance leads to partial or complete loss of photochromic properties, which may be associated with the transfer of the excitation energy from the photochromic addend to the carbon cluster. By varying the nature of the carbon material and the structures of the photochromic molecule and the connecting spacer, it is possible to control the charge transfer and charge separation processes in the hybrid molecules and, hence, to affect the efficiency of their photochemical transformations.

The data covered in the review encourage the researchers to develop industrially promising processes for the manufacture of materials with unique properties on the basis of photochrome-containing carbon clusters with the goal to design new-generation electronic technologies.

Currently, these studies are at the initial stage of development; however, the results obtained already demonstrate the great prospects of this research. In our opinion, further development of the studies dealing with functionalization of carbon clusters by known photochromic compounds may provide unique and unexpected results. The major effort should be directed toward the decrease in the response time, increase in the light sensitivity and electronic modulation of the photochromic hybrid systems. This would be of key importance for the development of new mulifunctional light-sensitive materials based on these systems.

This review was written with the financial support of the Russian Science Foundation (Project No. 14-13-00296).

References

1. B L Feringa, W R Browne *Molecular Switches* Vols 1, 2 (Weinheim: Wiley-VCH, 2011)
2. B L Feringa, R A van Delden, N Koumura, E M Geertsema *Chem. Rev.* **100** 1789 (2000)
3. V A Barachevskii *Khim. Vys. Energ.* **37** 8 (2003)
4. V Z Shirinian, A A Shimkin, in *Topics in Heterocyclic Chemistry* (Berlin, Heidelberg: Springer, 2008) p. 75
5. M Natali, S Giordani *Chem. Soc. Rev.* **41** 4010 (2012)
6. W Szymasski, J M Beierle, H A V Kistemaker, W A Velema, B L Feringa *Chem. Rev.* **113** 6114 (2013)
7. J Zhang, Q Zou, H Tian *Adv. Mater.* **25** 378 (2013)
8. S Erbas-Cakmak, D A Leigh, C T McTernan, A L Nussbaumer *Chem. Rev.* **115** 10081 (2015)
9. V A Barachevsky *Org. Photon. Photovolt.* **3** 8 (2015)
10. H Tian, S Wang *Chem. Commun.* 781 (2007)
11. H Tian, Y Feng *J. Mater. Chem.* **18** 1617 (2008)
12. D Gust, J Andreasson, U Pischel, T A Moore, A L Moore *Chem. Commun.* 1947 (2012)
13. S Chen, Y Yang, Y Wu, H Tian, W Zhu *J. Mater. Chem.* **22** 5486 (2012)
14. F Rios, S N Smirnov *Chem. Mater.* **23** 3601 (2011)
15. T Nakagawa, K Atsumi, T Nakashima, Y Hasegawa, T Kawai *Chem. Lett.* **36** 372 (2007)
16. V Balzani, M Gomez-Lopez, J F Stoddart *Acc. Chem. Res.* **31** 405 (1998)
17. *Organic Photochromic and Thermochromic Compounds* (Eds J C Crano, R'J'Guglielmetti) (New York: Plenum Press, 1999)
18. M Irie *Chem. Rev.* **100** 1685 (2000)
19. Y Yokoyama *Chem. Rev.* **100** 1717 (2000)
20. G Berkovic, V Krongauz, V Weiss *Chem. Rev.* **100** 1741 (2000)
21. J A Delaire, K Nakatani *Chem. Rev.* **100** 1817 (2000)
22. H Tian, S Yang *Chem. Soc. Rev.* **33** 85 (2004)
23. V I Minkin *Russ. Chem. Rev.* **82** 1 (2013)
24. V Z Shirinian, D V Lonshakov, A G L'vov, M M Krayushkin *Russ. Chem. Rev.* **82** 511 (2013)
25. M Irie, T Fukaminato, K Matsuda, S Kobatake *Chem. Rev.* **114** 12174 (2014)
26. L Fabbrizzi, A Poggi *Chem. Soc. Rev.* **24** 197 (1995)
27. V Balzani, A Credi, F M Raymo, J F Stoddart *Angew. Chem., Int. Ed.* **39** 3348 (2000)
28. I G Panova, I N Topchieva *Russ. Chem. Rev.* **70** 23 (2001)
29. V Balzani, A Credi, M Venturi *Molecular Devices and Machines: a Journey into the Nano World* (Weinheim: Wiley-VCH, 2003)
30. A H Flood, R J A Ramirez, W-Q Deng, R P Muller, W A Goddard III, J F Stoddart *Austral. J. Chem.* **57** 301 (2004)
31. H Tian, Q-C Wang *Chem. Soc. Rev.* **35** 361 (2006)
32. E R Kay, D A Leigh, F Zerbetto *Angew. Chem., Int. Ed.* **46** 72 (2007)
33. J L Zhang, J Q Zhong, J D Lin, W P Hu, K Wu, G Q Xu, A T S Wee, W Chen *Chem. Soc. Rev.* **44** 2998 (2015)
34. R Klajn *Chem. Soc. Rev.* **43** 148 (2014)
35. Y Wang, Q Li *Adv. Mater.* **24** 1926 (2012)
36. E Merino *Chem. Soc. Rev.* **40** 3835 (2011)
37. L Sun, Y A Diaz-Fernandez, T A Gschneidtner, F Westerlund, S Lara-Avila, K Moth-Poulsen *Chem. Soc. Rev.* **43** 7378 (2014)
38. E Orgiu, P Samori *Adv. Mater.* **26** 1827 (2014)
39. R Güstl, A Senf, S Hecht *Chem. Soc. Rev.* **43** 1982 (2014)
40. H W Kroto, J R Heath, S C O'Brien, R F Curl, R E Smalley *Nature (London)* **318** 162 (1985)
41. P A Liddell, G Kodis, J Andreasson, L de la Garza, S Bandyopadhyay, R H Mitchell, T A Moore, A L Moore, D Gust *J. Am. Chem. Soc.* **126** 4803 (2004)
42. S D Straight, J Andreasson, G Kodis, A L Moore, T A Moore, D Gust *J. Am. Chem. Soc.* **127** 2717 (2005)
43. M E El-Khouly, J H Kim, K-Y Kay, C S Choi, O Ito, S Fukuzumi *Chem. – Eur. J.* **15** 5301 (2009)
44. H Zhang, A Borgschulte, F A Castro, R Crockett, A C Gerecke, O Deniz, J Heier, S Jenatsch, F Nüesch, C Sanchez-Sanchez, A Zoladek-Lemanczyk, R Hany *Adv. Energy Mater.* 1400734 (2015)
45. H Zhu, T Li, Y Zhang, H Dong, J Song, H Zhao, Z Wei, W Xu, W Hu, Z Bo *Adv. Mater.* **22** 1645 (2010)
46. G Vives, J M Tour *Acc. Chem. Res.* **42** 473 (2009)
47. R Wortmann, P M Lundquist, R J Twieg, C Geletneky, C R Moylan, Y Jia, R G DeVoe, D M Burland, M P Bernal, H Coufal, R K Grygier, J A Hoffnagle, C M Jefferson, R M Macfarlane, R M Shelby, G T Sincerbox *Appl. Phys. Lett.* **69** 1657 (1996)
48. K D Harris, R Ayachitula, S J Strutz, L M Hayden, R J Twieg *Appl. Opt.* **40** 2895 (2001)
49. K A Muszkat, S Sharafy *J. Am. Chem. Soc.* **93** 4119 (1971)
50. M Irie, M Mohri *J. Org. Chem.* **53** 803 (1988)
51. G Hohlneicher, M Muller, M Demmer, J Lex, J H Penn, L-X Gan, P D Loesel *J. Am. Chem. Soc.* **110** 4483 (1988)
52. J H Frederick, Y Fujiwara, J H Penn, K Yoshihara, H Petek *J. Phys. Chem.* **95** 2845 (1991)
53. M Hanazawa, R Sumiya, Y Horikawa, M Irie *J. Chem. Soc., Chem. Commun.* 206 (1992)
54. V Z Shirinian, M M Krayushkin, V A Barachevskii, L I Belen'kii, A A Shimkin, Yu P Strokach *Mendeleev Commun.* **14** 202 (2004)
55. V Z Shirinian, M M Krayushkin, B V Nabatov, O Yu Kuznetsova, A A Shimkin *Bull. Chem. Soc. Jpn.* **79** 889 (2006)
56. M Irie, K Sakemura, M Okinaka, K Uchida *J. Org. Chem.* **60** 8305 (1995)
57. G M Tsivgoulis, J-M Lehn *Angew. Chem., Int. Ed. Engl.* **34** 1119 (1995)

58. L N Lucas, J V van Esch, R M Kellogg, B L Feringa *Tetrahedron Lett.* **40** 1775 (1999)
59. L N Lucas, J J D de Jong, J H van Esch, R M Kellogg, B L Feringa *Eur. J. Org. Chem.* 155 (2003)
60. S Kobatake, K Uchida, E Tsuchida, M Irie *Chem. Lett.* **29** 1340 (2000)
61. D Kitagawa, K Sasaki, S Kobatake *Bull. Chem. Soc. Jpn.* **84** 141 (2011)
62. M Prato, M Maggini, C Giacometti, G Scorrano, G Sandona, G Farnia *Tetrahedron Lett.* **52** 5221 (1996)
63. H-Y Hu, M-Z Zhu, Z-P Zhang, G-T Wen, Y Fu, Q-X Guo *Chin. J. Chem. Phys.* **19** 433 (2006)
64. A R Tuktarov, A A Khuzin, L M Khalilov, A R Tulyabaev, A R Akhmetov, U M Dzhemilev *Mendeleev Commun.* **25** 470 (2015)
65. S Castellanos, A A Vieira, B M Illescas, V Sacchetti, C Schubert, J Moreno, D M Guldi, S Hecht, N Martin *Angew. Chem., Int. Ed.* **52** 13985 (2013)
66. A R Tuktarov, A A Khuzin, A R Akhmetov, V A Barachevsky, O V Venidiktova, U M Dzhemilev *Tetrahedron Lett.* **56** 7154 (2015)
67. A Osuka, D Fujikane, H Shinmory, S Kobatake, M Irie *J. Org. Chem.* **66** 3913 (2001)
68. A R Tuktarov, A A Khuzin, A R Akhmetov, L M Khalilov, A R Tulyabaev, V A Barachevskii, O V Venidiktova, U M Dzhemilev *Mendeleev Commun.* **26** 143 (2016)
69. J Jeong, E Yun, Y Choi, H-Y Jung, S-J Chung, N W Song, B H Chung *Chem. Commun.* **47** 10668 (2011)
70. J L Bahr, G Kodis, L de la Garza, S Lin, A L Moore, T A Moore, D Gust *J. Am. Chem. Soc.* **123** 7124 (2001)
71. J M Endtner, F Effenberger, A Hartschuh, H Port *J. Am. Chem. Soc.* **122** 3037 (2000)
72. P A Liddell, G Kodis, A L Moore, T A Moore, D Gust *J. Am. Chem. Soc.* **124** 7668 (2002)
73. T Tsujioka, K Masuda *Appl. Phys. Lett.* **83** 4978 (2003)
74. X F Guo, D Zhang, Y Gui, M X Wax, J C Li, Y Q Liu, D B Zhu *Adv. Mater.* **16** 636 (2004)
75. P Andersson, N D Robinson, M Berggren *Adv. Mater.* **17** 1798 (2005)
76. Q Shen, L Wang, S Liu, Y Cao, L Gan, X Guo, M L Steigerwald, Z Shuai, Z Liu, C Nuckolls *Adv. Mater.* **22** 3282 (2010)
77. H T Zhang, X F Guo, J S Hui, S X Hu, W Xu, D B Zhu *Nano Lett.* **11** 4939 (2011)
78. P Lutsyk, K Janus, J Sworakowski, G Generali, R Capelli, M Muccini *J. Phys. Chem. C* **115** 3106 (2011)
79. N Crivillers, E Orgiu, F Reinders, M Mayor, P Samori *Adv. Mater.* **23** 1447 (2011)
80. C Sciascia, R Castagna, M Dekermenjian, R Martel, A R S Kandada, F Di Fonzo, A Bianco, C Bertarelli, M Meneghetti, G Lanzani *J. Phys. Chem. C* **116** 19483 (2012)
81. R C Shallcross, P O Korner, E Maibach, A Kohnen, K Meerholz *Adv. Mater.* **25** 4807 (2013)
82. E Orgiu, N Crivillers, M Herder, L Grubert, M Patzel, J Frisch, E Pavlica, D T Duong, G Bratina, A Salleo, N Koch, S Hecht, P Samori *Nat. Chem.* **4** 675 (2012)
83. R Hayakawa, K Higashiguchi, K Matsuda, T Chikyow, Y Wakayama *ACS Appl. Mater. Interfaces* **5** 3625 (2013)
84. Y Ishiguro, R Hayakawa, T Yasuda, T Chikyow, Y Wakayama *ACS Appl. Mater. Interfaces* **5** 9726 (2013)
85. K Borjesson, M Herder, L Grubert, D T Duong, A Salleo, S Hecht, E Orgiu, P Samori *J. Mater. Chem. C* **3** 4156 (2015)
86. J C Hummelen, B W Knight, F Lepeq, F Wudl, J Yao, C L Wilkins *J. Org. Chem.* **60** 532 (1995)
87. Y J He, H Y Chen, J H Hou, Y F Li *J. Am. Chem. Soc.* **132** 1377 (2010)
88. T D Anthopoulos, C Tanase, S Setayesh, E J Meijer, J C Hummelen, P W M Blom, D M de Leeuw *Adv. Mater.* **16** 2174 (2004)
89. H Yu, H H Cho, C H Cho, K H Kim, D Y Kim, B J Kim, J H Oh *ACS Appl. Mater. Interfaces* **5** 4865 (2013)
90. A C Whalley, M L Steigerwald, X Guo, C Nuckolls *J. Am. Chem. Soc.* **129** 12590 (2007)
91. D Dulic, S J van der Molen, T Kudernac, H T Jonkman, J J D de Jong, T N Bowden, J van Esch, B L Feringa, B J van Wees *Phys. Rev. Lett.* **91** 207402 (2003)
92. M Irie, T Eriguchi, T Takada, K Uchida *Tetrahedron* **53** 12263 (1997)
93. M K Ashraf, N A Bruque, J L Tan, G J O Beran, R K Lake *J. Chem. Phys.* **134** 024524 (2011)
94. P Zhao, P Wang, Z Zhang, C Fang, Y Wang, Y Zhai, D Liu *Solid State Commun.* **149** 928 (2009)
95. C Motta, M I Trioni, G P Brivio, K L Sebastian *Phys. Rev. B* **84** 113408 (2011)
96. E Fischer, Y Hirshberg *J. Chem. Soc.* 4522 (1952)
97. V I Minkin *Chem. Rev.* **104** 2751 (2004)
98. V A Lokshin, A Samat, A V Metelitsa *Russ. Chem. Rev.* **71** 893 (2002)
99. R Guglielmetti, in *Photochromism. Molecules and Systems* (Eds H Durr, H Bonas-Laurent) (Elsevier: Amsterdam, 1990) p. 314
100. V Lokshin, A Samat, A V Metelitsa, V I Minkin, in *Modern Approaches to the Synthesis of O- and N-Heterocycles* Vol. 1 (Eds T S Kaufman, E L Largi) (Kerala: Research Signpost, 2007) p. 187
101. J-H Xu, Y-L Li, D-B Zhu *Acta Chim. Sinica* **60** 541 (2002)
102. J-H Xu, Y-L Li, D-B Zhu *Synth. Commun.* **32** 1647 (2002)
103. A R Tuktarov, A A Khuzin, A R Tulyabaev, O V Venidictova, T M Valova, V A Barachevsky, L M Khalilov, U M Dzhemilev *RSC Adv.* **6** 71151 (2016)
104. J Frey, G Kodis, S D Straight, T A Moore, A L Moore, D Gust *J. Phys. Chem. A* **117** 607 (2013)
105. L A Frolova, P A Troshin, D K Susarova, A V Kulikov, N A Sanina, S M Aldoshin *Chem. Commun.* **51** 6130 (2015)
106. M Yoshida, K Suemori, S Uemura, S Hoshino, N Takada, T Kodzasa, T Kamata *Jpn. J. Appl. Phys.* **49** 04DK09 (2010)
107. C-W Tseng, D-C Huang, Y-T Tao *ACS Appl. Mater. Interfaces* **4** 5483 (2012)
108. L A Frolova, A A Rezvanova, B S Lukyanov, N A Sanina, P A Troshin, S M Aldoshin *J. Mater. Chem. C* **3** 11675 (2015)
109. A A Rezvanova, L A Frolova, P A Troshin *Mendeleev Commun.* **26** 26 (2016)
110. X Guo, L Huang, S O'Brien, P Kim, C Nuckolls *J. Am. Chem. Soc.* **127** 15045 (2005)
111. I V Ciapurin, S V Robu, E V Rotari, O Y Korshak, R A Lessard *Proc. SPIE* **4642** 50 (2002)
112. I Ciapurin, S V Robu, O Y Korshak, C Lafond, A Tork, R A Lessard *Proc. SPIE* **4342** 589 (2002)
113. N M Kronenberg, V Steinmann, H Bürckstümmer, J Hwang, D Hertel, F Würthner, K Meerholz *Adv. Mater.* **22** 4193 (2010)
114. N M Kronenberg, M Deppisch, F Würthner, H W A Lademann, K Deing, K Meerholz *Chem. Commun.* 6489 (2008)
115. A Ojala, A Petersen, A Fuchs, R Lovrincic, C Pölking, J Trollmann, J Hwang, C Lennartz, H Reichelt, H W Höffken, A Pucci, P Erk, T Kirchartz, F Würthner *Adv. Funct. Mater.* **22** 86 (2012)
116. A Ojala, H Bürckstümmer, M Stolte, R Sens, H Reichelt, P Erk, J Hwang, D Hertel, K Meerholz, F Würthner *Adv. Mater.* **23** 5398 (2011)
117. V Steinmann, N M Kronenberg, M R Lenze, S M Graf, D Hertel, K Meerholz, H Bürckstümmer, E V Tulyakova, F Würthner *Adv. Energy Mater.* **1** 888 (2011)
118. F Würthner, K Meerholz *Chem. – Eur. J.* **16** 9366 (2010)
119. H Bürckstümmer, E V Tulyakova, M Deppisch, M R Lenze, N M Kronenberg, M Gsanger, M Stolte, K Meerholz, F Würthner *Angew. Chem., Int. Ed.* **50** 11628 (2011)

120. N M Kronenberg, H Bürckstümmer, M Deppisch, F Würthner, K Meerholz *J. Photon. Energy* **1** 011101-1 (2011)
121. A Ojala, H Bürckstümmer, J Hwang, K Graf, B von Vacano, K Meerholz, P Erk, F Würthner *J. Mater. Chem.* **22** 4473 (2012)
122. V Steinmann, T E Umbach, M Schadel, J Krumrain, M R Lenze, H Bürckstümmer, F Würthner, K Meerholz *Org. Electron.* **14** 2029 (2013)
123. A Zitzler-Kunkel, M R Lenze, N M Kronenberg, A-M Krause, M Stolte, K Meerholz, F Würthner *Chem. Mater.* **26** 4856 (2014)
124. V N Bliznyuk, J Gasiorowski, A A Ishchenko, G V Bulavko, N A Derevyanko, N Serdar Sariciftci *Org. Electron.* **15** 1105 (2014)
125. J Dikova, S Kitova, D Stoyanova, A Vasilev, T Deligeorgiev, S Angelova *J. Phys: Conf. Ser.* **514** 012019 (2014)
126. R Augulis, A Devizis, D Peckus, V Gulbinas, D Hertel, K Meerholz *J. Phys. Chem. C* **119** 5761 (2015)
127. K-W Chen, C W Huang, S-Y Lin, Y-H Liu, T Chatterjee, W-Y Hung, S-W Liu, K-T Wong *Org. Electron.* **26** 319 (2015)
128. R F Khairutdinov, M E Itkis, R C Haddon *Nano Lett.* **4** 1529 (2004)
129. I W Cheong, S Wang, H S Ki, S-H Kim *Curr. Appl. Phys.* **9** 1269 (2009)
130. E Del Canto, K Flavin, M Natali, T Perova, S Giordani *Carbon* **48** 2815 (2010)
131. E Malic, C Weber, M Richter, V Atalla, T Klamroth, P Saalfrank, S Reich, A Knorr *Phys. Rev. Lett.* **106** 097401 (2011)
132. P Bluemmel, A Setaro, C Maity, S Hecht, S Reich *J. Phys.: Condens. Matter* **24** 394005 (2012)
133. P Bluemmel, A Setaro, C Maity, S Hecht, S Reich *Phys. Status Solidi, B* **249** 2479 (2012)
134. A Perry, S J Green, D W Horsell, S M Hornett, M E Wood *Tetrahedron* **71** 6776 (2015)
135. Y Li, Y Duan, J Zheng, J Li, W Zhao, S Yang, R Yang *Anal. Chem.* **85** 11456 (2013)
136. P Joo, B J Kim, E K Jeon, J H Cho, B-S Kim *Chem. Commun.* **48** 10978 (2012)
137. A-R Jang, E K Jeon, D Kang, G Kim, B-S Kim, D J Kang, H S Shin *ACS Nano* **6** 9207 (2012)
138. M Andresen, A C Stiel, J Folling, D Wenzel, A Schonle, A Egner, C Eggeling, S W Hell, S Jakobs *Nat. Biotechnol.* **26** 1035 (2008)
139. J Balapanuru, J X Yang, S Xiao, Q Bao, M Jahan, L Polavarapu, J Wei, Q-H Xu, K P Loh *Angew. Chem., Int. Ed.* **49** 6549 (2010)
140. A-A Nahain, J-E Lee, J H Jeong, S Y Park *Biomacromolecules* **14** 4082 (2013)
141. S M Sharker, C J Jeong, S M Kim, J-E Lee, J H Jeong, I In, H Lee, S Y Park *Chem. Asian J.* **9** 2921 (2014)
142. S X Wang, X M Wang, L J Li, R C Advincula *J. Org. Chem.* **69** 9073 (2004)
143. S Jurt, A Aemissegger, P Guntert, O Zerbe, D Hilvert *Angew. Chem., Int. Ed.* **45** 6297 (2006)
144. Y Norikane, N Tamaoki *Org. Lett.* **6** 2595 (2004)
145. C Zhang, M H Du, H P Cheng, X G Zhang, A E Roitberg, J L Krause *Phys. Rev. Lett.* **92** 158301 (2004)
146. Y P Wang, N Ma, Z Q Wang, X Zhang *Angew. Chem., Int. Ed.* **46** 2823 (2007)
147. T Murase, S Sato, M Fujita *Angew. Chem., Int. Ed.* **46** 5133 (2007)
148. K Oh-ishi, J Okamura, T Ishi-i, M Sano, S Shinkai *Langmuir* **15** 2224 (1999)
149. K-Y Kay, K-J Han, Y-J Yu, Y D Park *Tetrahedron Lett.* **43** 5053 (2002)
150. Y Shirai, T Sasaki, J M Guerrero, B-C Yu, P Hodge, J M Tour *ACS Nano* **2** 97 (2008)
151. T Sasaki, J M Tour *Org. Lett.* **10** 897 (2008)
152. J Zhang, K Porfyrakis, J J L Morton, M R Sambrook, J Harmer, L Xiao, A Ardavan, G A D Briggs *J. Phys. Chem. C* **112** 2802 (2008)
153. K S Kumar, A Patnaik *J. Comput. Chem.* **31** 1182 (2010)
154. K S Kumar, A Patnaik *J. Chem. Sci.* **125** 237 (2013)
155. K S Kumar, A Patnaik *Chem. Phys. Chem.* **11** 3645 (2010)
156. K S Kumar, A Patnaik *Chem. – Eur. J.* **17** 5327 (2011)
157. K S Kumar, A Patnaik *Langmuir* **27** 11017 (2011)
158. D I Schuster, K Li, D M Guldi, A Palkar, L Echegoyen, C Stanisky, R J Cross, M Niemi, N V Tkachenko, H Lemmetyinen *J. Am. Chem. Soc.* **129** 15973 (2007)
159. W Feng, W Luo, Y Feng *Nanoscale* **4** 6118 (2012)
160. D M Guldi, B M Illescas, C M Atienza, M Wielopolski, N Martin *Chem. Soc. Rev.* **38** 1587 (2009)
161. M E El-Khouly, J-H Kim, K-Y Kay, S Fukuzumi *J. Porphyr. Phthalocyanin.* **17** 1055 (2013)
162. K-J Han *J. Korean Oil Chem. Soc.* **31** 50 (2014)
163. S Ma, H Ting, L Zhang, Y Ma, L Zheng, L Xiao, Z Chen *Org. Electron.* **23** 1 (2015)
164. K Yuan, Y-J Guo, X Zhao *Phys. Chem. Chem. Phys.* **16** 27053 (2014)
165. P G Collins, P Avouris *Sci. Am.* **283** 62 (2000)
166. Y Yang, X Wang, L Liu, X Xie, Z Yang, R K Y Li, Y-W Mai *J. Phys. Chem. C* **111** 11231 (2007)
167. Y Feng, W Feng, H Noda, T Sekino, A Fujii, M Ozaki, K Yoshino *Carbon* **45** 2445 (2007)
168. Y Feng, X Zhang, X Ding, W Feng *Carbon* **48** 3091 (2010)
169. T Hu, H Xie, L Chen, G Zhong, H Zhang *Polym. Int.* **60** 93 (2011)
170. T J Kucharski, N Ferralis, A M Kolpak, J O Zheng, D G Nocera, J C Grossman *Nat. Chem.* **6** 441 (2014)
171. W Luo, Y Feng, C Cao, M Li, E Liu, S Li, C Qin, W Hu, W Feng *J. Mater. Chem. A* **3** 11787 (2015)
172. W Luo, Y.Feng C.Qin M.Li S.Li C.Cao P.Long E.Liu W.Hu K.Yoshino W.Feng. *Nanoscale* **7** 16214 (2015)
173. J M Simmons, I In, V E Campbell, T J Mark, F Leonard, P Gopalan, M A Eriksson *Phys. Rev. Lett.* **98** 086802 (2007)
174. V Schneider, T Strunskus, M Elbahri, F Faupel *Carbon* **90** 94 (2015)
175. S W Basuki, V Schneider, T Strunskus, M Elbahri, F Faupel *ACS Appl. Mater. Interfaces* **7** 11257 (2015)
176. X Zhou, T Zifer, B M Wong, K L Krafcik, F Leonard, A L Vance *Nano Lett.* **9** 1028 (2009)
177. Y Cao, S Dong, S Liu, Z Liu, X Guo *Angew. Chem., Int. Ed.* **52** 3906 (2013)
178. X Zhang, Y Feng, D Huang, Y Li, W Feng *Carbon* **48** 3236 (2010)
179. X Zhang, Y Feng, P Lv, Y Shen, W Feng *Langmuir* **26** 18508 (2010)
180. Deepshikha *Russ. J. Gen. Chem.* **85** 2167 (2015)
181. P Nguyen, J Li, T S Sreeprasad, K Jasuja, N Mohanty, M Ikenberry, K Hohn, V B Shenoy, V Berry *Small* **9** 3823 (2013)
182. Y Feng, H Liu, W Luo, E Liu, N Zhao, K Yoshino, W Feng *Sci. Rep.* **3** 3260 (2013)
183. J H Lee, J Jaworski, J H Jung *Nanoscale* **5** 8533 (2013)
184. D Saini *Mater. Res. Innovat.* **19** 287 (2015)
185. M Min, S Seo, S M Lee, H Lee *Adv. Mater.* **25** 7045 (2013)
186. D Saini *Int. J. Mater. Res.* **106** 176 (2015)
187. A Nurbawono, C Zhang *Appl. Phys. Lett.* **103** 203110 (2013)
188. N Peimyoo, J Li, J Shang, X Shen, C Qiu, L Xie, W Huang, T Yu *ACS Nano* **6** 8878 (2012)
189. N Peimyoo, T Yu, J Shang, C Cong, H Yang *Carbon* **50** 201 (2012)
190. J P Trinastic, H-P Cheng *Phys. Rev. B* **89** 245447 (2014)
191. M Kim, N S Safron, C Huang, M S Arnold, P Gopalan *Nano Lett.* **12** 182 (2012)

192. X Wang, Y Ouyang, X Li, H Wang, J Guo, H Dai *Phys. Rev. Lett.* **100** 206803 (2008)
193. M Y Han, B Ozyilmaz, Y Zhang, P Kim *Phys. Rev. Lett.* **98** 206805 (2007)
194. M Kim, N S Safron, E Han, M S Arnold, P Gopalan *Nano Lett.* **10** 1125 (2010)
195. N S Safron, A S Brewer, M S Arnold *Small* **7** 492 (2011)
196. P S Johnson, C Huang, M Kim, N S Safron, M S Arnold, B M Wong, P Gopalan, F J Himpsel *Langmuir* **30** 2559 (2014)
197. S Chen, L Bao, E Ou, C Peng, W Wang, W Xu *Nanoscale* **7** 19673 (2015)
198. D Shin, J H Kang, K-A Min, S Hong, B H Hong *APL Mater.* **2** 092501 (2014)
199. C-L Lee, T Liebig, S Hecht, D Bleger, J P Rabe *ACS Nano* **8** 11987 (2014)