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Photoconductive Interlocked Molecules and Macromolecules

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Abstract

Organic compounds and materials with photoconductive properties have been studied for many years because of their importance in many technological applications such as dye-sensitized solar cells, photodiodes, photoresistors, electronics, biomolecular sensing, etc. For multiple purposes, such molecules require intense protection from various factors which can decrease their durability and cause fatigue. Interlocked molecules and macromolecules involving photoconductive organic components and various types of macrocycles, such as cyclodextrins, cyclophanes, or macrocyclic ethers, are promising candidates for new photoconductivity-related applications. In this chapter, a review in this emerging research area in materials science and technology is provided. Focus is placed on photoconductive (poly)rotaxanes and (poly)catenanes. Various types of such materials and compounds are reviewed, and recent examples are provided. The relation between their structure and photoconductive behavior is discussed.

Keywords: photoconductivity, interlocked molecules, rotaxanes, catenanes, photocurrent responses, photosensitivity

1. Introduction

In recent years, a new class of supramolecular assemblies has gained the attention of the scientific community [1]. Supramolecular chemistry is a rapidly increasing research field which focuses on the study of complex systems that consist of more than one molecule, where order originates from the weak, non-covalent binding interactions between different chemical building blocks [2, 3]. The kinetic and thermodynamic control of covalent bonds has become a challenge for the synthetic community in order to create discrete molecules performing specific functions. This has accelerated chemists to attain precise control over kinetic and thermodynamic courses

utilizing weaker inter- and intramolecular interactions, such as hydrogen bonds, van der Waals forces, dipole-dipole interactions, etc. Controlling these weak interactions allows for targeted architectures of new class of molecules containing distinctive kinds of chemical bonds also known as “mechanical bonds.” Assemblies derived by the aforementioned forces consist of a distinct number of molecular components that explore mechanical-like movements (output) in response to pre-definite stimulation (input) [4]. The expression is often more generally applied to molecules that modestly mimic functions that occur at the macroscopic level. After organization and assembly, they are capable of linking molecular motions and reactions to complex macroscopic functions including actuation and signal modulation enabling “molecular machines.” The combination and coordination of organic, inorganic, and supramolecular chemistry made it possible to build various mechanically interlocked molecular architectures (MIMAs). The field of interlocked molecules is immense, and up to date, research in this field receives high interest and attention. In 2016, Jean-Pierre Sauvage, Sir J. Fraser Stoddart, and Bernard L. Feringa were awarded the Nobel Prize in Chemistry for the “design and synthesis of molecular machines.” The term has become state of the art in nanotechnology where a number of favorably complex molecular architectures have been investigated intended to construct MIMAs, estimated to fuel the cutting-edge miniaturization of multifunctional devices (electrical, optical, and chemical) in the near future. The profound investigation of these architectures is endeavored to proceed rapidly due to their valuable properties and potential future applications in biomechanics, molecular electronics, catalysis, drug delivery, electronic materials, and sensing including in general the targeted design of smart novel materials. Photoconductive multifunctional materials involving interlocked molecules and macromolecules are of high importance as they might result in novel hi-tech applications spanning from solar cells and molecular photodiodes to sensing biological applications. In this chapter, we provide a review to published photoconductive interlocked molecules and macromolecules, and we indicate the potentials of various classes of interlocked organic photoconductive dyes.

2. Rotaxanes and catenanes

Molecular machines can be divided into two main categories: synthetic and biological. Large, synthetic molecular machines refer to molecules that are artificially designed and synthesized, whereas biological molecular machines are going deep back in history and can be found under various forms in the nature (transport proteins such as kinesin, myosin, and dynein) [5]. Following a self-assembly process, the formation of large molecular and macromolecular structures can be achieved. These assemblies are mainly interlocked, and no covalent bond is responsible for their stability. Stabilizing interaction may be (i) donor/acceptor forces, (ii) metal/ligand coordination, (iii) hydrogen bonding interactions, (iv) π - π stacking, (v) solvophobic repulsion, and/or (vi) electrostatic forces. Non-covalent interactions enable new properties and smart functional materials by the emerging synergy between molecular recognition and advanced chemistry. The introduction of a mechanical bond enters within the well-recognized chemistry of the subcomponents of supramolecular architectures such as catenanes and rotaxanes. Catenanes and rotaxanes are among the simplest examples of mechanically interlocked molecules with nanometer-scale structures [6]. Many of these molecular assemblies

constitute nanomaterials that have been intensively investigated because of their ability to act as molecular machines and/or switches by giving controllable and reversible transformations. The interlocked components can be forced through a combination of chemical, optical, or electrochemical stimuli to change their orientation with respect to one another [7]. These reversible transformations may exhibit high response rates to various highly controllable physical or chemical external stimulations such as pH changes, electricity, light irradiation, heating or cooling, etc. Rotaxanes and catenanes are promising systems for the construction of artificial molecular machines. Catenanes were among the first supramolecular structures that have been reported, in which two or even more cyclic molecules have been mechanically interlocked together and did not disassembly by any external stimuli [4]. In 1964, the first catenane was synthesized by Schill and Lüttringhaus [8]. Synthetic strategies were improved in the late 1980s and beginning of 1990s, in large extent by Stoddart and coworkers [1]. According to the IUPAC nomenclature, $[n]$ catenanes consist of n -interlocked rings. In their simplest form ($[2]$ catenanes), two rings are non-covalently bound forming a structure like the one depicted in **Figure 1** [11]. One of the most synthetically challenging examples of catenanes has been reported in 1994 by the group of Stoddart which was composed of five interlocking macrocycles representing a $[5]$ catenane also known as olympiadane [12].

The disassembly of catenanes into its individual chemical components requires the breaking of one or more covalent bonds within the mechanically linked molecule. One of their fascinating functions is their ability to act as molecular machines where within these assemblies one or more of the macrocyclic ring(s) change position with respect to one another [13]. High synthetic challenges surround the synthesis of catenanes since a macrocyclization reaction is required in order to achieve the interlocked architecture with attendant competition between cyclization and oligomerization. In order to overcome this challenge, catenanes are typically formed under highly diluted conditions which lead consequently to prolonged reaction times,

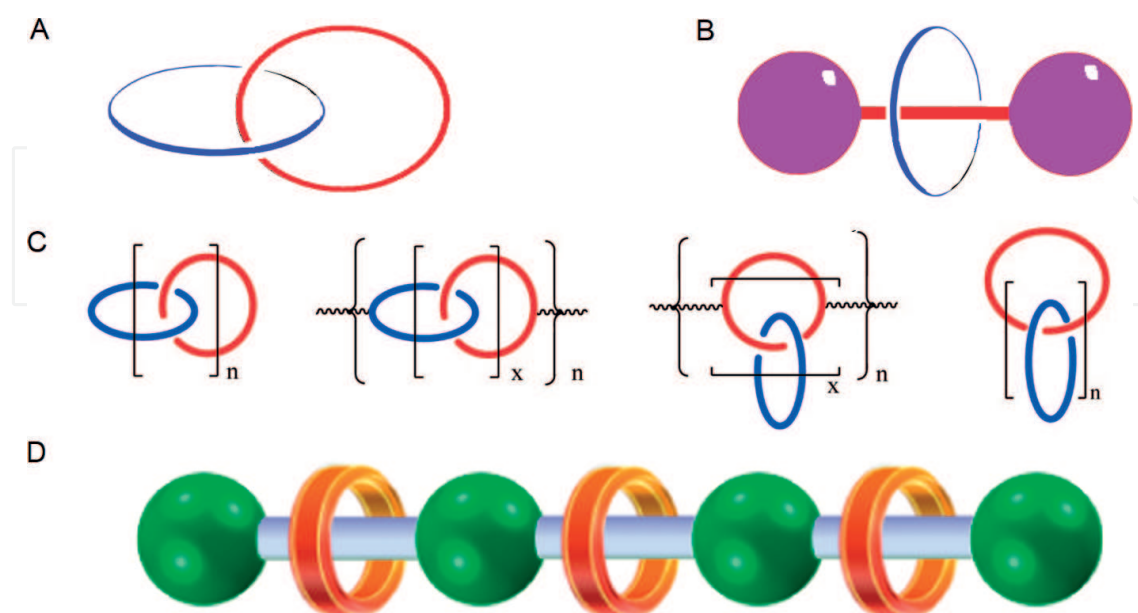


Figure 1. Symbolic representations of a $[2]$ catenane (A) and a $[2]$ rotaxane (B). (C) Various types of polycatenanes. Reprinted with permission from Niu and Gibson [9]. (D) Topological alignment in a polyrotaxane. Reprinted with permission from Yu et al. [10].

since the association between the ring and a macrocycle precursor is weak which diminishes yields. Immense amount of work has been published altering the synthetic protocols as well as introducing a variety of macrocyclic molecules, e.g., crown ethers, cyclophanes, cyclodextrins (CDs), cucurbituril, calixarene, etc. In contrast to catenanes, rotaxanes are composed of one or more macrocycles and “dumbbell-shaped” molecule(s) threaded through them. Stoppering bulky end groups also called “stoppers” prevent disassembly [14]. The word rotaxane is derived from the Latin words “rota” meaning wheel and “axis” meaning axle. The formal naming of rotaxanes according to IUPAC rules is [n]rotaxane, where n indicates the number of chemically independent components in a rotaxane assembly. The simplest form is “[2] rotaxane” which consists of one macrocycle and one dumbbell-shaped molecule. There are several interactions that can initiate self-assembly, needed for the formation of these supramolecular structures in a more efficient manner. These interactions may be hydrophobic, hydrogen bonding, or donor-acceptor interactions. The strength of these interactions varies, and this introduces different stability of the formed complexes depending on the nature of interaction, e.g., Van der Waals forces (2–4 kJ/mol), hydrophobic interactions (4–12 kJ/mol), and hydrogen bonds (8–40 kJ/mol). When considering the strategies of chemical synthesis of rotaxanes, one can distinguish three general approaches: Strategy I, threading of a macrocycle onto a rod molecule and subsequent interaction of the complex formed with the blocking reagents; Strategy II, cyclisation in the presence of compounds having a dumbbell-like structure; and Strategy III, temperature-induced “slipping” of the macrocycle onto bulky terminal groups of the dumbbell-shaped molecule. Accordingly, mechanically interlocked rotaxanes constitute some of the most appropriate candidates to serve as molecular switches and machines in the rapidly developing fields of nanoelectronics and nanoelectromechanical systems (NEMS). Numerous organic cyclic host compounds such as donor-acceptor complexes [15], crown ether complexes [16], and hydrogen bonded complexes involving cyclic amides [17] have been used for rotaxane synthesis. Herein, we shall focus on various rotaxanes and catenanes exhibiting photoconductive properties.

3. Photoconductivity

Photoconductivity is the phenomenon in which electrical current is generated in materials under light radiation. When a material such as a semiconductor absorbs photons of sufficient energy, the electrons in the valence band can be excited, cross the bandgap, and lead to the formation of electron-hole pairs resulting in increased conductivity (**Figure 2**). In principle, photoconductivity is a common physical phenomenon of a material, and it is particularly prominent in semiconductors due to their small bandgaps. Thus, photoconductivity generates great interest for the investigation of the electronic structure, transportation properties of materials, electron-hole pair dynamics, as well as practical applications such as photodetectors, photoresistors, and charge-coupled devices. The classic photoconductive materials consist of doped semiconductors, e.g., Si, Ge and Se [18–20], metal oxides, and sulfides as well as conductive polymers. Apart from these classic materials, the photoconductivity is also observed in an ultracold fermionic gas that is trapped in an optical lattice [21] as well as various organic compounds [22].

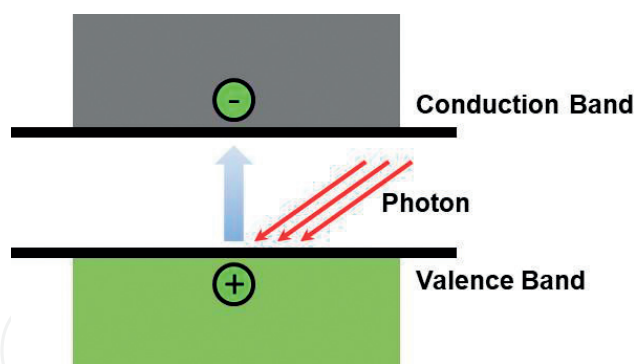


Figure 2. Excitation process leading to photoconductivity in a condensed matter system, in which incoming laser light ($h\nu$) excites an electron to the valence band, leaving a positively charged hole behind.

4. Photoconductivity measurements

The most prominent method to measure the photoelectrical properties is xerography (method shown schematically in **Figure 3**) [22]. The target sample is mounted and grounded on a sample holder, which can move forward or backward through a driving chain (**Figure 3a**). When the sample is moved to position (2) where the corotron is just above, the sample can be charged either positively or negatively. When the sample is moved to position (3), its surface potential can be measured by using an electrometer. A typical scheme of a photodischarge curve produced using this method is shown in **Figure 3b**. When the electronic shutter is closed, the sample is under totally dark conditions, and dark conductivity can be measured. When the shutter is open, the sample can be under exposure of either an intense erase light to measure the residual potential or a monochromatic light with known intensity to measure the photosensitivity.

This technique is simple and allows for the determination of first-order xerographic properties. Therefore, it has been widely used in the study and evaluation of photoconductive organic material properties [22]. Another intensively utilized method to investigate the photoconductivity of the material is graphically shown in **Figure 4**. By illuminating the sample with light of various wavelengths and plotting the current evolutions as a function of time, the generated photocurrent can be measured as well as different photoeffects [23, 24], e.g., photodoping,

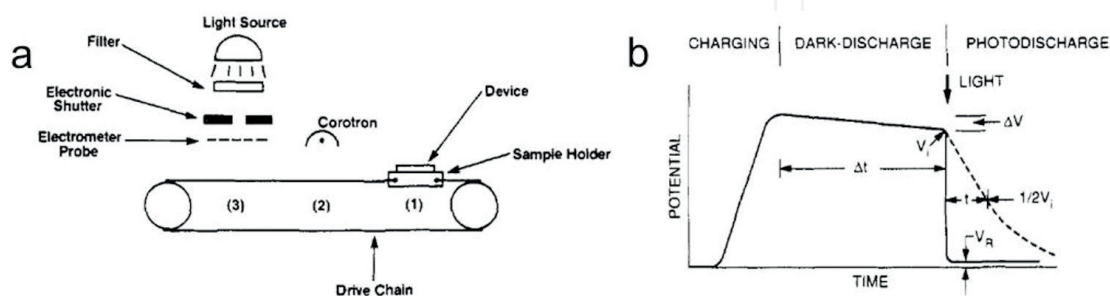


Figure 3. A schematic of the apparatus (a) and photodischarge curves (b). Reprinted with permission from Law [22].

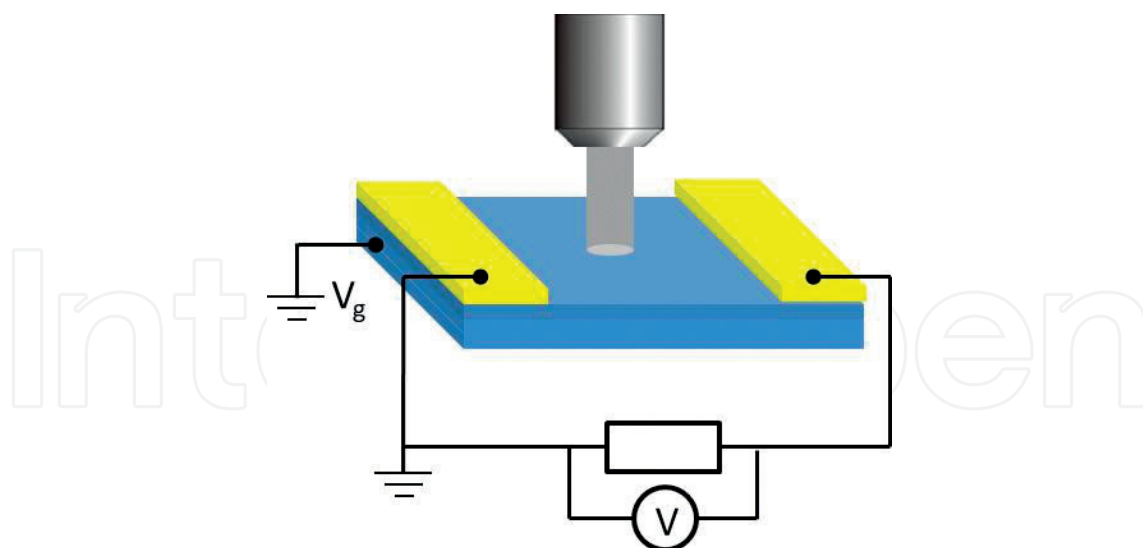


Figure 4. A schematic of photoconductance experimental setup.

photogating, etc. can be well studied. In addition, by tuning the back-gate voltage of the device, more phenomena such as photoconductive gain effect can also be studied [25].

5. Photoconductive interlocked molecules

5.1. Photoconductive rotaxanes and polyrotaxanes

5.1.1. Why rotaxanes?

Rotaxation, i.e., the inclusion of an axial molecule in the cavity of a macrocyclic molecule, is an interesting approach for the design of novel photoconductive materials which can efficiently introduce a number of beneficiary characteristics to these materials. There are different reasons which could justify why designing rotaxane photoconductive structures can lead to promising new materials. First of all, the moieties or functional groups which introduce photoconductivity to a compound are often unstable and chemically labile. The cavities of suitable macrocycles could offer protection to such entities, and this is vital for the durability and proper function of a photoconductive compound or material. That is, for instance, the case of azo dyes and squaraines, the rotaxanes of which will be examined in this chapter. Moreover, in many cases of photoconductive materials, prevention of intermolecular interactions is sought after. Encapsulation of photoconductive axial molecules in molecular rings often reduces the intermolecular interactions such as π - π stacking without hampering the charge transport. This is especially important in photoluminescent compounds where parallel alignment and interaction of π -conjugated molecules are obstacles. In addition to that, the non-covalent interactions developed between the axial and macrocyclic components in a rotaxane are overly important as they provide geometry stabilization and optimal orientation of these components so that charge transfer and transport are efficient. Such interactions are essential for the photoconductive behavior of a number of viologen-involving rotaxanes bearing electron-donating counterparts; a few such systems are reviewed herein. Furthermore, the

encapsulation of long conductive/photoconductive macromolecules within macrocycles such as CDs could result in the development of polyrotaxane molecular wires which, in a similar fashion to their macroscopic wire analogues, possess a conducting internal and insulating external part. The insulating part could prevent short-circuit problems in future molecular circuits involving these wires. The role of the insulating macrocycles in the photoconductivity of polyrotaxanes is also reviewed in this chapter. The last but substantially beneficiary feature of the development of photoconductive rotaxanes and polyrotaxanes is multifunctionality. Up to date a vast number of rotaxanes have been reported undergoing fully controlled shuttle motions, exhibiting switchability, photo- and electro-chromic, and photoluminescent properties. Combining one or more of these promising properties with photoconductivity could result in novel types of materials able to perform multiple functions upon demand.

5.1.2. Azo dyes and rotaxanes thereof

Azo dyes constitute a widely known class of organic pigments with significant industrial interest. These dyes exist in numerous products of everyday use, ranging from textile and leather dyeing agents to food colorants and DVD-R/+R disc recording layer materials. All azo compounds contain one or more units of the azo ($-N=N-$) chromophore connected to carbon atoms in both sides. The vast majority of azo dyes bear an azo group coupled to aromatic substituents such as benzene or naphthalene rings. To date a remarkable number of azo dyes have been synthesized and characterized [26]. This large number comes as a consequence of the ease of synthesis of azo compounds mainly relying on azo coupling, which involves an electrophilic substitution reaction between an aryl diazonium cation and a coupling partner. Typical coupling partners can be various aromatic compounds possessing electron-donating groups such as $-OH$, $-OR$, or $-NR_2$ functional groups [27]. Numerous rotaxanes comprising the arylazo units have been also reported [26].

The properties of azo dyes are not merely related to their color/light absorption properties but also to their vivid photochemistry, as they readily undergo reversible E/Z isomerizations (see **Figure 5**) in most of the cases via excitation with near UV or even visible light [28]. The reversibility as well as the low light energy demand for the accomplishment of this photochemical process renders azo compounds and materials thereof even more attractive for a number of optoelectronic applications [26–28]. Indeed, this photoreaction has been exploited in plenty azo-bearing materials including rotaxanes. Murakami et al. described 20 years ago the first light-driven molecular shuttle based on an azo rotaxane [29]. Deligkiozi et al. have reported controllable shuttling motions of α -cyclodextrin in [2]rotaxanes bearing a fully conjugated arylazo-based linear part [30]. Tian and coworkers reported on an azo-involving light-driven rotaxane molecular shuttle with dual fluorescence addresses comprising two different fluorescent naphthalimides and α -CD [31]. Indeed to date numerous other examples of photo-sensitive azo-involving rotaxanes have been reported [32]. Importantly, many azo compounds are known to exhibit photoconductive behavior. In 1969, Rau was the first to report the photoconductive behavior of azo dyes and specifically observed the photocurrents that form thin layers of a simple azo compound: 1-(phenylazo)-2-naphthol (**Figure 5**) [33]. Six years after the pioneering work of Rau, Champ and Shattuck reported the use of chlorodiane blue, a bis-azo compound (a derivative of 1-(phenylazo)-2-naphthol) as a photogenerating pigment in xerographic devices [34]. These two early scientific reports initiated a huge endeavor for the

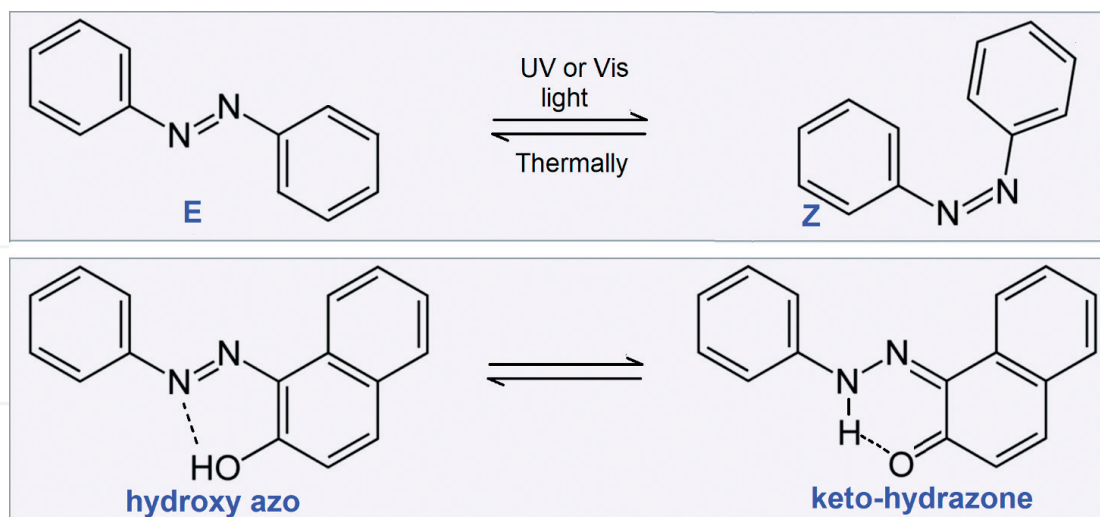


Figure 5. Scheme depicting the reversible E/Z isomerization of azobenzene (upper panel). The hydroxyl azo/ketohydrazone tautomerism of 1-(phenylazo)-2-naphthol (lower panel).

development of novel azo pigments with photoconductive properties, an endeavor which continues to date. Many research groups have come out with various photoconductive azo compounds mostly with structures relative to the parent 1-(phenylazo)-2-naphthol, over the years [22]. The photoconductive behavior of this parent azo pigment is narrowly connected to its structure and specifically to the hydroxyl azo/ketohydrazone tautomerism that this molecule and its derivatives exhibit (**Figure 5**) [22].

Nonetheless, there are also recent reports of photoconductive azo dyes with structure different from the “inspiring” structure of 1-(phenylazo)-2-naphthol. Recently, Deligkiozi et al. observed photocurrents from a [2]rotaxane of an azobenzene-based dye encapsulated in α -cyclodextrin (α -CD) as shown in **Figure 6** [35]. The photoconductivity of this interlocked azo dye measured using a wet method [35] was proved to be significantly higher than its α -CD-free precursor. The aforementioned [2]rotaxane was one of the first examples of rotaxanes involving an axial linear part with full π -conjugation [30, 36]. This robust aromatic skeleton provides the α -CD-free precursor some conductivity even in the dark which is reinforced when the dye is irradiated with white light. Remarkably though, the corresponding [2]rotaxane with α -CD appears to exhibit a significantly higher photoconductivity than the α -CD-free dye. Here, it is important to note that supramolecular insulation provided by α -CD (an insulating compound) is expected to result in a reduced conductivity of the [2]rotaxane when compared to its α -CD-free analogue. Yet, Cacialli et al. have shown that CD-encapsulated conductive polyrotaxanes with poly(para-phenylene) and poly(4,4'-diphenylene vinylene) continue to exhibit high conductivity despite the cyclodextrin insulating impact. It was concluded that cyclodextrin encapsulation inhibits parallel arrangement of the molecules without causing elimination of charge transport [37].

In the case of [2]rotaxane by Deligkiozi et al., photoconductivity was rationalized in terms of the non-covalent interactions of the cavity of α -CD and the encapsulated part of the azobenzene unit of this compound. These interactions result in stabilization of the geometry of the azobenzene part of the molecule [35]. Presumably, this stabilizing geometry effect resembles the corresponding effect observed in the case of the tautomeric 1-(phenylazo)-2-naphthol derivatives (**Figure 5**).

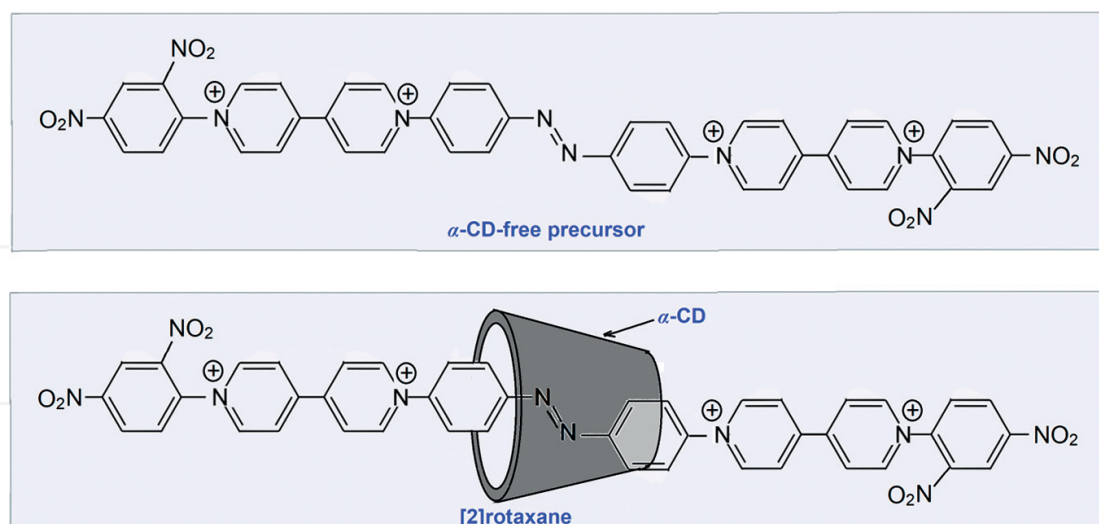


Figure 6. The chemical structure of the tetracationic part of the [2]rotaxane by Deligkiozi et al. [35] (lower panel) and that of the tetracationic linear α -CD-free precursor (upper panel).

The supramolecular insulation provided by encapsulation of an azo dye in α -CD has been earlier utilized by Haque et al. [38]. In their work they managed to thread π -conjugated tri-azo dye molecules through α -CD and then immobilize the resulting [2]rotaxanes onto nanocrystalline TiO_2 films (**Figure 7**). Transient absorption spectroscopy experiments supported that charge recombination was considerably retarded in the case of the as formed TiO_2 films when compared to non encapsulated dyes. This finding is very stimulating as it indicates that photocurrents are still generated by the conjugated encapsulated molecules, while the insulating α -CD part maintains a slow charge recombination. In the light of that, these photoconductive interlocked azo compounds are considered as promising for dye-sensitized solar cell (DSSC) applications [39].

5.1.3. Viologen-involving rotaxanes

Viologens constitute a class of heterocyclic compounds with remarkable properties [40]. They are 4,4'-bipyridine derivatives having both their nitrogen atoms quaternized, i.e., they are substituted by a chemical group which is often an aliphatic chain or an aryl group (see **Figure 8**) [40]. Due to their intense electron withdrawing (EW) character, aromaticity, as well as photo- and electro-active nature, they have been utilized as key components in a vast number of new materials [40, 42]. Viologens are also well known for their intense electrochromism which is attributed to the reversible one-electron reduction they readily undergo electrochemically or by means of reducing agents. They readily form charge transfer complexes (CTCs) with a variety of electron-donating species, e.g., ferrocyanides [43], tetrathiafulvalene (TTF) derivatives [41], as well as phenols [44]. In these complexes charge is reversibly transferred from the electron-donating part to the viologen upon absorption of visible light. Because of that, CTCs are colorful compounds and very photosensitive. Today, there is clear evidence that CTCs involving viologens exhibit photoconductive properties. This is, for instance, the case in some recent reported viologen/TTF CTCs (see **Figure 8**). Huo et al. observed marked photocurrent responses directly from such crystalline CTCs or from

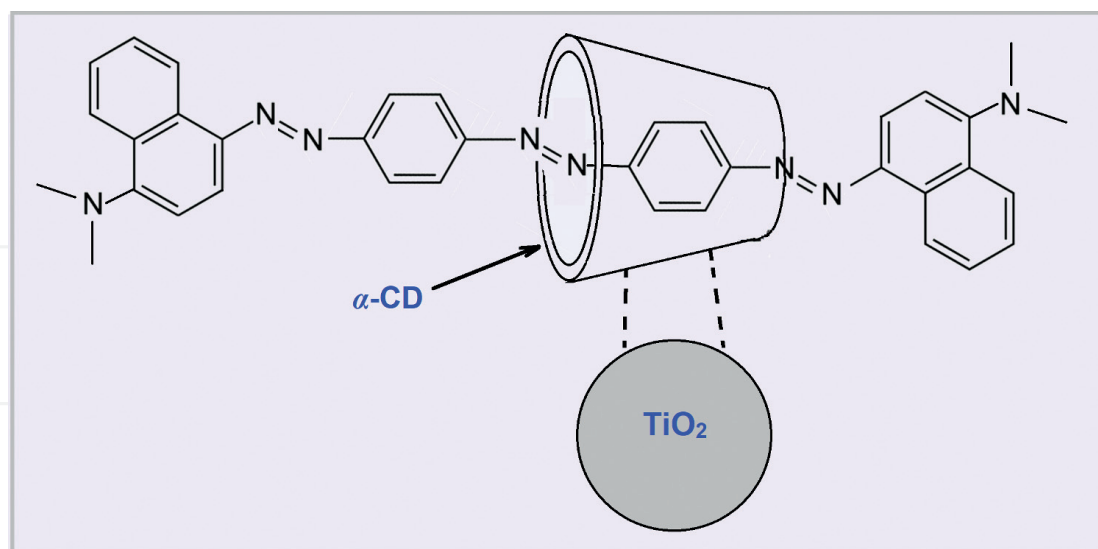


Figure 7. Schematic representation of the α -CD-encapsulated tri-azo dye onto TiO_2 nanocrystalline films utilized by Haque et al. (see Ref. [38]).

prepared film electrodes involving the CTCs depicted in **Figure 8**. A large number of rotaxanes involving viologens have also been reported exhibiting donor-acceptor interactions in which viologens play an important role as strong EW species [32, 45]. In these rotaxanes, viologen units are encountered either as parts of the axial or as parts of the macrocyclic components. In the latter class of rotaxanes, they are often used in cyclophane structures (see **Figure 9**). Such rotaxanes are considered for high-tech applications due to the ease of control of their function through electrical or light triggering. Feng et al. have achieved reproducible nanorecording on rotaxane thin films comprising TTF-involving axial and viologen cyclophane components [47]. A few years ago, Sheeney-Haj-Ichia and Willner reported that pseudorotaxane monolayers comprising viologen cyclophane units exhibit photocurrents eightfold higher than the ones observed in the case of the control monolayers lacking the viologen component (**Figure 9**) [46].

These significantly amplified photocurrents observed in the pseudorotaxane assembly were attributed to vectorial electron transfer of photoexcited conduction-band electrons to the strong electron accepting component. According to the authors [46], this fact leads to charge separation and retardation of electron-hole recombination. This finding is also in line with the photoconductive character of viologen CTCs and indicates that interlocked molecules and macromolecules comprising viologen CTC entities are promising materials with potential photoconductive properties.

In 2007 Saha et al. [48] reported on a redox-driven multicomponent rotaxane shuttle comprising a linear component which involved TTF, a naphthyl ether, and a porphyrin. The macrocyclic component employed was the same bis-viologen cyclophane utilized by Sheeney-Haj-Ichia and Willner [46]. C_{60} was utilized as a strong electron acceptor/bulk ending group. The authors emphasized that such donor-chromophore-acceptor system could generate photocurrents. This example constitutes one interesting case of a multifunctional material with potential photoconductive properties being able to also function as a molecular shuttle.

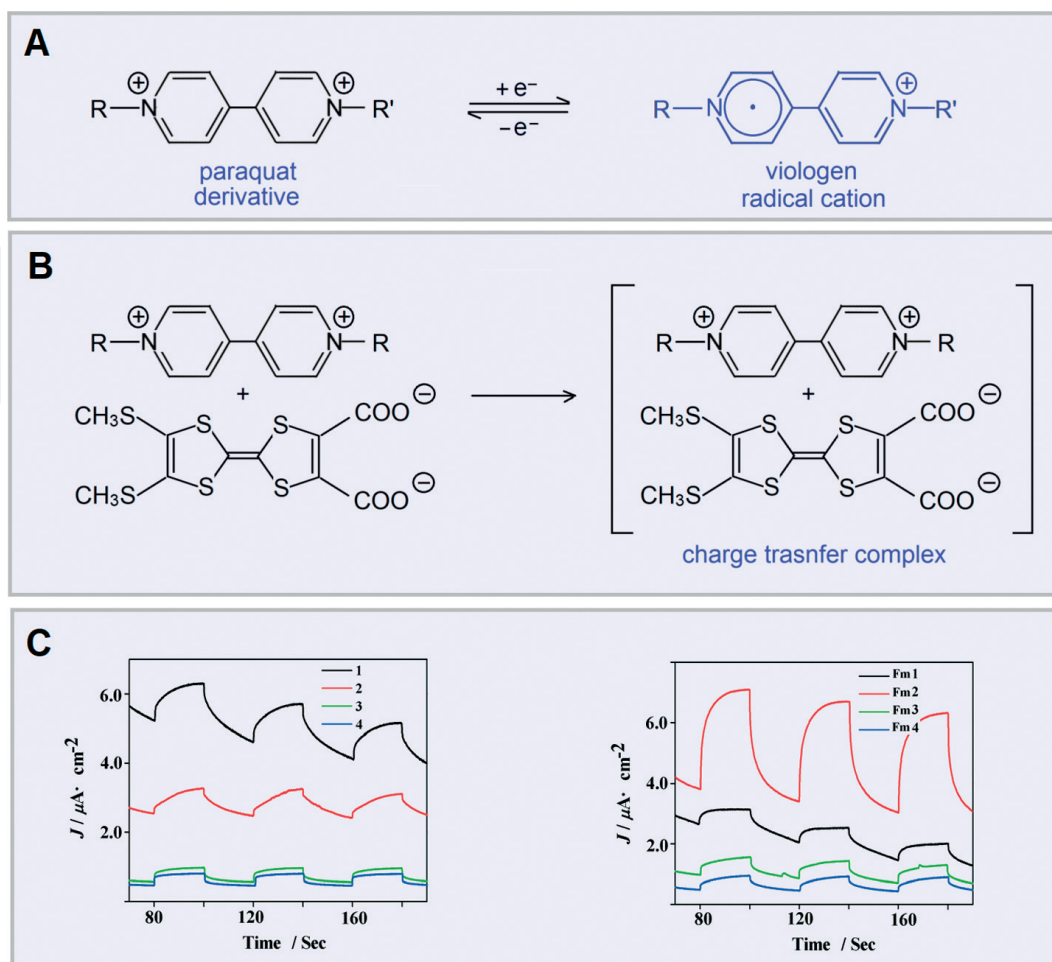


Figure 8. (A) Scheme representing the reversible one-electron reduction of a viologen dication comprising two different substituents (R and R'). (B) Scheme depicting the formation of photoconductive CTC complexes of a group of viologens and a dianionic TTF derivative according to Huo et al. [41]. (C) The photocurrent responses observed from the CTCs of middle panel, measured in crystals of the CTCs (left) and in thin-film electrodes (right). Plots of panel (C) reprinted with permission from Huo et al. [41].

5.1.4. Squaraine rotaxanes

Squaraine compounds constitute a widely known class of organic photoconductive compounds [22]. It was as early as 1966 when Sprenger and Ziegenbein reported the synthesis of intensely colored compounds derived from squaric acid (see Structure I in **Figure 10**) [49]. It was observed that the compound produced is characterized by a unique electronic structure resulting in interesting properties. Many relative compounds were subsequently synthesized. These fascinating compounds bear an internal donor-acceptor-donor (D-A-D) structure which can be represented through the resonance structures depicted in **Figure 10** [22, 50]. Around 40 years ago, Schmidt proposed the name squaraine for these compounds [22]. In 1974 Champ and Shattuck were the first to report the photoconductive properties of squaraine dyes [51]. They revealed that squaraines are able to generate electron-hole pairs in bilayer xerographic devices through light irradiation [51]. Awhile before this report, squaraines had already been proposed as sensitizers for ZnO photoconductors [52]. As mentioned squaraines are deeply colored compounds, and their absorption and emission are situated in the deep-red and near-infrared (NIR)

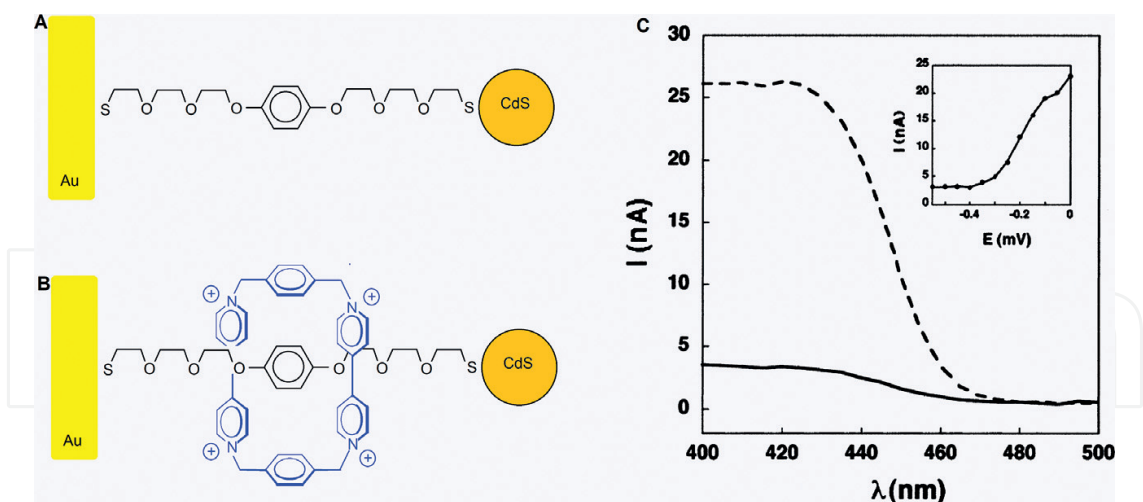


Figure 9. (A) Illustration of the setup used by Sheeney-Haj-Ichia and Willner without cyclophane. (B) The setup after inclusion in a tetracationic cyclophane. (C) Plot depicting the photocurrent response observed for the system in panel A (solid line) and that in panel B (dashed line) vs. the irradiation wavelength. Plot of panel (C) reprinted with permission from Sheeney-Haj-Ichia and Willner [46].

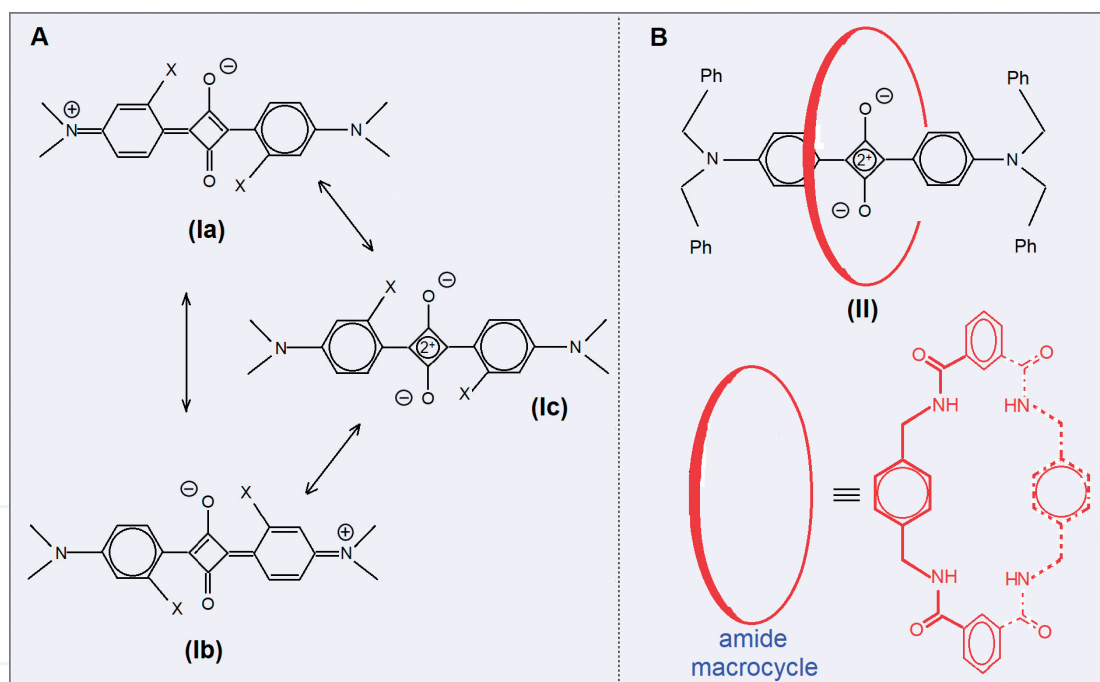


Figure 10. (A) The resonance structures of squaraines (Ia–c). (B) A squaraine rotaxane involving an amide macrocycle.

region [50]. These features along with their photoconductivity render squaraines important candidates for DSSC applications. In these technologies novel sensitizers absorbing in NIR wavelength region are required in order to boost the photoconversion efficiency. Indeed Yum et al. reported a photoconversion efficiency as high as 4.5% when using an unsymmetric squaraine dye (structure **III** depicted in **Figure 11B**) [54]. This work essentially indicated that squaraines are useful candidates for DSSC (details in **Figure 11**). Apart from marked photoconductive compounds, squaraines are generally very photosensitive and fluorescent [50].

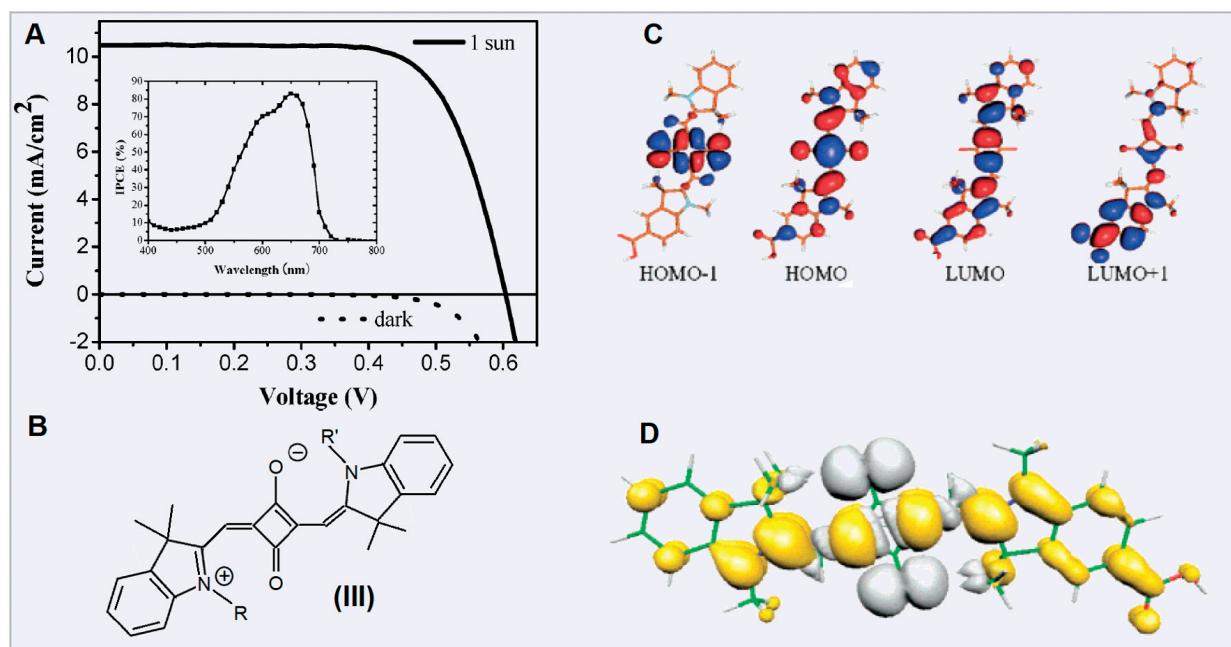


Figure 11. (A) Current-voltage characteristics for a squaraine dye (type II) with R = C₈H₁₇ and R' = Et and photocurrent action spectrum (inset). (B) Chemical structure of squaraine **III**, (C) frontier orbitals, and (D) charge density of dye **III**. Figures in Panels A, C, and D reprinted with permission from [53].

All these features are narrowly connected to their electronic structure, and they are essential for a vast number of imaging applications [50]. A significant drawback of squaraines is their instability against strong nucleophiles as well as their aggregation propensity which pulls down their fluorescence and potentially photoconductivity. These problems can be solved by the use of protecting threading macrocycles, i.e., through rotaxation of the sensitive core. This approach was first employed by Leigh and coworkers who managed to synthesize [2] rotaxanes utilizing normal squaraine structures and suitable amide-macrocyclic compounds (**Figure 10B**) [55, 56]. The as structured rotaxanes are characterized by significantly higher chemical and photophysical stabilities than the non encapsulated squaraines. This revolutionary study inspired a lot of other research groups to design and synthesize a wide variety of squaraine-based rotaxanes with potentials in a number of applications [50]. The corresponding rotaxanes do not hamper the properties of squaraines, but instead the properties are retained or even improved. Due to their high photoconductivity, promising performance in DSSC applications as well as other biologically relevant applications of rotaxanes of squaraines, their use is currently seriously considered.

5.1.5. Photoconductive polyrotaxanes

In recent years there is an increasing interest in the design and synthesis/fabrication of molecular wires, i.e., conductive conjugated polymers of high conductivity. Even though the research endeavors to develop molecular wires were initiated theoretically already in the 1940s using quantum mechanics [57], there is today a tremendous interest in this type of nanosized wires for a range of high-tech applications. In such systems prevention of short circuits could be achieved through threading of a conductive polymer within the

cavities of insulating (protecting) macrocycles [58]. These polyrotaxane-structured wires also called insulated molecular wires (IMWs), with nanometer dimensions, could be used in nanosized circuits [53]. The role of the insulating components (usually α - and β -CDs) is an important research subject as it clearly affects the conductivity and photoconductivity of polyrotaxane wires. In 2009 Terao et al. [59] studied a permethylated α -CD (PM- α -CD) polyrotaxane of a poly(phenylene ethynylene)-based polymer (**Figure 12A**) and reported the formation of a prominently insulating organic semiconductor wire exhibiting remarkably high hole mobility along the core π -conjugated polymer. They also reported light-induced currents observed upon excitation at $\lambda = 355$ nm (**Figure 12A**). Terao et al. some years later [61] based on previous theoretical publications compared experimentally the charge mobilities of linear and zig-zag polyrotaxanes involving conjugated polymers and permethylated α -CD.

They reported increased charge mobilities for the zig-zag polymer and confirmed the light-induced formation of charge carriers in the case of the linear polyrotaxane. However, they observed that rapid free carrier-formation processes were overlapped in the zig-zag polyrotaxanes. These stimulating findings indicate that IMWs do exhibit photoconductivity, but clearly the geometry of the macromolecules affects their photoconductive behavior. Encapsulation of a conjugated polymer such as the aforementioned π -conjugated polymer in the insulating cavities of PM- α -CD leads to increased lifetimes of charged radicals on the conjugated core via hindering charge recombination processes [62]. Moreover encapsulation results in marked fluorescence enhancement in this kind of polyrotaxanes, particularly in the solid state, suggesting that encapsulation is crucial for the achievement of efficient fluorescence properties [62]. More recently, Kostromin et al. [60] studied the photovoltaic effect and charge carrier mobility of some bithiophene conducting polymers, both “bare” and encapsulated in β -CD units (see **Figure 12B**). They concluded that the β -CD introduced marked insulation of

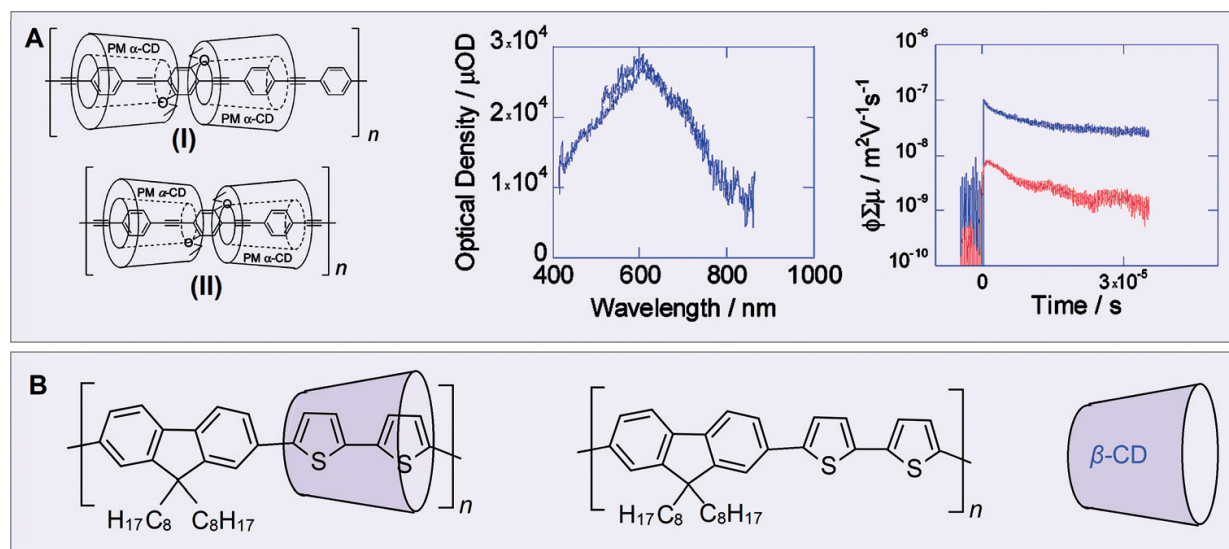


Figure 12. (A) Structure of the IMWs studied by Terao et al. [59] along with the transient absorption spectrum of IMW (I) after pulse exposure and conductivity transients observed for (I) (blue) and (II) (red) upon 355 nm excitation. Figures reprinted with permission from [59]. (B) Structure of the conjugated polymer and IMW investigated by Kostromin et al. [60].

thiophene fragments of the macromolecule, and this lead to hampering the transport of carriers which in turn yielded in a limited photovoltaic effect [60].

5.2. Catenanes and polycatenanes

5.2.1. *The structure of catenanes and its benefits*

Catenanes constitute another important class of interlocked molecules. Just like rotaxanes they are stabilized through mechanical bonds [9, 32]. Yet, they consist of two or more macrocycles interlocked in a way that resembles the connectivity of rings in a chain (Latin: *catena* = chain). There is a large variety of catenated structures reported to date with numerous applications. There are various reasons why catenanes could become important candidates for new photoconductive materials. As also mentioned for rotaxanes, encapsulation of a sensitive photoconductive moiety or functionality in a molecule could significantly increase the durability of the material and protect the desired photoconductive properties. Thus, interlocking photoconductive (or more generally photosensitive) macrocycles could potentially lead to promising stable catenated materials with optoelectronic applications. Moreover, geometry fixation and proper orientation in catenanes can give rise to intermolecular interactions (e.g., π - π stacking, etc.) facilitating efficient charge transfer in such materials. This is a key property which is discussed in more detail in this chapter. Finally, polycatenanes involving photoconductive parts could be perfect candidate multifunctional materials, as in such structures one can introduce photoconductivity via embedding repeated photoconductive catenane units in macromolecules with special properties, e.g., electrical or thermal conductivity, mechanical strength, etc.

5.2.2. *Photoconductive catenanes*

Even though numerous examples of catenanes and polycatenanes have been reported, there is a limited number photoconductive catenanes and polycatenanes. However, there is strong indication that such materials could also exhibit promising photoconductive behavior. The main types of organic photoconductive molecules utilized in rotaxanes and polyrotaxanes can be also utilized in catenanes and polycatenanes.

About 15 years ago, Simone [63] reported on the synthesis and characterization of some polycatenane repeated units of cyclophane connected to thiophene rings (red-colored part in **Figure 13**) interlocked with a bis-viologen tetracationic cyclophane (blue-colored species in **Figure 13**). This approach involving the aforementioned two cyclophanes was initially employed by Stoddart and coworkers [15] and is a very popular combination for numerous rotaxanes and catenanes (see, for instance, the pseudorotaxane in **Figure 9**). The resulting polycatenane of Simone and Swager is stabilized through π -stacking between the aromatic bipyridinium and benzene-1,4-diether rings of the interlocked macrocycles. The catenane in **Figure 13** which is colored green exhibits a charge transfer visible band situated at $\lambda = 626$ nm. This polycatenane as well as another variant was reported to be conductive (linear part is a π -conjugated polymer) [64] but also to exhibit significant photocurrent responses [63]. This example constitutes an important case enabling the design of novel photoconductive polycatenanes.

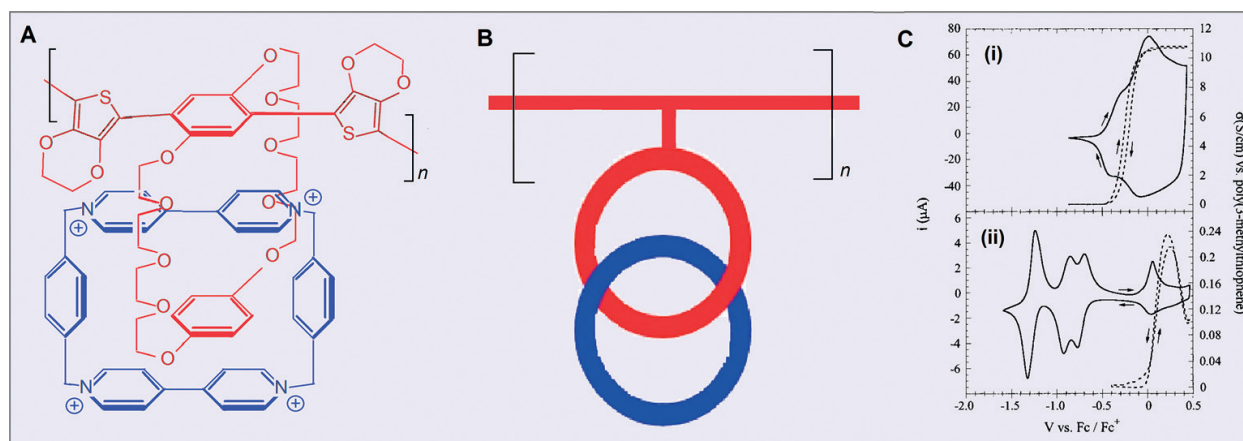


Figure 13. (A) The polycatenane synthesized by Simone [63]. (B) Symbolic representation of the polycatenane in panel A. (C) Cyclic voltammograms (solid lines) and conductivity profiles (dashed lines) for the polymer lacking the cyclophane units (colored blue) (i) and polycatenane (ii). Panel C plots reprinted with permission from [64].

It is very important to stress that (poly)catenanes do not exhibit disadvantages when compared to (poly)rotaxanes in terms of their photoconductive behavior/properties. The “strategies” for photocurrent generation are essentially the same for both classes of interlocked (macro)molecules. The downside in the case of (poly)catenanes can sometimes be the more tedious synthetic methodology required, when compared to (poly)rotaxanes (see paragraph 2). To some extent, this might explain the limited number of reported photoconductive (poly)catenanes. Nevertheless, catenated structures are certainly capable of introducing stability and shielding of the photoconductive parts. Additionally, catenated structures could potentially maintain efficient photocurrent generation and slow charge recombination in photoconductive materials. Thus, they should be considered as promising photoconductive interlocked materials/compounds, and they should clearly be given more attention.

6. Applications of rotaxanes and catenanes

Rotaxanes and catenanes are gaining more and more attention due to their applicability in modern technologies. They have been proposed for numerous biological applications such as smart drug-delivery systems corresponding to anticancer drugs [65, 66], imaging of biological matter (e.g., mitochondria) [67], or as useful materials for the enhancement of MRI imaging [68]. Especially, the squarain-involving interlocked molecules described are prominent examples of fluorescent bio-imaging agents and chemosensors [50]. Furthermore, both types of interlocked molecules are prominent candidates for new smart future applications acting as (multi)functional materials and undergoing fully controllable switching, shuttle motions, as well as molecular motor functions [69–71]. Medium- and photo-responsive interlocked molecules are also currently considered as new sensing materials with various possible applications [30, 35, 36, 72]. Taking into account the potentials of the photoconductive interlocked molecules described in this chapter, one could foresee a bright future for new optoelectronic materials, molecular wires, photoconductors, photovoltaics, and many other novel applications. Especially,

(poly)catenanes and (poly)rotaxanes encompassing CTC units are of high importance as materials with significant photoconductivity and photosensitivity. It is high time this fascinating class of interlocked (macro)molecules was given more attention.

7. Conclusion

This chapter has provided a review of the research field of interlocked molecules and macromolecules placing emphasis on rotaxanes, catenanes, and polymeric structures thereof. Various categories of organic photoconductive rotaxanes and catenanes have been reviewed, and the main structural and photoconductive characteristics have been provided. The (photo)conductive properties of the molecules and macromolecules with and without encapsulation are compared. A range of examples and potential applications has been also provided.

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