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Chapter

Nonlinear Optical Responsive Molecular Switches

Mahadevappa Y. Kariduraganavar, Radha V. Doddamani, Balachandar Waddar and Saidi Reddy Parne

Abstract

Nonlinear optical (NLO) materials have gained much attention during the last two decades owing to their potentiality in the field of optical data storage, optical information processing, optical switching, and telecommunication. NLO responsive macroscopic devices possess extensive applications in our day to day life. Such devices are considered as assemblies of several macroscopic components designed to achieve specific functions. The extension of this concept to the molecular level forms the basis of molecular devices. In this context, the design of NLO switches, that is, molecules characterized by their ability to alternate between two or more chemical forms displaying contrasts in one of their NLO properties, has motivated many experimental and theoretical works. Thus, this chapter focuses on the rational design of molecular NLO switches based on stimuli and materials with extensive examples reported in the literature. The factors affecting the efficiency of optical switches are discussed. The device fabrication of optical switches and their efficiency based on the optical switch, internal architecture, and substrate materials are described. In the end, applications of switches and future prospectus of designing new molecules with references are suitably discussed.

Keywords: nonlinear optical materials, optical switches, chromophores, simulation, DFT

1. Introduction

There is a strong demand for the advancement of high-performance NLO materials, owing to the emergence of photonic technologies in the area of telecommunication where the information is coded, transported, and routed through optically. Thus, NLO materials have created enormous interest among the scientific community due to their role in optical switching, sensor protection, light modulators, memory storage devices, information processing devices [1–3].

A considerable number of NLO materials have been developed over the last two decades. As a new method of communication, optical signal achieves faster network speed and broader bandwidth, and thus, the optical switch is an essential device for optoelectronic and integrated optics. Optical switches play the role of protecting, testing, monitoring, and management of the network. In this context, the design of NLO switches based molecules, which are characterized by their ability to alternate between two or more chemical forms displaying contrasts in one of their NLO properties, has motivated much experimental and theoretical work [4, 5].

Understanding these, researchers have been tried to synthesize and characterize the several molecular NLO switches that differ by the stimulus used to provoke the commutation. These stimuli can include light irradiation, redox reaction, pH variation, ion recognition, and others. The design of multistate and multifunctional systems has also provoked a large amount of work, aiming for the enhancement of the storage capacity of the optical memories or the diversification of the relevant devices [6, 7].

Generally, most of the molecular switches can be divided into two categories, namely stereoisomerism and structural isomerism. Other mechanisms are covered in the literature, such as dipole, charge, or spin switching, but these processes generally include some kind of structural change as well [8, 9]. As possible candidates for integration into responsive materials, researchers have been intensely studying the organic, organometallic molecules and other highly advanced materials like supramolecules, carbon nanotubes, etc. with switchable hyperpolarizability over the past two decades [10–13].

Realizing the importance of the factors as mentioned above, in this chapter, we illustrate the design and categorize the highly efficient NLO molecular switches based on stimuli and materials. After a critical overview, we provide numerous case studies, including organic, organometallic molecules, supramolecules, carbon/graphene materials, nanoscale structures, polymers, and crystalline solids [14, 15]. Finally, we illustrate the influence of the environment on the NLO switching properties with examples. The rational design of molecular NLO switches with recent device fabrication is also discussed. The chapter also explains the experimental and the theoretical approaches, which have reached maturity in obtaining NLO responsive molecular switches. The prime objective of the chapter was to examine the different systems with particular reference to their photophysical properties as well as the switching mechanism at the molecular level.

2. Factors affecting the efficiency of switches

Many scientists have been working for the last three decades, to develop the optical switches, in which one light beam can switch another beam on and off, the same way that one electrical signal can switch another on and off in an electrical transistor [16]. This type of light switch could be the basic building block for optical circuits and even for optical computers. In principle, such a device could work at terahertz frequencies or higher, and the dissipation of power could be far less. For an ideal device of an optical switch, there could be five crucial factors. They are: (1) amplification (a weak beam is used to switch a strong beam); (2) compact size, preferably small enough to make millions on a chip; (3) fast response time; (4) possibility of cascading devices (the output of one device can act as the input for a subsequent device) and (5) room-temperature operation [17–19].

3. Molecular switches based on stimuli

Functional materials, which are exhibiting distinct functionalities in response to a specific stimulus, are highly desirable for the fabrication of advanced devices with superior dynamic performances [20]. The stimuli can include light irradiation, temperature variation, redox reaction, induced ion recognition, and so on.

3.1 Light-induced optical switches/photoswitches

The photochemical isomerization of an olefinic bond is one of the fundamental processes in the vision. The structural perturbations induced by the *cis*/*trans* isomerization of the retinal moiety results in conformational changes in the protein molecule, and through a cascade of reactions, the neural pulse responsible for vision is generated. This principle was mimicked to design molecular systems that can undergo light-induced structural changes for signaling applications.

Light mainly offers several advantages over the chemical stimuli, viz., its spatial and temporal control, ease of implementation, remote addressability, and low toxicity. These optimistic attributes have led to the development of various photoswitching moieties for the applications in photo-pharmacology, sensing, energy production, and actuation [21].

The azobenzene moiety enjoys widespread popularity, and thus a number of artificial systems based on the azobenzene functionality have been investigated. Owing to its ease of synthesis, reasonable quantum yields, large extinction coefficients, and so azobenzenes exist in two forms, *E* (*trans*) and *Z* (*cis*) forms and their interconversions can be induced by irradiation with appropriate wavelengths [22]. For instance, upon photochemical excitation, structural changes occur in molecular systems having azobenzene functionality, and such changes were utilized for modulating the host-guest properties, phase changes in liquid crystals, photo-triggered reversible gel formation and photoinduced switching of conductivity. However, thermal reactions prohibit the use of azobenzene based molecular systems from their use in information storage systems. Chen et al. [23] reported dual-mode optical switch by conjugating helicene and bis-azobenzene moieties in proximity with highly diastereoselective photochromic and chirochromic switching both in solution as well as in nematic liquid crystals with tunable pitches and handedness by modification of four different metastable states. In 2013, Roldan et al. [24], for the first time, investigated the conductance properties of a photoswitchable dimethyl-dihydro pyrene derivative in single-molecule junctions using the mechanically controllable break junction technique. They studied the reversible photo-thermal switching of a bipyridine appended dimethyl-dihydro pyrene/cyclophane-dienephotochromic system. The photo-thermally triggered conductance switching between these two isomers is fully reversible, stable over more than five sequential cycles, with on/off ratio up to 104. This study represented highly promising candidates for constructing nanoscale molecular building blocks. Deng et al. [25] designed and synthesized two nonlinear optical chromophores based on dithienylethene as the ultraviolet NLO switches. They investigated open/close behavior using the UV–Vis spectra. The dipole moments, first and second hyperpolarizabilities, etc. have been calculated and analyzed for both opening and closure states of the chromophores using quantum chemical calculations. The switching ability of the NLO chromophores was studied through monitoring the SHG at the opening/closure states. The results suggested that indicate that the maximal SHG changes were observed at energy density equal to about 90 J/m^2. The resulting induced second-order susceptibilities remained up to 150 h without decreasing, even after switching off of the external UV light, which indicated that the chromophores have the potential application as the NLO switches widely applied in photonics. Another example where the purple merocyanine exhibits strong absorption at 563 nm and can completely block an incoming signal, the colorless spiropyran allows the beam to pass, depicted through the structures in **Figure 1**. Through these types of systems, the building of logic operations possible, which also lay an attractive foundation for digital processing at the molecular level [26].

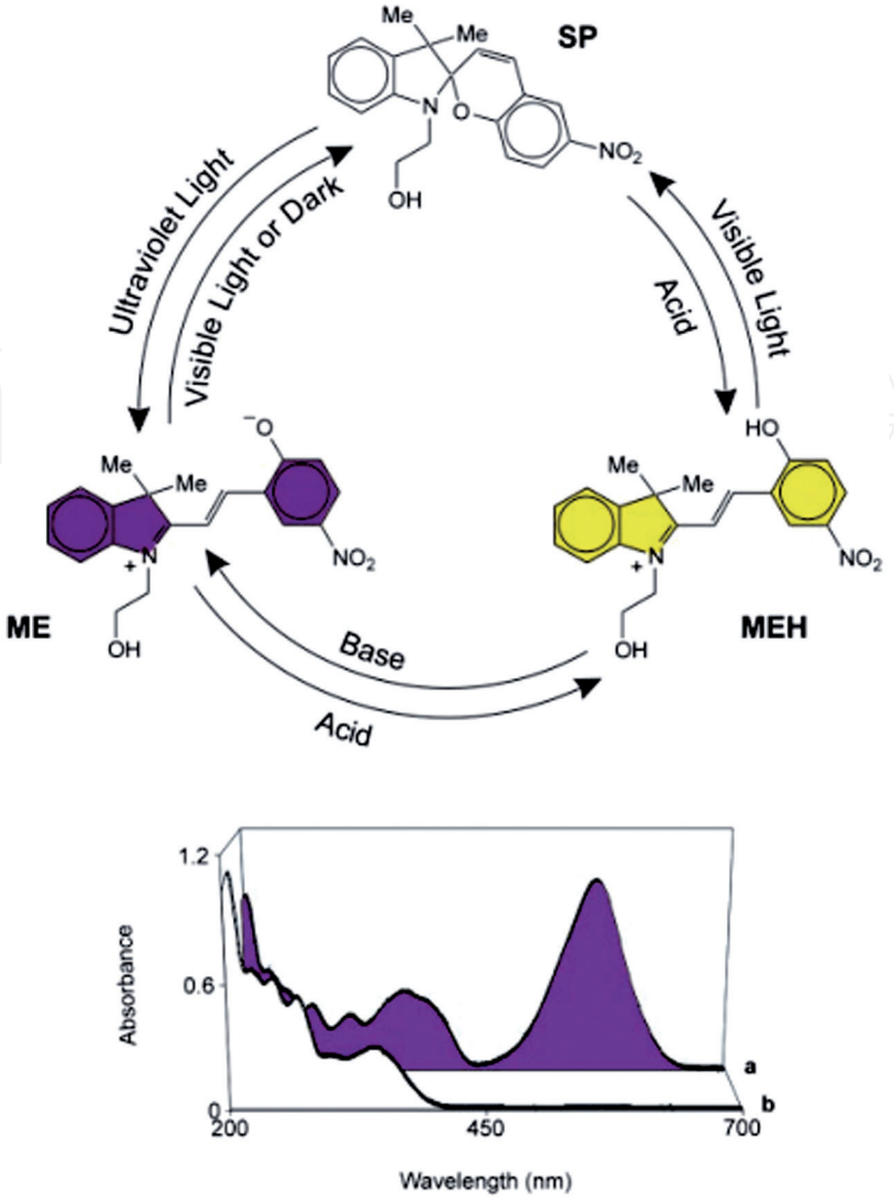


Figure 1.
The UV light, visible light, and H^+ induce the interconversion between the three states of SP, ME, and MEH. Absorption spectra of SP (in MeCN, 10^{-4} M, 25°C) recorded after (a in lower) and before (b in lower) irradiation at 254 nm for 5 min (Adopted from [26] with consent; National Academy of Sciences, 2002).

Similarly, it revealed [8] that five-membered and cyclic biradicals developed based on 15 elements are robust and efficient photochemical switches that can be activated by a red light with the quantum yield of the photoisomerization as high as 24.6%, and the thermal equilibration of the photo-activation product proceeds swiftly at room temperature, which is completely reversible. As demonstrated, the biradical character could be completely turned on and off, so that the system could be employed to control the chemical equilibria that involve activation products of the cyclic biradicals. Similarly, Li et al. [20] designed and synthesized two novel light-driven chiral fluorescent molecular switches that are able to exhibit unprecedented reversible *Z*/*E* photoisomerization behavior along with tunable fluorescence intensity in both isotropic and anisotropic media are described in **Figure 2**. Szukalski et al. [27] introduced all-optical switches that are based on deoxyribonucleic acid (DNA) in the form of electrospun fibers, where DNA is semi-intercalated with a push-pull, luminescent nonlinear pyrazoline derivative. Hansel et al. [28] have studied the switching ability and the nonlinear optical contrast

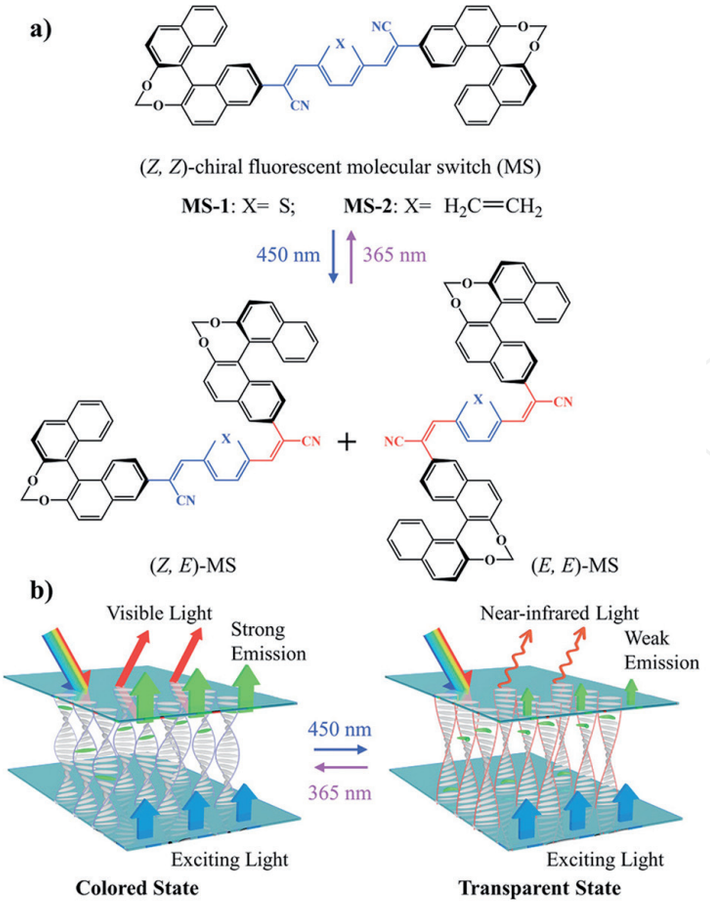


Figure 2.
(a) The chemical structures and reversible photoisomerization process of light-driven chiral fluorescent molecular switches MS-1 and MS-2. (b) The schematic illustration of the self-organized helical superstructures in the cholesteric LCs tuned by visible/UV light, reflecting different wavelengths, and fluorescing with different intensity when excited by blue light (Adopted from [20]; Springer Nature, 2012).

between different switching states of three unequal fulgimide-functionalized self-assembled monolayers (SAMs) on Si(111), facilitated a very efficient reversible photoisomerization, using second harmonic generation, density functional theory, and wave function method calculations.

In order to obtain high NLO contrasts, controlled variations of the linker system and the fulgimides were performed. In all the fulgimide-functionalized interfaces, a photoinduced reversible ring-opening/closure reaction demonstrated via the NLO response. The closed-form of the fulgimide demonstrated a higher SHG signal amplitude than that of open-form, and this is mainly because of the extended π-electron system of the closed state. Also, by chemical modifications, large cross-sections for the light-induced reversible switching process in the order of 10^{-18} cm^{-2} have been observed, which are similar to the values known for fulgimides in solution (shown in **Figure 3**). Based on the results, it is concluded that chemical modifications of both the molecular switch and the linker system may even enhance the NLO contrast between the open and closed fulgimides. From the theoretical study, it is predicted that the switching unit and the extended peripheral π-system are the potential targets for enhancing NLO contrasts, in particular. In general, the generation of two-dimensional NLO switching materials using functionalized photoswitchable silicon interfaces may pave the way for applications in photonic and optoelectronic devices [29].

Ping et al. [30] employed density functional theory (DFT) and time-dependent density-functional theory (TDDFT) methods in solution to study the effect of

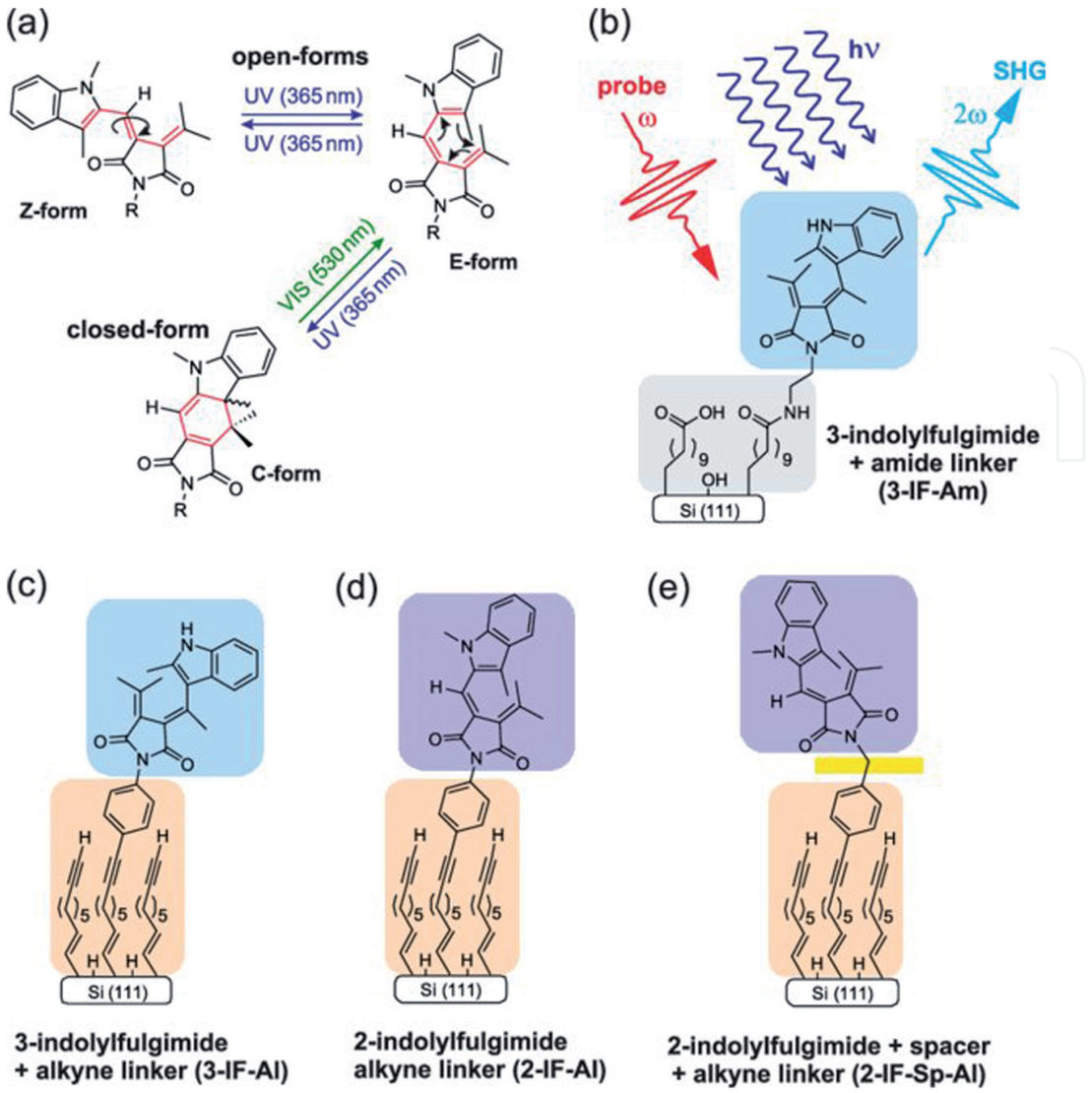


Figure 3.
(a) Photochromism in fulgimide upon irradiation with UV (λ = 365 nm) and visible (λ = 530 nm) light. Fulgimides yield a reversible reaction between the closed-form and a mixture E/Z-isomers of the open-form. (b) the scheme of the SAM containing fulgimide moiety, immobilized via an amide (Am) linker, called as 3-indolylfulgimide (3-IF-Am). SHG is used to study the switching state via the NLO response. (c)–(e) Fulgimide-containing SAMs on Si(111) (c) 3-indolylfulgimide (3-IF-Al), (d) 2-indolylfulgimide (2-IF-Al), and (e) 2-indolylfulgimide with a $-CH_2$-spacer group (2-IF-Sp-Al) connected via an alkyne (Al) linker to the Si substrate (Adopted from [28]; ACS Publications, 2018).

photoisomerization for dithiazolylarylene. The weak interaction of S···N and hydrogen bond of CH···N restrain the rotation of side-chain thiazolyl ring in open isomer 1a, the higher stability of which favors showing a high quantum yield of photoisomerization.

The UV–Vis spectrum at around 320 nm for open-isomer 1a is bathochromically shifted to 647 nm for closed-isomer 1b, in good agreement with the experimental photochromic phenomenon. The electron transition in electron CD (ECD) spectra for closed isomer 1b with two chiral carbon atoms is dominated by intramolecular charge transition (ICT) and local excitation (LE). Which attributes to one negative cotton effect (650 nm), one positive (440 nm) and one negative cotton effect (650 nm) where the two chiral carbon atoms play a slight role in these transitions. The potential energy surface (PES) in the S1 and S0 states, respectively, suggest that the cyclization reaction is allowed from open-isomer 1a to closed-isomer 1b in the photoexcited state with high-conversion quantum efficiency. At the same time, it is prohibited in the thermodynamic process. Besides, the second-order NLO response

for closed-isomer 1b is nearly six times higher than that of open-isomer 1a. Further, it is confirmed that the photoirradiation excite the photoisomerization property to show a significant difference in the second-order NLO response, which could be employed in designing the photochromic materials and reversible NLO switches.

3.2 Thermal optical switches

The thermal-optical switch (TO), as the essential part of the optical switch, acts as a pivotal part of low-speed fiber-optic communication systems. Currently, the wavelengths of the reported thermal-optical switches are usually at 1550 and 650 nm, and the thermal-optical switch working at 650 nm is mainly used in a system of short-range communication [31]. The switchable NLO materials are essential for photonic as well as optoelectronic technologies. One crucial concern for NLO photoswitching, the most studied physical switching strategy, is how to enhance the switching contrast of SHG in crystals because the known values are generally below three times [32].

These devices are polymer-based to obtain flexibility. In order to make the molecular switch to be useful in the future technological applications, the system should retain its properties when incorporated in a processable matrix, to offer a photoswitchable film for data storage. Flexible and wearable optoelectronic devices are the current trend for an active lifestyle [33].

In this context, Sun and coworkers [34] developed waveguide optical switches, as shown in **Figure 4** for a flexible photonic integrated circuit using poly(methyl methacrylate) (PMMA) polymer. The optical field of the device was accelerated by beam propagation to optimize the position of the electrode. The properties of switching of the flexible optical switch at different working conditions, such as contact to the polymer, silicon, and skin, were studied using simulation. The device was constructed based on the photo curved polymer and lithography method. Using an excimer laser, the end faces of the flexible film device were processed with optimized parameters of 15 Hz and 28 mJ/cm^2. The measured response rise time and fall time on the substrate were respectively 1.98 and 2.71 ms. The consumption of power and the ratio of extinction were 16 mW and 11 dB, respectively. The properties indicated that the resulting flexible optical waveguide structure could be used in the light control area of a wearable device.

Further, novel polymer (fluorinated photopolymer) based thermo-optic switch arrays were successfully designed and fabricated based on dielectric-loaded surface plasmon polariton waveguide (DLSPPW) structure by Zheng and research group [35]. Briefly, the DLSPPW model included highly fluorinated

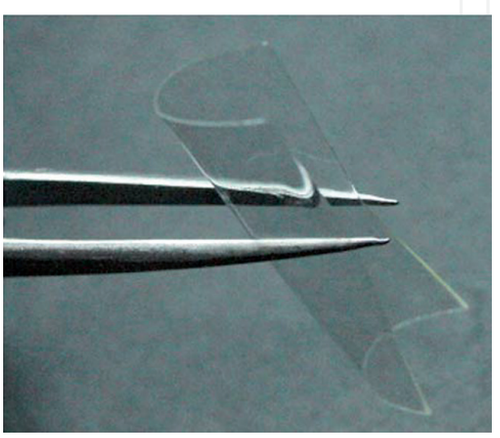


Figure 4.
Flexible polymeric film (Adopted from [34]; OSA Publishing, 2018).

low-loss photopolymers and organic–inorganic grafting materials that were used as the waveguide core and cladding and with PMMA substrate. The operation of the device at signal wavelengths was controlled via the thermo-optic effect by electrically heating the gold stripes of dielectric-loaded surface plasmon polariton waveguides. At 1550 nm wavelength, the propagation loss of 4 μm wide straight DLSPPW was performed as 0.55 dB/cm. The insertion loss of the device was around 4.5 dB. The fall time and switching rise of the device measured by 200 Hz square-wave voltage was found to be 370.2 and 287.5 μs, respectively. The switching power was about 5.6 mW, and the extinction ratio was about 13.5 dB. The flexible low-loss multifunctional waveguide switch arrays were realized to be suitable for large-scale optoelectronic integrated circuits. Zhen et al. [36] summarized the fundamental realization principles, novel configurations, superior materials, improved performance indexes, and ameliorated trigger methods of ultrafast optical switching.

Thermoswitching has shown impressive high SHG-switching contrasts, but the fast decay of thermally induced states demands constant heat sources to maintain the specific SHG intensities. Xing and coworkers [32] synthesized a photochromic and thermochromic bistable acentric compound, β-[(MQ)ZnCl3] (MQ+ = N-methyl-4,4′-bipyridinium), which represents the first crystalline compound with both heat- and photoinduced SHG switching behavior and the first example of a thermo-switchable NLO crystal that can maintain its expected second-order NLO intensity without any heat source. The SHG-switching contrast could reach about eight times after laser irradiation or two times after thermal annealing. The former value happens to be the highest recorded for photoswitchable NLO crystals. This work evidences that the higher SHG switching contrasts could be obtained by increasing the electron-transfer efficiency, self-absorption, and variation of permanent dipole moment.

3.3 Chemically activated optical switches

In the field of Biology, chemically responsive switches and machines are used to regulate the myriad of processes, which include the creation of protein folding, proton gradients, and viral entry and translocation [37]. Sakata et al. [38] reported the design, synthesis, and characterization of a family of thiol-reactive optical switches for labeling the proteins and other biomolecules. The site-selective introduction of photochromic probes within biomolecules is being employed as part of a new approach for optical control of bio-molecular activities and interactions within the cells. The thiol-reactive photochromic probes presented in this report cover spironaphthoxazine and five spirobenzopyrans. The location of the thiol-reactive group on the spirobenzopyran is different for each probe, and this feature could be used to control the geometry of the optical switch within a bio-conjugate. As indicated in **Figure 5**, the photochromes undergo rapid and reversible, and optically driven transitions between the states of a colorless spiro (SP) and a brightly colored

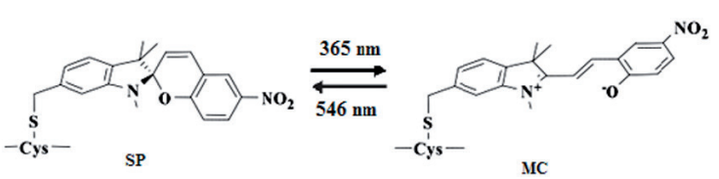


Figure 5.
Schematic representation of the reversible optical switching between the SP and MC states of a spirobenzopyran linked to a cysteine residue in a protein (Reused from [38]; American Chemical Society Publication, 2005).

merocyanine (MC). The absorption of MC of a spironaphthoxazine conjugate was red-shifted by more than 100 nm compared to the equivalent spirobenzopyran, which could be exploited for the independent control of the transition of MC to SP for up to two different spironaphthoxazine and spirobenzopyran conjugates within the sample.

4. Molecular switches based on materials

4.1 Optical switches based on organic chromophores

4.1.1 Design of chromophores

One of the major advantages of employing organic materials is that their physical and chemical properties can be customized through specific and well-defined synthetic modifications of the molecular structures. The properties such as positions and strengths of the low-energy one-photon and two-photon electronic resonances, the solubility, the aggregation propensity, the nonlinear polarizabilities, the strength of ion-pairing interactions in case of molecular salts dissolved in polymer hosts or in solution, the compatibility with various polymer host materials. Moreover, the photochemical and thermal stability of the NLO molecules can be logically controlled [39].

In NLO switches, most of the systems synthesized to date are π-conjugated donor-acceptor molecules, which consist of strong electron-donor (D) and electron-acceptor (A) groups anchored onto a π-conjugated linker. Coe [40] proposed to categorize the several systems based on the part of a molecule that could be altered while performing the reaction, i.e., the donor part (type I), the acceptor part (type II), or the conjugated bridge (type III), as shown in **Figure 6**. The NLO switches of type I and type II rely on redox switching, where the electron-donating capability of the donor group is reduced by oxidation, or on acido-switching, wherein the capability of the electron-donating group is reduced by protonation. The NLO switching based on redox interconversion has been established in a wide range of organometallic complexes. Most of the NLO switches of type III are photochromic compounds characterized by different commutation processes, including intramolecular proton transfer as in aniline derivatives, cis-trans photoisomerization in azobenzenes, and opening/closure of a conjugated ring in diarylethenes or spiropyrans [6].

Hales et al. [39] designed a class of chromophores using a relatively simple model, namely cyanine-like polymethines. The challenges associated with changing these microscopic properties of the chromophores into macroscopic properties for the suitable device applications are discussed in detail, along with the molecular engineering approaches to overcome these drawbacks.

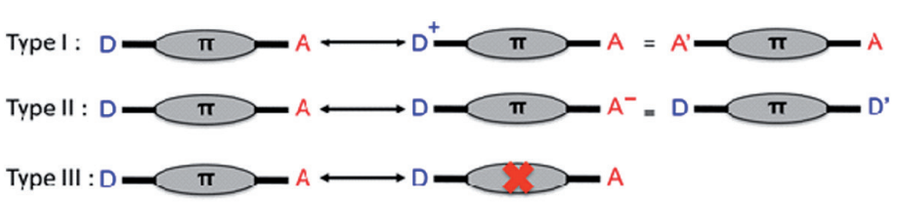


Figure 6.
The different types of NLO switching in dipolar D-π-A molecules, wherein the push-pull character is tuned upon switching, Type I = redox/proton transfer on D; TYPE II = redox/proton transfer on A; Type III = alteration of the bridge π-conjugation (Adopted from [6]; American Chemical Society, 2013).

Prabhu et al. [41] synthesized and crystallized a new chalcone compound (2E)-3-(3-methyl phenyl)-1-(4-nitrophenyl)prop-2-en-1-one based on the results obtained by Hirshfeld analysis, and nonlinear optical studies showed that the material is of a potential candidate for optical device applications such as optical limiters and optical switches. Tomas et al. [42] synthesized two molecules namely, 2,2′;-(1,4-phenylene-bis(ethyne-2,1-diyl))bis(N,N-diethyl-4-nitroaniline) (PDNA) and 2,2′-(1,4-phenylene bis(ethyne-2,1-diyl))bis(4-nitroaniline) (PNA), built up from two p-nitroaniline "push-pull" NLO chromophores slightly conjugated through a 1,4-phenylene bis(ethyne-2,1-diyl) bridge. The crystal structure of PNA reveals that the ground (off) state conformation corresponds to the centrosymmetric anti-conformer in which the molecular hyperpolarizability is equal to zero. Also, a computational investigation performed by the group reveals that once submitted to an intense electric field, the two p-nitroaniline subunits are gradually aligned in the direction of the field with the appearance of a metastable (on) state, stabilized by conjugation. During the on/off cycle, a loop of hysteresis was observed and thereby formed molecular bistability. This behavior was evidenced by investigating the NLO response of PNA at different field intensities by the electric field induced second-harmonic (EFISH) technique.

Kumar et al. [43] in their work proposed an optical switch based on nonlinear one-dimensional photonic bandgap material with polystyrene and SiO_2 as chosen constituent materials. The propagation of optical waves through these multilayered structures was studied for different intensities. The simulation of the device and its performance was carried out by transfer matrix method. The results suggest that the polystyrene/SiO_2 based nonlinear photonic bandgap material performed here can work as an optical switch. Also, the proposed device could be useful in optical time-division multiplexing (OTDM), demultiplexing, all-optical information processing, etc. This device could be a strong candidate for the variety of applications in the field of integrated optoelectronics, owing to its simple geometric structure and operating principle.

The physical properties of phase transition materials are directly linked to the transformation of structural moieties. In this context, Jing et al. [44] reported a new H-bonded binary crystal of cyclohexylaminium chlorodifluoroacetate, consisting of two distinct types of the anion-cationic structural moieties, which shows an order–disorder phase transition around 153 K (phase transition point, Tc). Thermal analyses, dielectric and second-order nonlinear optical measurements confirm the symmetry transformation from the point group mmm to mm2. It is noteworthy that cyclohexylaminium chlorodifluoroacetate exhibits a coexistence of switchable dielectric behaviors and bistable NLO effects. It exhibits NLO-activity below Tc, while its quadratic NLO effects disappear completely above Tc. Such an effect reveals the bistable feature of its quadratic NLO properties. The temperature variable-structure analyses reveal that the emergence of NLO effects below Tc is as to the partial ordering of anions as well as the small-angle reorientation of cations. This mechanism is different from that of the precedent NLO-switching materials, as it offers a potential way to design new electric-ordered molecular compounds as multifunctional materials.

4.2 Optical switches based on metallochromophores

The last two decades have been in the great boom in the development of metal–organic frameworks and coordination compounds. The resulting materials have proved to be excellent sorbents for catalysts, gases, objects for storing hydrogen as a fuel, elements of analytical devices for separating substances, as well as demonstrating unique physical properties in the field of nonlinear optics and

ferroelectricity magnetism. Recently, unique features such as strong optical anisotropy in the visible region have also been studied in addition to the existing scope of applications, and this is mainly due to a vast surface area [45].

In this context, Green et al. [46] reviewed the progress in employing metal alkynyl complexes as switchable NLO systems. The origin of NLO effects in molecules is summarized, molecular switching stimuli and read-outs were briefly reviewed, and switching NLO properties using other organic, inorganic, and organometallic molecules were also briefly discussed. NLO properties using other organic, inorganic, and organometallic molecules were also briefly summarized. Sarbjeet et al. [47], in their review, the aspects of new ferrocene-based chromophores have presented, and structure–property correlations have been studied, as the ferrocene unit behaves as an extremely strong donor or acceptor in its chromophore. This property has been used extensively in fine-tuning the electronic properties of the organometallic chromophores.

Juan et al. [48] reported three organic–inorganic hybrid analogs, (1) $[Et_3(n\text{-}Pr)P][Mn(dca)_3]$, (2) $([Et_3(CH_2CHCH_2)P][Mn(dca)_3])$ and (3) $([Et_3(MeOCH_2)P][Mn(dca)_3])$ (dca = dicyanamide, $N(CN)_2$-), and showed similar 3-dimensional perovskite frameworks, wherein the cavities are occupied by the guest phosphonium cations. At room temperature, the analogs 1 and 3 correspond to the orthorhombic noncentrosymmetric space group P212121, while analogue 2 crystallizes in the monoclinic centrosymmetric space group P21/c. Both DSC and dielectric measurements confirmed the phase transitions in 1–3, where subtle structural distinctions of guest cations affect the crystal lattices, phase transition temperature, and physical properties. The analogs 1 and 3 are SHG active at room temperature and which can be used as NLO switches tuned by guest cations.

A series of dipolar bis(dibutyl-amino styryl)bipyridine M(II) dichloride complexes (M = Co, Ni, Cu, Zn) and octupolar tris(bipyridine) M(II) coordination compounds of D_3 symmetry (M = Fe, Ru, Os, Ni, Cu, Zn) was studied by Bozec et al. [49]. The quadratic NLO susceptibilities of these complexes were evaluated with the harmonic light scattering technique and found to be at 1.91 mm. From the study, it was clear that the nature of the metallic centers strongly influenced the optical and NLO properties, and the first hyperpolarizability could be tuned by changing the nature of the metal ion. Thus, this could be a competent approach to the design of switchable NLO materials. This is the reason; the photochromic metal complexes yielded an efficient on/off reversible switching μβ values as determined by EFISH at 1.91 mm.

Qiang et al. [50] successfully synthesized and grown block crystals of $[trimethyl(chloromethyl)ammonium]_2[ZnCl_4]$ $[(TMCM)_2\text{-}ZnCl_4]$, which undergoes two reversible solid-state phase transitions at 337 K (Tc_1) and 258 K (Tc_2), respectively, with coexisting switchable nonlinear optical and dielectric properties. Exceptionally, variable-temperature x-ray single-crystal structural analyses also revealed that the unusual space group changes between Tc_2 and Tc_1 and above Tc_1. As expected, the dielectric value of $(TMCM)_2\text{-}ZnCl_4$, indicated that it exhibits a low dielectric state, an intermediate dielectric state, and a high dielectric state. The transitions of $(TMCM)_2\text{-}ZnCl_4$ could be intrinsically ascribed to the sequential order–disorder transformations of both the cations and anions. In particular, the second harmonic generation efficiency shows a sharp step-like increase from almost zero to 0.47. All these results demonstrate its potential application as a switchable and tunable molecular dielectric and NLO material. By Ming and coworkers [51] proposed and numerically investigated all-optical switching based metal–insulator–metal (MIM) waveguide resonator with an outer portion smooth bend structure containing Kerr nonlinear materials. In the structure, pump light locates at mixed-modes (the dips overlap), and then resonance in the resonator, which supports for

the improvement of nonlinear response. Light signal locates at split modes, which provides the full width at half-maximum of dips decrease significantly, and increase the difference of signal light transmittance; as a result, when pump light is on or off. This was also verified by the finite-difference time-domain simulations, with tiny optical bistability with signal light appear by varying the control-light intensity, and the switching time is at approximately the picosecond level.

Further, Benoit et al. [52] developed a robust and multi-usage detection tool that could recognize cations by molecular switches with a significant contrast of the second-order NLO optical properties. The concept of proof is given by evidencing by *ab initio* calculation, the ability of spiropyran/merocyanine systems to detect alkali, alkaline earth, and transition metal cations selectively. The complexes can have a broadband spectral and temporal response and strong reverse saturable absorption and two-photon absorption in the visible and near-IR region. Accordingly, Sun et al. [53] Pt (II) provided tridentate or bidentate complexes containing heterocyclic ligands with excellent nonlinear optical properties. As such, the complexes were useful for organic light-emitting diodes and optical-switching or sensing devices. To switch quadratic nonlinear optical effect has become an exciting branch of material science. However, solid-state molecular crystals exhibiting tunable and switchable NLO behaviors remain scanty. Herein, Adnan et al. [54] reported the picrate-based binary organic molecular crystal, triethylammonium picrate (TEAP), which undergoes a phase transition at Tc = 319 K above-room-temperature, being solidly confirmed by the dielectric and thermal measurements. A sizeable thermal hysteresis of ~7 K reveals the first-order feature for its phase transition. The quadratic NLO effects of TEAP can be switched in the vicinity of Tc, i.e., TEAP exhibits NLO-active response of ~1.5 times as large as that of KDP below Tc (NLO-on state); however, its NLO effects completely disappear above Tc (NLO-off state). The structure analyses reveal that the order–disorder transformations of triethylammonium cations and picrate anions together contribute to its both switchable NLO behavior and phase-transition. This work provides a new direction to the designing and assembling of stimuli-responsive materials. Efficient NLO properties of topological switches can be obtained from the push-pull chromophores with π-conjugated spacer and strong electron-withdrawing and releasing groups located on opposite sides of the skeleton ring. Sucarrat et al. [55] achieved this, as they generated unique Huckel-to-Mobius topology switches, with the macrocyclic ring of expanded porphyrins, which presents a conformational versatility that leads to original structural motifs. These systems could act as optoelectronic materials, and their range of applicability depends on the values of the nonlinear optical properties as well as the on substantial differences between the Huckel and Mobius structures.

Ting et al. [56] studied spirooxazine molecular switches, a photochromic material, which transform into open-form of metallic merocyanine by molecular switching and giving rise to significant contrasts in its second-order NLO properties as selective cation sensors. The resulting merocyanine derivatives exhibit 10–21 fold higher static second-order NLO responses. The large first hyperpolarizability relies on the alkaline earth metals present, causing values to increase nearly 21 fold, as evidenced by the larger charge distribution, lower transition energy, and separation distribution of the first hyperpolarizability. Therefore, spiropyran-to-merocyanine molecular switching could be employed to distinguish alkaline earth metals and determine the efficiency of cation detection.

4.3 Optical switches based on supramolecular systems

Chemically, photochemically and electrochemically controllable conformational motion of interlocked molecules such as catenanes, rotaxanes (as shown in

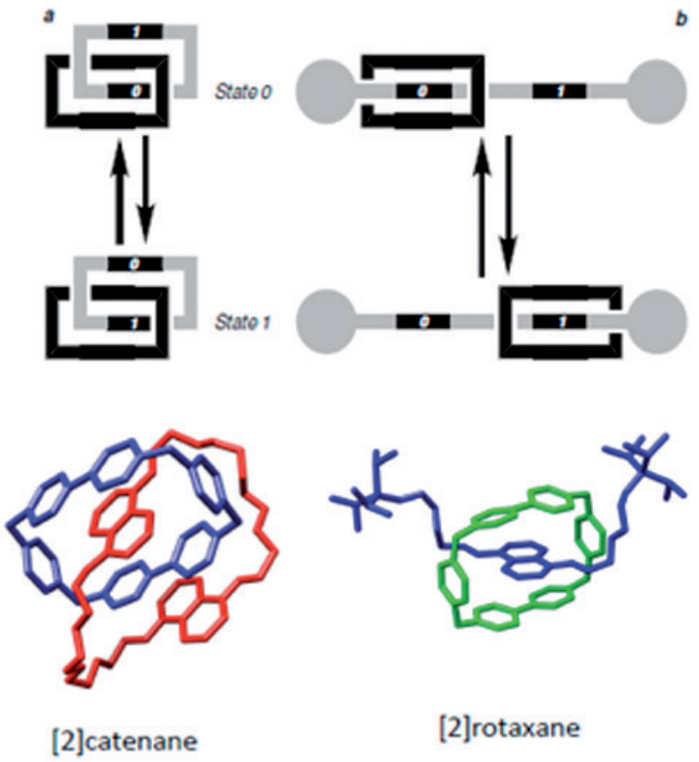


Figure 7.
Interlocked molecules: (a) Catenanes and (b) Rotaxanes (Adopted from [57]; American Chemical Society, 2001).

Figure 7), and pseudorotaxanes have been extensively investigated and reviewed [58]. The stimuli induced molecular motions in these systems may undoubtedly play a key role in the development of optoelectronic devices.

The nonlinear optical properties of phthalocyanines (Pcs) depend not only on the chemical structure of component monomers but also on their packing arrangement, which provides the possibility to incorporate switchability into the third NLO behavior of such materials at supramolecular level. Based on this, Hui et al. [59] rationally designed three series supramolecular third-order NLO photochromic moiety (switching materials) containing Pcs. By utilizing the photoinduced changes in the geometry and electronic delocalization distributions of photochromic moieties under the alternative illumination of suitable UV and visible light, the self-assemblies of Pcs were successfully photo-controlled in an efficient manner. Besides, they also showed large molecular second hyperpolarizabilities at the order of 10^{-30} esu both in "on" and "off" states. The results suggest that these materials would be of potential in emerging optoelectronics and photonic technologies.

Important features of the rotaxane system derived from noncovalent interactions between a component that contains complementary recognition sites. Such interactions, which are also responsible for the efficient template-directed synthesis of rotaxanes, include electron donor-acceptor ability, hydrogen bonding, hydrophobic–hydrophilic character, π-π stacking, electrostatic forces, metal-ligand bonding. Rotaxanes have, therefore, both molecular and supramolecular character: molecular because the components are held together mechanically and can be unlinked only by breaking strong covalent bonds; supramolecular because of the presence of weak noncovalent interactions [60].

Similarly, solid-solid-state reversible phase transitions are widely used in the switchable dielectric, ferroelectric, piezoelectrical, and pyroelectrical and NLO materials. For instance, Yi [61] reported a new crown ether clathrate, [Habf-(18-crown-6)1.5]$^{+}$ [PF6]$^{-}$ (Habf = p-ammonium benzene formamide) synthesis scheme as shown in **Figure 8**, which showed an interesting reversible phase transition and

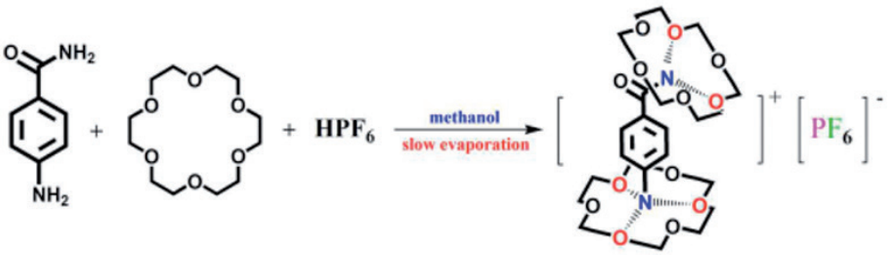


Figure 8.
The preparation of [Habf-(18-crown-6)1.5]$^{+}$ [PF6]$^{-}$ (Habf = p-ammonium benzene formamide) (Adopted from [61]; Royal Society of Chemistry, 2013).

switchable dielectric behaviors near room temperature (263 K) which was triggered by rotation and order–disorder motions of crowns. The synergetic rotation motion between the 18-crown-6 crown ethers and the order–disorder motions of both hexafluorophosphate guest anions and 18-crown-6 crown ether host molecules was analyzed by X-ray single-crystal diffraction. The apparent step-like dielectric change around the phase transition indicates that it has potential applications in dielectric switches.

Khan et al. [62] synthesized a novel molecular phase transition material, 1-methylpiperidinium perchlorate [18-crown-6] monohydrate, which exhibited reversible switchable dielectric anomalies near room temperature (260 K). The phase transition is from noncentrosymmetric to noncentrosymmetric, exhibiting a second harmonic generation response of ~0.8 times high than that of potassium dihydrogen phosphate. The temperature-dependent single-crystal X-ray diffraction reveals that the origin of its phase transition was attributed to the order-disorder transformation of perchlorate anion, the Me group of cation and the torsional angular change in the crown molecule; i.e., all three components contribute to the appearance of this phase change. The results of the work suggest that the synthesized compound could be conceived as a potential switchable dielectric and NLO material. Work also provided a practical approach to design novel NLO switch materials.

4.4 Optical switches based on graphene/carbon materials

The optoelectronic properties of graphene attracted much interest in recent years. Shiramin and Van [63] reported a comprehensive study, investigating the different design trade-offs involved in realizing, in particular, graphene-based modulators and switches. This involved the comparative study of representative hybrid graphene-waveguide configurations, focusing on optimizing their dimensions, the gate-oxide thickness, the polarization, the operating wavelength, and contact definition. Minmin et al. [64] fabricated MoS_2/graphene nanocomposite films with high optical homogeneity and large scale. Using a Z-scan technique with a femto-second laser at 800 nm, the saturable absorption of MoS_2/graphene nanocomposite films was enhanced as compared to pristine MoS_2 film and graphene film. The nonlinear absorption coefficient of MoS_2/graphene nanocomposite film measured at the same condition was close to −1217.8 cm/GW, and this is higher than those of MoS_2 film (−136.1 cm/GW) and graphene film (−961.6 cm/GW) [45].

In the same line, Amos et al. [65] reviewed on the optical properties of carbon nanotube (CNT) and their most relevant applications, including saturable absorption for the passive mode-locking of fiber lasers and optical switching for wavelength conversion. Several demonstrations of integrated graphene-based modulators, switches, detectors, and nonlinear devices have been reported [63].

4.5 Optical switches based on nanoparticles

Recent studies have shown an NLO response in inorganic nanocomposite materials with enhanced SHG coefficient. Some studies have reported the preparation and NLO properties of inorganic nanocomposite materials with noble metals [66]. Herein, Sun et al. [67] reviewed on recent theoretical progress in understanding the nonlinear optical response of noble metal nanocomposite materials with an enhanced third-order nonlinear susceptibility application on optical switchers and optical limiters. The enhanced third-order nonlinear susceptibility results from the surface plasmon resonance of noble metal nanoparticles, which strongly depends on irradiation light wavelength, concentration, and surrounding medium of noble metal particles. Furthermore, their applications as optical switchers with ultrashort time response and optical limiters of intense laser radiation were also reviewed and discussed.

Jagannath et al. [68] fabricated gold nanoparticles (NPs) embedded in sodium antimony borate glass system, and their optical, physical, structural, and ultrafast nonlinear optical properties were studied and analyzed. UV–visible spectroscopy measurements revealed the characteristic surface plasmon resonance of Au NPs at 565 nm and attributed to interband transition. The ultrafast NLO properties of gold doped glasses were studied by the Z-scan technique at a non-resonant wavelength (λ = 800 nm, 80 MHz repetition rate) with femtosecond Ti: sapphire laser pulses. The Z-scan data demonstrated that the investigated glasses are potential materials for the applications in NLO devices, particularly in optical switching devices.

5. Device fabrication of optical switches

The molecular switch is a multifunctional device, which identifies in telecommunication networks to even human body muscles as a modern optical device. In this context, light is a critical element of optical switches, which influences the switching mechanism to bring on/off state [69]. Fabrication of such optical switches mainly depends on the functions of the optical switch, internal architecture, and substrate materials. Most of the optical switches are based on the silicon platform; in some cases, SiGe is also used. The deposition of the material on the substrate is broadly classified into two classes, viz., physical vapor deposition and chemical vapor deposition. To reduce the errors in device fabrication, generally, the chemical vapor deposition technique preferred.

Light guided through couplers by varying the coupling ratio comes under the section of electro-optic switches. In telecommunication networks, they operate between the wavelengths 850 and 1550 nm, and the widely used materials are based on LiNbO, III-V group conductors, GaAs or InP, polymers, silicon. However, these switches always suffer from fabrication errors [70–78]. Qiao et al. [70] developed optical switches with a complementary metal-oxide-semiconductor (CMOS) and microfabrication techniques having low power consumption, high-speed cross talk, high insertion loss, nanosecond response speed and with excellent long-term stability which implies to be suitable for lightwave circuit applications. Abel et al. [79] designed and developed the high speed ultrafast low power consumption optical switch with CMOS combined monolithic integrated fabrication technique.

Wavelength multiplexing divisions-based operation in optical switches is preferably carried out with a variation of the refractive index of the material by thermo-optic coefficient. The phase changing materials are generally preferred in the thermo-optic switches as they have thermo optic effect. These switches are classified into interferometric and digital optical switches [78]. Thermo optical switches are relatively slow, and the biggest problem is in tuning the material properties

with the limiting switch speed and thermo isolation problem [80–84]. Zequin et al. [81] designed with low energy consumption Mach Zehnder Interferometer (MZI) based switch with improved compatibility for configurable and high-bandwidth wavelength division multiplexing application. The fabrication techniques used were CMOS and Silicon-on-Insulator (SOI), which are proved to be the best. Thermo optic switches are highly applicable for MZI, as can have suitable configuration, operating between wavelengths 850 and 1500 nm.

A combination of optical switches based on reflecting surface-micromirror operation called micromechanical electro-mechanical system (MEMS) optical switches which have replaced various optical switches to overcome the various issues. These are the most dominant and promising switches in switching technology, available in 2D, 3D configurations as they possess advantages of good potential in high volume and with low cost with its compactness and optical transparency. It is well-known that silicon is the dominant material for the fabrication process. Surface micromachining, which sounds similar to surface milling, whereas one can only subtract the material from a device, with exterior micromachining, one can both add and subtract material, or one can match layers of material more precisely. **Figure 9** [82] gives a detailed schematic of the process from a plain silicon substrate to an entire surface assembled micromotor. The patterning is performed using a lithography mask, a thin film of metal wrapped within the glass with the fancy pattern on it (in this case, the shape of a micro-cantilever). Ultraviolet light is then illuminated through the holes in the mask, which suppresses some parts of the photoresist, allowing it to be quickly washed away. For instance, Sattari et al. [85] designed and experimentally demonstrated 64 × 64 silicon photonic switches with 3.7 dB on-chip losses, 0.91 μs switching times, digital operation and broadband response from 1460 to 1580 nm. These are scalable when compared to previously reported silicon photonic switches, through its MEMS-actuated adiabatic couplers with high on/off ratios, with no loss in the off state. In its present embodiment, this switch integrated 4096 MEMS-actuated adiabatic couplers on a 7 mm × 7 mm area, as reported is the largest silicon photonic integrated circuit so far demonstrated.

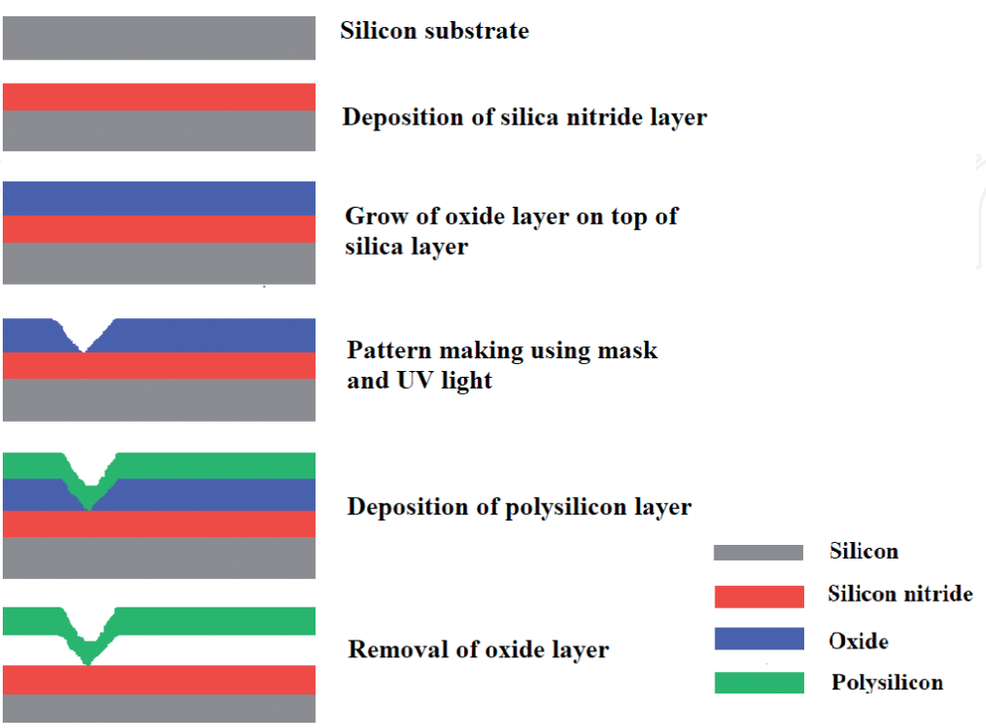


Figure 9.
Simple process for fabricating a micro-cantilever using surface micromachining technique (Reused from [82]).

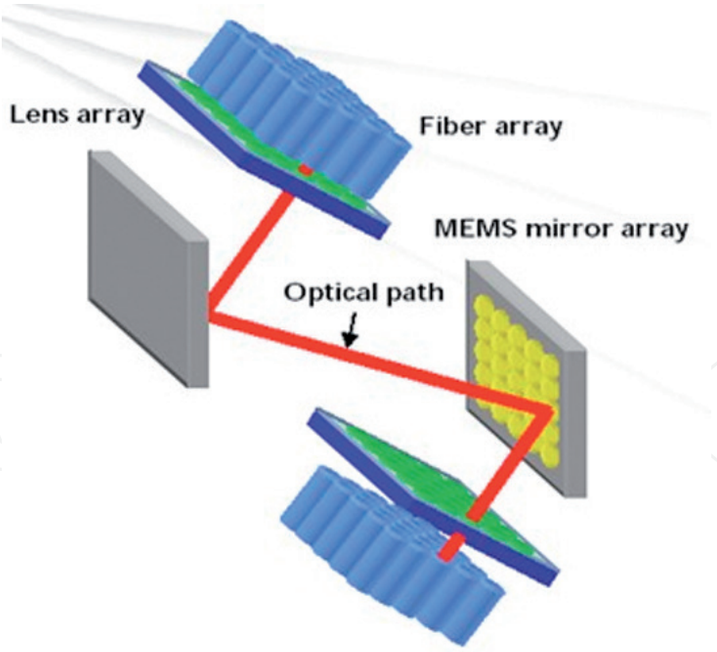


Figure 10.
Ideal MEMS optical switch (Reused from [86]; OSA Publishing).

MEMS optical switches are promising with low cost, lightweight, high speed, high resolution, and high sensitivity [6, 81]. **Figure 10** shows the operation process of the MEMS switching [86]. Based on the various advantages, the MEMS-based optical switches are the dominant and promising switches in switching technology. Primarily switches are fabricated with silicon platform and CMOS fabrication technique, which is compatible with other techniques. The internal architecture also matters in the efficiency of the performance of the device.

6. Applications of switches and future prospectus of designing new molecules

This chapter addresses the molecular design strategies to engineer new SHG materials, which are quite advanced and well employed. It is hoped that the recently introduced algorithm by which the SHG-relevant D-π-A motif can be identified and assessed its strength, which will help to move this field towards a more rational approach to materials discovery of dipolar SHG chromophores. Future challenges depend on extending the investigated objects to supramolecular (e.g., rotaxanes) architectures, which involves many NLO-responsive units, in order to exploit their cooperative effects for enhancing the NLO responses and contrasts [87].

The discovery of more materials is essential before sufficient data are available for establishing the generic relationships between the structure and SHG properties. Nevertheless, the SHG materials have exciting prospects for the NLO applications that employ SHG in a more 3D fashion, in particular to optical switches. Thus, this chapter focused on numerous examples of discrete molecules, as reflects the natural progress of the field [88]. Through these representative examples, one could demonstrate that the rational design of molecular NLO switches, which combines experimental and theoretical approaches.

In order to compare the performance of memory devices, the specifications are yet to be determined. The literature does not fulfill these requirements. Then one should ask whether any structure, with the right materials, is eventually competent in achieving the expected performance. To reply this, it is essential to know

the mechanisms accountable for switching and conductance as the active mechanisms are still the subjects of debate, complicated by the fact that the experimental results are not always reproducible, even within the same laboratory. Therefore, it is not easy to study the trade-offs between, for example, in the case of switching and retention times or on-state current and retention time. Endurance may vary in a system that involves mass transport like electrochemistry, electromigration, and molecular reorientation as compared to the one in which only charge transports [89].

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