



Multifunctional conjugated 1,6-heptadiynes and its derivatives stimulated molecular electronics: Future moletronics

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ABSTRACT

Over the past decade conducting polymers have been studied for electronic applications, among them, molecular electronics: the study and investigation of molecular building blocks is a next-generation demanded area of research. Hence, the moletronic equivalent multi-functional advantages of cyclopolymerized 1,6-heptadiyne (HD) systems explored in this review. Further, this report elucidates physical properties via conditional cyclopolymerization methodologies, it describes the chemistry of tethering molecular-chains facilitated intrinsic-conductivity. HD and its derivatives induce superior conductivity characteristics via doping elements, wherein, significant electronic conductivity mechanism is attributable to the solitons and anti-solitons, which was described in this context. HD and their derivatives molecular mechanism, its compatibility are expounded for moletronic application, which is new insight of the article. Moreover, required inherent characteristics, for e.g., thermal-stability, chemical-resistance, mechanical properties, magnetic, and electronic properties have been discussed. Furthermore, failures, physical limitations, and its realizable similarity solutions for moletronics have described. Though electronic or moletronic components having failures and other physical limitations, HDs offers excellent conductivity with wide functional and physical properties that could lead to potential candidates to deliver efficient and low-cost moletronic devices.

1. Introduction

Molecular electronic (moletronics) field is an expeditiously developing field in nanotechnology that leads to the development of future electronics that includes modern circuits and devices [1–5]. For example, electroactive phase instigated hybrid molecular, monomolecular and miscible molecular-based devices embedded in between electrodes to perform the basic function of electronics [6–9]. Also, smart switchable molecular electronic devices for ex: hybrid nanocomposites obtained by the homogeneous dispersion of zinc oxide nanowires as a dopant into hydrogen-bonded liquid crystalline compounds or smart in-plane switchable nanowires embedded liquid crystal matrix-based devices, CdS nanowires encapsulated liquid crystal in-plane switching of LCD device and metallic nanowire-based smart structures for transport of electrons without any scattering [10–14]. Moreover, molecular electronic advancement in medical sector such as molecular electronics-based medical implants, which have collectively transform the

diagnosis and treatment of many diseases [14–16]. While many characterization techniques have been practiced from the last decade such as microscopy, new techniques are constantly emerging. In particularly STM, high-resolution electron microscopy and secondary ion mass spectroscopy has revolutionized. Such kind of advanced methods and evolutionary characterization techniques allowing the image and analysis of structure and compositions leading to an increase in the level of understanding the behavior at molecular scale [17–20]. In order to understand the molecule electronic functions, it is important to understand intrinsic molecular electronic states and its properties such as its electronegativity, molecule length, Fermi level, and energy gap [21–24]. Recently, intrinsic functional and structural properties have been explored widely by the researchers from the theoretical and quantum chemical calculations [25–28]. Among them, they suggested that the electrical and electronic properties such as charge transport, magnetic and optical properties are preminent characteristics of moletronic systems, which probably attributable due to their interrelated

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molecular orbital and its states. Charge transport of molecule depends on the nature of the molecule and its electronegativity, backbone structure induced solitons, anti-solitons and electrode material [29–33]. More importantly, electrodes are prominent to understand the conduction mechanism in-between metallic electrode and molecular systems, i.e., the energy levels of metallic (Fermi level) system and the molecular orbital system needs to be matched. This significant phenomenon can be understood via impedance matching phenomena, it suggested that the maximum power transfer while maintaining minimum of the signal obstruction from a molecular system to the metallic system [34–36]. In general, these two system's energy levels are not systematically synchronized within the equilibrium axis [37], thus mismatch approach predicts the barrier contact level, which is analogous to the Schottky effect. LUMO-HOMO difference is related to the bond length, the height of the barrier, effective barrier thickness, presence of defects, thermoelectric emission [38], direct tunneling and hopping, these LUMO-HOMO barrier width influencing key factors to enable the electron transport properties of a molecule since conduction is improved by decreasing HOMO-LUMO gap (HLG) energy [39–45]. Recently, researchers have widely explored and demonstrated the conducting properties of conjugated molecules, they have small band gap energy of about ~2–4 eV. This band gap energy, i.e., HOMO-LUMO band gap energy is interrelated with the molecular chain length, which was experimentally demonstrated by Li *et al.* [46–48]. Among the conjugated polymers, polyacetylene (PA), where Acetylene triple bonds have a rich number of electrons, and these monomers are used during polymerization to yield linear conjugated systems, which has been widely used as an engineered polymer for functional applications due to its simplicity and high conductivity [49,50]. Though this polymer exhibits superior electronic conductivity, insolubility and infusible low oxidation resistance make PA difficult to adopt for functional electronic applications. Functional substituents with wide range to overcome the drawbacks of polyacetylene and causes a dramatic change in properties relative application development [28,29,32]. PHD is a new type of conjugated polymeric system that can produce via ring forming polymerization (cyclopolymerization) technique [51].

In this context, cyclopolymerization of PHDs and its derivative synthesis methodologies and the chemistry have described. Further this extends the explanation of intrinsic conductivity, and its significant interrelation mechanism with the solitons and anti-solitons have described in this context, which is prevalent characteristics for moletronics. Also, the molecular mechanism for moletronics, and PHDs, its derivatives compatibility towards moletronic application have been enunciated. Moreover, other inherent characteristics for moletronic applications such as PHDs and its derivative induced functional properties like thermal stability, chemical resistance, mechanical properties, and magnetic and electronic properties have been discussed. Furthermore, failures, physical limitations, and its realizable similarity solutions for moletronics have also been described in this review.

2. Poly(1,6-heptadiyne)s significance

Though PA's dimensional conjugated structure induced electronic properties to facilitate functional electronic applications, processability, reactivity, moisture, and oxygen stability are the substantial problems that make them incompatible for electronic applications. To overcome these drawbacks, low dimensional PHDs systems were widely explored by the researchers, specifically, PHDs with high potential conductivity has led to an investigation of the number of electronic components and devices. 1,6-heptadiynes were extensively considered as di- or tri-block conjugated cyclo-co-polymers by introducing wide range derivatives rendered desirable functional advantages. Cyclopolymerization of 1,6-heptadiyne monomers catalyzed via various catalytic systems, for example, Grubbs 3rd generation catalyst, etc., is an efficient living rapid polymerization technique to synthesize well controlled over both number average molecular weight and molecular weight distribution

with a conjugated polyene backbone structure leads to soluble characteristics in organic solvents such as tetrahydrofuran (THF), etc. [52]. More importantly, adjoining amelioration in this field was the discovery of organic polymeric systems with metallic properties. Metallic properties with long-chain polyenes such as PHDs as a potential material for semiconductor electronics, which can be described via π -conjugation instigated structural change, the longest polyene chains π -conjugation were less than 20 units long was reported, later on, in 1958 researchers have demonstrated polymerization of infinite polyene chains had been successively carried out in the presence of Ziegler catalyst [53]. Thus, long chain possesses large number of conjugated double bonds lead to intensified electronic conductivity and optical characteristics. Moreover, Buchmeiser group examined Grubbs catalyst (Ruthenium-based user-friendly Grubbs catalysts) based polymeric systems suggested that these diynes with greater air, and moisture tolerance probably attributable to the functional groups reactivity via cyclopolymerization of diynes. Later on, they developed interesting architecture rendered a wide range of macromolecules with superior multi functionalities, thereby copolymerized system extended scope to various molecular level electronic applications.

Conjugated soluble polymers possess significant interest due to their anisotropic functional advantages such as electrical and optical advantages while maintaining the solubility parameter [54]. Similarly, significant progress has been made to develop PHD and its derivatives with both conductivity and solubility [55,56]. The developed heptadiyne systems possess solubility in organic solvents such as benzene, and chloroform [57–60]. Schrock type catalysts offer soluble polymeric systems that contain only one type of repetitive unit to form either five-membered or six-membered ring structures, although the fine-tuned quaternary system is used for this purpose [53,61]. This relative catalyst induced heptadiyne structures can be realized via stereo- and regioselective way [53]. Resulted 1,6-heptadiynes possess improved co-planarity corresponding to the λ_{\max} , reversible thermochromic behavior and excellent film building probabilities. Also, it exhibits thermal and air environment stability for months either in solution or in solid form [58].

Large voltages enabled molecular design field effect transistors (FETs) induce extensive power consumption, though high dielectric materials can facilitate for this purpose, negatively affected charge carrier mobility leads to energetic disorder [62]. To overcome this, low- k dielectrics are feasible which compensate reduce capacitance effect [62]. 1,6-heptadiynes possess low dielectric characteristics; this significant property suggests that it could be a potential candidate for electronic and moletronic applications. Also, these conjugated systems exhibit superior magnetic, optoelectronic and charge transport properties [33], which are attributed due to conjugation in the main backbone chain in addition to the solitons or anti-solitons effect. Thus, above all delineations reveal the 1,6-heptadiyne and its derivatives with desired functionalities enabled under conditional synthetic routes could lead to futuristic materials for electronic or moletronic applications. The 1,6-heptadiyne functional characteristics have been illustrated in Fig. 1, the advantages of five- and six-membered ring structure's are reported in Table 1.

3. Poly(1,6 – heptadiyne)'s cyclopolymerization, conductivity, and doping

In current technological applications such as inorganic semiconductors, optoelectronics, and photonics, polyenes are potentially utilized due to its conjugated structure [63–67]. PHDs are derivatives of PA, though there are many synthetic roots to assess these systems and its derivatives, cyclopolymerization of α,ω -diynes represent a powerful technique due to its multi-functionality and assessability [52,68]. The 1,6-heptadiyne can be synthesized with the help of monomers such as Diphenyldipropargylmethane, Dipropargylmalonate as well as various catalyst i. e. NbCl₅, TaCl₅ and MoCl₅, the cyclopolymerization of 1,6-heptadiyne with MoCl₅ (100%) resulted highest yield compared to

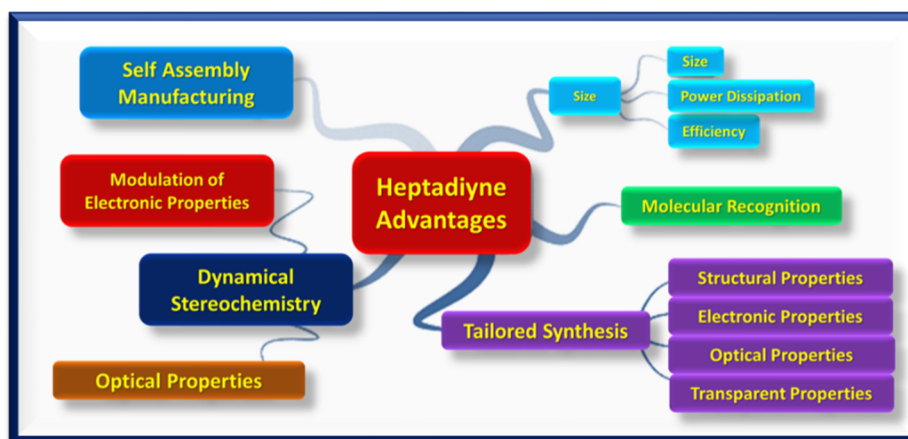


Fig. 1. Advantages of 1,6-heptadiyne.

NbCl_5 (40%) and TaCl_5 (35%) and Methanol was used to terminate the cyclic polymerization of PHDs. It is observed that irrespective of polymerization condition and type of catalyst, PHD is vulnerable to oxidative forces in air and insoluble in an organic solvent, therefore small amount of methanol was used to terminate cyclic polymerization of PHD [69]. Thus typical polymerization procedure was reported, where all the procedures for catalyst, solution preparation, and polymerization were carried out under atmospheric nitrogen conditions. Solvent, catalyst solution, and co-catalyst solution are injected into a polymerization reactor cell. Subsequently, monomer in each solvent mixture injected into a reaction chamber. After a certain period, the polymerization is terminated by adding a small amount of methanol. The resulting polymer is then dissolved in chloroform followed by precipitation with a large amount of excess methanol [69]. Moreover, other research reports suggested that the functional solubility is attained due to ligands in the 4th position of PHDs via cyclopolymerization. Though the performance of defined polymer is endowed by catalytic systems, and oxidation, the long term stability, nevertheless, effective conjugation lengths are facilitated with the help of the cyclopolymerization technique [59,60,70,71]. The possible ring structures in PHD polymer through the synthetic cyclopolymerization route is shown in Fig. 2(a-d).

The narrow range of five-membered ring structure or six-membered ring units can be attained via living regioselectivity process. The polymers with a five-membered ring structure possess a high magnitude of conductivity than the six-membered ring structure due to its expeditious cyclization, which is further related on doping metallic

elemental catalysts [67,72]. Potential Molybdenum-based Schrock initiators have been explored, for example Diethyl dipropargylmalonate (DEDPM) (Fig. 2(d)), but Ruthenium-based pseudo halide complexes provided high reactivity during copolymerized metathesis reaction. Also, the possible similarity was realized with modified Grubbs' catalyst and Grubbs – Hoveyda catalyst which were explored recently, suggests that for living systems, a handful of pseudo – halide Ruthenium – catalyst enabled initiators are feasible [53,72]. However, PHDs are difficult to polymerize with standard Ruthenium – alkylidenes, since Ruthenium-based initiators possess a rich number of electrons. Hence, electron-withdrawing pseudo – halide catalysts are preferred [73]. Enhancement in the polarity and increased activity of Ruthenium – alkylidene induced by di-chlorides with fluoro-carboxylates lead to unique cyclopolymerization of PHDs. Thus, diynes are extensively explored to form conjugated polyenes via cyclopolymerization technique and soluble PAs are more favorable with this technique. However, major challenge is mainly due to reactions that enabled the controlling process of the regiochemical outcome, which is attributable to the α and β terminal alkyne catalyst discrimination deficiency. Olefinmetathesis catalysts via cyclopolymerization route is an effective synthetic process to produce controlled molecular weight and narrow dispersity systems [60,74–76]. Five – membered ring structure in conjugated polymers resulted in α – addition of metal carbene to alkynes and similarly, β – addition leads to six – membered ring structures. This selectivity of five or six-membered ring structure was reported by Schrock and Buchmeiser *et al.* in which they had demonstrated the regioselectivity of PHD with Molybdenum-catalysis

Table 1

Advantages of 1,6-heptadiynes five-membered and six-membered ring structures.

| Five-membered ring | Six-membered ring |
|--|---|
| Formed by α -addition in heptadiynes | Formed by β -addition in heptadiynes |
| α -addition of the metal carbene to alkynes results in conjugated polymers containing a five-membered ring structure | β -addition gives six-membered ring structures |
| Forming by fast cyclization | Six-membered rings form slow cyclization than five-membered rings |
| Oxidative stability via cyclized vinylene groups | Sterically unfavoured orientation |
| Sterically and electronically favorable structure | Insoluble in an organic solvent, except oligomers |
| Insoluble in an organic solvent, except oligomers | Solubility in common organic solvents |
| Solubility in common organic solvents | The conductivity of six-membered ring structures are low as compared to the five-membered ring structures |
| Conjugation leads to the electronically and ionically conductive | Optoelectronic properties are low as compared to the five-membered ring structure |
| Optoelectronically tolerable | |
| Five-membered rings possess stable and efficient blue electroluminescence characteristics | 1D- or 2D-nanostructures are possible with the advanced synthetic routes |
| 1D- or 2D-nanostructures are possible with the advanced synthetic routes | |
| Metathesis polymerization of dendronized five-membered ring structure provides good thermal stability with the highest decomposition temperature of 300 °C and with electrochemical stability. | |

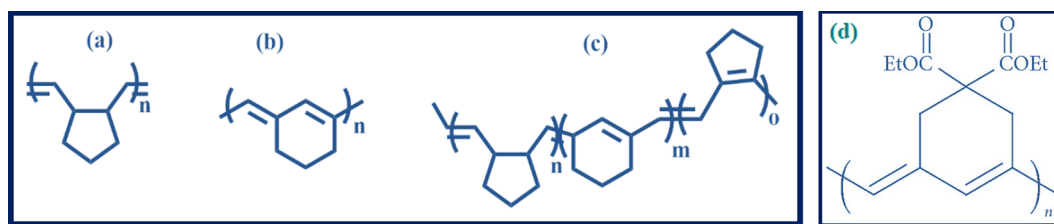


Fig. 2. Cyclopolymerized PHDs ring structure (a) polycyclopent-1-enevinylenes, (b) polycyclohex-1-ene-3-methylidenes, (c) mixed structure of polycyclopent-1-enevinylenes and polycyclohex-1-ene-3-methylidenes, (d) Diethyl dipropargylmalonate (DEDPM).

[58,77–82]. Subsequently, researchers had reported the cyclopolymerized of PHD derivatives α -fashion regioselectivity utilizing Grubbs' catalyst. Joung Hoimin *et al.* reported highly efficient regioselectivity of PHD via third-generation Grubbs' catalyst, which offers controlled molecular weight and dispersity of five-membered ring polyenes [83–86]. Grubbs' 'Z' selective catalyst creates the N-heterocyclic carbene (NHC) ligand which leads to a respectable selectivity of about > 70–80% in six-membered rings [87–90]. Though the improved experimental selectivity of five-membered and six-membered PHD configurations are well studied, researchers have not explored theoretical regioselectivity estimation and the control of regioselectivity. Recently, Choi *et al.* reported the combined experimental and computational studies to establish conceptual foundations of regioselectivity using Ruthenium-based catalyst which leads to a new cyclopolymerization process possessing efficient selectivity for β -addition. This type of optimized study could be thought of research activities to enhance the understanding of the regioselectivity α -addition in PHDs that influence functional properties, for example, the origin of optimized regioselectivity of Ruthenium2-catalyst leads to increasing β -addition regioselectivity which facilitates electronic demands (Fig. 3(a-d)) [54,90,91]. Also, Ruthenium1-carbene catalysts are Fischer carbenes, where carbene acts as a natural ligand and provides σ -donor and π -acceptor, these carbenes induce orbital interactions such as $sp^2 \sigma$ -donor and enthalpy p-orbital π -acceptor [54,90,91]. These orbital interactions facilitate both electronic and steric forces induce cyclopolymerized regioselectivity, which attributes due to more nucleophilic and less substituted terminal position among alkyne-carbons. Thus, electronically preferred base-substrate alignment to catalyst resulted from α -addition [54,90,91]. In other cases, steric forces lead to the opposing properties (Fig. 3(b)) [54,90,91]. The steric hindrance between substituents and metal carbene in heptadiyne disfavors β -addition, these two types of techniques elucidate that the Ruthenium catalysts (Ruthenium1 and Ruthenium2) dominate the regioselectivity process via cyclopolymerization. Considering both electronic and steric demands five-membered ring structure produced by α -addition of Ruthenium1 catalyst is favored and the sterically preferred side bound the system to enable Ruthenium2-catalyst with β -addition [54,90,91], but however, due to the catalyst structure the electronic control cannot be avoided which leads to different carbene induced electronic properties. Enforcing stringent trigonal-bipyramidal geometry, this can improve the electronic effect at metal-center results Ruthenium - dxy energy (Fig. 3(c)). This suggests that the heptadiynes and its derivatives via controlled conditional synthetic routes lead to the improved electronic properties with defined molecular weight, which further facilitate heptadiynes as a potential possible candidate for electronically rendered future molecular electronics [54,90,91].

3.1. Conductivity and doping

In general organic, polymers come under insulators since their electrons in sp^3 orbital are tightly bound together with individual atoms in backbone structure likewise sigma-bonds between the atoms. Whereas in the case of conjugated polymers, π -bonds and delocalized π -electrons extend down to one-dimensional chain axis and the plane of

conjugation with significant overlap lies in one direction along the backbone [92]. Many theoretical results have been proposed, which suggests that the diyenes exhibit such type of electronic conductivity characteristics, although theoretical results proved the stability of electronic conductivity of diyene systems, experimental results are not stable due to their instability induced undoped systems are insulators. Acetylene or 1,6-heptadiynes systems can be chemically dopable and this can be quantified with the aid of cyclic voltammetry. Both the n-type and the p-type electrochemical doping advantages can be successfully feasible, the degree of doping can be controlled via charge alteration, which can easily switch the direction of either p-type or n-type leads to diyene's electronic conductivity characteristics. Similarly, charge inducing strategy via photoexcitation in acetylene or 1,6-heptadiynes without utilizing chemical dopants was realized by the researchers, though the sub-gap transition and its virtual configurations are same as those revealed from the chemically dopable samples [93]. Friend *et al.* reported that the long-lived excitation states concentration is low via photoexcitation doping mechanism and hence it was not a feasible technique and suggested that chemical doping as the mature way to improve electrical conductivity to enhance moletronic device or component performance. Moreover, it might lead to thermal and chemical stability by choosing proper dopants during chemical doping for conductivity improvement [94]. Thus suggested that the chemical doping can be either donor or acceptor doping to the diyene system, which further leads to the metallic state of conductivity. Electron acceptors such as Diodene: I_2^- , Arsenic pentafluoride: AsF_5^- , Perchlorate anion: ClO_4^- can oxidize the chains and induces a positive charge, this mechanic process is known as p-type doping. Similarly, the electron donors such as Potassium: K^+ , Magnesium: Mg^{2+} , Sodium: Na^+ , tetrabutylammonium: Bu^4N^+ etc., are negative charge inducers, thus it is n-type mechanic doping. However, due to the nature of the hole's or electron's moment the conductivity can be improved even though both processes are reversible, the dopant and level of mechanistic doping most likely influence on the specific mechanism of doping (donor or acceptor) [95]. Though the improved characteristics realized via dual doping mechanisms (either p-type/n-type), the origin of outstanding electronic functional properties, i.e., electronic conductivity attributable to the process of solitons. It is postulated that the soliton is accountable for cis-to-trans isomerization of diynes as well as conductivity and the chain reconstruction leads to soliton defect, which is due to an odd number of carbon in the backbone chain. Thus, forming and breaking of the backbone chain bond during the isomerization action has been illustrated for acetylenes in Fig. 4(a and b). Yamabe *et al.* demonstrated the mechanism of p-type doping resulting in cis-to-trans formation [96], in this mechanism, the electron transferred from conjugation to the dopant, which resulted in one unpaired electron. Adjacent subsequent electron moment shifts down to the chain to create a double-bond until single-electron makes a new path that accepts the unpaired electrons and the direction of bond alteration is due to the series process of electron jumps, consequently, electron conduction [45]. The results of spectroscopic measurement reveal that the net reaction has no unpaired electrons, thus the spin density remains unchanged [97]. This result supports the spin density stabilization phenomena if unpaired electrons transfer to other molecule. Thus, soliton is

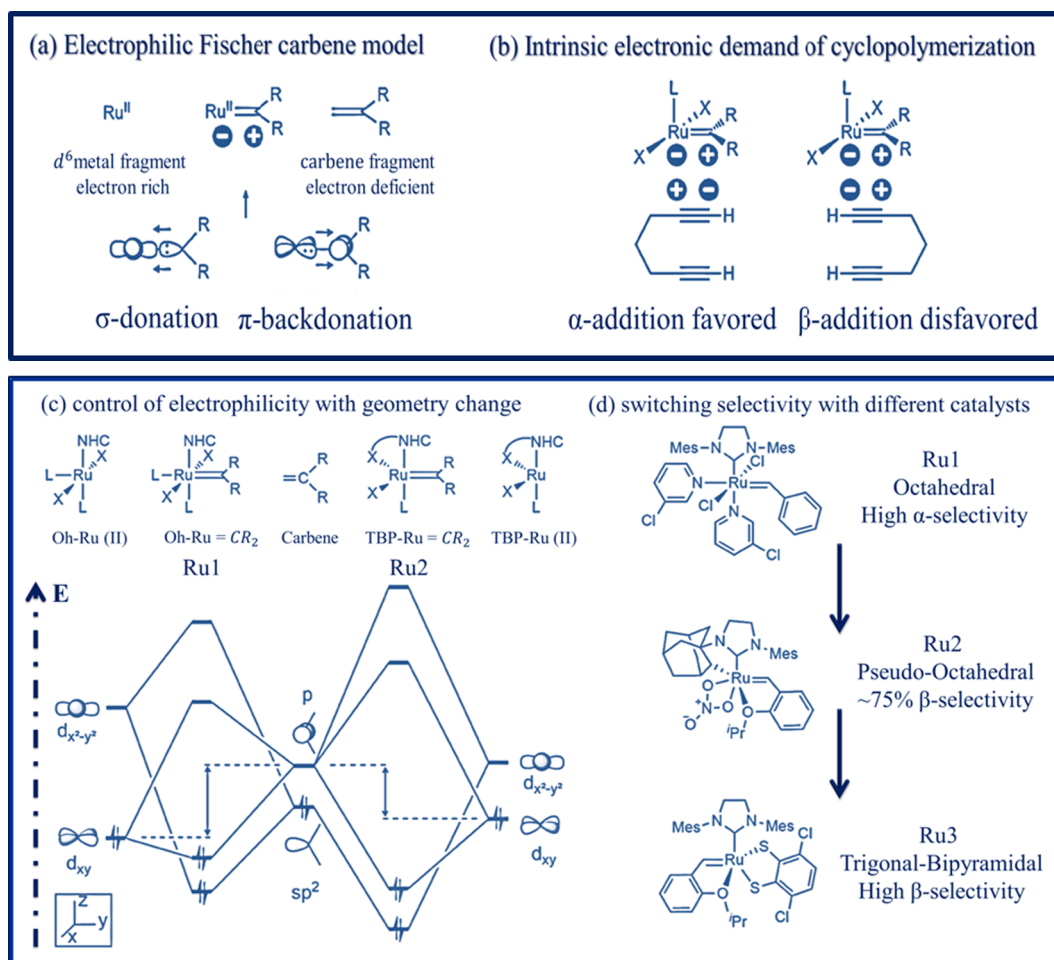


Fig. 3. (a) Electrophilic Fischer carbene model, (b) copolymerized PHD intrinsic electronic demand, (c) control of electrophilicity with geometry change, (d) Different geometries possessed switching regioselectivity of Ruthenium-catalysts. (Copyright permissions: <https://doi.org/10.1021/jacs.7b11968>).

a topological kink as a defect can lead to a single or pair of an electron in the backbone structure of the conjugated system, the mass of soliton is small having a domain wall of predefined carbons making it kink mobile [98,99]. Odd number of carbons generally leads to the solitons in a backbone chain of polymer (for example: existence of odd-number of carbons in a PA and possibility in poly(1,6-heptadiene), and its derivatives) arising from chain oxidation or chain cleavage or chain reconstruction, the solitons created in other way are called as anti-solitons, therefore even-numbered carbons reside on the backbone chain of the molecule. These dual states lead to breaking of double bonds in a polymer molecule soliton or anti-solitons as result conduction of electrons [100]. The bipolaron rendered doubly charged state (spin = 0) forms two positive solitons on a conjugated chain network further responsible for the electronic conduction [101]. Like charges repels each other present on the same chain and then move back respective to their other half of bipolaron due to their repulsive forces. Another mean, especially separated combination of positive charge and negative charge gives a polaron. These two types of solitons, such as charged solitons, create a defect, thus the spectroscopic study reveals that these solitons induce conductivity and are preeminently depends on the doping level and doping mechanism, for example, light doping exhibits the charge stored in polaron and likewise high level of doping exhibits charge stored in the bipolaron [102]. Rigid band of PA and PA derivatives is similar to semiconductors. In $-(CH-CH)n-$ structure, atomic orbitals are classified as n-anti-bonding (conduction orbitals) and n-bonding (valence orbitals) and are derived from the $2n$ -huckle type atomic orbitals [103]. Therefore, organic molecule band gap energy, i.e., in-between lowest occupied orbital of the molecule (π^*) and

highest occupied molecular orbital (π) decrease while double bonds and conjugation lengths are increased. For example, trans-PA (Fig. 4(a)) exhibits 1.4 eV, and cis-PA exhibits 1.8 eV for an infinite – degree of conjugation [104]. Herein, when PA or its derivatives are excited by external means either electrical forces or thermal forces, though the chain relaxation of electrons relaxes to a mid – gap energy level, re-organization of backbone chain results in the bond alteration and consequently, bond electrons can conduct from valence – band to conduction – band. This suggests that the highest occupancy of conjugated double bonds leads to metallic state conductivity of PA derivative as in 1,6-heptadiyne. So, the conductivity of conjugated polymers, for example, PA or poly(1,6-heptadiynes) increases with incremental doping levels, and it depends on a wide range of doping elemental compatibility and further increment in doping level leads to metallic state conductivity. PA and poly(1,6-heptadiynes) can absorb light at the highest level of doping where concentrations are usually measured in the form of molar fractions. However, at a high level of concentrations, though the polymeric systems exhibit metallic conductivity, high concentrations induced major structural changes to impede the conductivity at low temperatures [105]. At a higher level of doping, the formation of solitons resides on the chain begin to overlap. During these overlapping, the whole backbone chain structure experiences overall suppression, consequently changes insulator state to the metal transition state and then the chain can provide conductivity at room temperature in the metallic regime [100]. The charge transport occurs down to the backbone in PA or poly(1,6-heptadiynes); however, the probability of PA chain to fold back into themselves can be made by introducing different molecules or dopants via different synthetic

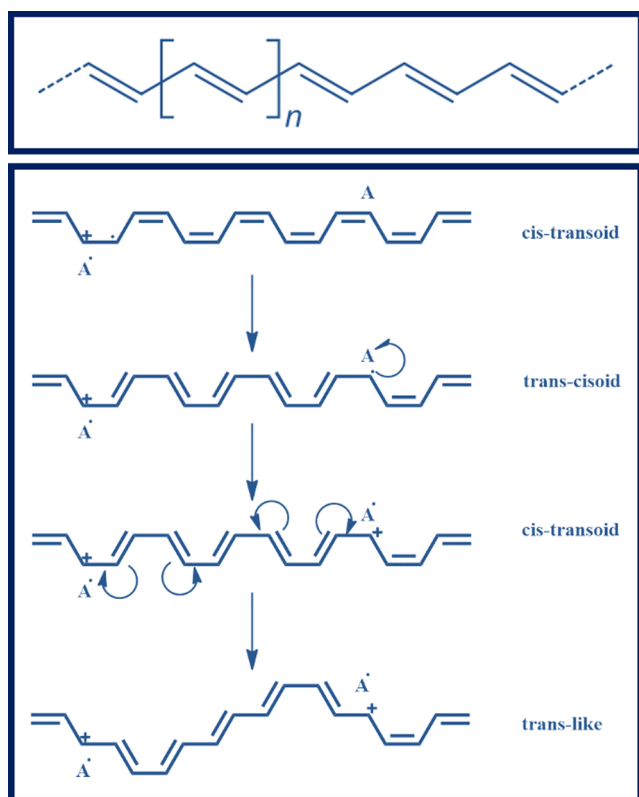


Fig. 4. (a) Trans-polyacetylene structure. (b) cis – trans doping enabled PA isomerization.

routes. This induces probability of electron to jump to another chain when they are intrinsically connected which, as a result attains the ability to conduct electrically. This can be attained by maintaining close contact and the right geometrical factors of backbone structure, which are necessary conditions for charge hopping [106]. In the backbone chain, hope phenomena can also depend on alignment between chain, degree of crystallization, and conjugation length [107].

4. Molecular mechanism for moletronics, 1,6-heptadiyne, it's derivatives compatibility

Since last 20 years, monodispersed polymeric systems has been developed via ring-opening-metathesis-polymerization (ROMP) [108–112]. Under mild conditions, not only macromolecule of defined length is attained but also key-metal-alkylidene permits sequential attachment of additional blocks. This advancement in synthesis probably allow moletronic molecule fabrication, where molecular electronic potential (MEP) is an important task to understand molecular electronic properties. Molecule's electron-withdrawing and gaining further enable us to understand interatomic interactions [113]. Additionally, well researched molecular electron configuration also elucidates accurate switching mechanism. However, MEP voltage illustrates complicated-topology and this is different from an exponential decay or decreases as expected from the linear or bilinear electronic components [113]. Thus, experimental results are different from theoretical results, for example, Tour *et al.* described theoretical concepts of the single molecular potential profile, which was performed under an applied voltage [114,115]. This suggests that the molecule exhibits different functional characteristics (storage or switching), which are beneficial for moletronic applications. Also, the electronic performance of benzene rings was investigated by Seminario and Derosa *et al.* which suggests that the benzene rings with nitro and amine groups render negative ions that are more stable than the neutral state of the same benzene ring. Thus, different single stable molecules exhibit different electronic properties, which can

behave as memory device. The main advantage of this molecule is that they exhibit storage or switching properties [116–118].

Thus either experimental or theoretical switching/storage performance of a molecular system chiefly depends on potential molecular profile, the MEP of potential 'V' indicates that at any point of radius 'r' induces by a molecule system (nuclei is surrounded by the electrons) which is also known as quantification of electron density, can be mathematically expressed as in Eq. (1) [113].

$$V(r) = \sum \frac{Z_i}{|R_i - r|} - \int \frac{\rho(r')}{|r - r'|} dr' \quad (1)$$

In Eq. (1), $\rho(r)$ is the density, which can be obtained from the molecule wave function. The distinguishing site of positive and negative potentials corresponding to molecular energy potential for doublet and triplet excited molecule exhibits electronic potentials, which is strictly describing that any molecule or atom could be used as electronic devices. Thus the growing of molecule technological advance demanding for the fabrication of molecular electronics, for example, logic gate operation with electronic potentials are feasible, etc. [119]. A simple operation of Trifluorobenzene molecule, which could be a thought of futuristic molecular electronic device and is shown in Fig. 5. In this case, the trichlorobenzene molecule can be excited by two water molecule MEP, which is located as two types of four possible inputs for the trichlorobenzene molecule leads to an AND gate operation (Fig. 5: AND logical gate). Herein, considered water molecule as an input to excite the logical gate operations. Likewise, we can also use HCl or similar molecules with a positive or negative potential profile. The expected logical gate inputs are $V_1 = 0$ and $V_2 = 0$ yields output = 0, likewise $V_1 = 0$ and $V_2 = 1$ yields output = 0 which is in symmetry to $V_1 = 1$ and $V_2 = 0$ that yields output = 0 and $V_1 = 1$ and $V_2 = 1$ yields output = 1.

Gibson *et al.* demonstrated the copolymerized 1,6-heptadiyne molecule, homogeneous Ziegler – Natta catalyst solution leads to metallic luster enabled insoluble free-standing film via 1,6-heptadiyne molecule. The experimental results suggest that these molecular system via doping mechanism enabled by acceptance treatments produce high conductivity of about $\sim 1 \text{ S cm}^{-1}$. Further, these results revealed that the number of divergences are attained in molecular and solid-state structure via cyclopolymerization. The differentiation in the structure was manifested by differential scanning calorimetry; the measurement outcome demonstrated that the PHDs exhibited two different structures at different temperatures of 107 °C and 275 °C. In which, exo-double bond rearrangement of polymer leads to helical to a more planar backbone structure was attained at a lower temperature (107 °C). It was therefore believed that the process was exo to endo transition influenced by the backbone structure of 1,6-heptadiyne. The exothermic

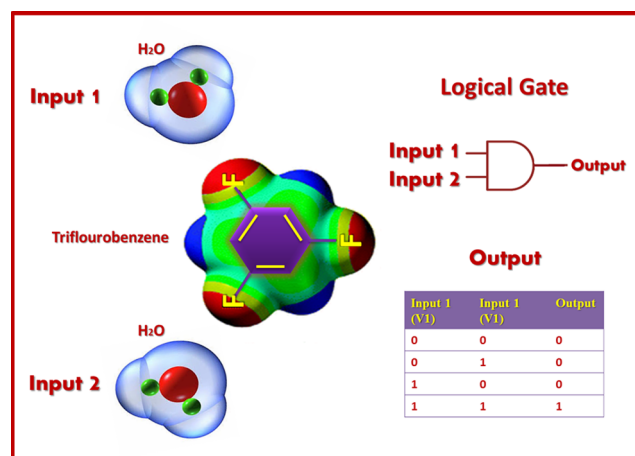


Fig. 5. Logical AND gate operation of trifluorobenzene molecule [120].

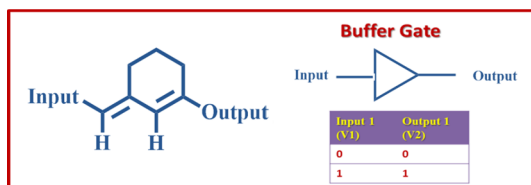


Fig. 6. The exothermic process enabled 1,6-heptadiyne planar structure (moletronic switch) [121].

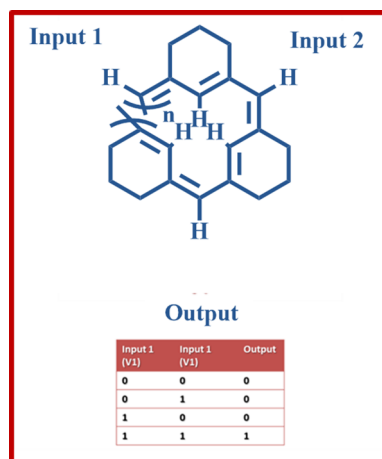


Fig. 7. The endothermic process enabled 1,6-heptadiyne helical structure (moletronic logical gate) [121].

process enabled 1,6-heptadiyne planar structure and endothermic process enabled 1,6-heptadiyne helical structure which has been illustrated in Figs. 6 and 7. The illustrated different copolymerized 1,6-heptadiyne structures possessed different characteristics which could be possible potential candidates for moletronic switch (buffer logical gate) and moletronic logical gate (AND logical gate), analogous molecular electronic operations are illustrated in Figs. 6 and 7 [121]. Curcumin: 1, 7 - bis - (4 - hydroxy - 3 - methoxyphenyl) - 1, 6 - heptadiene, - 3, 5 - dione which was established in 1910 and till date the technological advancement in curcumin structure and its properties suggest that these compounds and its derivatives has tremendous medicinal characteristics due to potential biological activity. Chemical modification induced curcumin derivatives have been developed for various applications, for example water-soluble polymorphs of curcumin [122], curcumin nanoparticles for cellular uptake improvement [123], and nano-formation of curcumin as a cancer medicine [124]. Also, this compound was well explored in moletronics application, for example, Kim *et al.* reported NOR logical gate using curcumin in aqueous solution with Hg^{2+} [125], this logical gate was implemented in electrochromism cell where curcumin- Hg^{2+} complex compound was sandwiched in-between indium tin oxide electrodes. Electrochromism is a reversible change of the absorption spectrum of a substance due to the application of potentials leads to electrochemical redox reaction [126]. These logical gate functions exhibited curcumin compound suggest that if relative modification of backbone structure of curcumin is enabled by 1,6-heptadiynes rather than 1,6-heptadienes, the resulting compound could lead to logical AND gate functions and the proposed structure based of 1,6-heptadiynes has been illustrated in Fig. 8.

Molecule realized rods provide an opportunity to connect two-functional moieties at a defined length to enable desired functional characteristics and such types of molecular rods are extensively explored and are demanded in areas of material and in life sciences. For example, Tour *et al.* explored molecular electronic wires concerning single or small packets of the molecule as a fundamental unit can able to conduct and

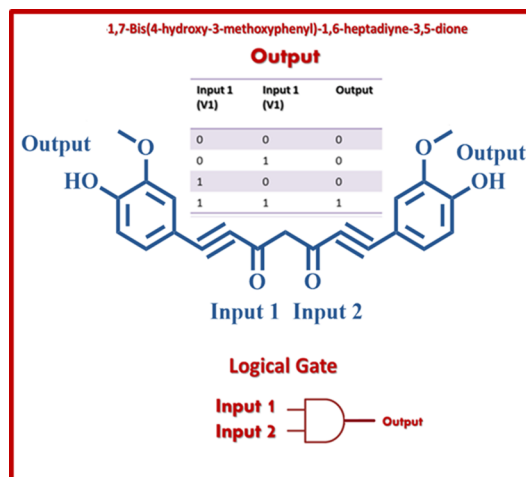


Fig. 8. Curcumin modified via 1,6-heptadiyne molecule.

switch electronically [127]. In biological-sciences, such kind of wires or rods have been used as a mediator to mimic biological-functions, for example synthetic ion channels or wires or rods in bilayer membrane to mediate ion transport or electron transport [45,128–132]. A new class of molecular rods are six- and five-membered ring saturates joined in a helical or straight planar direction have been explored by the researchers, these backbone structures enabled electronic and optoelectronic properties with the aid of 1,6-heptadiynes can be attained via conditional synthetic routes [68,133]. However, the molecular structure clarifies the size of the molecule, and it is clearly described that the probability of molecule adopts with another molecule, thus research reports suggests that the 1,6-heptadiynes can easily be coupled with the other molecule bearing with the alkyl moiety established by a most relevant synthetic click reaction [68,134–137]. This further suggests that a wide range of 1,6-heptadiyne derivatives can be feasible with the compatible doping elements which leads to desirable functional electronic properties rendered electronic devices. This propounds that 1,6-heptadiyne and its derivative systems with functional moieties could lead to functional moletronic applications, however for connecting two different sections/components or molecular electronic devices, switch as a junction is desirable to comprise at least one material specifically, in molecular electronics one molecule, such kind of molecule realized electronics were widely explored [138,139]. Meiran *et al.* demonstrated ionic PAs via metathesis polymerization of dendronized triazolium functionalized 1,6-heptadiynes (Fig. 9).

The results suggested that the dendronized triazolium functionalized PHD exhibits relatively high intrinsic ionic conductivity 7.3×10^{-5} , further, they have improved conductivity to 1.4×10^{-4} via doping of lithium bis(trifluoromethanesulfonyl)imide. The improved conductivity is attributed to the dual conductivity states, such as ionic and electronic conductivity i.e., 7.1×10^{-5} and $5.0 \times 10^{-5} \text{ Scm}^{-1}$ [140]. Similarly, other research group demonstrated mono or bidisperced ionic polyacetylenes (iPAs) with branched 1, 2, 3 - triazolium pendants via cyclopolymerization induced relatively rich intrinsic conductivity of about $1.4 \times 10^{-5} - 2.1 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and experimentally

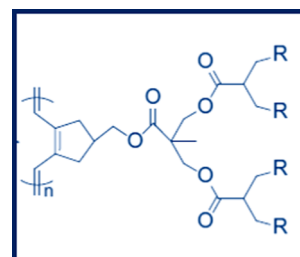


Fig. 9. Dendronized triazolium functionalized 1,6-heptadiynes.

proved that the conductivity can be improved via doping with lithium bis(trifluoromethanesulfonyl)-imide, which had improved ionic conductivity ranging between 2.5×10^{-5} – 4.3×10^{-5} S cm⁻¹. Further, increment in doping level has lead to two states of conductivity i.e., ionic and electronic conductivity in the range of 4.5×10^{-5} – 7.1×10^{-4} and 1.5×10^{-6} – 4.5×10^{-6} S cm⁻¹ respectively. The above experimental delineations suggest that desired level of doping in conjugated polymeric systems for example PHDs, could lead to two different energy state characteristics, such kind of two energy levels exhibited molecules that could be promising candidates in the field of molecular electronic switches or wires or interconnects [141]. However, both experimental and theoretical concepts are elucidating that the molecule conductivity depends on the various factors including the molecule-electrode coupling strength, charge transport pathway, the energy of molecular frontier orbitals and electron spin state [33,142]. Among them, molecule-electrode coupling strength is a considerable important characteristic to maintain efficient operation applicable to wide molecular applications. Recently, researchers have developed molecular level electrodes with hydrogen-terminated Silicon-100 (Si(1 0 0)) with 1,8-nonadiyne with robust-surface, where the oxidation is not evident. Also, they have extended the research to investigate functional properties of diverse chain lengths of α,ω -diynes (for example 1,15-hexadecadiyne, 1,10-undecadiyne, 1,8-nonadiyne (ODY) (Fig. 10) and 1,6-heptadiyne (HDY)) under different experimental-test conditions rendered reacting hydrogen-terminated Si(1 0 0).

The diyne monolayers showed oxide levels below the X-ray Photoelectron Spectroscopy (XPS) detection limit with lengths ranging from 7 to 11 carbons, results indicate that the apparent rate of electron transfer is affected not only by the self-assembled monolayer thickness but also the presence of tiny oxidative defects act as electron hopping between ferrocene hotspot moieties [45,143]. These defects induced monolayers facilitate excellent coupling strength along with the improved conductivity, hence such type of molecular level electrodes are potential candidates of key applications at the interface of biology and electronics, for example polymer electrodes are feasible in neurological diseases treatment, to record and stimulate nerve activity [56,143]. Furthermore, these attractive organic molecules due to their mixed condition rendered distinct properties, i.e., the ability to transport both electron/holes and ionic species are potentially required for molecular electronics [56,144]. Also, properties such as chemical reactivity or wettability tuning by changing their oxidation state via doping mechanisms are promoting or hindering of biomolecule adhesion [56,144]. This feature especially valuable for improving the biocompatibility of implantable-electrodes [56,144]. The probability of these all functionalities could be attained via doping mechanisms of 1,6-heptadiynes. Hence 1,6-heptadiynes and its derivatives could be a potential electrode material for enhancing the biological activity due to its intermolecular forces driving the moieties towards hydrophilicity or hydrophobicity. In molecular electrodes, charging mechanism is significant for switching, molecular charging charge transfer may probably occur via electron-donor-acceptor complex, which is an association of two or more molecules or of different parts of one large molecule in which fraction of electron charge is transferred between molecular entities followed by the generic reorganization. Moreover, it probably attains from external gating mechanism where Fermi level of contacts leads to changes in the energetic position of the molecular energy level renders electron charging [24]. Recently conjugated cyclopolymer with

bulky substituents was synthesized via the Molybdenum chloride: MOCl_2 -catalyzed diethyle-dipropargylmalonate and 4,4-bis[(tert-butyl)diphenylsiloxy)methyl]-1,6-heptadiyne and the synthesized polymer showed a characteristic UV-visible absorption band and absorption maximum value of 507 nm. Photoluminescence spectrum exhibited maximum peak at 594 nm corresponds to the photon energy of 2.09 eV and band gap of the cyclic copolymer was 2.01 eV the [145]. Such types of polymeric systems are extensively utilized in electrochemical gating systems in the molecular level, this approach of molecular junction is immersed in an electrolyte, where molecule connected in between two-metal-electrodes as drain and source electrodes. Since the electrochemical electrode module the atomic-bridge through the arrangement of twofold layer, it is displayed as a more proficient electivity to control charge transport with independent electrochemical potential control of source and drain [33,139,146]. However, both ionic and electronic conductivity plays a role in molecular gating systems. Recently researchers have utilized click chemistry to synthesize branched triazole group via a controlled approach for HD substituent. Monomer cyclopolymerization is favored without weakly coordinating branched-triazole itself can stabilize living propagating chain to generate pendent-enbale polyacetylene with five-membered-ring repetition-units and trans-double-bonds. Bis(trifluoromethane)-sulfonimide lithium doped acetylenes experimentally proved ionic conductivity is 2.45 to 1.8×10^{-6} S cm⁻¹, further iodine doping leads to electronic and ionic conductivity states of 1.2×10^{-7} S cm⁻¹ and 1.3×10^{-5} S cm⁻¹ respectively at room temperature [147]. Also, Wu *et al.* synthesized branched 1,2,3-triazolium functionalized polyacetylene with enhanced conductivity. Monobissubstituted HD undergo to produce ionic-PAs with branched-1,2,3-triazolium-pendents cyclopolymerization, this polymer gives high-intrinsic-ionic conductivity between 1.4×10^{-5} to 2.1×10^{-5} S cm⁻¹ at 300 °C. Further doping this polymer by lithium – bis(trifluoromethanesulfonyl)imide leads to superior ionic-conductivity between 2.1×10^{-5} – $4, 3 \times 10^{-5}$ S cm⁻¹. The reported doping mechanism elucidating electronic and ionic conductivities ranging between 1.5×10^{-6} – 4.5×10^{-6} S cm⁻¹ and 4.5×10^{-5} – 7.1×10^{-4} S cm⁻¹ [141]. Further this result suggest that the PAs derivative as 1,6-heptadiyne act as two energy state instigated new electrolytic material for molecular gating systems thus experimental evidence propound that probability of 1,6-heptadiynes could be a functional material for molecular electronic devices [147]. Recently, Song *et al.* developed bridge-like structures via metathesis-cyclopolymerization, with the high-resolution transmission electron microscopy (HRTEM) analysis propose that the parallel stripes like ladder in the same direction attributed flat aromatic perylene bisimide (PBI) core close edge on orientation with respect to the substrate surface and strong interaction is present between the molecules. Presumably, π - π interactions between the polymeric backbone in the horizontal dimensions may account for this highly oriented ladder like morphology with a ladder length of around 4.1 nm and each ladder consists of 12 monomeric units [148]. Such a kind of ladder network form of polymers and their binary blends were widely explored for molecular electronic devices due to their ladder structure endows a smaller optical band-gap, greater electronic delocalization and substantially enhanced electron transport [149]. Similarly, ladder like polyacetylene with excellent optoelectronic properties and regular architecture was developed by Song *et al.* [150]. Novel double slandered polyacetylene with perlene bismide bridge has been efficiently synthesized by metathesis

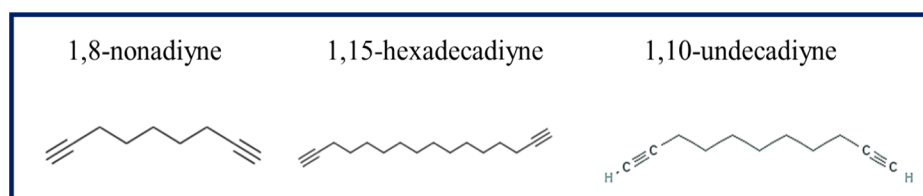


Fig. 10. 1,8-nonadiyne (ODY), 1,15-hexadecadiyne and 1,10-undecadiyne structures.

cyclopolymerization of bis(1,6-heptadiyne) derivatives and exhibited good solubility, highly thermal and oxidative stability low LUMO energy levels narrow bandgaps [150]. Therefore the new type of ladder like PA bearing PBI bridge would be expected as the attractive alternative to fullerenes as photovoltaic materials and also may be used as the constructing unit to build complicated new polymers enabled future molelectronic systems [150]. Though Grubbs catalyst gives efficient cyclopolymerized products, only expensive and highly active Grubbs-catalyst enabled N-heterocyclic carbines are known to efficiently stimulating cyclopolymerization. Well controlled cyclopolymerization via 3G-Grubbs-catalyst is a fast-initiating and widely coordinating pyridine additives as stabilizing agents in noncoordinating solvents or widely coordinating in tetrahydrofuran solvent. These advances in cyclopolymerization enhances scope of monomer, which reduces complexity of resulting polymer to produce various brush structures, bridged, star-shaped, and ionic-PAs and heterostructures as well [151]. Star kind of advanced architectures of block-copolymers have been explored via cyclopolymerization technique. These advanced architectures and nanostructural forms are attained due to the inherent properties of controlled cyclopolymerization technique. Cyclo-polymerization living nature enabled block-co-polymers leads to substituents facilitated brush and dendronized-polymers, similarly, monomer crystallinity or insolubility lead to spontaneous-self-assembly polymers into various 1 or 2D nanostructures [68]. Structural-diversity of functional PAs by preparing blockcopolymers (BCPs) via cyclopolymerization has been well explored along with varying ring sizes of BCPs with various doping elements. 5-, 6-, and 7-membered-ring triblock-copolymers were also expounded via sequential-polymerization of heptadiyne, octadiyne and Nonadiyne. All the above results suggesting that the conjugated block-copolymers with divorce functionality obtained via cyclopolymerization. Moreover, dendronized and brush polymer nanostructures are interesting morphologies realized via cyclopolymerization technique. It suggests that when the dendronized polymers via graft through approach, it produces well-defined nanostructures of defect-free-dendrons, also dendrone are located in each repeating unit. Prepared functionalized heptadiynes were realized by the researchers with the aid of second/third-generation ester based dendrones with elongated-structures due to its steric-repulsion between dendrones. Further researchers have synthesized brush kind of structures via cyclopolymerization and using living ring polymerization, from heptadiynes initiators, poly(ϵ - caprolactone) and poly(L - lactide) macro-monomers were prepared. Using Hoveyda-Grubbs Second Generation (HG2) they have produced insulated molecular wire architectures as their backbones conjugated structures are insulated via non-conjugated-macromolecules [68]. Thus experimental reports suggesting that the complicated nano-structures which are preeminently required for molelectronic devices could be possible via cyclopolymerization. Further this experimental evidence revealing the probability of implementation of 1,6-heptadiynes to the functional molecular electronics. Moreover, in recent years, polymer's self-assembly into a nanoparticle has been renewed research it facilitates accessing of various intriguing advanced-nano-structures. Recently Choi *et al.* investigated and envisioned that using cyclopolymerization as new process to produce new monomers or polymonomers lead to semi-conducting nanostructures as nano-particles. Meldrum acid was used for preparing of HDY based blockcopolymer (BCP) in which which they have observed spontaneous

micellization during cyclopolymerization. For more example: the cyclopolymerization of neoheptyl side-chains with fluorine moiety enabled HDY monomers led to the formation of two-dimensional (2D) nano-sheets with different solvents enabled shape variation was observed. By adding increased phenyl groups between neoheptyl-side-chains and fluorine-moiety, tunable width enabled one-dimensional (1D) nano-ribbons were obtained via in-situ-nanoparticlization conjugated-polymers (INCP) mechanism [152]. This describes conjugated BCPs having polyene-backbone potentiality for investigation of various-nano-structure morphologies via phase-separation. 1D-organic nanowires have been developed for nano-electronics by various organic-semiconductors. For example; to prevent shortcircuits in nanoelectronics, insulated form of nanowire has been developed. That is the versatility of cyclopolymerization for producing different nanostructures could facilitate for future electronic device realization [68]. Furthermore, generated potential instigated wide spectrum of chemical molecule investigation could be possible via nanostructures. Nanogenerator, these can generate change electron motion via changes in molecules or gaseous species. Generated voltage probably due to their change in dipole-moment and interacted surface-area [153]. Recently semiconducting polymers have been widely explored due to their strong driving force for self-assembly, although various reports on successful self-assembly of nanostructures using semiconducting polymers, direct in-situ self-assembly of these polymers into two dimensional nanostructures have proven difficult. Recently, Yang *et al.* reported the synthesis of a simple conjugated homopolymer by living cyclopolymerization of a 1,6-heptadiyne and its efficient in-situ formation of large surface area 2D fluorescent semiconducting nano-structures. It is observed that solvent dependent self-assembly behaviour of homopolymer i.e., starting polymer formed 2D nano-sheets with different shapes, such as rectangle, raft, and leaf when dissolved in different solvents. This study providing importance insight for their shape modulation during the self-assembly could be a possible candidates for fabricating nano-generators for biological functions as well as for electrical components [86]. Overall these experimental evidences suggesting that the versatility of cyclopolymerization for preparing various semiconducting nanostructures leads to future molelectronic component [68]. Though polymerization of 1,6-heptadiynes by Ring Closing Metathesis Polymerization has been attracted due to its unique way of generating conjugated polymers with multiple functionalities [55,145]. Its optical property to its functionality leads to molecular electronics for frequency domain optical storage. It is believed that the functionality defined local environments of wide derivative induced various molecules to absorb slightly different laser frequencies even though the same electronic transition is being probed. In effect various bits are addressed by the laser frequency or wavelength at which they are stored, hence the name frequency domain optical storage [145,154]. However, researchers have reported that the conformational behavior of conjugated polymers differ from classicrandomcoilmodel due to π - electron delocalization derived longer persistence lengths [155]. These results suggests that the polymeric systems exhibit electronic and optical characteristics, which are altered because of their combination of conformation of single-chain and individual-chains interactions within a single system [156]. Similarly, Choi *et al.* demonstrated model polymer (poly(dihexyldipropargylmalonate)) coil to rod formation, then the measurement was conducted to reveal absorption spectra at

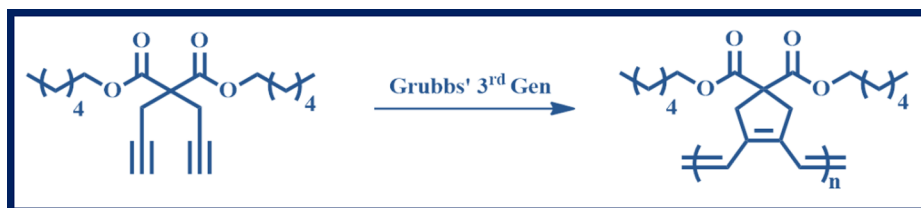


Fig. 11. Synthesis of PDHDPM 1,6-heptadiyne.

different aging times in tetrahydrofuran (Fig. 11).

Theoretical estimation of configurational displacement can be attained by 'S' Huang Rhys Factor via potential energy curve upon excitation, which elucidates conjugated polymer conformational disorder [157]. Increase in absorption spectra described intensities of 0–0 vibronic peak lowers the 'S' value and commensurate to more extended conformation for CPs. When a dilute solution was aged, λ_{max} of 0–0 vibronic peak shifted (~ 13 nm) and the vibronic signal increase was perceived with aging time. 'S' can be easily calculated from the relative intensities of 0–1 and 0–0 vibronic peaks in absorption spectra, the mathematical representation is given as $\frac{I_{0-1}}{I_{0-0}} = S$. Moreover, SEC-viscometry suggests that α as a coil to rod transition shape parameter and dynamic light scattering (DLS) was used to measure the hydrodynamic radius of polymer with the decrease in S and the shift of SEC trace to the left concerning aging, which further support confirmation transition. For poly-(dihexyldipropargylmalonate) (PDHDPM) and poly-(cyclopentenylene-vinylene) (PCPVs) (Fig. 12(a) and (b)), this correlation between S and α suggests coil to rod transition in cyclopolymerized conjugated systems with a five-membered ring structure [158].

This method of experimental and theoretical analysis and confirmation of coil to rod transition suggests that the cyclopolymerization assisted heptadiynes coil to rod formations activity could be predicted based on experimental and theoretical distress factors and this makes molecular rods or molecular wires or switches favorable for moletronics in electronic components. Molecules contain conjugated-linear- π -network lead to excellent electronic properties [159,160]. For example, alkylidene catalyst enabled PHDs such as poly[dialkyl dipropargylmalonates] are via cyclopolymerization. Also, these polymers and its derivatives exhibit highly conjugated structures, which are relatively stable in air-environment [54,67,121,161,162]. Czekelius *et al.* investigated five-membered ring polyene oligomers with ~ 15 double bond configurations forming PHDs via cyclopolymerization of diisopropylidipropargylmalonate. Wittig like reactions were introduced between aldehydes and Molybdenum-alkylidene to produce oligomers [163]. Moreover, Scriban *et al.* demonstrated improved conjugated chain in oligomers of 1,6-heptadiynes having ~ 23 double conjugated bonds via wittig-like-reaction between aldehyde-capped-oligoenes and bimetallic-molybdenum-alkylidene compounds and relative structures were alternative to cis-trans conjugated double bonds. Molecular weight and optical measurements were similar to that of polyenes and carolenoids, which suggested that electronic transition energies depend on conjugated lengths. Thus, the study revealed different energy-related even allowed transitions with the bond length ranging from 5 to 23 indicate that the asymptotic-convergence [164]. Such type of improved conjugated double bonds via conditional synthetic processes facilitate for further improvement in electronic conductivity and structural stability, which leads to efficient stabilized moletronic activities under critical conditions. Improved conjugated lengths can be further assessed via HOMO-LUMO energies, for example phosphole analog of pyrrole possess low lying LUMO due to σ - π orbital interaction between phosphorus centre and the polarizable diyene, the HOMO-LUMO energy level of phosphorus and polarizable dienes can be controlled by chemical functionalization at their centre and these

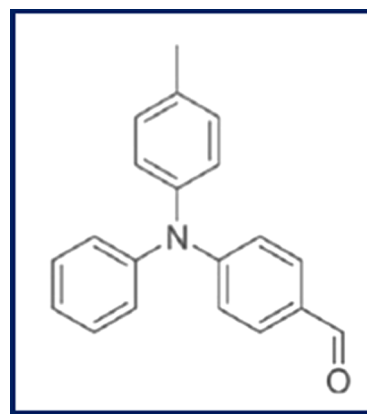


Fig. 13. Triphenylamine-functionalized polyacetylenes (TPA-PAs) structure [170].

properties of phosphorous are essential for construction of optical and electronic materials [165]. Significant efforts have been made by the researchers to access interesting optoelectronic properties via π -conjugated systems with various structures. Introduction of siloles and germales into a conjugated system is of potential interest and computational studies suggest that derivatives from 1,6-heptadienes have small band LUMO energy [68,103,105,166–169]. Triphenylamine-functionalized polyacetylenes (TPAs) by third-generation Grubbs-catalyst via metathesis-cyclopolymerization produces 1,6-heptadiyne derivatives; this synthetic selectively generates the TPA-PAs (Fig. 13) with five-membered-ring and trans-microstructure.

The results were suggesting that the TPA pendants endowed PAs with good-solubility and excellent optoelectronic properties (absorption wavelength: 592–605 nm in chloroform, -5.0 eV of HOMO energy level and energy band gap range: 1.82–1.77 eV). When bis-TPA side group introduced into the PA backbone, the resultant polymer displayed desirable oxidative stability and high fluorescence quantum yield among the PA derivatives family. Also, the polymer exhibits spontaneous-self-assembly with the specialized nanocylinder-architecture without requiring tedious post-synthetic treatments. Thus immobile and rigid conjugated PA segment assembled into the novel cylindrical nanostructure with π - π transition-interaction of TPA side groups [170,171]. This can be expected with the incorporation of conjugated units that lead to novel charge transport properties for use in molecular electronic devices [172,173]. The intermolecular zirconocene coupling of 4,4-bis(hexyloxymethyl)-1,7-bis-p-halophenyl-1,6-heptadiynes introduces 2,5-bis-p-halophenylzirconocyclopentadienyl, which undergoes efficient transmetalation with GeBr_4 . Resulting derivative after metallization i.e., bis-p-halophenyl-2,5-germales were induced by dihalogermoles with MeLi lead to poly(2,5-diphenylgermole) (Fig. 14) with excellent optical properties and exhibited efficient photoluminescent characteristics at the high molecular weight ($\phi = 0.79$) [174].

Moreover, the third-order optical nonlinearity was investigated by Park *et al.* [175] According to this research report, the soluble conjugated structure induced large third-order-optical-nonlinearity was attained via cyclopolymerization of 4,4-disubstituted-1,6-heptadiynes and further suggested that optical properties were dependent on chemical

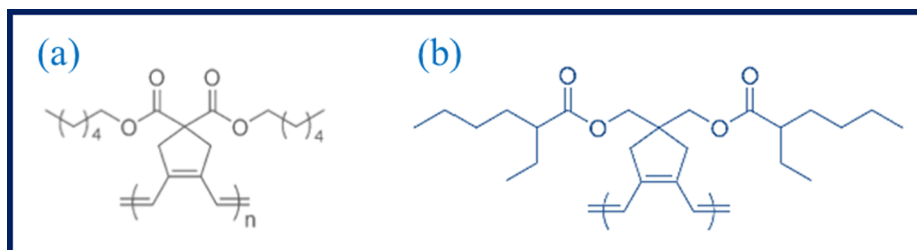


Fig. 12. (a) Poly-(dihexyldipropargylmalonate) (PDHDPM) and (b) poly-(cyclopentenylene-vinylene) (PCPVs) structure.

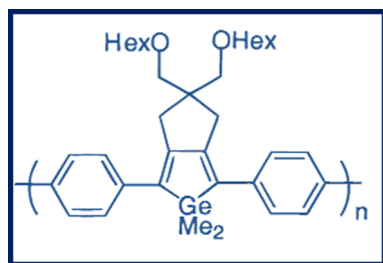


Fig. 14. Poly(2,5-diphenylgermole) structure.

structure configuration. Thus, $\pi - \pi^*$ conjugated chain transition induced π -electrons lead to optical absorption peak at 540 nm. Nevertheless, the optical density dependent on the substituents molar configuration thus third-order non-linear optical-coefficient was observed to be $2.6 - 6.5 \times 10^{-11}$ [175]. These kinds of heptadiynes and its derivative systems resulted from conditional synthetic processes with various doping elements, and concentrations that could lead to improved functionalities such as electronic conductivity, photorefractive and photoconductive, optoelectric characteristics thereby realizing structural properties rendered molecular electronic devices.

Though organic heptadiyne systems provide excellent conductivity due to the flow of electrons by breaking the bonds down on the backbone chain, but inorganic semiconducting materials are used in various modern electronic applications, for example logical gates, molecular switches, light emitting diodes, printing electronic circuits [176–181]. To attain suitable organic material (1,6-heptadiynes) for those applications, chemical and physical configurations such as electronic structure and viscosity, melting temperature, glass transition temperature, morphology, oxidation stability, and thermal stability need to be improved, which can result in fine-tuning of materials for applications. Buchmeser *et al.* prepared diblock copolymers with 1,6-heptadiynes i.e., DEDPM to get fully conjugated diblock copolymer via selective α -addition comprising of five and six membered ring units. The results revealed that the formation of highly tactic polymers (> 80%) with predominantly trans-configured exotic double bonds [182]. Such type of organic diblock or triblock copolymers suggested 1,6-heptadiyne compatibility with another molecule could lead to improved functional characteristics mostly required for moletronic operation. Moreover, a broad range of doping elements induces excellent electronic conductivity for applications while maintaining functional advantage and such type of moletronic application suggested 1,6-heptadiynes were extensively explored by the researchers. Firstly, cyclopolymerized ω -diynes was used to derive a special kind of PA. In 1961, researchers polymerized cyclically conjugated 1,6-heptadiynes ($X = CH_2$) by Ziegler – Natta catalysts [183], the synthesized conjugated polymeric system was in red and soluble and the conductivity was around $10^{-10} - 10^{13} \text{ S cm}^{-1}$. Later on, Gibson *et al.* demonstrated the conductivity, which is due to exo-endo double-bond location and proposed that the maximum conductivity is due to the chemical rearrangement of catalyzed dopant. Saturated solution of iodine was used during temperature (at -78°C) enabled doping process which exhibits conductivity of 0.4 S/cm and upon rising temperature from 0 to 25°C the conductivity began to decrease [121]. However, the value of >0.4 S/cm at -78°C transforms to >4 S/cm at 25°C , in spite of differences in solid-state and molecular configuration, this doping attributable to the chemical-rearrangement absence to bring about the same level of conductivity as PAs [121]. Moreover, Palladium (Pd(II)) based catalyst doped α,ω -diynes have been demonstrated, these monodisperse diynes solvable in organic solvents and are lightweight structure [184]. However, the cyclic structure was determined based on both cyclic backbone structure and side chain structure. Furthermore, Choi *et al.* demonstrated α,ω -diynes via synthetic cyclopolymerization route, which had induced various functionalities by doping of various catalytic systems, for example Molybdenum- and W-based catalysts etc. [94–96,185–187]. The number average molecular

weight of this polymer was about $\sim 10^5 \text{ g/mol}$. This α,ω -diynes were solvable and even exhibited high conductivity because of double bonds in a continuous backbone chain structure. Molybdenum(V) chloride ($MoCl_5$) and Tungsten hexachloride (WCl_6) catalysts were utilized to cyclopolymerize photoconductive monomer and a monomer containing nonlinear optical chromophores [188], and resulting polymer exhibited photorefractive and photoconductive properties. The maximum photoconductive properties was recorded at 350 nm and 700 nm. Moreover, photovoltaic properties were elucidated under lightweight conditions and the response was $\sim 640 \text{ nA}$ and photodark current ratio was established for undoped polymer in the range of 30 – 5. The gel-permeation-chromatography was utilized to find average number molecular-weight and it was around 23000–45000 g/mol and the poly dispersity index (PDI) was in 2.1 – 3.1 range. Schrock *et al.* cyclopolymerized diethyle dipropargylmalonate ($X = C(CO_2Et)_2$) using molybdenum catalyst [77] and C-NMR quantification results describe equal six-membered and five-membered ring structure. The selective five-membered ring structure arose from a tail to tail insertion similarly head to tail insertion to form a 2msix-membered ring structure. The cyclopolymerization of 1,6-heptadiyne, whose structure was unambiguously identified due to DEDPM [59,185]. This polymerization leads to the mixture of five and six-membered ring structure with the $Mo(N-2,6iPr_2-C_6H_5)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$. These structures can be identified with the aid of C-NMR spectroscopy since their carbonyl carbon and the quaternary carbon are especially sensitive to the ring size. Carbon resonates at 172.0 ppm (carbonyl carbon) and 57–68 ppm (quaternary carbon) which are the characteristics of the five-membered ring structure, similarly, 170.8 and 54 ppm are characteristics of six-membered ring structure. Cis/trans configuration of exocyclic-double-bond or backbone single bond s-cis-trans configuration in poly(cyclohex-1-ene-3-methyldiene)s and double-bonds configuration in poly(cyclopent-1-enylene-1-vinylene)s, has shown in Fig. 15. The reason of this variation in elements of symmetry are mirror planes, the axis of rotation and centers of the invention, which can be revealed by poly(cyclopent-1-enylene-1-vinylene)s, which further relate each repetitive unit to each other [189]. The cationic and anionic centres are constrained to the repeating units in the polymer chain. Thus monomers to tune the distribution of species along the polymer chain and modify the physical properties. The above all delineations and experimental evidence suggest that the 1,6-heptadiynes and its derivatives enabled under conditional synthetic environment rendered five- and six-membered ring instigated various kind of nanostructures with functional activities could lead to chief candidates for electronics.

5. Potential properties applicable to the moletronics

Current prestigious electronic technology is moletronics, which require adaptability, flexibility, and functionality of advanced resist materials that make them attractive. Material simplicity and novel functional properties well permit independent moletronic analogous/digital components to be dedicated for a wide range of electronic applications. Organic light emitting diodes (OLEDs) for flat panel applications and the most stringent conditions facilitated flexible devices that are fabricated by these molecules considering their functionalities. To gain equivalent functionalities and compatibilities in organic polymers concerning the traditional light emitting diodes (LEDs), including clarity, dimensional stability, thermal stability, barrier properties, solvent resistance, low coefficient of thermal expansion, smooth surface and electronic conductivity [190,191]. Polymer need to be mimicked to that of functional material. Many conductive polymers that have been synthesized are often based on five and six-membered ring structure to improve certain electronic features, for example band gap energy and electron conductivity such as polypyrrole, polythiophene, polyaniline, PA, and polyphenylenevinylene, these polymer structures have been illustrated in Fig. 16. Among them, though PA shows higher conductivity, solubility, low moisture and thermal stability and low processability, insufficient functional characteristics make them

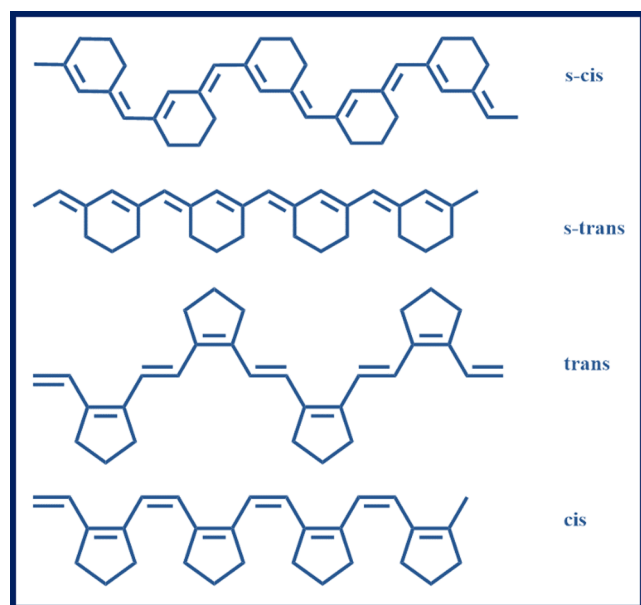


Fig. 15. Poly(cyclopent-1-enylene-1-vinylene)s and poly(cyclohex-1-ene-3-methylidene)s configuration probability.

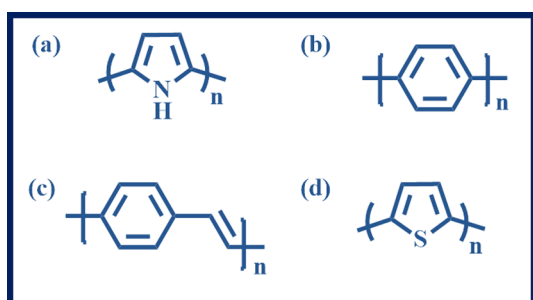


Fig. 16. Chemical structure of conjugated polymers (a) polypyrrole, (b) poly-paraphenylene, (c) polyphenylenevinylene, (d) polythiophene.

incompatible for the electronics even in moletronic devices [192]. Poly(1,6-heptadiynes) are derivatives of PAs, which provide a wide range of organo-solvent facilitated solubility, high thermal and moisture stability and high processability. Thus, poly(1,6-heptadiyne)s and its derivatives could be futuristic materials for moletronic devices and

components with considerable improvements assessed by the most feasible doping mechanisms enabled synthetic route as cyclopolymerization.

5.1. Thermal stability

Thermal stability is essentially required characteristic feature of a polymer that is useful during moletronic device fabrication and operation, polymers or their molecules are exposed to high thermal stress during the fabrication process of moletronic components or devices, for example barrier coatings [193], electrode deposition [194], patterning [195] and thin film transistors (TFTs) fabrication [196,197]. Particularly during TFTs fabrication, thermal and mechanical stresses are the most preeminent strategies which can change dimensional and structural parameters leading to heat dissipation that enabled inefficient electronic components or devices [198]. Therefore, during the selection of polymeric materials for moletronic, thermal factors need to be considered to avoid thermal and mechanical stresses. Polymeric materials with proper thermal stability such as coefficient of thermal expansion and glass transition temperature relate molecular chain relaxation of thermal stresses that are stored during the fabrication. Barriers or electrode coating layers enabled inorganic or metallic materials have a low coefficient of thermal expansion (CTE) than the organic materials, for example the dimensional change of polymer in polymeric substrates significantly starts at a glass transition temperature (T_g) (Fig. 17) [199]. Hence, the polymers with high T_g s are essentially required, such as polyethersulfone (PES) is possible suited in this regard. Though this polymer exhibit high T_g , the potential possibility of electronic conductivity is low, on the other hand poly(1,6-heptadiyne)s and its derivatives exhibit high T_g (Fig. 17) with excellent electronic properties similar to that of PAs which could be a potential candidate for moletronic [200,201]. Though high T_g is an essential parameter for moletronic, low coefficient of linear expansion (CLE) and coefficient of thermal expansion (CTE) are also administrable and advantageous for making dimensionally stable components for electronic devices with polymers [202]. However, different CLE and CTE of internal substrate layers leads to induced strain and cracking probability, which is probably due to thermal cycling during fabrication process hence leading to the deterioration of device functionality and efficiency. Therefore, polymeric systems that can withstand high temperature with low CLE and CTE are required for high-temperature process, for example low-temperature to high-temperature polysilicon (LTSP) process to enable film deposition and also, high-temperature stability enabled plastic substrates with low CTEs: $10-20 \frac{ppm}{K}$ or less

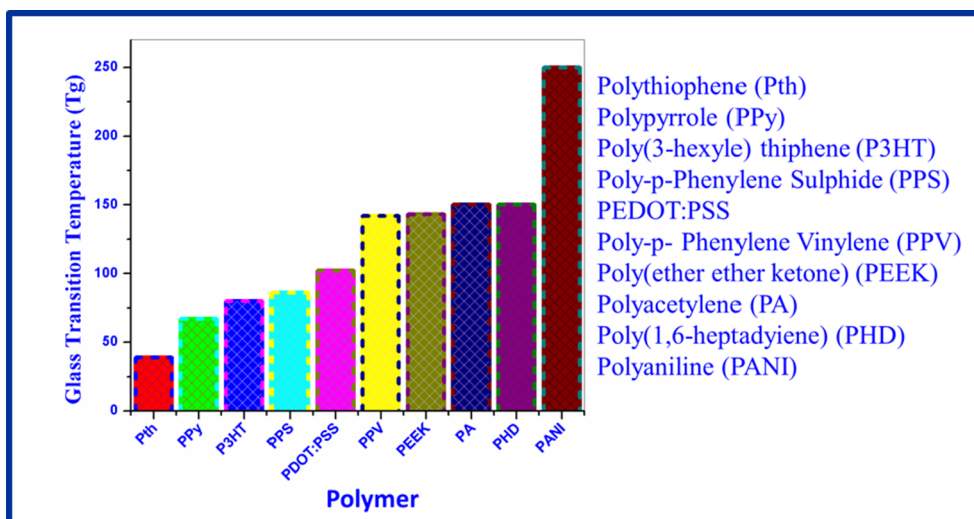


Fig. 17. Polymer glass transition temperature (T_g).

facilitates deposition of films, which leads to the device anneal temperatures of above 350 °C [202]. Polyesters such as polyethylene terephthalate (PET) [203] and polyethylene naphthalate (PEN) [204] have extensively been investigated for electronics due to their processability, although having T_g of 78 and 120 °C and these polymers are not compatible with OLEDs since they have very low T_g . MacDonald *et al.* developed a process, that facilitates thermal and dimensional stability and necessarily support flexible moletronic devices or components during fabrication [205]. The thermal and mechanical analysis indicates that, when exposed to a temperature of up to 180 °C for 5 min, heat-stabilized films demonstrate minimal-shrinkage. Furthermore, the analysis states that once the heat is stabilized, the effects due to T_g are negligible and the polymeric films remain dimensionally reproducible. Though this improvement is good enough within the performance requirements of moletronic components or devices, processing conditions deteriorate the functional properties such as insulating characteristics, intrinsic conductivity, and stimulated charge carriers. To facilitate these characteristics, efficient regioselective synthesis technique enables a wide range of dopable elements like poly(1,6-heptadienes) and its derivatives which could be an ideal candidate with stabilized T_g of 91–160 °C or even more with a low linear coefficient of expansion while maintaining electronic conductivity [201]. So, polymers formed via stereoselective cyclopolymerization evidence unique thermal properties corresponding to those of stereoregular polynorbornene and poly(1,3-cyclohexadiene) [206–208]. In Co-promoted cyclopolymerization, olefin coordinated chelate with closed structure isomerizes to a transoid structure before the cyclization [209,210] and from the conclusion it suggests that it is thermodynamically favorable for the formation of trans-fused cyclopentane ring [209,210]. The cyclization of Iron (Fe) and Cobalt (Co) catalyzed complex demonstrate the further formation of thermodynamically favorable structure. Though the cyclization of Fe and Co catalyzed complex demonstrate selectivity of formation of cis- or trans- five-membered rings, catalyst play a critical role during selectivity, for example Fe catalyzed cyclization yield with cis- and trans-fused polymer five-membered ring structure [209,210]. Ito *et al.* demonstrated flexible-fibrous-glass reinforced polymerically (FRC) flexible display substrates exhibit 89% transparency (at 400 nm) with low CLE and CTE of 14 ppm/°C [211], and in addition to this, researchers have reported thermally stable polymer substrates like AryLite [212,213]. Although poly(1,6-heptadiene) is not reconcilable with the processability of fibrous elements, but terpolymer/poly(1,6-heptadiynes) blends reported by Balasubramanian *et al.* facilitated fibrous substrates or devices with high dimensional accuracy in nanoscale while maintaining electrical conductivity via electrospinning technique, which further enhanced thermal stability of poly(1,6-heptadiynes) that can be attained by choosing proper catalyst, synthetic conditions and fibers and thermal stability can be achieved by assortment of proper blended polymeric material, for example acrylonitrile butadiene styrene (ABS) [34,61].

Such type of thermally stable micro or nano scale fibrous materials with high electronic conductivity are imperative for the moletronic interconnects during self-assembled molecular deposition. Such type of monolayer diffusion barriers using self-assembled molecular deposition had been reported by the Ramanath *et al.* [214,215] In which one end of bifunctional organosilicon ligand diffused on to the inter-layer-dielectric (ILD) while the other end was anchored to the Cu interconnect [216].

5.2. Surface properties

Surface functionalities such as roughness, roughness induces compatibility as well as hydrophobicity and cleanliness, which are the desirable prerequisites to ensure the integrity of subsequent layers (conductive and barrier coating). Amorphous polymers possess required surface functionalities as compared to that of semiconductor oxide materials and semi-crystalline polymeric substrates. However, surface-defects

create abnormalities during operation moletronic components or devices. For examples, pinhole defects arrived during the fabrication of thin films for barrier and electrodes consequently creates dark spots in OLEDs [217] and the molecular strategy implemented on the thin film transistor displays enabled pinhole defects to lead to the origination of deep states, these are probably consistent with the molecular bonds reflected over a wide range of energy due to variation in local environments [218,219]. At zero volts of a thin film transistor the bonds are interconnected with flat bond conditions, with positive or negative gate voltages the bonds bend upwards or downwards and thus result in change in Fermi level occupancy [24]. The occupancy of these states is low because they are well situated above the Fermi level profile, even though space charge is located in band tail states and this indicates the dominated deep states are the preeminent factors to induce total space charge effect. Thus, a small fraction of band-tail electrons above the conduction band mobility edge foment an increase in source-drain current. However, in deep states gate voltage is directly proportional to the space charge, but as the bending of the band increases there is exponential increment of current, that leads to losses instigated in inefficient devices [219]. To avoid these defects and the defects caused due to mechanical breakdowns, engineered planarizing of layers underlying substrates needs to be explored which is done by removing the defects from the surfaces and making them scratch resistant [220]. Such type of defect-free engineering technologies with efficient strategies enabled PHDs ensures the integrity of subsequent layers and conductive coatings for moletronics.

Surface-initiated polymerization refers continuously adding of repeated monomers at the terminal of surface-treated chains which provides a wide range of functional advantages over traditional methods, including rapid processing, improved adhesion in between substrate and polymer coating, uniform thickness, complex shape feasibility and tunable grafting densities. These engineered thin film technologies (dielectric layers, lithography resists, responsive polymer films, and membrane separators) are potentially applicable for moletronics and its profound impact probably attributes to the compositions facilitated by film growing capability due to its architecture and properties. Jennings *et al.* demonstrated surface-treated poly(n-alkylnorbornene) films by bound catalyst reacted monomer via ring-opening-metathesis-polymerization (ROMP) [221], also Hatjopoulos and Register demonstrated elastomeric properties of poly(n-alkylnorbornene) and their hydrogenated derivatives synthesized via ROMP [222]. The results suggested that attained elastomeric properties are due to a decrease in glass transition temperature with an increase in chain length, which was attributed to alkyl polymer chains acting as a plasticizer. Although reduced thermal stability was attained via surface triggered ROMP technique, other functionalities such as water resistance surfaces, elastomeric properties, surface and barrier properties, low surface energy, high resistance, and capacitance potentially improved the performance characteristics make them fundamental for moletronics. The barrier properties of hydrocarbon facilitated surface initiated thin films via ROMP technique have widely demonstrated and this method presented excellent resistance to water and ion transport, making them suitable for numerous applications as a functional surface coating. This result suggests that heptadiene and its derivative systems with improved functionalities while maintaining the electronic conductivity via doping mechanism enabled cyclopolymerization route leads to an efficient material for electronics and moletronics.

5.3. Chemical resistance

Organo-electronic materials with obligatory qualities such as chemical exposure of organic substrates, trapping of moisture during fabrication including patterning, cleaning, and coating process [223] and chemically stable materials are potentially required for organo-electronic and moletronic applications. Currently, chemically stabilized materials such as polyethylene terephthalate and polyethylene

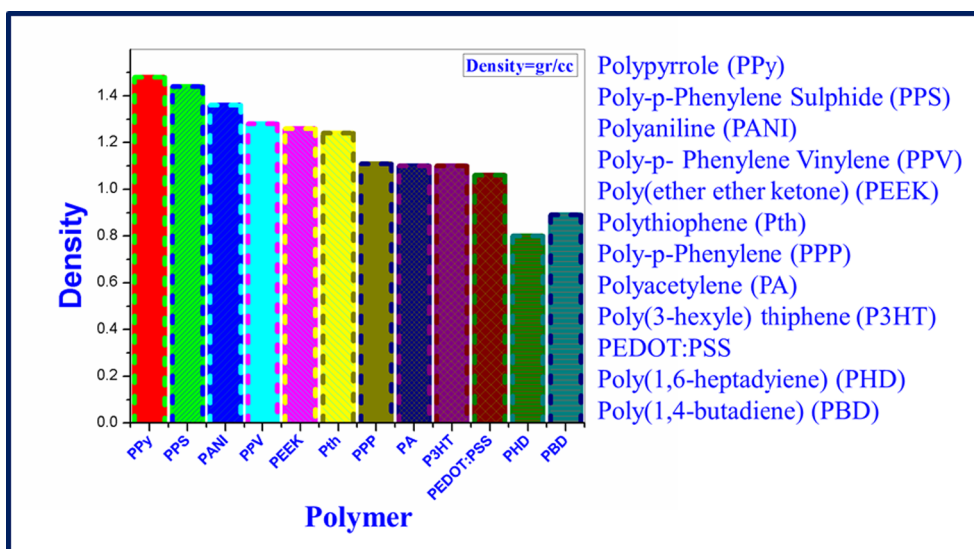


Fig. 18. Representation of polymer density.

naphthalate are studied because of their strong solvent resistance when compared to other polymers. Inorganic or organic layer coatings are probably utilized for preventing solvent and moisture invasion, wherein fluorine-contained aliphatic cyclic structures with little crystallinity are superior to hydrocarbon resins with moisture, chemical and dry etching resistance. Further, it provides a low cost production of semiconductor devices as moletronics [224]. Khar *et al.* reported Curcumin (1,7-bis-[4-hydroxy phenyl]-1,6-heptadiene-3,5-dione) a well-known biologically active compound which possesses anti-inflammatory, antimutagenic, and anticarcinogenic effects [224]. Many permutations are available for modifying the properties of a polymer, incorporation of polar groups or nonpolar groups that can control adhesion, solvent resistance, and chemical resistance [224]. So, if curcumin could be modified concerning the PHD rather than 1,6-heptadiene, it could lead to chemical resistance characteristics similar to that of curcumin system [225]. These delineations suggest that PHDs and its derivatives could be chemically stable, which can be attained via implemented conditional synthetic routes leads to a well suitable moletronic bioimplantable devices.

5.4. Mechanical properties

For flexible moletronic devices or components, validated mechanical properties need to be contemplated [226]. Flexible organic light emitting diodes (FOLEDs) demands stringent constraints among other light emitting layer, a brittle transparent inorganic anode, metal cathode, TFT layer and encapsulated layer [227]. The probability of mechanical failure is attributed to mechanical discrepancy in-between organic and inorganic interfaces when the devices are bent and the main causes of failure is attached to the brittleness property of thin organic films in the FOLED system [228]. To overcome these drawbacks, organic materials are extensively suggested for moletronics and these materials are the best choice for reliable devices [229]. Hence, understanding of organic material properties are important potential parameters to improve mechanical limits [190]. The components failure predominantly by their thickness, properties, flexible as well as adhesion between layers under applied external stresses, wetting characteristics, environmental characteristics, and robustness during the usage [205]. Fluorine contained aliphatic cyclic structured films are protective films that serves as buffer stress against heat stress and mechanical stress. Although the single-layered organic films are mechanically stable, the most effective way to retain reliable mechanical properties is by using multilayer thin-films and altering the chemical

structure. The understanding of multilayer mechanism of polymeric substrates integrated thin film barrier coatings remains an as challenging task [230] and spectroscopic characterization or direct imaging of sizes, defects special density <100 nm in diameter are difficult. Moreover, material properties and their functionalities like in-situ-solubility and effective-diffusivity [231]. Furthermore, analysis and quantification of the single oxide layer or organic or inorganic layer deposited on a polyethylene terephthalate may not precisely exemplify independent layer in multilayer desk [229,232]. Conjugated amorphous polymers have a wide area of surveillance as perspective substitutions for indium tin oxide in optoelectronic and electronic applications, principally for moletronics due to their magnificent flexibility and mechanical-strength. Chemical and physical evidence suggested that the structure of poly(1,6-heptadiene) polymer containing backbone with alternating single and double bonds and cyclic repetition ring units resulted from stereospecific head to tail coupling of acetylene groups [233]. Such polymer structure to property relation findings is still contradictory, however, mechanical as well as other functional properties are controlled by the structural parameters. Inhomogeneity such as microvoids and flaw mechanics suggest mechanical strength, toughness, free volume and related segmental mobility, packing and cross-linked structural characteristics can tailor the mechanical properties by altering structural parameters. Micro-voids, flaws and other structural defects induced strength and toughness are inherently controlled during deformation of polymers and the influence of crosslink density on mechanical properties are explored. The impact strength is more pronounced on molecular weight, which is interrelated with the density of a polymer (conjugated conducting polymers density has been illustrated in Fig. 18) and results relate energy absorption capacity to the intensity and localized segmental mobility [229,232]. Such type of low-density polymers is desirable candidates for stealth electronics [229,232].

Due to the absorbed energy impacting probably increases with molecular weight, composition and effect of the composition may dominate the influence of crosslink density. Physical aging and post-curing also seriously affected the physical properties of polymers. Kong *et al.* demonstrated physical properties that are relatively dependent on post-curing and sub-Tg [229,232]. Moreover, Schroeder *et al.* demonstrated the hypothesis of Tg influenced strain properties probably influenced by the polymer MW, the tensile strength was probably affected due to bulk density, which is interrelated to the crosslink density [234].

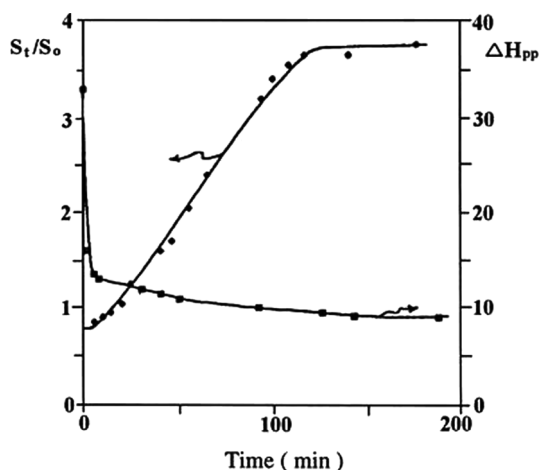


Fig. 19. Poly(DPDPDM) line width (■) and free spin population (◆) versus exposure time to iodine at 25 °C in vacuum S_0 initial spin population and S_t spin population at each time 't'. (Copyright permissions: <https://doi.org/10.1021/cr960080i>).

5.5. Electrical and electronic properties

5.5.1. Dielectric

Dielectric properties are extremely paramount to incorporate proper gate insulator, for example non-volatile field-effect transistors (FETs). High on-state current is enviable for efficient molecular design FETs, this can be attained via molecular design of FETs that are operated at very larger voltages V_D or V_C [235]. However, large voltages enabled molecular design FETs to induce extensive power consumption. This energy consumption is not economical and eco-friendly hence researchers have demonstrated a plausible approach which deals higher I_D at lower bias voltages while increasing dielectric constant of capacitance [236].

$$I_D = W/L\mu C_1 V D [(V_G - V_{th}) - V_D/2] \quad (2)$$

However, crucial parameters are $D_{max} = \epsilon_0 k E_B$, which can be sustained by the gate insulator as well as the capacitance $C_i = \frac{\epsilon_0 k}{d}$, where ϵ_0 = vacuum permittivity, k = dielectric constant, E_B = breakdown energy field and d = thickness [235]. Reduced bias voltages and improved ON/OFF ratio can be possible with high dielectric materials [237]. Though the high- k dielectric materials can improve all configurations required by a device, it negatively affects charge carrier mobility as a result of an energetic disorder in semiconductor devices [112]. To improve this low- k dielectric in terms of its feasibility, which results in low energy losses, consequently, high-quality factor for reducing capacitance [112], PHDs and its derivatives facilitate low dielectric- k values and has been reported by Magisetty *et al.* [238]. Hence, these cyclopolymerized polymeric systems could be a appealing for molecular device fabrication and the additional advantage of low- k dielectrics is the reduced hysteresis loop, which further facilitates defect free interfaces in semiconductor devices [112]. In switches or logic gates, dielectrics without hysteresis are preferable for faster response in molecular design LEDs. For applications like non-volatile memories, the dielectric with electret properties is required for longer time retention of charge [181,239], and the dielectrics that are to be used in capacitors can be polarized under an external potential and that evince additional dipole polarization or quasi-charge storage. These functional properties can probably be enabled by 1,6-heptadiynes and their derivatives via cyclopolymerization synthesis process suggested by Magisetty *et al.* and have demonstrated electronic properties and charge storage using PHDs [238].

5.5.2. Magnetic and optoelectronic properties

Researchers have suggested that PA and its derivatives can exhibit

magnetic, optoelectronic properties, which is imputable to the conjugation in the main backbone chain. Further, the researchers have revealed that solitons may yield magnetic, transport and optical properties and this phenomenon was endorsed for the PA [121]. Also, researchers were focused on conjugated systems which probably attributable to the magnetic and optical characteristics [240]. Masuda *et al.* suggested that these non-linear optical and magnetic properties were due to the carbon-carbon alternating double bonds in the main backbone chain of substituted PAs [241]. The magnetic properties can be advocated due to the spin dynamics and further improvements in spin dynamics was accomplished by doping phenomena. Thus, undoped poly(DPDPDM) spin density was 1018 spin/g and line width (H_{pp}) was 33G at $g = 2.0011$ [242]. According to Fig. 19 of poly(DPDPDM), researchers have suggested and proved that the changes in spin population and line width was attained with the aid of in-situ doping [242]. Doping the substituents initiated radicals and non-equivalent double bonds in the backbone chain that induces spin density [243,244] and these results showed similarity to that of poly(1,6-heptadiynes). Also, electron spin resonance (ESR) of poly(1,6-heptadiynes) has been shown in Fig. 20, the spin density is interrelated with ESR spectra i.e., in poly(dihexyldipropargyl ammonium bromide) (PDHPAB), where 1020 spin/g spin density was obtained upon doping and the time was decreased, these results were consistent with PA, which can be further interpreted by solitons. Moreover, at 90 MHz proton NMR spin-spin (τ_1) and spin-lattice (τ_2) relaxation measurement were conducted in the range of temperature 140 – 440K. Results suggested that relaxation anisotropies of spin-spin states within the relaxation $\tau_1 = 10$ ms (140K) to $\tau_2 = 14$ ms (440 K). The relaxation of spin-lattice states (Fig. 21) were revealed in the absence of τ_2 transition, τ_1 is minimum which was due to spin diffusion to spin sites, for example to induce relaxation, motion of spin side or end groups was initiated with a slight shift of τ_1 towards longer values the behavior exhibited and appeared to be similar to the molecular process which was further responsible for ESR change line width [121]. This recommends that heptadiyne systems could exhibit magnetic properties depending on the doping level and element as a result of conjugation.

Organic polymers with π -conjugation such as PA, polydiacetylene, polythiophene, and phenylenevinylene are third-order nonlinear optical χ^3 materials with optical nonlinearity of about 10^{-12} to 10^{-9} esu

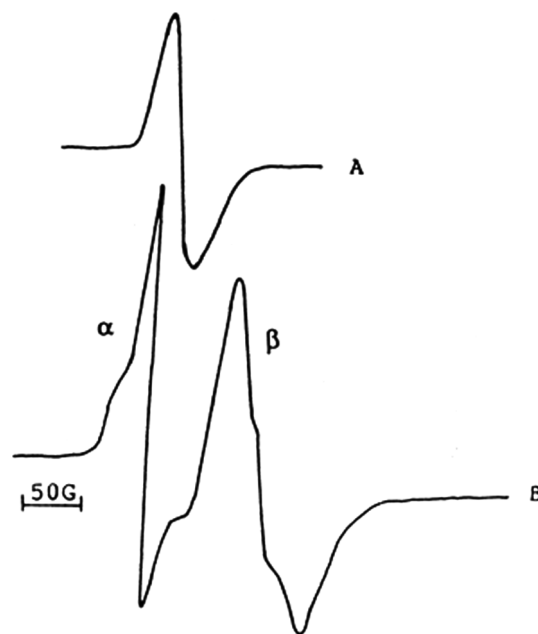


Fig. 20. Poly(DPDPDM) electron spin resonance (ESR) spectra versus heating time at 230 °C under nitrogen gas: (A) Zero time; (B) after 15 min. (Copyright permissions: <https://doi.org/10.1021/cr960080i>).

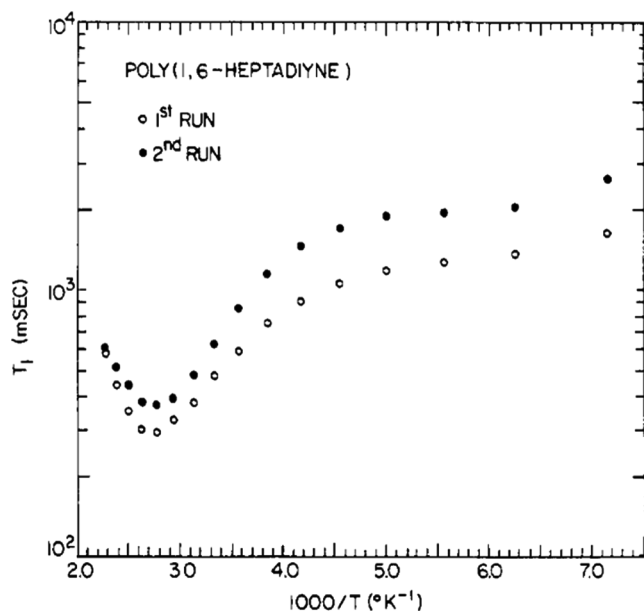


Fig. 21. Temperature dependence (140–440 K) of spin–lattice interaction time in poly(1,6-heptadiynes) measured by the 180-T-90 sequence at 90 MHz at broker CXP spectrometer. (Copyright permissions: <https://doi.org/10.1021/ja00351a048>).

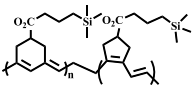
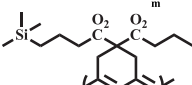
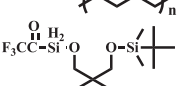
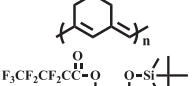
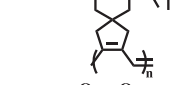
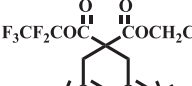
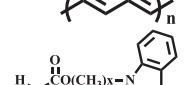
[245–247], which are potentially suggested for applications such as moletronic switches and ultrafast – optical devices [248,249]. This optical nonlinearity could be effectively monitored, analyzed, and optimized with the aid of current molecular design and optimization tools, but due to limitations of suggested conjugated polymers, practical applications are less explored. Heptadiynes and its derivatives are promising candidates as a 3rd order optical materials due to their functional advantages over the above suggested organic materials. The non-linear optical properties can be measured via degenerate four-wave mixing method (DFWM) as this method was implemented for poly(1,6-heptadiynes and its derivatives) during the measurement of optical susceptibility, the measured values have been illustrated in Table 2. The incremental change in the concentration of polymer solution results in increment in χ^3 values (Fig. 22) and alternatively, the third order nonlinear optical susceptibility parameters were intensified by increasing substituents at the 4th site of 1, 6 – heptadiynes in accord to the UV–vis spectroscopic characteristic bathochromic shift, which enforced π -conjugation of heptadiynes system to more planar form and leads to incremental χ^3 values of the polymer [250].

In summary all the functional properties are interlinked and these are either directly or indirectly instigated by the conjugated backbone chemical structure of the compound, this has been illustrated as Representation of heptadiynes functional properties in Fig. 23.

6. Failures, physical limitations and its realizable similarity solutions for moletronics

Materials when approaching the molecular or nanocluster gains functional properties while loosing of their bulk properties and that are used to handle logical operations [251]. This phenomenon applies to all materials and is utilized to generate a moletronic device as they depend on physics of governing the small amount of matter, for example diode is a smallest electronic device with ideally zero-resistance in forward-bias and infinite-resistance in reverse-bias indicates ON/OFF states of the diode [251]. This significant feature can be seen in diodes using in vacuum tubes but certainly far from the ideal characteristics which is still acceptable, however, when using semiconductor diodes, the practical diodes can instigate few ohms in forward bias as well as few Giga ohms in reverse bias

Table 2
Linear and non-linear optical properties of 1,6-heptadiynes.

| Polymer | λ_{max} (UV) nm | χ^3 (10^{-3}) esu | References |
|--|--------------------------------|----------------------------|------------|
|  | 540 | 2.6 | [60] |
|  | 560–590 | 3.1 | [60] |
|  | 540–595 | 3.6 | [60] |
|  | 560–590 | 4.3 | [60] |
|  | 530–570 | 4.1 | [60] |
|  | 540 | 0.99 | [60] |
|  | 550–640 | 0.44 | [60] |

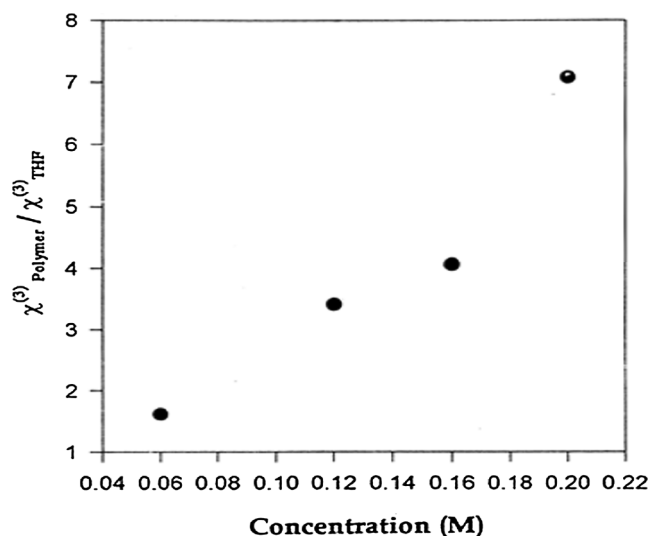


Fig. 22. Concentration dependence of susceptibility χ^3 of poly(1,6-heptadiynes) dissolved in THF. (Copyright permissions: <https://doi.org/10.1021/cr960080i>).

mode and their typical ON/OFF ratios are in the range of 10^3 – 10^6 [251]. However, single-molecule enabled diodes can give few kilo ohms in the forward and reverse bias modes. Hence the ON/OFF ratio ranges bigger by one magnitude, which attributes to the resistive component and is negligible when the diode is considered as macro-level device, but it induces higher magnitude of losses when the diode is considered as a molecular level device. The physics of tunneling and hopping phenomena conspicuously describes this feature in which electrons tunnel through

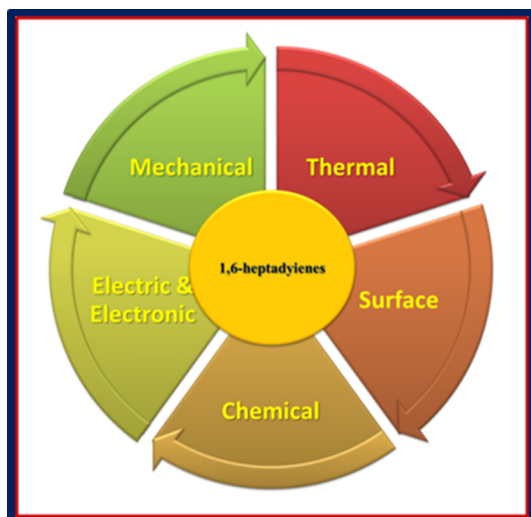


Fig. 23. Representation of heptadiynes functional properties.

potential barriers and stimulate the alteration in ON/OFF ratio of that device simultaneously causing thermal losses because of resistance [251]. The photolithography technique is widely explored for molecular electronic device fabrication. The design and fabrication of moletronic devices or components based on mask preparation and exposure on the silicon-based substrate via electromagnetic radiation [251] have certain drawbacks that is interconnected to fabrication of transistors smaller than the minimum feature cannot be performed and heat dissipation is the stringent problem of integrated electronic devices or integrated circuits (ICs) [251]. To overcome these drawbacks the 1,6-heptadiynes with an infinite number of conjugating double bonds leads to the reduction of intrinsic resistance can reduce the heat dissipation since heat losses are due to electron flow in a resistance medium [238]. Therefore, heptadiyne systems and its derivatives with functional characteristics could be suggested for the efficient electronics or moletronics.

Polar covalent compounds probably attract moisture like anti-static agents, which leads to nanoscale defects (conductive defects) between traces and ionic compounds like chlorides that tends to have corrosion problem. And the fluorinated hydrocarbons residues may hydrolyze and release corrosive chlorides and thus the polar molecules dissipate high-frequency energy causing parasitic dielectric losses [252]. Above the glass transition temperature, the molecule softens and becomes susceptible to contaminant diffusion, for example polyglycolic solder flux can lead to increase its humidity intake and results in deterioration of electronic properties and facilitate corrosion [253]. Similarly, electrostatic discharge is caused due to electrical overstresses by applied external forces, these stresses may cause device failure due to parameter shift and degradation rate causing latent damage, localized device failure, high current density and high electric field gradient. In reality, the electrostatic discharge (ESD) in moletronics may cause damped waves with rapidly altering polarity [254] and the current induced failures are also more apparent in bipolar junction devices, where Schottky and PN junctions are predominant [139,255]. Simultaneously, parasitic resistance which are in series or parallel are often frequency dependent and the alteration in any of these may lead to the parameter shift and failure. Shorted failures and leakage occur due to an increase in parasitic resistance, which is the most common failure modes in moletronic devices. All electronic devices under moletronics category are supposed to be extremely sensitive to the water and oxygen or else device degradation takes place. Many mechanisms have proposed the detractor of moletronics which includes emitting material diffusion into transparent hole layer, cathode oxidation, anode layer detachment, cathode layer detachment, electrical short circuits, the electrochemical reaction at electrodes, oxygen activated photochemical damage. To

reduce moletronic device failures, understanding of above mechanistic concepts are requisite and their analysis is essentially required as they can probably act as a root cause to protect devices from failures.

Additionally, exposure to ambient conditions resulted in dark spots deteriorates the device performance. Also, the influence of oxygen and water is significant for example, water at the cathode/organic layer electrochemical reduction leads in hydrogen production, which creates bubbles at the cathode surface and such type of oxygen driven dark spots is different from the water induced dark spots and deteriorates the kinetic efficiency of devices. The black spots at the electroluminescent devices for example black spots at polyfluorene with poly(styrenesulfonate) doped poly(3,4-ethylene dioxathiophene) (PEDOT/PSS) on an anode and Cu/A as cathode system reducing electroluminescence efficiency and also caused by dust contamination thus forming dark spots. Chua *et al.* revealed that roughening of polymer/electrode interfaces lead to incremental current induced charge carrier flow that degrades the device performance by degrading the polymer characteristics. To protect from that degradation, isolation/encapsulation of devices or active materials are prescribed to improve the lifetime.

Furthermore, there are four systematic failure areas that have been widely observed from the analyzation of modern density theories and are more relevant and applicable to molecular electronics [142]. The generic failures are dispersion interactions, charge transfer, extended conjugation and bond dissociation, which are all induced by a common element involving long-range non-local electron moment induced resistive parameter. Although the advancement in technologies makes inferior to overcome these failures, density functional theory (DFT) [142,256] methods are also possible by enabling the inbuilt advanced functional advantages within the DFT such as local density approximation (LDA) or generalized gradient approximation (GGA) or hybrid functional are common in nowadays. DFT can be applied to problems involving in moletronics, which includes dispersive interactions, interconnections, bond cleavage, long-range charge transfer, properties related to the extended π -configuration and anomalously high polarizabilities [142,256]. The ability of DFT to do accurate charge partition flow across the electrode-molecule junction by screening of applied electric fields through molecules, molecular HOMO-LUMO EGs concerning the electrode Fermi level energy and the distance-dependent conductivity are a particular area of concern of direct relevance to molecular electronics. Also, various methods have been suggested for these purposes, such as Krieger-Li-Lafrate exchange-correlation potentials [33,142,257], current density potentials [71] and the use of alternate density functional formalisms to Kohn Sham Theory [258]. These methods and advocate techniques elucidate to improve the described problem-solving strategies in moletronic, although the present DFT methods and advocate techniques can facilitate improving problem-solving skills, the future DFT in moletronic applications may confidentially apply and routinely solve the problems. Suggested methods and approximations applicable for probability in DFT, for example advancement in self-consistent charge density functional tight binding DFT theory [259], intermediate neglect differential overlap (INDO) [260–263] and minimal neglect differential overlap (MNDO) [259] methods, these methods may overlap with the DFT and that are intended to deal with all known systematic problems, providing a powerful tool for nanotechnology.

Organic materials are promising candidates for molecular memories due to their attractive features include good processability, miniaturized dimensions such as molecular dimensional designs [264]. Electrical switching is a process of domain nucleation and growth in molecular memories, which is a dominant switching mechanism in the ferroelectric polymer [181,265,266], however, domain growth leads to lower conductivity which further enable slower switching mechanism [267–269]. To improve the nucleation, the planar nanostructures are feasible and is possible to control the precise location of nucleation and direction of domain wall motion consequently deterministic switching

[265]. The poly(1,6-heptadiynes) and their derivatives or liquid crystal poly(1,6-heptadiynes) can be a possible candidate to improve the nucleation which results in reduced defects (because as we know that the nucleation is an inverse relation with the defects) facilitating efficient moletronic devices. Also, the poly(1,6-heptadiynes) exhibits high thermal stability, self-organized conjugated structure and conductivity, as well as wide doping enabled poly(1,6-heptadiynes) derivatives are essential requirement to alter the functional properties for efficient moletronic devices [265]. Hence poly(1,6-heptadiynes) and its derivatives could be thought of a polymeric material that reduces failures in moletronic devices [270,271]. The additional benefit of poly(1,6-heptadiynes) is its low dielectric constant, which probably reduces hysteresis loop steps, as a result, continuous uniform non-polar and defect-free interface leads to efficient performance [62].

Heat dissipation is the major drawback of the electronic industry, several attempts have been taken to look for better material to reduce heat dissipation, but they assess marginal improvements. The reason is that in moletronics signals are coded with the use of charge carriers and variations in currents, these transformed quantities can lead to the measured quantity. These coded signals make large excitations of vibrations that induce the heat dissipation, which also depends on the resistive nature of material since the materials exhibit resistive property. The low resistance large charge carrying capability results in high-end vibrations then the large energy dissipated via conversion of electric to heat energy. To reduce heat dissipation, researchers have proposed two scenarios. First one is molecular electronic potential (MEP) to code, which detect and process information, similarly, the second one is the use of vibrational states to transfer the information. Molecular electronics with molecular level operations, for example MEPs of HCl and Triflorobenzene further suggested that heptadiyne systems were explained in the above basic mechanism of the molecule for moletronics. These moletronics may be overcome the drawbacks of traditional electronics generated heat losses by minimizing energy consumption, for example, though the excitation energy is required to initiate the logical gate operations etc., or as the gates that are directly interconnected, losses in interconnections are perhaps small functions of energy that require to change states. Though the existing one or two orders of magnitude of errors and power consumption can still operate and represent an excellent result. Moreover, when comparing to the molecular devices to the microelectronic devices and bulk electronic, devices gain should be concerned.

7. Future scope

The advancement in electronic industry has been driven by the current electronic needs, hence, the development of electronic device technologies are preferred with experimental evolutionary improvements [272]. Researchers have widely explored and suggested the role of organic materials, particularly polymers role in electronic advancement leads to reliable electronic components/devices. However, molecular electronics enables the manipulation of information at the molecular level, simple molecules are nanometer dimensions offering the prospect of very dense circuitry in 3-dimension. Various techniques that can permit molecular level fabrication and evaluation, among them, Langmuir-Blodgett technique helps to permit the manipulation of materials at molecular scale, with this technique Langmuir-Blodgett (LB) films can be possible to construct and even films can be enabled with the interaction of more than one type of molecule. The control over molecular architecture using LB technique permits the fabrication of organic superlattices with precisely defined symmetry properties. Such molecular assemblies can exhibit pyroelectric, piezoelectric and non-linear optical phenomena [273,274]. Similarly, molecular beam epitaxy have several advantages over LB technique such as film stability, different chemical compounds enabled molecular structures, near tendency of organic/biological molecules for self assembly into complex structures [275]. Similarly, evaluation techniques such as STM and

AFM, that may be used to provide direct images of surfaces with nanometer resolution. We therefore have several technologies for evaluation and fabrication at molecular level to investigate ultrathin layers of organic compound functional properties. However, extensive effort need to be made on building of organic information processing system, how will the information be stored? How will it be manipulated? Most importantly how will be the interface connection between the molecular system and the outside body are most important to forward the area of functional advancement. One way of forwarding of advancement in molecular electronics is to use molecular microscopic techniques to reveal the alteration of individual organic molecules. For example; molecular materials can exhibit a variety of reversible and irreversible processes. Interrogation using STEM would either leave the molecular entities intact, i.e., change of molecular orientation or confirmation or induce reactions such as complexation, dimerization or polymerization [17–20,276]. However, major issues in dealing with moletronics are experimental verification and the controlled fabrication of devices. Robust and focused work on stable modeling of molecular devices is necessary in order to fill gap between the synthesis and realization of relevant molecules and solid-state molecular-devices. Experimental predictions, validation and clear analysis would be possible with the molecular simulation tools, molecular dynamics can be used to explore conformational space, and is often the method of choice for large molecules such as proteins, etc. [277,278]. In molecular dynamics, energy of surface is explored by solving Newton's laws of motion for the system. Moreover, molecular dynamics simulates the natural motion of the molecular system. The energy provided in a molecular dynamic procedure allows the atoms move and collide with the neighbouring atoms. This is a form of conformational searching since enough thermal energy is provided, Also, simulated annealing is a type of molecular dynamic experiment which is popular when optimizing of protein models [277,278]. More challenging in molecular electronics is the behavior of individual organic molecules or groups of molecules and the precise three dimensional positional control of individual atoms and molecules. This topic as diverse as molecular switching, DNA electronics and molecular manufacturing have all been described in the literature. Much of research activity is directed towards computational architectures that may one day rival silicon technologies [277–280].

Two approaches are outlined in molecular electronics to exemplify the top-down and bottom up themes of nanotechnology. The former one refers to the making of nanoscale structures, for example by machining, whereas the bottom-up or molecular nanotechnology applies to building organic and inorganic architectures atom by atom or molecule by molecule [277]. These kind of molecular electronic devices are considered to exhibit unlimited functionality. In addition molecules could exhibit piled up-into three dimensional layers, thereby increasing overall efficiency of the system lead to many application field areas such as in physics, chemistry, engineering and nanorobotics. For example, nanotube molecular wires have a wide range of applications in the field of chemical sensors, etc. [34,229,281–283]. Another recent trend in molecular electronics is its application in the field of refrigeration and the flow of heat at the microscopic level. In connection with this molecular based refrigeration is a current research area. Peltier cooling at molecular junctions, which is an important step for this research and was considered to be almost inaccessible, has been reported. With this finding more research has become possible in the field of thermoelectric transport through molecular junctions. For a smooth transport between the molecular junction conductance should be relatively high. It has been reported that two similar molecules are kept in parallel between top and bottom graphene electrodes, electrical conductance is more than doubled. Beyond the discoveries and experiments discussed in this article a new technology that will connect these molecules to the outside world is not very distinct and constant effort toward the advancement of this goal is essential [238,284–290].

8. Conclusion

Cyclopolymerization of 1,6-heptadiynes and its derivatives are organic electronic polymers. Hence, the moletronic equivalent multifunctional advantages of cyclopolymerized 1,6-heptadiyne (HD) systems suggested as the most desirable materials for molecular electronics. 1,6-heptadiyne's significant molecular mechanism, its derivatives compatibility towards moletronic applications were presented. This is further supported by a conjugated system with its functional characteristics (electronic conductivity, magnetic and optical properties, light weight, flexibility, robustness, oxidation stability, and thermal stability) can be realized via various catalytic dopant enabled conditional cyclopolymerization synthesis route. Further, this can be described by solitons and anti-solitons interaction mechanisms, solitons and anti-solitons intensified conductivity is dependent on mechanistic doping and doping level. Moreover, potential characteristics, failures, physical limitations and its realizable similarity solutions for moletronics have been described. In summary, all the above delineations could suggest that the heptadiynes and its derivatives foment efficient moletronic performance due to its functional advantages while maintaining excellent conductivity characteristics.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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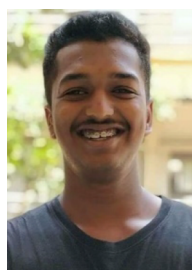
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