

Review

Organic Semiconducting Polymers in Photonic Devices: From Fundamental Properties to Emerging Applications

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Abstract: This review examines the distinct advantages of organic semiconductors over conventional insulating polymers as optically active materials in photonic applications. We analyze the fundamental principles governing their unique optical and electronic properties, from basic conjugated polymer systems to advanced molecular architectures. The review systematically explores key material classes, including polyfluorenes, polyphenylene vinylenes, and polythiophenes, highlighting their dual electrical–optical functionality unavailable in passive polymer systems. Particular attention is given to polymer blends, composites, and hybrid organic–inorganic systems, demonstrating how semiconductor properties enable enhanced performance through materials engineering. We contrast passive components with active photonic devices, illustrating how the semiconductor nature of these polymers facilitates novel functionalities beyond simple light guiding. The review explores emerging applications in neuromorphic photonics, quantum systems, and bio-integrated devices, where the combined electronic–optical properties of organic semiconductors create unique capabilities impossible with insulating polymers. Finally, we discuss design strategies for optimizing these distinctive properties and present perspectives on future developments. This review establishes organic semiconductors as transformative materials for advancing photonic technologies through their combined electronic–optical functionality.

Keywords: organic semiconductors; photonic devices; conjugated polymers



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1. Introduction

The rapid evolution of photonic technologies has created an increasing demand for optically active materials that can efficiently manipulate, generate, and detect light. These materials play crucial roles in various applications, including optical communications, information processing, sensing, and emerging quantum technologies. While traditional inorganic materials have dominated the field, there is a growing interest in organic materials, particularly organic semiconductors, due to their unique advantages and versatile properties [1].

The fundamental requirements for photonic applications include precise control over optical properties, efficient light–matter interactions, and compatibility with existing fabrication technologies. In this context, polymeric materials have emerged as promising candidates due to their inherent advantages in processing and scalability [2–4]. Polymer-based materials offer exceptional flexibility in manufacturing, enabling cost-effective production methods such as printing and roll-to-roll processing, which are particularly attractive for large-area applications [5]. These processing capabilities, combined with the potential

for chemical modification and tuning of optical properties, make polymers increasingly relevant for next-generation photonic devices.

Within the broader class of polymeric materials, organic semiconductors represent a particularly interesting subset due to their unique combination of optical and electronic properties. These materials, characterized by their conjugated molecular structure, exhibit strong light–matter interactions and can be engineered to display specific optical characteristics. Their semiconductor nature, arising from delocalized π -electron systems, enables both electronic and optical functionality, making them suitable for active photonic components [6,7]. Furthermore, organic semiconductors often exhibit significant nonlinear optical properties, which are essential for applications in optical switching, frequency conversion, and signal processing.

The integration of organic semiconductors as optically active polymer materials in photonic applications represents a convergence of several advantageous properties: solution processability, which enables low-cost manufacturing; structural flexibility, allowing for diverse device architectures; and tunable optoelectronic properties, providing versatility in application design. These materials have demonstrated potential in various photonic applications, ranging from conventional devices such as light-emitting diodes and photodetectors to more advanced applications including optical amplifiers, modulators, and nonlinear optical devices [2,8,9].

Recent advances in molecular design and synthesis techniques have further expanded the possibilities for organic semiconductor-based photonic materials [10,11]. The ability to precisely control molecular structure and organization has led to enhanced optical properties and improved device performance. Additionally, the development of new processing methods and device architectures has facilitated better integration of these materials into practical photonic systems.

This review aims to provide an overview of the current state of the art in organic semiconductors as optically active polymer materials for photonic applications. We will examine the fundamental principles governing their optical properties, discuss various material systems and their characteristics, and explore emerging applications and future prospects in this rapidly evolving field.

2. Fundamental Principles

The electronic and optical properties of organic semiconductors stem from their unique molecular structure, particularly their conjugated backbone. To understand these properties, it is instructive to compare conventional saturated polymers with conjugated systems. In saturated polymers like polyethylene (PE), carbon atoms form only σ -bonds, resulting in a large highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap typically approaching 7 eV [12]. This electronic structure makes PE an electrical insulator with minimal interaction with visible light. In contrast, conjugated polymers like polyacetylene (PA) feature alternating single and double bonds, where each carbon atom contributes one electron to the π -system. This conjugation creates delocalized π -electron clouds extending over multiple monomer units, significantly reducing the HOMO-LUMO gap to 1–1.5 eV [13], placing it in the semiconductor regime and enabling strong interactions with visible light.

The π -conjugated system forms the basis for the semiconductor nature of these materials, creating an energy band structure analogous to inorganic semiconductors, though with important distinctions. The HOMO and LUMO in organic semiconductors correspond to the valence and conduction bands in inorganic materials. However, the localized nature of electronic states in organic semiconductors leads to fundamentally different light–matter interactions.

When organic semiconductors absorb photons, they primarily generate excited states known as excitons, rather than the direct formation of free charge carriers typical in inorganic semiconductors. These excitons are electron–hole pairs bound by Coulombic interactions, with binding energies typically ranging from 0.3 to 1.0 eV [14,15]. This high binding energy, resulting from the low dielectric constant of organic materials and strong electron–hole correlation, means that room temperature thermal energy (≈ 0.026 eV) is insufficient for spontaneous exciton dissociation into free carriers.

Excitons in organic semiconductors can be classified into several types based on their character [16–19]. Frenkel excitons, localized on individual molecules or polymer chain segments, are the most common. These excitons can migrate through the material via energy transfer mechanisms, primarily Förster energy transfer for singlet excitons and Dexter energy transfer for triplet excitons, as illustrated in Figure 1. The exciton diffusion length, typically 5–20 nm in conjugated polymers, is a crucial parameter that influences device design and performance.

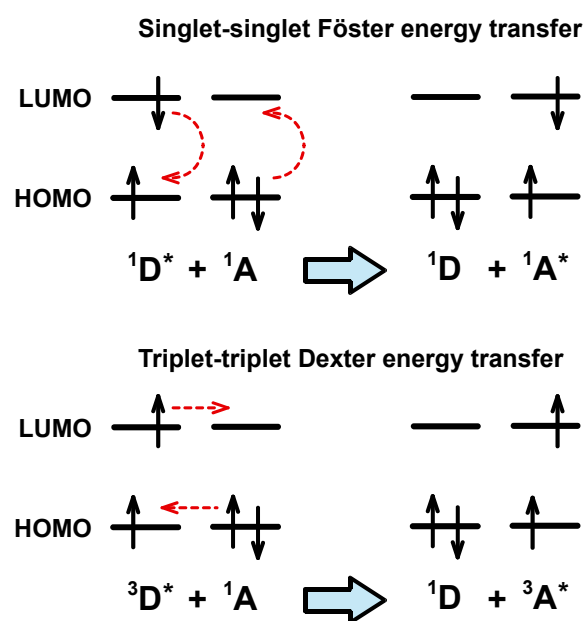


Figure 1. Schematic view of the Förster energy transfer for singlet excitons and Dexter energy transfer for triplet excitons.

The generation of free charge carriers from excitons requires additional energy or suitable interfaces. In photovoltaic applications, this is commonly achieved through the use of donor–acceptor heterojunctions, where the energy level offset between materials provides the driving force for exciton dissociation. The process involves exciton diffusion to the interface, followed by electron transfer to the acceptor material, resulting in charge separation. Understanding and controlling these processes is crucial for developing efficient photonic devices.

In the context of light emission, the process operates in reverse. Injected electrons and holes form excitons, which can then recombine radiatively, producing photons. The efficiency of this process depends on various factors, including spin statistics, competing non-radiative decay pathways, and the molecular packing that influences both electronic and optical properties.

The optical properties and phenomena in organic semiconductors arise from their unique electronic structure and can be understood through their energy band diagram. The absorption and emission processes are fundamentally linked to electronic transitions between the HOMO and LUMO levels, modified by vibrational states that create character-

istic spectral features. When a photon is absorbed, electrons are excited from the HOMO to LUMO, creating a vibronic progression in the absorption spectrum due to coupling with molecular vibrations. Similarly, emission occurs when excited electrons return to the ground state, typically showing a Stokes shift due to geometric relaxation in the excited state. This vibronic structure leads to characteristic absorption and emission bands rather than sharp transitions, with the spectral shape influenced by both electronic and vibrational states.

There are several known nonlinear optical effects in polymer organic semiconductors. In organic semiconductors, Second Harmonic Generation (SHG) arises from the non-centrosymmetric molecular structure and occurs when two photons combine to produce a single photon at twice the frequency [20,21]. The efficiency of this process depends strongly on the molecular hyperpolarizability and the degree of polar ordering. Conjugated polymers with push–pull structures exhibit particularly strong SHG responses, making them valuable for frequency conversion applications in integrated photonic circuits. However, maintaining the non-centrosymmetric order in polymer films remains challenging and often requires special processing techniques.

Electro-optic effects manifest as changes in refractive index under applied electric fields [22,23]. In organic semiconductors, the effect primarily originates from molecular re-orientation and electronic polarization. The fast response times (femtoseconds for electronic processes) make these materials particularly attractive for high-speed optical modulators and switches. Polymers with large dipole moments and extended π -conjugation typically show enhanced electro-optic coefficients, enabling efficient modulation at relatively low voltages [24].

Third Harmonic Generation (THG) in organic semiconductors converts three photons into one photon at triple the frequency. Unlike SHG, THG does not require non-centrosymmetric structures, making it more generally accessible in polymer systems [25,26]. The effect scales with the third-order susceptibility $\chi(3)$, which can be enhanced through extended conjugation and appropriate molecular design. THG finds applications in frequency conversion and optical signal processing, though thermal management can be challenging due to the high intensities required.

Optical Kerr effect, this third-order nonlinear effect manifests as an intensity-dependent refractive index change. In conjugated polymers, the effect can be particularly strong due to the delocalized π -electron system [27]. The fast response time makes it useful for all-optical switching and signal processing. However, the same mechanism can lead to unwanted self-phase modulation in high-power applications, potentially distorting optical signals in waveguides.

Two-Photon Absorption (TPA) occurs when two photons are simultaneously absorbed to excite an electron across an energy gap equivalent to the sum of their energies. In organic semiconductors, TPA can be enhanced through molecular design strategies that increase the two-photon cross-section [28]. While this effect can be detrimental in some applications by causing optical losses, it is deliberately exploited in others, such as 3D optical data storage, photodynamic therapy, and high-resolution imaging. The quadratic dependence on intensity provides inherent 3D selectivity in these applications [29].

These nonlinear optical phenomena are particularly interesting in organic semiconductors because their strength can be tuned through molecular design and processing conditions. The ability to engineer these properties at the molecular level, combined with solution processability, makes organic semiconductors versatile materials for photonic applications. However, practical implementation often requires careful consideration of trade-offs between nonlinear optical response, optical losses, and material stability.

Understanding and controlling these optical properties and nonlinear phenomena is crucial for developing effective photonic devices. The challenge lies in optimizing molecular structures and processing conditions to enhance desired effects while minimizing unwanted ones, ultimately achieving the performance requirements for specific applications.

3. Material Systems

The diversity of polymer materials suitable for photonic applications is extensive and still continuously expanding. The ability to tailor molecular structures through synthetic chemistry enables precise control over optical, electronic, and physical properties. Rather than providing an exhaustive list of all available materials, this review focuses on fundamental polymer families that have demonstrated significant impact in photonic applications and serve as platforms for understanding structure–property relationships in these systems.

At the core of polymer-based photonic materials are conjugated polymers, which feature alternating single and double bonds along their backbone. This conjugation creates delocalized π -electron systems that extend over multiple monomer units, enabling unique optical and electronic properties not found in conventional polymers. Unlike saturated polymers with localized σ -bonds, conjugated polymers possess significantly reduced bandgaps (typically 1.5–3 eV), placing them in the semiconductor regime and enabling strong interactions with visible light. This semiconductor behavior, combined with solution processability, has positioned conjugated polymers as versatile materials for a wide range of photonic applications, from simple light guiding to complex nonlinear optical phenomena.

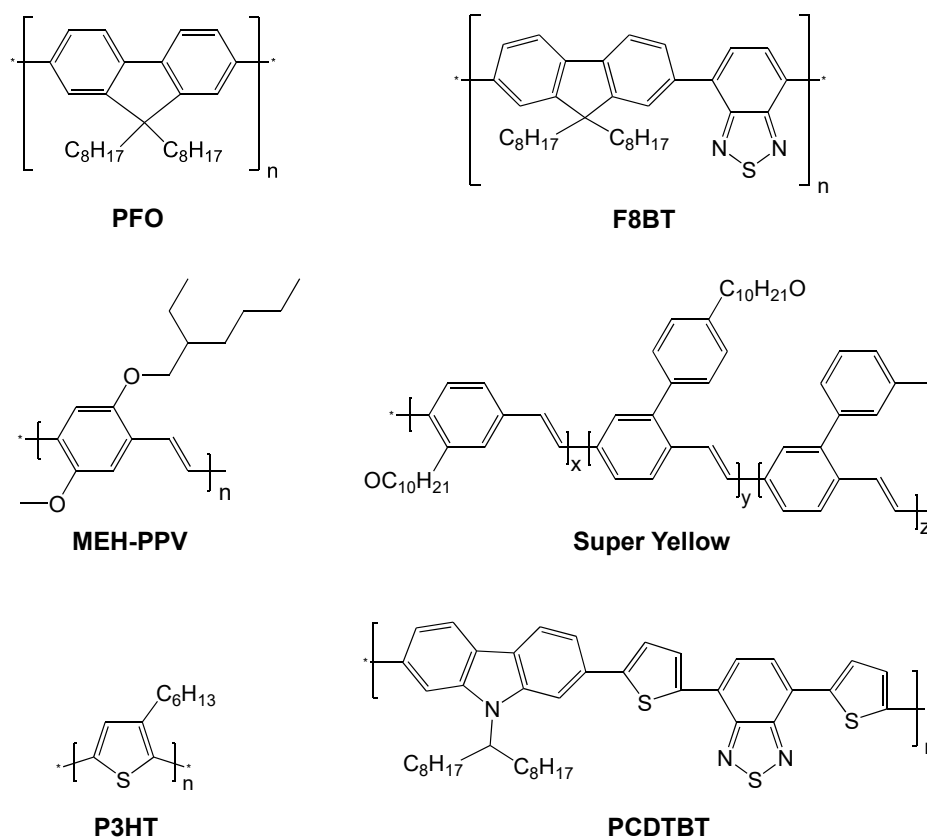
The development of conjugated polymers has evolved from early systems like polyacetylene to increasingly sophisticated architectures designed to enhance specific optical properties. Contemporary materials often incorporate various functional moieties that influence light absorption, emission, charge transport, and processing characteristics. This molecular engineering approach has yielded a rich landscape of materials with properties tailored for specific photonic applications. Among these, several key conjugated polymer families have emerged as particularly important platforms, which we discuss in detail below.

Conjugated polymers can be divided into several classes. Polyfluorenes (PFs) feature a rigid biphenyl unit with a bridging carbon atom at the 9-position, allowing for side-chain substitution that influences solubility and processing [30]. Their rigid backbone structure promotes extended conjugation and high photoluminescence quantum yields. The prototypical poly(9,9-dioctylfluorene) (PFO) exhibits excellent blue emission and can form different conformational phases affecting its optical properties [31]. More complex systems like F8BT (poly(9,9-dioctylfluorene-*alt*-benzothiadiazole)) incorporate electron-accepting units to red-shift emission and enhance charge transport [32,33]. Polyfluorenes find applications in light-emitting devices, optical amplifiers, and lasers, though their susceptibility to oxidative degradation requires careful encapsulation.

Polyphenylene vinylenes (PPVs) comprise phenylene units connected by vinylene bridges, creating a highly conjugated system with strong visible light absorption and emission [34,35]. The archetypal poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) shows efficient yellow-orange emission and good solution processability [36,37]. Derivatives like “Super Yellow” PPV offer improved stability and quantum yield [38]. These materials excel in electroluminescent devices and have shown promise in optical switching applications. Their relatively large Stokes shift helps minimize self-absorption in waveguide applications, though photo-oxidation of the vinylene bonds can limit long-term stability.

Polythiophenes (PTs) feature five-membered sulfur-containing heterocycles in their backbone, providing good environmental stability and strong π - π interactions [39,40]. Poly(3-hexylthiophene) (P3HT) represents the most studied system, showing good charge transport and optical properties that depend strongly on molecular weight and regioregularity [41–43]. More complex systems like poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT) incorporate electron-deficient units for enhanced absorption and charge separation [44,45]. Polythiophenes find applications in photodetectors and optical sensors, with their strong interchain interactions enabling efficient energy transfer in well-ordered films.

Recent advances in polymer chemistry have led to the development of novel architectures that extend beyond traditional conjugated polymer systems. Donor–acceptor copolymers have emerged as a particularly promising class, incorporating alternating electron-rich and electron-poor units within the polymer backbone, as shown in Scheme 1. This design strategy enables precise control over energy levels and optical gaps, leading to materials with optimized properties for specific applications. For instance, PCDTBT derivatives and related low-bandgap polymers extend absorption into the near-infrared region, opening new possibilities for telecommunications applications and bio-imaging [44,46].



Scheme 1. Molecular structures of poly(9,9-dioctylfluorene) (PFO), poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT), poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), “super yellow” polyphenylene vinylene, poly(3-hexylthiophene) (P3HT), and poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT).

Another significant development is the introduction of spiro-based polymers, where spiro-linkages maintain conjugation while effectively suppressing aggregation. This molecular architecture leads to improved photoluminescence efficiency and solution processability, making these materials particularly attractive for light-emitting applications [47,48]. The

unique spatial arrangement of the conjugated segments also allows for three-dimensional charge transport, potentially beneficial for complex photonic circuits.

Dendrimeric systems represent another innovative approach, combining the processing advantages of small molecules with the robust film-forming properties of polymers [49–53]. These branched architectures enable precise control over chromophore spacing and orientation, leading to enhanced energy transfer efficiency and improved optical properties. The multiple functional end groups in dendrimeric structures also provide opportunities for surface functionalization and integration with other materials.

Cross-linkable conjugated polymers have also gained attention, particularly for multi-layer device fabrication [54,55]. These materials incorporate functional groups that enable post-processing cross-linking, significantly enhancing film stability and allowing for the construction of complex device architectures without compromising existing layers. This approach has proven particularly valuable in creating stable waveguide structures and integrated optical circuits.

The continued development of new polymer systems, coupled with a deeper understanding of structure–property relationships, enables increasingly sophisticated control over optical and electronic properties. This evolution drives progress in both fundamental research and practical applications in photonic devices.

Polymer blends and composites are another interesting topic [56]. The blending of different polymers offers a powerful strategy to combine desirable properties of individual components into a single material system. In photonic applications, polymer blends can enhance light emission, improve charge transport, or introduce new functionalities unavailable in single-component systems. For instance, blends of PFO with F8BT have demonstrated efficient energy transfer, enabling color tuning and improved emission efficiency in light-emitting devices [57–59]. Similarly, blends of MEH-PPV with electron-transport polymers like PBD (2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole) have shown enhanced electroluminescence efficiency through improved charge balance [60].

Another successful example includes blends of P3HT with high-electron-affinity polymers like poly(2,5,2',5'-tetrahexyloxy-7,8'-dicyanodi-p-phenylenevinylene) (CN-PPV), which create efficient heterojunctions for photodetector applications [61]. The incorporation of poly(methyl methacrylate) (PMMA) into conjugated polymer systems has proven effective in reducing aggregation-induced quenching and improving film formation properties, as demonstrated in blends with polyfluorene derivatives, as illustrated in Figure 2 [62,63].

However, the development of effective polymer blends faces several challenges. The primary limitation stems from the thermodynamic immiscibility of many polymer pairs, leading to phase separation at various length scales. For example, while PFO and F8BT can form relatively stable blends at certain compositions, phase separation often occurs during thermal annealing, affecting device stability [64–66]. While controlled phase separation can sometimes be beneficial, creating specific morphologies for optimal device performance, uncontrolled segregation often leads to poor device performance and stability.

The compatibility of polymer blends depends strongly on their molecular structure, molecular weight, and processing conditions. Even small changes in processing parameters can significantly affect blend morphology. Solutions to these challenges include the use of compatibilizers, such as block copolymers that can stabilize the interface between immiscible components, careful selection of common solvent systems that enable uniform mixing during processing, and the development of processing protocols that kinetically trap desired morphologies. For instance, the addition of small amounts of rod-coil block copolymers has been shown to stabilize blends of conjugated polymers with insulating matrices [67–69].

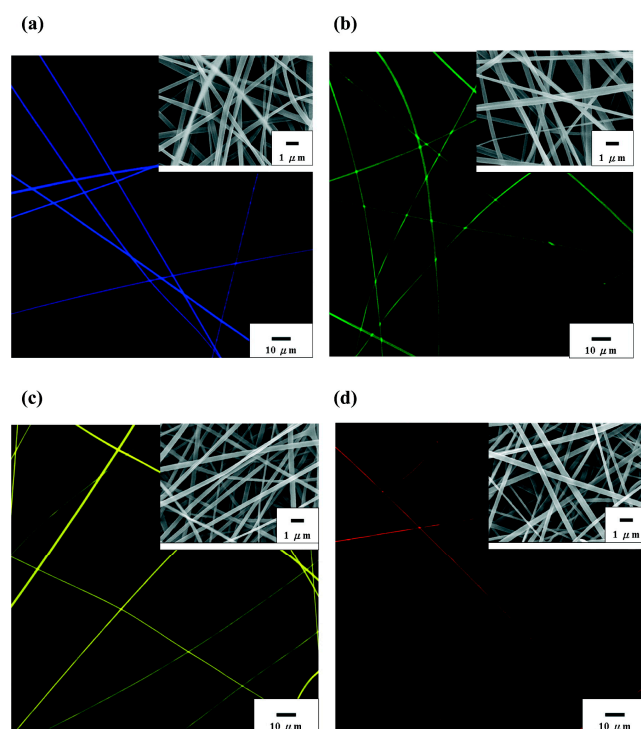


Figure 2. Laser confocal microscopy images of 5 wt% polyfluorene derivative/PMMA blend ES nanofibers with (a) PFO; (b) PFQ; (c) PFBT; (d) PFTP [62]. Reprinted (adapted) with permission from [62]. Copyright 2007 American Chemical Society.

Additionally, the optical properties of blends can be affected by energy transfer between components, requiring careful consideration of energy level alignment and spatial distribution of the constituents. Förster resonance energy transfer (FRET) between donor and acceptor polymers can be either beneficial or detrimental depending on the application, necessitating precise control over blend composition and morphology to achieve desired optical properties [70–72].

Besides blends of organic materials, the hybrid organic–inorganic systems offer another alternative approach. The integration of organic polymers with inorganic nanostructures has emerged as a promising approach to creating materials with enhanced or complementary functionalities. Semiconductor quantum dots (QDs) can be incorporated into polymer matrices to achieve spectrally tunable emission through quantum confinement effects. For example, CdSe/ZnS core–shell quantum dots embedded in MEH-PPV matrices have demonstrated efficient energy transfer from the polymer to QDs, resulting in enhanced red emission useful for display applications [73,74]. Similarly, PbS quantum dots integrated with polyfluorene derivatives have enabled near-infrared emission and detection capabilities, extending the spectral range of polymer-based devices [75]. Another successful implementation includes hybrid systems of P3HT with zinc oxide nanoparticles, where the inorganic component enhances charge transport while maintaining the solution processability of the polymer matrix [76].

Metal nanoparticles introduce localized surface plasmon resonance (LSPR) effects, which can enhance light absorption and emission through near-field coupling. Gold and silver nanoparticles are particularly useful due to their strong plasmonic responses in the visible region [77]. For instance, silver nanoparticles embedded in F8BT have shown significant enhancement of photoluminescence through plasmonic coupling [78]. The enhancement of local electromagnetic fields near metal nanoparticles can increase the efficiency of nonlinear optical processes and modify emission rates through the Purcell effect [79,80]. However, successful implementation of these hybrid systems requires care-

ful consideration of several factors. Surface modification of inorganic nanoparticles is often necessary to ensure compatible integration with the polymer matrix. For example, quantum dots capped with organic ligands like trioctylphosphine oxide show improved dispersion in conjugated polymer hosts [81,82]. Similarly, silane coupling agents have been effectively used to modify metal oxide nanoparticles for better compatibility with polymer matrices [83,84].

The concentration and distribution of inorganic components must be carefully controlled to optimize device performance. While higher concentrations of nanoparticles can enhance certain properties, they may also lead to aggregation and increased scattering losses. For instance, optimal plasmonic enhancement in polymer–metal nanoparticle systems typically occurs at relatively low metal concentrations (<1 wt%), above which aggregation and quenching effects become dominant. Additionally, the interface between organic and inorganic components plays a crucial role in determining energy and charge transfer processes, requiring careful engineering of surface chemistry and morphology control during processing.

The development of these hybrid systems continues to expand the possibilities for polymer-based photonic devices, combining the processability and flexibility of organic materials with the unique optical and electronic properties of inorganic nanostructures.

Since the material properties of polymer systems can be tailored according to the demand, the development of polymers with targeted optical properties requires a multifaceted approach combining molecular design, morphology control, and processing optimization. At the molecular level, several key strategies have emerged as particularly effective. Conjugation length control through backbone design and side-chain engineering enables precise tuning of absorption and emission wavelengths [85,86], as demonstrated in polyfluorene derivatives where the incorporation of different co-monomers allows the tuning of emissions from blue to red [87,88]. Energy level adjustment can be achieved via the incorporation of electron-rich or electron-poor substituents, exemplified by the development of donor-acceptor systems like PCDTBT, where the combination of carbazole donor and benzothiadiazole acceptor units enables broad absorption and efficient charge separation.

Aggregation control, crucial for maintaining high luminescence efficiency, can be accomplished through the careful introduction of steric hindrance or specific molecular architectures. For instance, the incorporation of bulky side groups in MEH-PPV reduces interchain interactions and enhances photoluminescence quantum yield [89]. The spiro-configuration in spiro-OMeTAD demonstrates how molecular architecture can prevent excessive aggregation while maintaining charge transport properties [90]. The incorporation of specific chromophores allows for desired optical transitions, as seen in F8BT where the benzothiadiazole unit introduces low-energy absorption and emission bands [91]. Control over interchain interactions through side-chain modification affects both optical and charge transport properties, demonstrated by the impact of alkyl chain length and branching in P3HT derivatives on film morphology and optical properties.

Processing strategies play an equally crucial role in optimizing optical properties. The choice of solvent and drying conditions significantly influences film morphology, as shown in the case of P3HT where slow drying from high-boiling solvents promotes crystallinity and red-shifted absorption [92,93]. Thermal or solvent annealing procedures can be employed to modify molecular organization post-deposition, exemplified by the dramatic changes in PFO optical properties upon formation of the β -phase through controlled solvent exposure [94]. Various alignment techniques enable the achievement of oriented structures for enhanced or anisotropic optical properties, demonstrated in mechanically aligned polymer films showing polarized emission. Surface modification strategies prove essential for controlling interfacial properties, particularly in multilayer devices or hybrid

systems, as shown in the use of polyelectrolyte layers to modify electrode interfaces in light-emitting devices [95,96].

The successful development of effective materials requires careful balancing of multiple factors. Optical performance requirements must be weighed against processing compatibility considerations, while environmental stability remains a crucial concern for practical applications. For instance, the development of air-stable blue-emitting polymers has required careful molecular design to prevent oxidation of fluorene units while maintaining high photoluminescence quantum yields. Cost considerations and scalability of both synthesis and fabrication processes play vital roles in determining commercial viability, as demonstrated by the industrial adoption of solution-processable light-emitting polymers in display applications. This complex interplay of factors necessitates an iterative approach to material development, where molecular design and processing strategies are continuously refined based on performance feedback and application requirements. The continued evolution of these design strategies, coupled with an improved understanding of structure–property relationships, enables increasingly sophisticated control over optical properties in polymer-based photonic materials.

4. Applications in Photonic Devices

Photonic devices manipulate and control light through various optical phenomena, enabling applications in communications, sensing, computing, and display technologies. These devices can be broadly categorized into passive and active components based on their interaction with light. Passive components guide, filter, or scatter light without external energy input, while active components require energy to modify, generate, or detect light signals. Polymer materials offer unique advantages in both categories, including solution processability, mechanical flexibility, and tunable optical properties.

4.1. Fabrication Approaches for Polymer Photonic Devices

The realization of polymer-based photonic devices relies on a diverse array of fabrication techniques that can be broadly categorized into solvent-based and solvent-free approaches. The selection of appropriate fabrication methods is often dictated by the solubility limitations of specific polymer systems, particularly conjugated polymers where extended π -conjugation can significantly reduce solubility in common solvents or even make certain polymers completely insoluble. These solubility challenges have driven the development of alternative processing strategies to ensure that the beneficial optical and electronic properties of these materials can be effectively incorporated into functional devices. Each method offers distinct advantages in terms of resolution, scalability, and compatibility with specific polymer systems.

Solvent-based techniques leverage the inherent solution processability of many polymers, enabling cost-effective and scalable device fabrication. Spin coating represents one of the most widely used methods, providing uniform thin films with precisely controlled thickness through adjustment of rotation speed and solution viscosity [97]. This technique has been successfully applied to create waveguide cores using various polymers, including PMMA, SU-8, and conjugated polymers like polyfluorenes. For more complex device geometries, inkjet printing offers the ability to directly pattern polymer structures without masks, though at somewhat lower resolution [98]. This approach has proven particularly valuable for fabricating multicomponent devices, where different polymers can be deposited in specific locations. Solution casting and dip coating provide additional options for creating films of varying thickness, with the latter being particularly useful for coating three-dimensional structures [99].

Solvent-free processing methods exploit the thermoplastic nature of many polymers and are particularly advantageous when solvent compatibility issues arise. Thermal nanoimprint lithography enables high-resolution pattern transfer by pressing a heated mold into a polymer, creating features with dimensions below 100 nm [100]. This technique has been successfully applied to fabricate polymer photonic crystals, gratings, and microresonators. Hot embossing represents a related approach suitable for larger-scale features [101]. For polymers with appropriate thermal properties, melt processing enables the creation of structured devices through techniques such as extrusion or injection molding, though typically with more limited resolution than nanoimprint approaches.

For certain applications, polymer vapor deposition techniques offer unique advantages, particularly for creating highly conformal coatings or working with materials insoluble in common solvents. Chemical vapor deposition of parylene, for example, produces pinhole-free films with excellent optical properties useful as waveguide cladding layers [102]. For conjugated polymers, oxidative chemical vapor deposition has emerged as a promising solvent-free approach for creating electronic and optoelectronic devices.

The patterning of polymer photonic structures employs several approaches, often adapted from microelectronics fabrication. Photolithography remains widely used, particularly with photosensitive polymers like SU-8, enabling the direct creation of waveguides and other photonic elements [103]. For non-photosensitive polymers, reactive ion etching following photoresist patterning provides an alternative route, though at the cost of increased process complexity [104]. Direct writing techniques using laser or electron beams offer maskless patterning with high resolution, particularly valuable for prototyping or creating gradient-index structures through selective polymer cross-linking [105].

The integration of multiple materials, crucial for many photonic devices, can be achieved through several approaches. Layer-by-layer assembly enables the creation of complex multilayer structures, though interface quality between dissimilar materials requires careful consideration to minimize optical losses [106]. Selective area deposition, using techniques such as microcontact printing or area-selective growth, provides another route to integrating different functional materials within a single device.

Post-processing techniques often play a crucial role in optimizing device performance. Thermal annealing can enhance crystallinity and alignment in semicrystalline polymers, improving both optical and electronic properties [107]. Similarly, solvent vapor annealing offers a gentler approach to reorganizing polymer chains and enhancing interchain interactions in conjugated polymer systems [108]. Surface treatments, including plasma processing or self-assembled monolayer deposition, can modify interfacial properties crucial for multi-material integration.

Table 1 summarizes the above-mentioned list of fundamental approaches to photonic device fabrication. The selection of appropriate fabrication approaches depends on multiple factors, including resolution requirements, material compatibility, scalability needs, and economic considerations. For high-performance devices, combinations of these techniques are often employed, with solvent-based methods providing the initial structure and post-processing techniques optimizing performance. The continued development of these fabrication approaches, coupled with advances in polymer design, drives progress toward increasingly sophisticated and capable polymer photonic devices.

Table 1. Overview of fabrication methods for photonic devices based on organic semiconductors, showing key features, resolution, application, and representative material families. N/A means ‘not applicable’.

Fabrication Method	Category	Key Features	Resolution	Application	Compatible Materials
Spin Coating	Solvent-based	Uniform thin films, precise thickness control	10 nm (thickness)	Waveguide cores, thin film layers	PMMA, SU-8, polyfluorenes
Inkjet Printing	Solvent-based	Direct patterning, maskless, multi-material	20–50 μm	Multicomponent devices, displays	Low-viscosity polymer solutions
Solution Casting	Solvent-based	Simple process, variable thickness	>1 μm	Large-area films, flexible devices	Most soluble polymers
Thermal Nanoimprint	Solvent-free	High-resolution, pattern transfer	<100 nm	Photonic crystals, gratings	Thermoplastic polymers
Hot Embossing	Solvent-free	Large-area patterning, cost-effective	>1 μm	Waveguides, microfluidic integration	Thermoplastic polymers
Polymer Vapor Deposition	Solvent-free	Conformal coatings, pinhole-free	10 nm (thickness)	Waveguide claddings, barriers	Parylene, some conjugated polymers
Photolithography	Patterning	Parallel processing, industry-standard	0.5–2 μm	Complex waveguide networks	Photosensitive polymers (SU-8)
Direct Laser Writing	Patterning	Maskless, 3D capabilities	100 nm–1 μm	Photonic crystals, complex structures	Photo-cross-linkable polymers
Reactive Ion Etching	Patterning	High anisotropy, vertical sidewalls	100 nm–1 μm	High-contrast waveguides	Most solid polymers
Layer-by-Layer Assembly	Multi-material	Precise thickness, multi-functionality	1–10 nm (layer)	Multilayer photonic structures	Polyelectrolytes, functional polymers
Thermal Annealing	Post-processing	Enhanced crystallinity, reduced defects	N/A	Improved optical transmission	Semi-crystalline polymers
Solvent Vapor Annealing	Post-processing	Controlled reorganization	N/A	Enhanced interchain interactions	Conjugated polymers

4.2. Passive Components

In the domain of passive photonic components, polymer materials have demonstrated remarkable versatility and functionality. Polymer waveguides serve as fundamental building blocks for integrated photonic circuits, offering capabilities beyond simple light guiding. For instance, PMMA waveguides doped with chromophores enable temperature sensing through thermo-optic effects [109], while SU-8 waveguides functionalized with specific receptor molecules have shown excellent capabilities for bio-sensing applications [110]. The incorporation of stimuli-responsive polymers like poly(N-isopropylacrylamide) (PNIPAm)

creates adaptive waveguides that respond to environmental changes, enabling switchable routing and sensing applications [111].

Polymer-based optical filters utilize various mechanisms for spectral selection, with Bragg filters fabricated from alternating layers of polymers with different refractive indices, such as PS/PMMA multilayers, providing efficient wavelength filtering [112,113]. More sophisticated approaches include holographic polymer-dispersed liquid crystals (H-PDLCs), where the periodic variation in refractive index creates selective reflection bands [114–116]. The incorporation of azobenzene-containing polymers enables photo-switchable filters whose spectral response can be modified with light, adding an active component to traditionally passive structures [117].

The field of polymer photonic crystals offers unique opportunities for creating responsive optical structures. Block copolymers like PS-*b*-PMMA can self-assemble into periodic structures with photonic band gaps, becoming particularly interesting when one component is responsive to external stimuli [118,119]. Hydrogel-based photonic crystals incorporating poly(acrylic acid) demonstrate color changes in response to pH or ionic strength, useful for sensing applications [120,121]. Similarly, photonic crystals based on cholesteric liquid crystalline polymers provide a tunable selective reflection that can be modified through mechanical strain or temperature [122–125].

More complex passive structures combine multiple functions or incorporate responsive elements. Multimode interference (MMI) devices using epoxy-based polymers enable optical power splitting [126], while ring resonators fabricated from fluorinated polyimides provide narrow-band filtering capabilities [127]. Photonic crystal fibers using PMMA or COC (cyclic olefin copolymer) offer specialty light guidance properties, and Mach–Zehnder interferometers incorporating electro-optic polymers demonstrate advanced sensing capabilities, as illustrated in Figure 3 [128–130]. In each case, the polymer material not only provides basic optical functionality but also enables additional features through mechanical flexibility, easy surface modification, response to environmental conditions, cost-effective fabrication methods, and integration possibilities with other materials and devices.

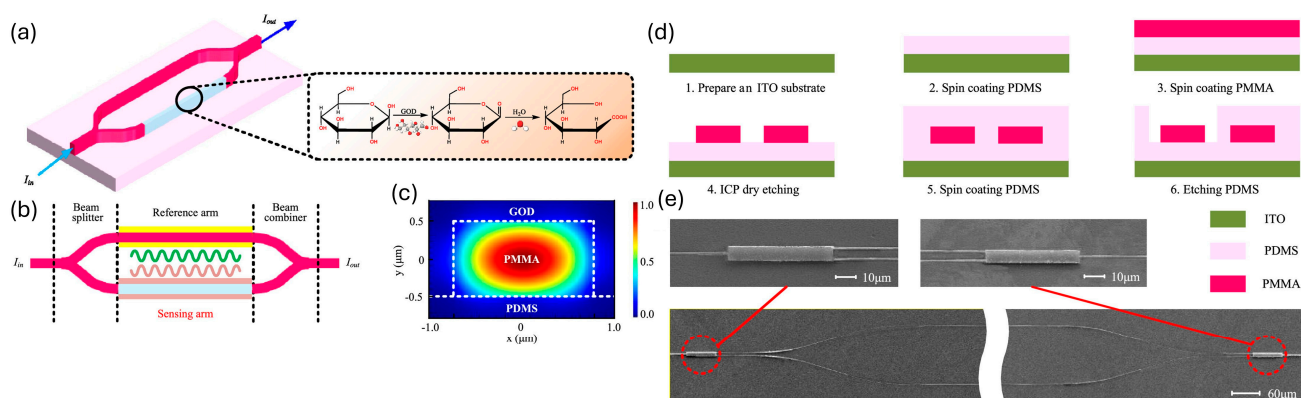


Figure 3. Architecture and working principle of the Mach–Zehnder interferometer (MZI) blood glucose sensor: (a) Working principle of the MZI blood glucose sensor. Glucose oxidase (GOD) catalyzes the production of gluconic acid and H₂O₂ from blood glucose. (b) Layout of the MZI, which consists of a 1 × 2 beam splitter, a 2 × 1 beam combiner, and two branch waveguides (sensing arm and reference arm) of the same length. The red line and the green line indicate the phases of the sensing arm and reference arm, respectively. The phase shift between the reference arm and the sensing arm is π . (c) TE electric field mode distribution of the single-mode waveguide at 1550 nm. (d) Schematic demonstration of the overall fabrication process for preparing the MZI blood glucose

sensor along with magnified detailed SEM images. Step-by-step illustration showing the overall fabrication process of the polymer-based MZI blood glucose sensor. The substrate (green) material is ITO, the cladding layer (pink) material is PDMS, and the core layer (red) material is PMMA. (e) SEM images of the MZI blood glucose sensor, including the 1×2 MMI coupler, 2×1 MMI coupler, input/output ports, and curved waveguides. The structure is symmetric, with a core size of $2952 \mu\text{m} \times 130 \mu\text{m}$ [130]. Reprinted (adapted) with permission from [130]. Copyright 2024 American Chemical Society.

The continued development of these passive components benefits significantly from advances in polymer science, with new materials and processing methods expanding the range of achievable functionalities and applications. The ability to combine different polymer systems and incorporate responsive elements opens new possibilities for creating adaptive and multifunctional photonic devices.

4.3. Active Components

The realm of active photonic components encompasses devices that interact with light through energy conversion or external control, with organic semiconducting polymers playing a crucial role in many applications. Light-emitting devices represent one of the most successful implementations, where polymers like PFO and its derivatives enable efficient electroluminescence across the visible spectrum. The incorporation of electron-transporting units, as demonstrated in F8BT, has led to improved device efficiency and color purity [33,57]. These materials have found commercial success in display applications, benefiting from solution processing and the ability to achieve large-area devices through printing techniques.

In the domain of photodetectors, conjugated polymers offer unique advantages for light-sensing applications. P3HT and its blends with electron-accepting materials have demonstrated high sensitivity and fast response times [41,42]. More sophisticated systems, such as low-bandgap polymers like PCDTBT, enable broader spectral coverage extending into the near-infrared region [45]. These materials prove particularly valuable in imaging applications and optical communication systems where flexible, large-area detection is required.

Optical amplifiers based on conjugated polymers exploit their strong stimulated emission properties. MEH-PPV has demonstrated optical gain in waveguide configurations, while more specialized materials like poly(9,9-dioctylfluorene-co-benzothiadiazole) enable amplification at specific wavelengths through careful molecular design [131,132]. These systems benefit from high gain coefficients and the ability to integrate directly with polymer waveguide structures, though challenges remain in achieving long-term stability under high-intensity illumination.

Modulators and switches represent another important category where polymer materials excel through their strong electro-optic and thermo-optic responses. Polymers containing chromophores with large dipole moments, such as DR1-PMMA (Disperse Red 1 functionalized poly(methyl methacrylate)), enable efficient electro-optic modulation [133–135]. More advanced systems incorporate cross-linkable units to improve stability while maintaining high electro-optic coefficients. Additionally, thermo-optic switches based on conjugated polymers like polyfluorenes demonstrate fast switching capabilities with relatively low power consumption.

The integration of these active components with passive structures has led to increasingly sophisticated photonic circuits. For example, the combination of polymer light-emitting regions with waveguide structures enables integrated light sources, while the incorporation of photodetector sections creates complete optical links [136–138]. The ability to pattern different polymer materials through solution processing enables the fabrication

of complex devices incorporating multiple active functions. Moreover, the development of new materials continues to expand the capabilities of these devices, with recent advances in stability and efficiency pushing toward practical applications in communications, sensing, and computing.

The success of active polymer photonic components relies heavily on molecular design strategies that optimize both optical and electronic properties while maintaining processability and stability. The continued development of new materials and device architectures, coupled with an improved understanding of structure–property relationships, drives progress toward more efficient and reliable devices for next-generation photonic applications. Table 2 demonstrates the versatility of organic semiconductors in both passive components (waveguides, filters, photonic crystals) and active devices (light-emitting devices, photodetectors, amplifiers, modulators), highlighting their broad applicability in photonic technologies.

Table 2. Overview of passive and active photonic devices based on organic semiconductors, showing different device categories, representative material families, and their primary applications.

Device Type	Category	Material Family	Example Material	Application	Ref.
Waveguides	Passive	Polyfluorenes	PFO	Light guiding, sensing	[62]
		Modified PMMA	Doped PMMA	Temperature sensing	[109]
		SU-8	Functionalized SU-8	Bio-sensing	[110]
Filters	Passive	PS/PMMA	Multilayer stacks	Wavelength selection	[112]
		Azobenzene polymers	DR1-PMMA	Photo-switchable filtering	[133]
		H-PDLCs	LC-polymer composites	Tunable reflection	[114]
Photonic Crystals	Passive	Block copolymers	PS-b-PMMA	Structural color	[118]
		Hydrogels	Poly(acrylic acid)	pH sensing	[120]
		Liquid crystals	Cholesteric polymers	Strain sensing	[125]
Light-emitting devices	Active	Polyfluorenes	F8BT	Light sources	[33]
		PPV derivatives	MEH-PPV	Light sources	[131]
Photodetectors	Active	Polythiophenes	P3HT	Light sensing	[41]
		Low-bandgap polymers	PCDTBT	NIR detection	[45]
Optical amplifiers	Active	PPV derivatives	MEH-PPV	Signal amplification	[132]
		Polyfluorenes	F8BT	Optical gain	[57]
Modulators/Switches	Active	Electro-optic polymers	DR1-PMMA	Signal modulation	[133]
		Thermo-optic polymers	PFO derivatives	Optical switching	[94]

4.4. Emerging Applications

The field of polymer photonics continues to expand into novel territories, with several emerging applications demonstrating particular promise. Neuromorphic photonics, which aims to emulate neural processing through optical systems, has begun to leverage the unique properties of conjugated polymers. For instance, P3HT-based photonic synapses have demonstrated spike-timing-dependent plasticity, mimicking biological learning processes through photo-induced charge transfer [139,140]. Similarly, devices incorporating poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno[3,2-b]thiophene)] (PDPP-TBT) have shown multi-level optical memory states useful for neuromorphic computing applications [141,142]. The ability to tune the photophysical properties of these materials through molecular design enables the creation of artificial synapses with controllable response times and memory retention.

Quantum photonic systems represent another frontier where polymer materials are making significant inroads. Conjugated polymers like MEH-PPV have demonstrated single-photon emission capabilities when properly isolated at the molecular level [143]. More sophisticated systems incorporating BODIPY-based polymers enable controlled quantum emissions with high purity and tunability [144,145]. The integration of quantum emitters with polymer waveguide structures creates opportunities for on-chip quantum information processing. Additionally, block copolymers like PS-*b*-PMMA provide self-assembled templates for organizing quantum emitters with precise spatial control, crucial for quantum optical circuits [146,147].

Bio-integrated photonics has emerged as a particularly exciting application area, leveraging the biocompatibility and flexibility of polymer materials. Water-soluble conjugated polymers such as poly(fluorene-alt-benzothiadiazole) (PFBT) derivatives enable direct integration with biological systems for sensing and imaging applications [148,149]. The development of biodegradable conjugated polymers based on modified PPV structures opens possibilities for transient photonic devices that can be safely absorbed by the body after use.

These emerging applications benefit from the convergence of multiple polymer technologies. For instance, neuromorphic systems often combine photoactive conjugated polymers with ion-conducting polymers to achieve synaptic-like behavior. Quantum photonic applications frequently utilize hybrid systems where polymer matrices provide precise control over the local environment of quantum emitters. Bio-integrated devices leverage the chemical versatility of polymers to combine optical functionality with biological interface capabilities. The continued development of new materials and processing methods, particularly those focusing on stability and reproducibility, drives progress in these emerging fields.

Furthermore, the intersection of these emerging applications creates opportunities for novel devices. For example, bio-inspired neuromorphic systems utilizing light-sensitive conjugated polymers offer new approaches to artificial intelligence, while quantum biosensors combining single-photon sensitivity with biological specificity enable unprecedented detection capabilities. The ability to process these materials using conventional techniques while achieving sophisticated functionality positions polymer photonics at the forefront of next-generation optical technologies.

5. Conclusions

This review has demonstrated the significant potential of organic semiconductors as optically active polymer materials in photonic applications. The unique combination of semiconductor properties with polymer processability makes these materials particularly attractive for next-generation photonic devices. The ability to tune optical and electronic

properties through molecular design, coupled with solution processability and mechanical flexibility, positions organic semiconductors as versatile building blocks for both passive and active photonic components.

The field has witnessed remarkable progress in fundamental material development, from well-established systems like polyfluorenes and polyphenylene vinylenes to emerging donor-acceptor architectures. The successful implementation of these materials in various photonic devices, ranging from simple waveguides to complex neuromorphic systems, demonstrates their versatility and potential. The development of polymer blends, composites, and hybrid organic–inorganic systems has further expanded the application space, enabling enhanced functionality and improved performance.

Looking forward, several trends are likely to shape the future of organic semiconductor photonics. The integration of multiple functionalities within single material systems, enabled by sophisticated molecular design, will drive the development of adaptive and self-regulating photonic devices. The emergence of bio-inspired and quantum photonic applications opens new opportunities for organic semiconductors, particularly in areas requiring biocompatibility or precise control over quantum states. Additionally, the development of materials with enhanced stability and improved processing compatibility will facilitate the transition from laboratory demonstrations to practical applications.

The convergence of organic semiconductors with advanced fabrication techniques, particularly additive manufacturing and roll-to-roll processing, positions these materials as enabling technologies for large-area, flexible photonic systems. As the field continues to mature, organic semiconductors are poised to play an increasingly important role in addressing challenges in communications, computing, sensing, and healthcare through innovative photonic solutions. The combination of synthetic versatility, processability, and tunable optoelectronic properties makes organic semiconductors a cornerstone of future photonic technologies.

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