Recent advances in open-shell mixed conductors—From molecular radicals to polymers

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Chem. Phys. Rev. 4, 041310 (2023)
https://doi.org/10.1063/5.0163747
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Cite as: Chem. Phys. Rev. 4, 041310 (2023); doi: 10.1063/5.0163747
Submitted: 19 June 2023 · Accepted: 26 October 2023 · Published Online: 12 December 2023

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ABSTRACT
Mixed conductors have recently garnered attention in the chemical physicist community due to their distinctive conducting nature and numerous potential applications. These species transport charges via both ionic and electronic pathways, where the coupling between these pathways facilitates an alternative mode of charge transport. Among the various mixed conductors examined, stable open-shell organic compounds are emerging as a promising class of materials. They have the potential to supplant existing organic mixed conductors thanks to their superior conductivity, ease of processing, environmental stability, and functional adaptability. Notably, recent advancements in open-shell macromolecules have been remarkable, ranging from their unprecedented solid-state electrical conductivity to their versatile roles in electrochemistry. Similarly, recent strides in small molecular open-shell species deserve attention. The solid-state electronic properties of these small molecular radicals can be compared to those of macromolecular (non-)conjugated organic materials, and they also play a significant role in wet (electrolyte-based) chemistry. In this review article, we offer a comprehensive overview of open-shell organic compounds, encompassing both small and macromolecular radicals. We particularly emphasize their role as a mixed conductor in various applications, the unique context of each species, and the interconnections between them.

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https://doi.org/10.1063/5.0163747

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I. INTRODUCTION
Open-shell mixed conductors, including both small- and macro-molecular radicals, have recently demonstrated their widespread impact in a range of fields. These are from industries and technologies
to the rapidly evolving area of chemistry, materials science, and biology.\textsuperscript{2–10} With the key distinction being the presence of unpaired electrons in their outermost valence shell, these (macro-)molecular species exhibit both micro- and macroscopic properties that are markedly distinct from conventional organic mixed conductors.\textsuperscript{4,11} The ambient stability of such open-shell mixed conductors is achieved through spin delocalization and/or steric protection of the unpaired electrons.\textsuperscript{4,6,12} Here, a minute change in their singly occupied molecular orbital (SOMO) translates readily into significant variations in the terminal properties. As a result, it expands the potential of these mixed conductors vastly in electronic and energy applications.\textsuperscript{1} In addition to the designer flexibility, they also possess excellent processability due to their non-conjugated nature.\textsuperscript{1,13,14} This makes the open-shell mixed conductors compatible with different manufacturing processes and allows for tailoring their mechanical, thermal, spin, and transport properties on demand (Scheme 1).

While the initial synthesis and observation of the paramagnetic properties of nitroxide-based radical polymers (one of the representative open-shell macromolecules) date back to 1972,\textsuperscript{15} it is only in the recent few decades that these macromolecules have been highlighted as key components in various electronic and electrochemical applications. In particular, the solid-state electronics of open-shell macromolecules has experienced a very recent breakthrough, with the discovery of radical systems possessing electrical conductivities comparable to that of conjugated small and macromolecules.\textsuperscript{13} Despite its current immaturity, the field is growing very rapidly, with increasingly specific demands for the understanding of the fundamental conduction mechanisms governing these conduction systems. Furthermore, the establishment of a structure–property relationship among derivatives of various macromolecular radicals is another driving force of the rapid growth. Pressing needs also arise in revealing ionic conduction processes associated with them as mixed conductors, the aspect of which has been elusive throughout the literature (Fig. 1).

Another key to comprehensively understanding open-shell mixed conductors is to elucidate the fundamental mechanics and the underlying interrelationship of their building blocks, namely, those of small molecular radicals.\textsuperscript{1,16} The discrete nature of these molecular species often provides a more precise description of the specific electronic and/or electrochemical properties, decoupling the backbone effects that the macromolecules inherently possess. This way, one can potentially predict and fine-tune the desired end-use properties, with a suitable combination of the radical moieties and the backbone structures. Up until now, however, the focus of open-shell mixed conductors has primarily revolved around macromolecular radicals, while the
The significance of small molecular ones has been relatively overlooked. One of the main purposes of this article, therefore, is to emphasize the recent accomplishments of small molecular radicals in the aforementioned fields, and to explore their contextual relevance and interrelationships.

The purpose of organizing this review is to provide researchers in relevant fields with a generalized overview of the advancements in open-shell mixed conductors, with a particular emphasis on their preparation and applications in electronics. Specifically, our review focuses on stable nitroxide-based radicals, given their substantial impact and extensive coverage in the existing literature. Considering our primary focus on nitroxides as mixed conductors, this review will commence with a concise summary of recent works on their fundamental conduction mechanism in Sec. I. Subsequently, Sec. II will explore synthetic strategies employed for various categories of small and macromolecular radicals. Section III will provide a comprehensive account of the recent advancements in small molecular radicals as mixed conductors, while Sec. IV will extensively summarize the progress made in macromolecular radicals. To conclude, Sec. V will evaluate the current state of the field and explore potential opportunities for future research. The objective of this review is to stimulate interest in the development of open-shell mixed conductors, by focusing on the most promising, but have largely overlooked, areas of investigation. By doing so, we aim to facilitate interdisciplinary collaboration among researchers and address the pressing challenges in this burgeoning field.

### A. Charge transport in small and macromolecular radicals

The characteristic open-shell nature of (macro-)molecular radicals leads to their charge transport behaviors markedly distinct from those of the conjugated small and macromolecules. These behaviors are characterized by the presence of highly localized charge carriers with weak coupling to each other with optional disorders. Specifically, the charge transport in this system can be viewed as a series of redox hopping events associated with self-exchange redox reaction among constituent species, under possible constraints of such as the presence of backbones or electrolytes. Therefore, while the charge transport behavior in small molecular radicals can be described in a relatively simple manner, the structural disorder in macromolecular radicals adds a significant level of complexity to its description. This is further complicated by the electrolytes added to the system. This subsection summarizes recent studies on the mechanistic aspects of charge transport processes governing small and macromolecular radicals, from the simplest case of small molecular radicals to the case of electrolyte-based macromolecular systems.

#### 1. Charge transport in small molecular radicals

Due to a relatively well-defined molecular structure and the crystallinity that is often encountered in many of the examples, the charge transport in small molecular radicals has shown good fits to the conventional charge transport schemes. As an example, Liang et al. recently reported the solid-state conductivity of model nitroxide compounds that are composed of a cyano-biphenyl moiety connected to the TEMPO, only differing the type of the linkage in between. From the fitting behavior of the electrical conductivity with respect to the temperature, a generalized charge transport scheme that follows the conventional variable range hopping (VRH) model was established [Figs. 2(a) and 2(b)]. Specifically, both of the molecular crystals showed a good fit to both the 3D Mott-VRH and Efros–Shklovskii VRH (ES-VRH), with only minor deviations. They also reported related small molecular radical crystals composed of alkyl-biphenyl moiety connected to the TEMPO, only differing the type of the linkage in between. From the fitting behavior of the electrical conductivity with respect to the temperature, a generalized charge transport scheme that follows the conventional variable range hopping (VRH) model was established [Figs. 2(a) and 2(b)]. Specifically, both of the molecular crystals showed a good fit to both the 3D Mott-VRH and Efros–Shklovskii VRH (ES-VRH), with only minor deviations. The molecular crystal again followed the VRH
model, further generalizing the conducting scheme governing the small molecular radical species. Of specific note is on the case of small molecular radicals that are amorphous in nature. In this case, it is expected that it deviates from the above-mentioned charge transfer schemes, as in the case of largely amorphous, non-conjugated macro-molecular radicals (see below). In addition, the presence of solvent or electrolyte can further make the situation complicated. For example, as will be discussed in Sec. III B, in the specific case of nearly insulating TEMPO crystal experimentally measured boosting up of its conductivity by addition of electrolyte—however, the presence of a solvent in general is expected to results in so-called solvent friction effect.17

2. Solid-state charge transport in macromolecular radicals

Radical polymers stabilize electronic charge through stable open-shell moieties, rather than through conjugation and delocalization. Similar to the case of small molecular radicals, it can be assumed that the electronic transport in the radical polymers happens through self-exchange between pendant groups that are brought into close proximity through chain motion (more specifically, it is generally described as neutral species reacting with either cation or anion for the exchange, rather than two neutral ones reacting with each other).14,18 Their ionic transport is known to show some similarity to the traditional polymer electrolytes, facilitated by radical moieties located in pendant groups and their movement through the chain motion.22,23 Unlike conjugated polymers, radical polymers in general do not need a rigid backbone for electronic transport (except for conjugated radical polymers), and both ionic and electronic conductivities are highly dependent on $T_g$ of the polymer.24,25

Unlike the charge transport in small molecular radicals, which, in many cases, display crystallinity,16 these macromolecular radicals have shown a notable deviation from conventional activated hopping models.1 This is mainly due to their more pronounced energetic disorder, originating from the interplay between the open-shell moiety and the amorphous region. With a representative example being the weak

![Figure 2](https://example.com/fig2.png)

**Figure 2.** Charge transport in (macro-)molecular radicals. (a) and (b) Electrical conduction measurements of TEMPO-derived single crystals, (a) TEMPO-BPCN-1 and (b) TEMPO-BPCN-2, spanning a temperature range from 10 to 340 K. Reproduced with permission from Liang et al., Cell Rep. 4, 101409 (2023). Copyright 2023 Authors, licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives (CC BY NC ND) license.17 (c) Theoretical RDFs of PTMA, including (a) nitroxyl N-N, (b) nitroxyl O-O, (c) nitroxyl N-O, and (d) the backbone distances. The cumulative (solid black lines), inter-chain (red with dash-dots), and intra-chain (dotted blue) RDFs are displayed. Reproduced with from Kemper et al., J. Phys. Chem C 118, 17213 (2014). Copyright 2014 American Chemical Society.18 (d) Density of states (DOS) of PTMA, illustrating the TEMPO groups’ SOMO influenced by the surrounding in a simulated film. The vertical ionization potential (vIP) represents the DOS stemming from steric disorder, and the shift in energy at the local electric potential (LEP) termed vPLEP, denotes the alteration in site energy due to the local potential. vPLEP displays of $\epsilon = 3.4$ and $\epsilon = 1.0$, which correspond to the DOS factoring in both steric and electrostatic irregularities with a dielectric constant of 3.4 and 1.0, respectively. Dashed lines, color-matched to their respective data, represent Gaussian fits with a bin size of 0.05 eV. Reproduced with permission from Kemper et al., J. Phys. Chem. C 119, 21369 (2015). Copyright 2015 American Chemical Society.19 (e) Scheme for electron self-exchange reaction ($k_{\text{ex,app}}$) and heterogeneous charge transfer ($k_0$) in a redox polymer. (f) Relationship between $k_{\text{ex,app}}$ and the concentration of redox sites, $C_e$, for a series of redox polymers. Reproduced with permission from Sato et al., J. Am. Chem. Soc. 140, 1049 (2018). Copyright 2018 American Chemical Society.20
temperature dependence of a few known radical polymers, which is contrary to what the hopping models predict, a better descriptive model that takes the interplay into account has been necessary.

In a recent effort, Kemper et al. utilized atomistic molecular dynamics (MD) simulations to explore the structure and morphology of polymer films, and the interplay between intermolecular packing and charge transport in a film of a model radical polymer, poly-(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl) methacrylate (PTMA). An amorphous film of PTMA was generated first by the classical MD, onto which quantum mechanical electronic structure methods to calculate the electronic coupling matrix element between radical sites were utilized. As a key result, the computed radial distribution functions (RDFs) indicated a “head-on” configuration of the TEMPO moieties resulting in a close contact distance of \( \sim 4.5 \text{\ Å} \), while a “parallel” nitrogen–oxygen bond stack showed the separation distance of \( \sim 6 \text{\ Å} \). Interestingly, the RDFs also indicated that the dominating coupling in the film to be inter-chain interactions, rather than the ones within the intra-chain TEMPO moieties [Fig. 2(c)].

In a series of efforts, Kemper et al. also established the charge transfer rate scheme that considers all the terms in the conventional Marcus rate, by calculating the rates between the sites. In detail, the basic assumption includes the consideration that (1) the mobility of a material with localized charge carrier sites is determined by the rate at which charge carriers can transfer from site to site, and (2) the connectivity of the localized charged sites. Among different terms taken into account, the reorganization energy was shown to have pronounced effect on the resultant probability density of the charge transfer coefficient, with the temperature displaying the least impact [Fig. 2(d)].

### 3. Charge transport in macromolecular radicals with electrolytes

Unlike the case of solid-state conduction, charge conduction of the macromolecular radicals in the presence of electrolytes is typified by so-called “diffusive hopping.” With the prominent issue being the observed bimolecular electron self-exchange reaction constant (\( k_{\text{ex,app}} \)) and the standard reaction rate constant (\( k_0 \)) of an immobilized redox site differing significantly to those of the dissolved species, a better descriptive model that captures the discrepancy has been required.

To this end, Nishide and co-workers recently proposed a universal electron hopping model that considers both the Marcus–Hush theory and the segmental motion of redox-active sites. The resultant diffusion-cooperative model successfully explained the aforementioned issue being the suppressed movement of the redox centers bound to macromolecules, which reduces the collision frequency of the charge transfer reactions. The derived equations successfully predicted both \( k_{\text{ex,app}} \) and \( k_0 \) of wide variety of radical species regardless of the types of the redox reactions, main chains, and states of the polymers [Figs. 2(e) and 2(f)].

### II. (MACRO-)MOLECULAR RADICALS—DESIGN FEATURES AND SYNTHESIS

The demand for materials with exceptional electronic and/or electrochemical properties in both solid-state and electrolyte-based systems is experiencing unprecedented growth. In this context, stable nitroxides as mixed conductors stand out as the most notable candidates owing to their synthetic versatility and remarkable physical and electrochemical properties. Specifically, the non-conjugated nature of the nitroxides enables relatively facile preparation of such compounds, where the resultant products exhibit excellent solubility and processability than those of conjugated small and macromolecules. This section summarizes the recent endeavors in synthesizing a diverse range of stable nitroxides in both small and macromolecular forms, with additional synthetic perspectives on conjugated radicals. For readers with a specific interest in nitroxide polymers, excellent review articles on the topic are recommended and can be found at the references cited here.

#### A. Preparation of nitroxide-based small molecular radicals

The long-lived small molecular radicals, 2,2,6,6-tert-butylpiperidinyl-1-oxyl (TEMPO) and its derivatives, are drawing great attention due to their synthetic versatility and rapid redox kinetics. Recently, Lia and co-workers demonstrated a comprehensive synthesis and characterization of a library of redox-active nitroxide radicals (Scheme 2). Here, 4-hydroxy TEMPO 2 was prepared through a two-step synthesis from triacetoneamine 1. First, the carbonyl group of 1 was reduced using NaBH4, followed by the oxidation of the secondary amine with hydrogen peroxide and a catalytic amount of sodium tungstate. This process yielded 2 as a precursor for subsequent transformations. A substitution reaction of 2 with propargyl bromide yielded 4-propargyl TEMPO 3, which could undergo further transformation through a copper-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction with azides. This reaction formed a 1,2,3-triazole linkage (Fig. 3). Another substitution reaction of 2 with acryloyl chloride resulted in 4-acryloyl TEMPO 4, which could be utilized as a monomer for the subsequent polymerization of PTMA. The bromination of 2 in the presence of triphenylphosphine and tetrabromomethane led to the formation of 4-bromo TEMPO 5, albeit with a low yield of approximately 30%. Furthermore, the tosylation of 2 resulted in the production of 4-tosylate TEMPO 6, which could be further converted into useful functionalities such as 4-azido TEMPO 7 and 4-ido TEMPO 8.

A nitrogen analog of 2, 4-amino TEMPO 12, which features a primary amine moiety useful in synthesis, can be synthesized through a two-step process involving oxidation and de-acetylation of 4-acetyl-2,2,6,6-tetramethylpiperidine 11 (Scheme 3). Subsequently, a carboxylic acid can be coupled with 12 through amide coupling to produce a TEMPO derivative 13. A condensation reaction between 12 and an acid anhydride results in a variety of amide products, with a representative example being 14 that is widely utilized in energy storage or field-effect transistor (FET).

#### B. Synthesis of nitroxide-based radical polymers

In this subsection, strategies for incorporating various types of backbone structures with pendant groups into nitroxide-based radical polymers will be illustrated. While the main focus of the discussion will be on polymers with non-conjugated backbones, a brief summary on conjugated radical polymers will also be presented (Fig. 4).

### 1. Non-conjugated backbones

A polymethacrylate-based radical polymer 15 (PTMA) has served as a representative macromolecular radical since the early stages of its synthetic development. Early approaches include anionic polymerization initiated by phenylmagnesium bromide, a Grignard reagent. In detail, the nitroxide radical monomer 4 was directly polymerized to

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yield polymer 15 [Scheme 4(a)], albeit with limited chain length ($M_n \sim 1$ kg mol$^{-1}$). The low molecular weight of 15 in the early approaches was attributed to side reactions between the Grignard reagent and the radical moieties. Recently, Nishide and co-workers demonstrated that polymerization of 4 initiated by methyl methacrylate-capped 1,1-diphenylhexylithium could reduce the extent of the side reaction, by forming a bulky organometallic system. This method resulted in a polymer with $M_n$ of up to 30.4 kg mol$^{-1}$, exhibiting remarkably low dispersity ($D < 1.10$) [Scheme 4(a)]. A few examples of group-transfer polymerization (GTP) were also reported as an alternative strategy for the direct polymerization of PTMA. This approach involved the polymerization of de-protected monomer 4 into PTMA, resulting in a polymer with $M_n$ of 13.9 kg mol$^{-1}$ and $D$ of 2.97 [Scheme 4(b)]. Although the high dispersity is generally considered undesirable, the GTP method maintained a high radical density of the polymer, which was approximately 100%.

While direct polymerization methods offer a straightforward, single-step synthesis of PTMA without the need for pre- and post-polymerization treatment, polymers with well-controlled, predictable molecular weight and narrow dispersity are also desired in many applications. Thus, subsequent efforts were made on the indirect polymerization of such polymers, which are characterized by the inclusion of a radical intermediate and post-treatment of protected pendant groups. Specifically, the indirect polymerization of PTMA involved the intermediate piperidine monomer and the post-oxidation of the PTMA precursor 17. The utilization of metal-free, reversible addition-fragmentation chain-transfer (RAFT) polymerization yielded 17 with tunable molecular weights and relatively low dispersity ($M_n = 5 - 24$ kg mol$^{-1}$ and $D = 1.2$) [Scheme 4(d)]. After the removal of the chain-transfer terminus using excess amount of azobisisobutyronitrile (AIBN), meta-chloroperbenzoic acid (mCPBA) was used to convert 17 into PTMA. The oxidation efficiency of the polymer was evidenced by UV/Vis spectra. Additionally, atom-transfer radical polymerization (ATRP) [Scheme 4(e)] has also been reported for the polymerization of 17 with low dispersity ($D \leq 1.2$) and controllable molecular weight. Recently, Bertrand and co-workers and Zhang and co-workers demonstrated an efficient protocol for the synthesis of the electroactive polymer 15 using the single electron transfer living radical polymerization (SET-LRP) method. The superior electron transfer activity of Cu(0), combined with specific ligands facilitated the synthesis of PTMA at ambient temperature. Polymers with controlled molecular
**FIG. 4.** Examples of polymer backbone structures and pendants to be incorporated in nitroxide-based radical polymers.4,11,38,39

**SCHEME 3.** Preparation of 4-amino-TEMPO and its transformations.30–32

**Non-conjugated polymer backbone**
- polyethylene
- polyether
- polyvinylether
- polymethacrylate

**Conjugated polymer backbone**
- polyacetylene
- poly(1,6-heptadiyne)
- polythiophene
- polypyrrole
- polycarbazole

**Types of nitroxide radical**
- TEMPO
- PROXYL
- aminyloxyl
- nitronylnitroxide
weights ($M_n = 11.0–187.4$ kg mol$^{-1}$) and a narrow dispersity ($D = 1.1$) were produced, supported by detailed kinetic studies. The synthesis of block copolymers with azide-containing monomers was also successfully conducted, showcasing the tolerance of functional groups under the specified polymerization conditions.

Similar to the ionic polymerization of PTMA, anionic ring-opening polymerization (AROP) of cyclic ethers offers a simple and straightforward preparation strategy for poly(ethylene oxide) with radical moiety [Scheme 5(a)]. The de-protected nitroxide monomer 18, 4-glycidyl-2,2,6,6-tetramethylpiperidinyl-1-oxy (4-glycidoxy TEMPO)
was one of the most studied monomers due to its ease of synthesis and purification. Several AROP schemes of 18 have been reported, employing crown-ether-assisted potassium tert-butoxide ($^t$BuOK), a diethyl zinc/water mixture, or a phosphazene base ('Bu-P4)/alcohol as the initiator. These methods have successfully produced poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl)19 (PTEO). The AROP scheme also successfully prepared poly(PROXYL ethylene oxide)21 (PPEO) from PROXYL monomer20, employing a diethyl zinc/water catalytic system.60,61

Recently, Nishide and co-workers have demonstrated anionic ring-opening polymerization of the episulfide monomer22, with initiation by the 1-butanol/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) system [Scheme 5(b)].62 Due to the stronger nucleophilicity of the thiolate anion compared to that of alkoxide, the polymerization of monomer 22 was feasible under milder reaction conditions. This method resulted in a higher molecular weight of the ethylene sulfide polymer 22 with $M_n$ of 12 kg mol$^{-1}$, in contrast to its ethylene oxide counterpart, PTEO, which had $M_n$ of 7 kg mol$^{-1}$.

A cationic polymerization scheme was also successfully employed for the synthesis of poly(TEMPO vinyl ether)25 (PTVE) from 4-vinylxoyl TEMPO 24.63,64 The polymerization was conducted at a low temperature (~25°C) using boron trifluoride diethyl etherate (BF$_3$/Et$_2$O) as a catalyst. The resulting product formed a gel, which was predominantly insoluble in organic solvents [Scheme 5(c)]. Although the polymerization was not highly controlled, the gel product still demonstrated utility in energy storage applications. Another direct polymerization method for producing stable radical polymers is the ring-opening metathesis polymerization (ROMP) using norbornene derivatives (Scheme 6). This approach yielded well-defined products with high molecular weight and narrow dispersity.65,66 The process was catalyzed by either second- or third-generation...
Grubbs catalysts, leading to the formation of high molecular weight polymers 27a, 27b, and 27c (with molecular weights of up to 272 kg mol\(^{-1}\)).

Additionally, a recent report on the synthesis of polyacetylene backbone from functional acetylene monomers with Ru catalysts is noteworthy, which generated high molecular weight polyacetylenes (M\(_n\) > 200 kg mol\(^{-1}\)) with excellent yields (> 90%).

2. Conjugated backbones

Conjugated radical polymers are characterized by \(\pi\)-conjugated units in their backbone structures and pendant radicals, which exhibit distinctive electronic properties due to the diverse conduction pathways they offer (Scheme 7). The polymerization process can be carried out by oxidative polymerization of thiophene derivatives using FeCl\(_3\), or their electrochemical polymerization on an ITO-coated glass substrate. As the resultant polymers from these methods suffered from uncontrolled chain growth and the presence of oxidative impurities, other polymerization methods, such as direct arylation polymerization (DArP), Stille coupling, and Grignard metathesis (GRIM) polymerization, have also been developed. These methods have provided excellent regio-regularity of the polymers with negligible to no impurities. Recent works also include the synthesis of 1,6-heptadiyne functional nitroxide monomers and their polymers through cyclopolymerization with the Grubbs third-generation catalyst.
III. RECENT PROGRESS IN MOLECULAR RADICALS

Building on the synthetic strategy described in Sec. II, this section continues the discussion on recent progress in small molecular radicals. As briefly mentioned in Sec. I, the literature on small molecular radicals has rarely been summarized despite recent advancements made in this area. We will start by discussing the initial work that discovered the possibility of small molecular radicals in solid-state electronics. The discussion will be followed by different strategies used to enhance solid-state conductivity and the structure–property relationships that govern this system. The section will conclude with a brief overview of the relationship between solid-state electronics and electrolyte-based systems.

A. Solid state electronics of small molecular radicals

Although somewhat counterintuitive, discussion on the exceptional solid-state conductivity of nitroxide-based small and macro-molecular radicals begins with their macromolecular form. However, it was only soon after that the conductivity of the small molecular radicals was found to be comparable to their macromolecular form. Among various derivatives of TEMPO, 4-substituted TEMPOs were the main subject of research owing to their synthetic versatility and/or commercial availability. In particular, 4-hydroxy TEMPO displayed robust solid-state conductivity above room temperature.

In a recent report, Yu and co-workers described a versatile processing method for 4-substituted TEMPOs to create single-crystalline active layers through physical vapor deposition. Specifically, a single crystal of 4-hydroxy TEMPO spanning the electrodes displayed very high conductivity of $\sim 10^{-2}$ S m$^{-1}$ at elevated temperatures, showing distinct thermal behavior other than the simple thermal activation. However, the same crystal at room temperature displayed only moderate solid-state conductivity. A careful crystallographic study revealed the observed discrepancy between the two states. At room temperature, the crystal featured a packing structure that is not favorable for electronic conduction (i.e., a doubly intercalated structure with the farthest proximity between the active sites). However, at an elevated temperature, the partially molten state of the crystal facilitated self-exchange redox reactions between the active sites, boosting the observed electrical conductivity.

One of the important points from the initial report is that the crystal structure and the resulting apparent proximity between the active radical sites are the factors determining the overall solid-state conductivity of small molecular TEMPO species. This trait of small molecular radicals also indicates the underlying conduction mechanism governing their behavior, namely, VRH models as described above. In this context, a recent work from Liang and co-workers is highly noteworthy. In the work, they devised two chemically identical, but structurally distinct 4-substituted TEMPOs [TEMPO-BPCN-1 and TEMPO-BPCN-2, Fig. 5(d)]. The resultant single crystals displayed markedly distinct crystallographic structures with each other, where TEMPO-BPCN-1 showed a monoclinic structure, while

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**FIG. 5.** Solid-state electronics of small molecular radicals. (a) Device configurations incorporating 4-hydroxy TEMPO crystal bridged between gold terminals. (b) Diagrammatic representation of electron self-exchange mechanisms facilitating charge movement in radical entities. (c) Variation in conductivity with temperature, paired with the relevant DSC plot. Reproduced with permission from Yu et al., Nano Lett. 20, 5376 (2020). Copyright 2020 American Chemical Society. (d) TEMPO variants bearing structural resemblance, namely, TEMPO-BPCN-1 and TEMPO-BPCN-2. (e) Computed crystal shape and a unit cell of TEMPO-BPCN-1 (monoclinic type) alongside TEMPO-BPCN-2 (tetragonal type). Reproduced with permission from Liang et al., Cell Rep. 4, 101409 (2023). Copyright 2023 Authors, licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives (CC BY NC ND) license. (f) Structures of radical molecules with n-alkyl substitutions. For C6BP-TEMPO, R is C6H13, and for C12BP-TEMPO, R is C12H25. (G) Measured electrical conductivity for the C12BP-TEMPO single crystal over a temperature spectrum of 10 $\leq$ T $\leq$ 300 K. The conductivity of the single crystal amplifies with rising temperature, and its dependence on temperature aligns with the variable-range hopping model. Reproduced with permission from Liang et al., Mol. Syst. Des. Eng. 8, 464 (2023). Copyright 2023 Royal Society of Chemistry.
TEMPO-BPCN-2 displayed a tetragonal one [Fig. 5(e)]. Interestingly, the difference in the active site proximity between the two resulted in approximately 1000-fold variation in conductivity, reemphasizing the importance of the apparent proximity between the radical sites. Specifically, they reported the highest solid-state conductivity of approximately $2 \text{ S m}^{-1}$ from TEMPO-BPCN-1, among the reported values of small molecular radicals. Furthermore, a mechanistic study revealed the two under VRH model, indicating its expansion toward different types of TEMPO derivatives. A series of efforts by the same group on other TEMPO derivatives following the VRH scheme further supports the generality of the charge conduction mechanism governing small molecular TEMPO derivatives [Figs. 5(f) and 5(g)].

Although chemical doping has been widely utilized in conjugated small and macromolecules, the conductivity of non-conjugated small and macromolecular radicals can also be enhanced by a suitable doping strategy. While these radicals can potentially feature comparable solid-state conductivity to that of the conjugated system without any doping strategy, one must be careful in considering possible tradeoffs that the doping process will bring about. These include the apparent conductivity, longevity of the devices, doping stability, and so on.

In a recent work, Joo and co-workers reported the potential of 4-substituted TEMPO as a mixed conductor. In the work, two different types of dopants were utilized: an electronic dopant tetrafluorotetracyanoquinodimethane (F4TCNQ) and an ionic dopant lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) [Fig. 6(a)]. Briefly, four different types of devices were prepared: pristine 4-substituted TEMPO, the electronic doping, the ionic doping, and the co-doping system. The observed total conductivity of 4-hydroxy TEMPO showed marked increases for each added step of the doping process [Figs. 6(b) and 6(c)]. Overall, the conductivity of the co-doped system showed an approximately 10 000-fold increase compared with that of the pristine device, demonstrating the possibility of different doping strategies for the non-conjugated small molecular radicals [Fig. 6(d)].

### 2. Relationship between solid-state and electrolyte-based systems

Although different types of TEMPO derivatives have been widely utilized in electrolyte-based systems owing to their redox versatility, their connection to solid-state electronics has mostly been unknown. Among relevant works, Ko and co-workers explored the effect of the presence of water in the solid-state system of TEMPO derivatives, targeting the revelation of the aforementioned relationship for broader understanding toward small and macromolecular radicals.

In the work, they first tested eight different 4-substituted TEMPO derivatives [Fig. 7(a)]. As an expansion of the previous study on the solid-state conductivity of 4-hydroxy TEMPO, the TEMPO derivatives displayed a temperature-dependent conductivity transition behavior, demonstrating the generality of the conducting mechanism governing small molecular radical species. Importantly, the apparent conductivity values were boosted at elevated humidity, with variation of conductivity from highly conducting (i.e., that of 4-hydroxy TEMPO) to virtually non-conducting (i.e., that of sterically less hindered TEMPO) [Figs. 7(b)–7(d)]. Interestingly, the structure–property relationship found throughout the solid-state conductivity measurement was consistent with that found in the electrolyte-based system, revealing the inherent link between the two systems. Specifically, the observed conductivity displayed linearity toward both variables associated with solid-state electronics (i.e., work function) and an electrolyte-based system (i.e., catalytic activity), respectively [Figs. 7(f) and 7(g)].

### 3. Small molecular radicals in electrolyte-based system

Building upon the connection established between solid-state electronics and electrolyte-based system of small molecular radicals, this subsection highlights recent field of research that the established knowledge above potentially finds its immediate application—that of rechargeable batteries. Small molecular radicals, especially those of nitroxides, have found their wide usage in a number of electrolyte-based systems, with that of catalysis being one of the representatives. Recently, the excellent redox stability and the solvolyphility that the small molecular nitroxides provide have largely been highlighted in the field of rechargeable batteries, especially that of redox flow batteries (RFBs). RFBs utilize the redox chemistry of two redox couples in solution, converting the stored chemical energy into electrical energy. Here, the solutions of redox species called either being catholyte or anolyte, which means positive and negative sides of the electrolytes, are pumped through the cell compartment. The electrodes are often physically separated by membranes or other similar components, preventing direct contact of the electrolyte systems. RFBs feature their decoupling between the energy storage and the power output, designer flexibility, and excellent scalability owing to the inherent design principle.

In a recent report, Wei and co-workers reported a non-aqueous RFB utilizing TEMPO as electroactive material, lithium hexafluorophosphate as supporting charge carriers, and ethylene carbonate/propylene carbonate/ethyl methyl carbonate mixture as a solvent. Owing to the characteristic solvolyphility of TEMPO, a very high solubility of 5.2 M in the solvent mixture system was achieved, at 2.0 M of TEMPO concentration in its actual operation and high operating voltage of 3.5 V. With small variation on the molecular structure, Liu and co-workers recently reported a totally organic aqueous RFB (OARFB) where 4-hydroxy TEMPO was utilized as a catholyte. As a redox couple, methyl viologen (MV) was adopted as an anolyte. In its operation, an exceptionally high cell voltage of 1.25 V, current densities ranging from 20 to 100 mA cm$^{-2}$, and capacity retention over 100 cycles with nearly 100% Coulombic efficiency were achieved. The high performance of the fabricated OARFB was attributed to the high redox potential and the solubility of 4-hydroxy TEMPO, and again its excellent redox stability [Fig. 8(a)]. In a recent example, Hu and co-workers reported an OARFB utilizing TEMPO derivatives as catholyte featuring low permeation through the membrane, high redox potential, and solubility [Fig. 8(b)]. Specifically, the synthesized TEMPO derivative with a dual-ammonium di-cationic group showed very low permeability through the membrane component, while showing an excellent stability. It resulted in a device with a high power density of 114 mW cm$^{-2}$ and 100% capacity retention for 400 cycles at 60 mA cm$^{-2}$, at an energy density of 9.05 Wh l$^{-1}$.

### IV. RECENT PROGRESS IN MACROMOLECULAR RADICALS

#### A. Solid-state electronics of radical polymers

In the significant work that opened up possibilities of solid-state electronics using radical polymers, Joo and co-workers demonstrated that a non-conjugated glass could exhibit solid-state conductivity...
comparable to that of conventional conducting polymers. In their study, they synthesized a radical polymer glass PTEO [Fig. 9(a)], which showed a marked improvement in electrical conductivity. Specifically, the percolation of the polymer network led to a 1000-fold increase in the solid-state conductivity of PTEO [Fig. 9(b)]. The percolation process was enabled by a simple thermal annealing of the glass, during which a significant improvement in connectivity between the chains was observed [Figs. 9(c) and 9(d)]. Similar to the case of small molecular radicals, further improvement in the solid-state conductivity of a radical polymer can be achieved through a suitable doping strategy. For example, Joo and co-workers have demonstrated in a series of works that the addition of an ionic dopant LiTFSI to PTEO enabled a markedly improved ionic conductivity of $10^{-1} \text{ S m}^{-1}$ at an elevated temperature in a long channel device (>50 $\mu$m). Significant amounts of ionic coupling between PTEO and LiTFSI were observed, implying the potential of radical polymers as mixed conductors [Figs. 9(e) and 9(f)].

Recently, small and macromolecular radicals have shown great potential in their incorporation into matrices of conjugated small and macromolecules. This often leads to a significant change in the...
FIG. 7. Relationship between solid-state electronic and electrolyte-based systems in small molecular radicals. (a) Molecular structures of small molecular radicals derived from nitroxide. (b) Diagrammatic depiction showcasing the conductivity improvement in TEMPO variants when subjected to a moisture-rich setting and elevated temperatures. (c) Graphical representation of TEMPO-based devices featuring a channel length of 50 \( \mu \)m and a film thickness of 90 \( \mu \)m (left), contrasted with the device in a moist environment (right). (d) and (e) Changes in conductivity for TEMPO derivatives in correlation to temperature, under a relative humidity of (d) 0\%, and (e) 90\%. (f) and (g) Structure–property relationship in TEMPO derivatives. (f) Graph plotting conductivity against the computed work function of chosen TEMPO variants. (g) Chart correlating conductivity with catalytic efficacy \((\eta_p / \eta_c)\) with activity metrics derived from prior studies. 4-substituted TEMPO derivatives and those with fewer steric impediments are denoted by blue and pink colored squares, respectively. Reproduced with permission from Ko et al., JACS Au 2, 2089 (2022). Copyright 2022 Authors, licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives (CC BY NC ND) license.

FIG. 8. TEMPO derivatives in RFB systems. (a) Diagrammatic depiction of the MV/4-hydroxy TEMPO organic aqueous redox flow battery (OARFB), showcasing both the discharged and charged conditions of the cell. Direction of electrolyte flow is marked with arrows. Constituents of the cell include the following: 1. MV anolyte reservoir; 2. 4-hydroxy TEMPO catholyte reservoir; 3. circulation pump; 4. copper current collector; 5. carbon terminal plate; 6. graphite electrode; 7. membrane facilitating anion exchange. Reproduced with permission from Liu et al., Adv. Energy Mater. 6, 1501449 (2016). Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Schematic illustration of \( \text{N}_2\)-TEMPO/\( \text{[NPf}_{6}]_2\text{VCl}_6 \) OARFB and its battery reactions. Reproduced with permission from Hu et al., Adv. Energy Mat. 12, 2102577 (2022). Copyright 2021 Wiley-VCH GmbH.
electronic properties of the host materials, enabling synergetic integration of mixed organic conductors for various applications in solid-state electronics. For this purpose, it is necessary to establish a deep understanding of how the radical moieties are functioning within the film of the host conjugate polymers. Wilcox and co-workers utilized the geometry of organic field-effect transistors (OFETs) to examine the interaction between a conjugated polymer poly(3-hexylthiophene) (P3HT) and radical moieties including nitroxides and galvinoxyl (Fig. 10). Key results include the switching of the host’s electronic properties from semiconducting to conducting by the incorporation of poly(galvinoxylstyrene) (PGSt), while the nitroxides did not result in such behavior. Specifically, the presence of only small amount of the macromolecular radical resulted in the increase in apparent carrier mobility. It is also worth noting that the incorporation of radical polymers is not limited to blending them into active components of OFETs. In a recent work on OFET utilizing pentacene as an active layer, Sung and co-workers discovered the introduction of a radical polymer interlayer in the device stack led to significantly increased mobility and device ON/OFF ratio (Fig. 11). In detail, the charge transport energy level of in the device stack led to significantly increased mobility and device ON/OFF ratio. The interfacial layer was tuned for the effective charge injection and/or extraction. This was attributed to a combined effect of the enhanced charge transport capability and the facilitated growth of the pentacene grain. Specifically, the latter is associated with the nucleation and growth of larger-sized pentacene resulting in a significant decrease in the roughness of the grain size and a reduction in the number of charge traps. This point is interesting in terms of device architecture, as it indicates that the physical properties of both small and macromolecular radicals can potentially helpful in mitigating the surface energy gap between the active layer of such device and the electrode.

Designing an advanced system of organic semiconductors that enables simultaneous transport of electronic and ionic inputs has garnered significant attention as an alternative for advancing intrinsically stretchable and flexible bioelectronic devices and biosensors. Among various types of volatile devices, organic electrochemical transistors (OECTs) have emerged as a promising option due to their unique ability to amplify coupled electronic and ionic signals. This characteristic has positioned OECTs as suitable devices for interfacing electronics with biological systems in diverse application fields, including biochemical sensing, cell culture analysis, and neuromorphic computing. To date, the mixed conductor of conjugated polymers has been predominantly employed and has made significant progress. However, challenges such as complicated synthesis, low yield, thickness control, and the complex internal charge exchange in conjugated polymers continue to hinder the widespread application of mixed polymer semiconductors in bioelectronic devices. In this context, radical polymers can potentially serve as a powerful alternative due to their excellent synthetic versatility and processability, as discussed in Sec. II. Although a complete description of the charge transport behavior of macromolecular radicals remains challenging, the inherent charge...
The transfer mechanism of radical polymers has an advantage over that of the conjugated polymers, given the possibility of significant crosstalk between species within conjugated polymers during device operation. To this end, Kim and co-workers reported an exciting study that employs a radical polymer PTEO and a conjugated polymer P3HT as integrated mixed conducting system, for an active channel of OECTs [Fig. 12(a)]. The novel aspect of this work is the use of the radical polymer as a voltage regulator, which tunes the ion injection to the desired potential for the device.

A pronounced dependency on the redox profile of the mixture containing radicals was observed, enabling the manipulation of the blend film’s threshold voltage based on varying amounts of pendant radicals. This alteration led to a shift in OECT operation. Moreover, incorporating PTEO’s polar chains has brought about planarization of conjugated polymer chains, boosting intra-chain exciton interaction. This affected the physicochemical and electrochemical characteristics of P3HT within the blend [Figs. 12(b) and 12(c)]. As a result, merely adjusting the composition of this conductive blend has yielded an exceptional performance of P3HT-based OECTs, achieving a figure-of-merit ($\mu$C/cm$^2$) of up to 150 F V$^{-1}$ cm$^{-1}$ s$^{-1}$ with 5 wt. % PTEO content [Figs. 12(d) and 12(e)]. Additionally, the blend’s kinetic behavior was influenced, which was a notable deviation from what has been observed in pure P3HT-based OECT devices [Fig. 12(f)].

This improved kinetic response can be linked to a rise in the ion percolating network due to increased PTEO content, facilitating greater ion doping into P3HT structures. While there was a balance between OECTs’ steady-state functionality and transient reactions, the ability to adjust the blend’s threshold voltage using minimal radical polymer content provides a valuable and straightforward strategy. This method involves merging a conjugated polymer semiconductor with an ion-conductive radical polymer counterpart to achieve superior organic mixed conductors [Fig. 12(g)].

V. DISCUSSION AND FUTURE OUTLOOK

Recent years have seen a surge in research and development centered on open-shell organic compounds, driven by their potential to cater to specific needs across a variety of end-use applications. For instance, within the realm of materials science, small and macromolecular radicals possess the potential to birth advanced materials characterized by superior mechanical, thermal, and electrical properties. Their synthesis through controlled polymerization techniques, which grant meticulous control over molecular weight, structure, and consequent properties, further accentuates their appeal. Moreover, small molecular radicals present diverse synthetic pathways while preserving a high radical density, thereby allowing for a customized design of polymer and molecular properties on demand. This has culminated in the advent of
FIG. 11. Influence of radical polymers at OFET interfaces. (a) Diagrammatic representation of the pentacene-based OFET, featuring a PTMA layer positioned between the metal contact and the organic semiconductor. (b) Microscopic view of PTMA droplets inkjet-printed atop the gold source and drain electrodes. Note that the precision of the inkjet printing technique ensures PTMA deposition solely over the gold contacts, excluding the OFET channel (specifically, the SiO₂ area between the two electrodes). The inset showcases the chemical composition of PTMA. Atomic force microscopy (AFM) showcases surface topographical visuals of pentacene on (c) unmodified gold and (d) atop a PTMA layer. (e) Display of output ($I_D-V_D$) and (f) transfer curves ($I_D-V_G$) for pentacene-based OFET setups without the inclusion of a PTMA layer. (g) Output and (h) transfer characteristics for pentacene-based OFET systems that incorporate an 8-nm PTMA layer between the organic semiconductor and the gold contact points. Reproduced with permission from Sung et al., Org. Electron. 37, 148 (2016). Copyright 2016 Elsevier B. V.

FIG. 12. Radical polymer-based organic electrochemical transistors. (a) Schematic representation of the OECT setup. (b) Characteristic forward and reverse output curves for the OECT containing 5 wt. % PTEO using a 0.1 M NaCl aqueous electrolyte and a solid Ag/AgCl reference electrode. (c) Voltage readings pertain to the applied gate voltages during measurements, noted with $V_D = -0.8$ V and a scan rate of 10 mV s⁻¹. The red graph in panel (c) mirrors the data of its black counterpart in the same panel but uses a logarithmic scale to accentuate the OECT’s ON/OFF distinction. An optical microscopic snapshot embedded in panel (c) showcases an OECT channel, with the guiding scale bar equating to 100 μm. (d) Derived $\mu_C^*$, plotted against PTEO content, deduced from their associated transfer curves. (e) An evident shift in the initial voltage, marked as $V_T$, was discerned at concentrations as minimal as 2.5% PTEO (by mass) within the blended films, stabilizing around $-0.72$ V when the compositions contained ≥7.5% PTEO (by mass). (f) Normalized transient responses, applying a $V_G$ of $-0.8$ V sourced at $t = 10$ s for a 200 s span with a static $V_D = -0.8$ V, revealed that increasing PTEO content fostered superior transient kinetics in the OECTs. (g) The switching delay inversely correlated with escalating volumes of PTEO. Reproduced with permission from Kim et al., ACS Macro Lett. 11, 243 (2022). Copyright 2022 American Chemical Society.
novel and enhanced materials and devices, thereby empowering the community of researchers to make significant contributions to a broad spectrum of both solid-state and electrolyte-supported systems.

However, while the application-driven research thrust on open-shell organic compounds has indeed led to significant advancements in materials tailored for specific applications, there exists a potential oversight of opportunities to cultivate more robust structure–property relationships. Addressing this requires a shift toward fundamental research, aiming to unravel the chemical and physical properties that dictate the behavior of open-shell entities, be it small molecules or polymers. This further underscores the importance of fostering an interdisciplinary consortium of chemists, materials scientists, physicists, and engineers. Such a collaborative approach promises a holistic grasp of the core essence of open-shell organic compounds in general, subsequently guiding innovative strategies for material design and synthesis.

Chemists, in particular, stand at a pivotal crossroads, uniquely positioned to lead research in open-shell chemistry. This holds the promise to usher in transformative changes in the design of macromolecular and small molecular structures in the near future.

Yet, characterizing the mixed ionic and electronic systems and performing assessments of open-shell chemistry of small and macromolecular radicals remain challenging, largely attributed to their typically amorphous disposition. This presents a hurdle in drawing connections between macromolecular design and inherent molecular attributes—a vital link for understanding the nexus between design and the inherent structure of small molecules and macromolecular properties in a systematic manner. To overcome these barriers, there is a call to employ advanced characterization modalities, building on existing accomplishments within this domain. Techniques such as in operando x-ray and neutron scattering, transmission electron microscopy, and solid-state nuclear magnetic resonance spectroscopy can shed light on molecular and nanoscale structures and dynamics. This knowledge is pivotal to a nuanced understanding of the behaviors of these materials. A deepened appreciation of the interplay between design and structure in the open-shell organic compounds can potentially catalyze the creation of groundbreaking materials tailored for specific utilities. Given the profound implications for diverse sectors, ranging from energy storage to biomedical innovations, it remains imperative for chemists and materials scientists to continually pioneer advancements in open-shell chemistry research.

ACKNOWLEDGMENTS

This work was supported by the Korea Institute of Science and Technology (KIST, Korea) Institutional Program. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (Nos. RS-2023-00208313 and 2022K1A3A1A91093969).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Jaehyoung Ko and Quynh H. Nguyen contributed equally to this work.

Jaehyoung Ko: Data curation (equal); Visualization (equal); Writing—original draft (lead); Writing—review & editing (equal). Quynh H. Nguyen: Data curation (equal); Formal analysis (equal); Writing—original draft (equal); Writing—review & editing (equal). Quyen Vu Thi: Data curation (equal); Formal analysis (equal); Writing—original draft (equal). Yongho Joo: Funding acquisition (lead); Investigation (lead); Project administration (lead); Supervision (lead); Validation (equal); Writing—original draft (equal); Writing—review & editing (equal).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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