

# Degradable $\pi$ -Conjugated Polymers

Azalea Uva, Sofia Michailovich, Nathan Sung Yuan Hsu, and Helen Tran\*



Cite This: *J. Am. Chem. Soc.* 2024, 146, 12271–12287



Read Online

ACCESS |

Metrics & More

Article Recommendations

**ABSTRACT:** The integration of next-generation electronics into society is rapidly reshaping our daily interactions and lifestyles, revolutionizing communication and engagement with the world. Future electronics promise stimuli-responsive features and enhanced biocompatibility, such as skin-like health monitors and sensors embedded in food packaging, transforming healthcare and reducing food waste. Imparting degradability may reduce the adverse environmental impact of next-generation electronics and lead to opportunities for environmental and health monitoring. While advancements have been made in producing degradable materials for encapsulants, substrates, and dielectrics, the availability of degradable conducting and semiconducting materials remains restricted.  $\pi$ -Conjugated polymers are promising candidates for the development of degradable conductors or semiconductors due to the ability to tune their stimuli-responsiveness, biocompatibility, and mechanical durability. This perspective highlights three design considerations: the selection of  $\pi$ -conjugated monomers, synthetic coupling strategies, and degradation of  $\pi$ -conjugated polymers, for generating  $\pi$ -conjugated materials for degradable electronics. We describe the current challenges with monomeric design and present options to circumvent these issues by highlighting biobased  $\pi$ -conjugated compounds with known degradation pathways and stable monomers that allow for chemically recyclable polymers. Next, we present coupling strategies that are compatible for the synthesis of degradable  $\pi$ -conjugated polymers, including direct arylation polymerization and enzymatic polymerization. Lastly, we discuss various modes of depolymerization and characterization techniques to enhance our comprehension of potential degradation byproducts formed during polymer cleavage. Our perspective considers these three design parameters in parallel rather than independently while having a targeted application in mind to accelerate the discovery of next-generation high-performance  $\pi$ -conjugated polymers for degradable organic electronics.

## 1. INTRODUCTION

The dynamic intersection between electronic devices and society is pushing existing boundaries as emerging technologies seamlessly integrate into our daily lives and transform the way we communicate, work, and engage with the world around us. Next-generation electronics will feature properties that make devices more harmonious with our bodies and the environment, including new stimuli-responsive properties and improved biocompatibility. For example, temporary skin-like health monitoring devices<sup>1–3</sup> can replace traditional bulky devices, providing increased comfort to patients (Figure 1). Sensors can be built into food packaging,<sup>4–7</sup> alerting consumers about the quality of the food they consume and preventing food waste (Figure 1). Other future applications include environmental monitoring,<sup>8–10</sup> where nutrient and humidity levels can be monitored remotely, implantable energy storage devices,<sup>11,12</sup> or on-demand drug delivery with integrated biosensors<sup>13–15</sup> for targeted release of medicines (Figure 1). As these technological advancements evolve, a question arises: what is the fate of these devices once they are no longer needed? Currently, only 17.4%<sup>16</sup> of global electronic waste (e-waste), including household, medical, and sensor devices, is properly recycled. While next-generation electronics will be diminutive volumewise compared to current devices, their widespread abundance may proliferate, especially with smart monitoring; how do we jumpstart this technology with sustainability in mind? One solution is to impart degradability

to future electronics, where devices would disintegrate over a set period of time,<sup>17–19</sup> leading to new use cases. For example, health monitoring devices with degradable properties would eliminate the need to be surgically removed from patients and diminish the risk of possible infections.<sup>20</sup> Also, as low-cost monitoring devices are integrated into compostable food packaging or used for large-scale environmental studies, imparting degradability offers the opportunity to minimize waste in unintended locations and eliminates the need for tedious retrieval. To achieve a future for degradable electronics, new synthetic strategies must be developed.

Within the past decade, significant progress has been made in the synthesis of degradable materials for encapsulants, substrates, and dielectrics,<sup>21–23</sup> integral components for building organic electronics; however, conducting and semiconducting materials that are degradable under specific conditions are still limited. While inorganic materials can be used, organic materials (e.g.,  $\pi$ -conjugated polymers) offer advantages such as stretchability, biocompatibility, and degradability while maintaining mechanical durability and

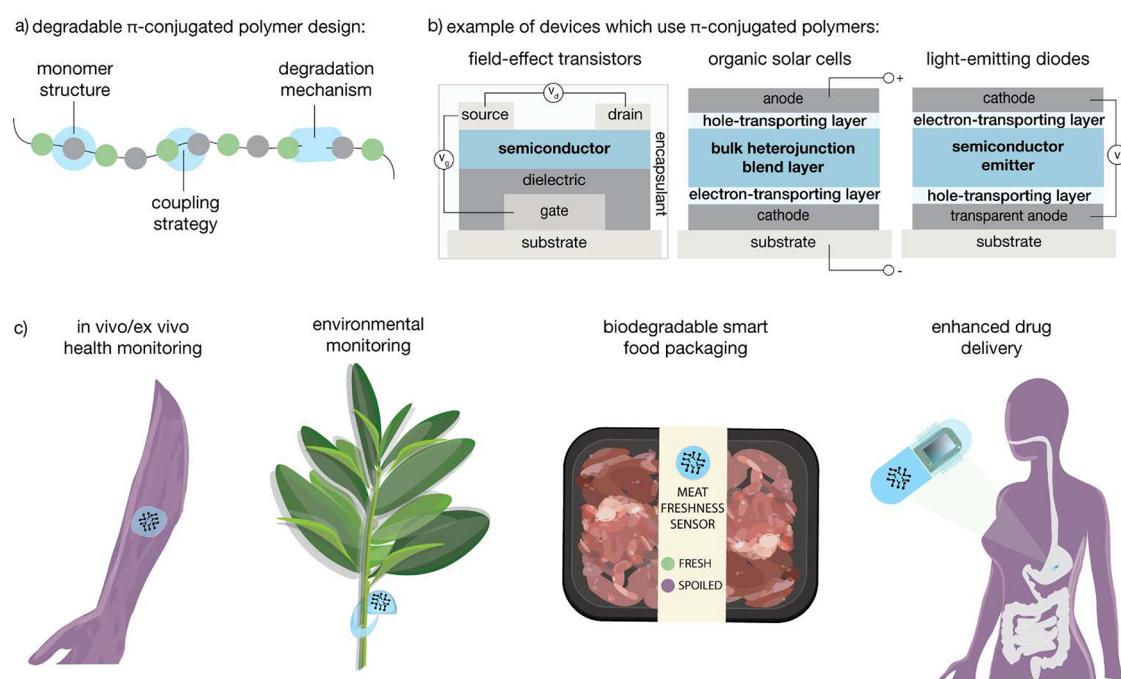
Received: March 4, 2024

Revised: April 10, 2024

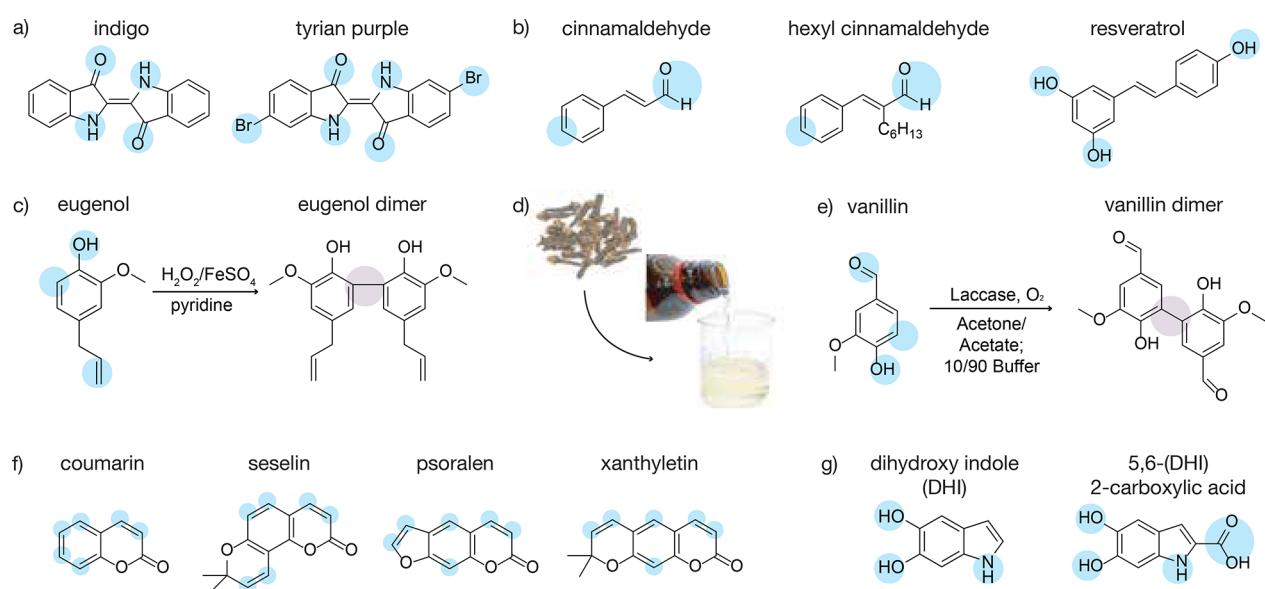
Accepted: April 11, 2024

Published: April 24, 2024





**Figure 1.** Designing degradable  $\pi$ -conjugated polymers for organic electronics. (a) Three major design considerations discussed in this perspective:  $\pi$ -conjugated monomer structure, synthetic coupling strategies, and degradation mechanisms. (b) Degradable  $\pi$ -conjugated polymers are used as conductors or semiconductors in a wide range of electronic devices including but not limited to field-effect transistors, organic solar cells, and light-emitting diodes. Blue layers of the devices represent  $\pi$ -conjugated polymers. (c) Applications that can benefit from using degradable electronics include (from left to right): temporary in vivo or ex vivo health monitoring devices, temporary environmental monitoring, biodegradable smart food packaging, and on-demand degradable capsules for enhanced drug delivery.



**Figure 2.** Overview of biobased monomers, their sites for functionalization (highlighted in blue), and their potential chemical transformations (highlighted in purple). (a) Isoindigo derivatives: indigo and Tyrian purple. (b) Biobased phenylpropanoids: cinnamaldehyde, hexyl cinnamaldehyde, and resveratrol. (c) Dimerization of eugenol by peroxide oxidation. (d) Eugenol monomer sequestration from clove buds. (e) Dimerization of vanillin by Laccase enzyme mediated oxidation. (f) Coumarin derivatives: coumarin, seselin, psoralen, and xanthyletin. (g) Eumelanin building blocks: dihydroxy indole (DHI) and 5,6-(DHI) 2-carboxylic acid. Images adapted with permission from refs 32 and 110. Reference 32 available under a CC-BY-NC-ND 4.0. Copyright 2021 American Chemical Society and 2020 American Chemical Society.

electronic properties. In the pursuit of designing degradable  $\pi$ -conjugated polymers, chemists must consider several factors, including but not limited to monomer selection, polymerization methods, and degradation mechanisms (Figure 1a), all of which must be tailored to the intended application. We propose having a targeted application in mind to help drive the

initial stages of the design process when synthesizing new degradable  $\pi$ -conjugated polymers. Specifically, one major pitfall to current degradable  $\pi$ -conjugated polymers is the lack of knowledge on degradation byproducts, specifically their identity, associated toxicity, and environmental impact. Herein, we provide our perspective on designing degradable  $\pi$ -

conjugated polymers using  $\pi$ -conjugated monomers, applying synthetic coupling strategies, and discussing their degradation modes and mechanisms. We highlight polymer examples developed for various applications, such as biosensors, batteries, and drug delivery. Moreover, we discuss various modes of depolymerization and approaches to enhance our comprehension of potential degradation byproducts formed during polymer cleavage. Throughout this perspective, we emphasize polymers with fully  $\pi$ -conjugated backbones; however, we do highlight select examples of nonconjugated systems that feature notable depolymerization mechanisms that would be of interest to apply toward fully  $\pi$ -conjugated systems. Our aim is to inspire the global polymer chemistry community to push the boundaries in designing the next-generation of high-performance  $\pi$ -conjugated polymers for degradable organic electronics.

## 2. $\pi$ -CONJUGATED MONOMERS

Molecular design considerations for degradable  $\pi$ -conjugated polymers include appropriate functional handles, solubilizing properties, the influence on electronic performance, chemical stability, and predictable degradability. Monomers for polymers require functional handles (e.g., aldehyde for imine polycondensations) suitable for polymerizations, or the functional handles should be readily transformable (e.g., alcohols to halides). As for solubility, the monomer should be soluble in polymerization conditions and contain solubilizing side chains to enable the resulting polymer to be processable. Since the monomer directly influences the eventual polymer electronic performance, monomers are selected to be conjugated for electron delocalization and suitable band gap energies. Chemical stability plays a multifaceted role in the synthetic preparation of the monomer and polymer, as well as their degradation. Moreover, understanding the monomer chemical stability can motivate the design of recyclable  $\pi$ -conjugated polymers, where monomers are recoverable upon degradation. Lastly, by using  $\pi$ -conjugated biobased (i.e., derived from renewable biomass or produced by living organisms) monomers or analogs, degradation mechanisms and byproducts can be deduced from known degradation pathways in Nature (Figure 2), noting that not all compounds in Nature are nontoxic. This section aims to showcase the existing catalogue of monomers that have been used for the synthesis of  $\pi$ -conjugated polymers with known degradation byproducts, highlighting opportunities to design biobased monomers and employ lesser-utilized monomers for degradability or recyclability purposes.

**2.1. Biobased Monomers.** In recent years, researchers have expanded the utility of biobased compounds to organic electronics and degradable materials. This is possible as the monomers possess natural conjugation for potential electron mobility and functional groups that can converted into labile chemical linkages in the polymeric state for degradation. Natural dyes, such as indigo extracted from *Indigofera tinctoria* leaves<sup>24</sup> (Figure 2a), melanin produced from *sepia* extract,<sup>25</sup> and systems derived from forest biomasses,<sup>26</sup> such as furans and vanillin, are naturally occurring  $\pi$ -conjugated monomers that have been utilized for organic electronics. Furans have been used to prepare various monomers for polymerizations, including  $\pi$ -conjugated polymers.<sup>27,28</sup> For example, Baillargeon and co-workers<sup>29</sup> synthesized lignocellulosic furfuryl biobased diacetylenes and generated polydiacetylenes via topochemical polymerization. Vanillin is another exemplary biobased organic

monomer that is used for synthesizing  $\pi$ -conjugated materials for organic light-emitting diodes, and others,<sup>30,31</sup> with notable contributions from Leclerc,<sup>32</sup> and Arndtsen,<sup>33</sup> among others. The chemical composition of this monomer, which includes substantial conjugation and synthetically transformable functional groups, enables its ability to be used in the creation of  $\pi$ -conjugated polymers with degradable, labile chemical sites. For example, Brochon, Cramail and co-workers<sup>34</sup> synthesized a divanillin monomer, which they polymerized with diamines to yield degradable poly(azomethine)s (Figure 2e). Although it has yet to be reported for  $\pi$ -conjugated polymers, vanillin's degradation via oxidation has been characterized<sup>35,36</sup> and its degradation byproducts have been identified.

Eugenol, a member of the same phenolic class of compounds as vanillin, is an underutilized biobased monomer that is promising for the design of degradable  $\pi$ -conjugated polymers. Eugenol features an aromatic ring, which can be used in the backbone of polymers, with the possibility of further derivatization from phenolic hydroxyl, methoxy or allylic bond functionalization (Figure 2c,d).<sup>37</sup> The compound has been extensively studied for the preparations of thermosets, as the functional groups on eugenol can easily be transformed into epoxy and methacrylate groups, which can be further used to react with amines, anhydrides phenols, and thiols.<sup>38</sup> Moreover, recent cross-linked polymers featuring eugenol have also been studied for their degradability,<sup>39</sup> but there are limited reports of its usage in  $\pi$ -conjugated polymeric systems, with most reports stemming from the early 2000s. Most notably is Masuda and co-workers<sup>40,41</sup> demonstration of polyacetylene derivatives containing eugenol moieties. In their first demonstration, polyacetylene with eugenol side chains was synthesized via a modified eugenol compound featuring an acetylene unit. Remarkably, the allyl side chain of eugenol was preserved in polymerization, opening avenues for postfunctionalization. Similar to vanillin, the degradation of eugenol-containing polymers has briefly been explored, but the in-depth characterization of eugenol degradation mechanisms and byproducts exists,<sup>42,43</sup> further demonstrating the advantage of using biobased monomers when designing degradable  $\pi$ -conjugated polymers.

Additional phenolic and naturally occurring  $\pi$ -conjugated compounds that have yet to be reported in conjugated polymeric systems but merit future investigation include resveratrol, flavonoids, cinnamaldehyde, catechins, anthocyanins, and coumarins (Figure 2b,f). A subcategory of lactones, coumarins are present in essential oils, fruits, and teas and feature photochemical properties, making them desirable for incorporation into polymeric systems for various electronic applications.<sup>44,45</sup> Choudhury and co-workers<sup>46</sup> designed a coumarin inspired monomer, which they then polymerized via Suzuki-coupling to yield a fluorescent conjugated polymer. Although this report did not explore the degradability potential of coumarin, the degradable properties of coumarins have been explored in hydrogels. Anseth and co-workers<sup>47</sup> utilized coumarins' photochemical properties as a degradable trigger in hydrogels: upon irradiation at 365 nm, coumarin linkers would break apart to yield coumarin methyl alcohol.

Another underexplored class of biobased molecules for  $\pi$ -conjugated polymers are carotenoids. A class of pigmentation molecules, carotenoids feature  $\pi$ -conjugated bonds, giving rise to their high single molecule conductance,<sup>48</sup> ability to scavenge reactive-oxygen species and role in photosynthesis.<sup>49</sup> Carotenoids can degrade via chemical oxidation, enzymatic

oxidative cleavage, or UV oxidation,<sup>50,51</sup> opening opportunities for various degradation pathways if incorporated into a polymeric system. Carotenoids, such as  $\beta$ -carotene, have been studied as semiconductors in the single molecule state for organic field-effect transistors.<sup>48,52</sup> However, their main caveat that prohibits their scalable application in electronic devices is their low electron hole mobilities values. Carotenoid copolymers exist naturally as a first step in the degradation process: for example,  $\beta$ -carotene spontaneously polymerizes in the presence of oxygen to yield a copolymer intermediate among numerous small molecule degradation products known as apocarotenoids.<sup>53–55</sup> To the best of our knowledge, only one report of a carotenoid monomer was used to synthesize a degradable  $\pi$ -conjugated polymer. Tran and co-workers<sup>56</sup> demonstrated the polymerization of an apocarotenoid, termed C10 dialdehyde, with diamines to yield poly(azomethine)s with dual modes of degradation: acid hydrolysis due to the imine linker in the backbone, and UV oxidation due to the carotenoid moiety in the backbone. Thus, there are ample opportunities to further investigate the use of other carotenoid molecules as monomers for  $\pi$ -conjugated polymers.

The highlighted examples thus far are biobased monomers that may display high electronic performance if incorporated into extended conjugated polymer chains. Little to no research has been conducted in the use of biobased materials for donor–acceptor monomers and polymers. This field requires more attention because it can be realized by complementing the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy gaps of common biobased monomers. Monomer pairings that possess the smallest energy gap are potential donor–acceptor pairs. Table 1 encompasses a noncomprehensive list of known HOMO–LUMO energy band gaps of biobased monomers. These limited data are a good starting point for the future design of  $\pi$ -conjugated polymers, whether they may be blended with synthetic organic donor–acceptors or used to create fully biobased systems.

**Table 1. Literature Reported HOMO and LUMO Energy Levels for Common Biobased Monomers**

Monomer	HOMO (eV)	LUMO (eV)	Band gap (eV)
Vanillin <sup>154</sup>	−0.24	−0.07	−0.17
Beta-carotene <sup>155</sup>	5.84	3.54	2.30
Indigo <sup>155</sup>	5.50	3.80	1.70
Tyrian purple <sup>155</sup>	5.80	4.00	1.80
Coumarin <sup>156</sup>	−6.50	−1.89	−4.61
Eumelanin (5,6-dihydroxyindole-2-carboxylic acid) <sup>157</sup>	1.16	−1.40	2.50
Cinnamaldehyde <sup>158</sup>	−2.48	−6.89	4.41

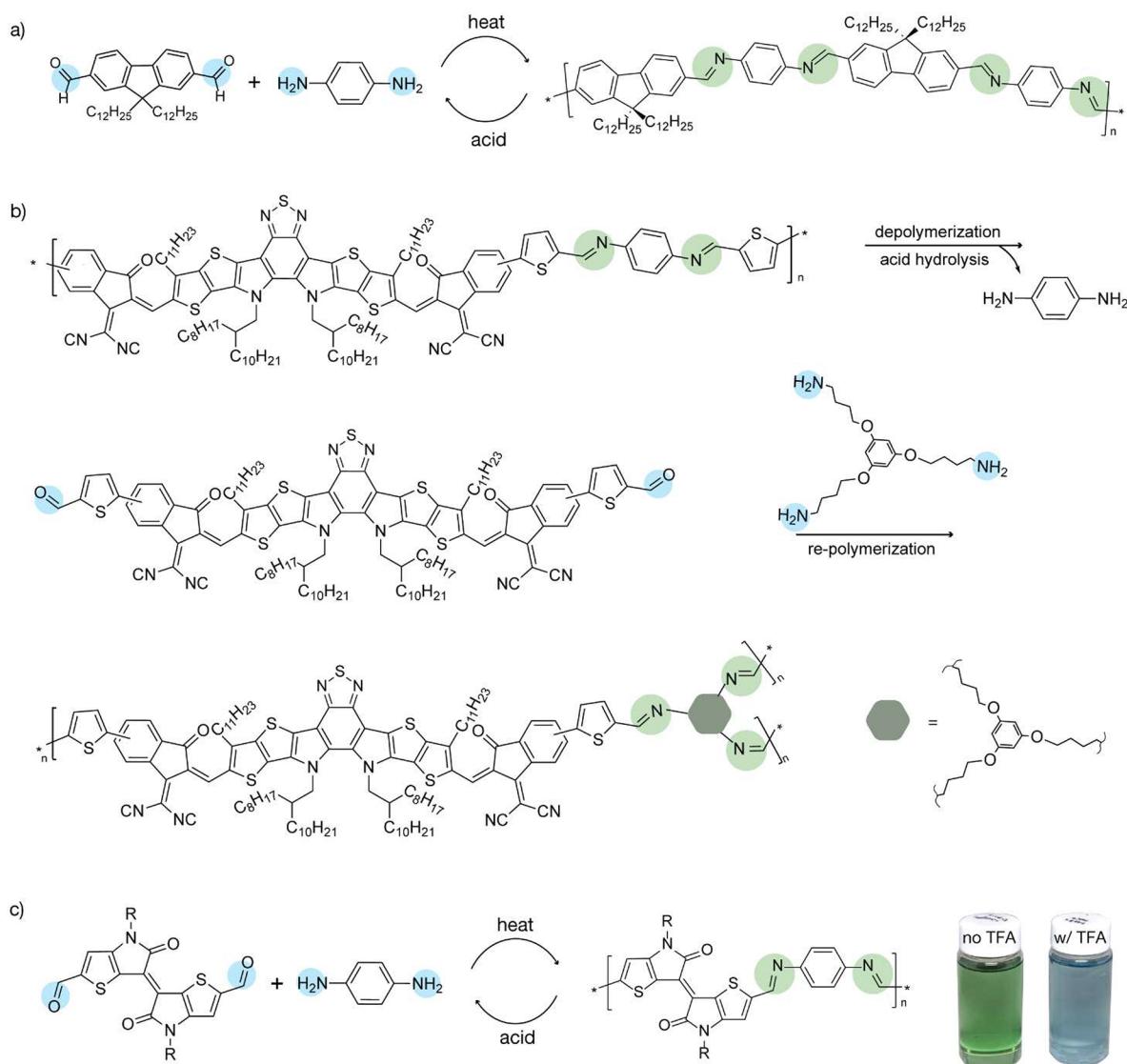
**2.2. Monomers for Chemically Recyclable  $\pi$ -Conjugated Polymers.** Understanding the appropriate demands for designing monomers suitable for chemically recyclable  $\pi$ -conjugated polymers provides insight on the degradation intermediates and eventual byproducts, which is an area of research not deeply explored to date (Figure 3). To be able to recover a monomer from a  $\pi$ -conjugated polymer postdegradation, the monomer must be chemically stable toward the degradation conditions which trigger depolymerization, a feat that is synthetically challenging. Although there are many reports of degradable  $\pi$ -conjugated monomers, few highlight

the preservation,<sup>57</sup> and reuse of degradation products. The first recyclable imine-based polymer was reported by Bao and co-workers<sup>58</sup> in which fluorene and *p*-phenylenediamine monomers were recovered in over 90% recycling yield upon degradation of the polymer via treatment with trifluoroacetic acid (Figure 3a). More recently, Son and co-workers<sup>59</sup> developed a recyclable  $\pi$ -conjugated polymer, PY-TIP, that is broken down through mild acid hydrolysis to yield a new monomer, YS-TA, and *p*-phenylenediamine (Figure 3b). Although the YS-TA monomer recovered is not the original monomer used for the initial polymerization, YS-TA is stable under acidic conditions, allowing it to be recovered and used to create new cross-linked polymers. While the group does not mention the targeted functionalization's made to maintain monomer recovery upon degradation, one may look to the findings of Ashizawa, Tran, and co-workers<sup>60</sup> to better understand the chemical properties required for recycling  $\pi$ -conjugated polymers. The group synthesized a thienoisoiindigo-based polymer with a cleavable imine bond in its backbone (Figure 3c). Upon introduction of mild acid, the polymer was shown to degrade back into its original monomers, which were recovered and used for subsequent polymerizations. Specifically, the thienoisoiindigo (TII) monomer is chemically stable under acidic degradation, allowing it to be recovered, unlike previously reported diketopyrrolopyrrole (DPP) imine-based polymers,<sup>61</sup> in which the DPP core would undergo ring-opening in the presence of acid. These findings reveal that the recycled monomers can be reused without sacrificing the overall quality of the polymer, as demonstrated by the comparable properties between pristine and recycled polymers.

The field of chemical recycling to monomers specifically for  $\pi$ -conjugated polymers is still in its infancy. While the previous examples highlighted feature this process with imine bonds, there are no reports on other degradable linkers that can produce monomers for chemically recyclable  $\pi$ -conjugated polymers. For future work with different labile linkages, chemists can turn to inspiration from advancements in chemical recycling to monomer with non  $\pi$ -conjugated systems,<sup>62</sup> where kinetics and thermodynamics parameters<sup>63</sup> provide great insight into the optimization of recovering pristine monomers from bulk polymers and self-immolative chemistries<sup>64,65</sup> enable precise control over depolymerization. With the development of new monomers that are stable toward depolymerization conditions, we envision an emergence in publications related to fully recyclable  $\pi$ -conjugated polymers in the coming years.

### 3. SYNTHETIC COUPLING STRATEGIES

In conjunction with monomer design, another design consideration is the synthetic coupling strategy to achieve a degradable  $\pi$ -conjugated polymer, which serves as one method for introducing labile bonds. The most cited deliberate method to introduce a labile linkage in the polymerization process is imine polycondensation (Figure 4a).<sup>61,66–70</sup> Requiring dialdehyde- and diamine-functionalized  $\pi$ -conjugated compounds, imine polycondensations proceed under mild conditions, requiring only a catalytic amount of acid to initiate the reaction and a drying agent to scavenge water that is produced in situ. The imine-based polymers, also known as poly(azomethine)s, have become the forefront of degradable  $\pi$ -conjugated polymers due to their facile depolymerization under acidic conditions, with creative polymeric designs and uses dominating the field of degradable organic materials in

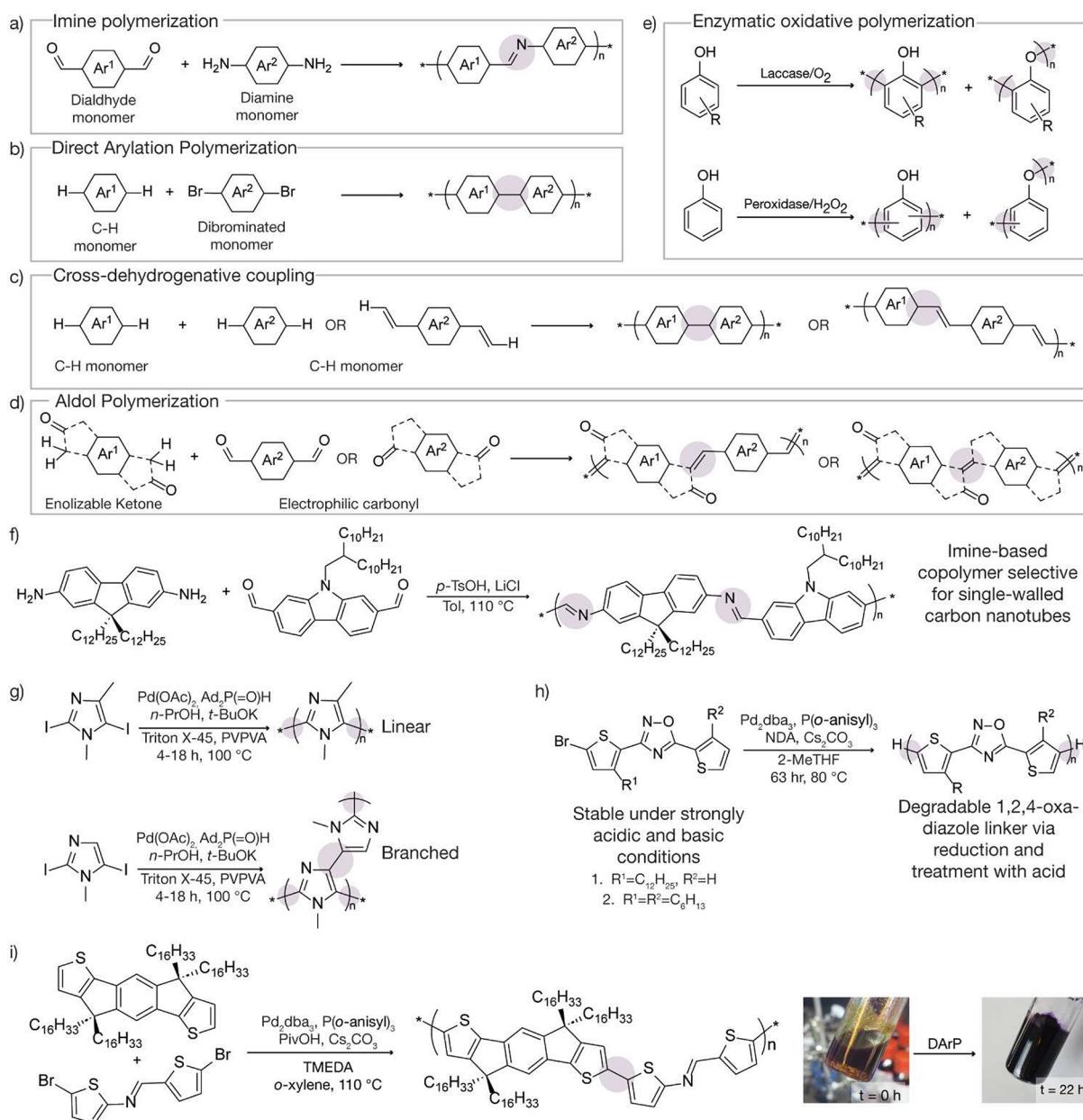


**Figure 3.** Schematic overview for the chemical recycling of  $\pi$ -conjugated polymers and the recovery of their monomeric components. (a) Chemical recycling of fluorene-based polymer, in which fluorene and diamine monomers are recovered. (b) Chemical recycling of polymer PY-TIP, and re-polymerization using the recovered monomer. (c) Chemical recycling of thienoisooindigo-based polymer in the presence of mild acid (trifluoroacetic acid, TFA), and polymer solution color change upon cleavage of the imine bond in the presence of TFA. Images reproduced or adapted from (refs 58, 59, and 60). Reference 60 available under a CC-BY 4.0. Copyright 2023 American Chemical Society, 2023 American Chemical Society and 2024 Royal Society of Chemistry.

recent years.<sup>60,61,66,67,71</sup> However, other chemistries can be employed to synthesize polymers with different degradable linkages besides imines, enabling alternate degradation conditions that depolymerize polymers into smaller monomeric units. This section aims to highlight more sustainable coupling strategies to employ for the polymerization of  $\pi$ -conjugated polymers and to inspire chemists to apply these conditions toward the design of degradable conjugated systems (Figure 4).

**3.1. Direct Arylation Polymerization.** The study of well-defined  $\pi$ -conjugated polymers requires the use of robust polymerization methods. To date, many recent reports of  $\pi$ -conjugated polymers have been prepared via Stille or Suzuki–Miyaura cross-coupling polymerization. These methods are atom-inefficient as one set of monomers is prefunctionalized with an organometallic moiety (i.e., stannylation or borylation for Stille and Suzuki, respectively), serving as a sacrificial

foothold to generate the cross-coupled product. In addition, Stille cross-coupling requires the use of toxic tin reagents and produces toxic tin waste. The atom-inefficiency during monomer preparation, purification, and polymerization as well as the stoichiometric waste poses a major obstacle to the large-scale production and feasibility of the use of  $\pi$ -conjugated polymers. Direct arylation polymerization (DArP) has been increasingly used to synthesize  $\pi$ -conjugated polymers in a more atom-efficient and benign approach, which has yielded  $\pi$ -conjugated polymers with comparable molecular weights and polymer performance to those synthesized by Stille or Suzuki.<sup>72–74</sup> DArP circumvents the requirement to prefunctionalize a coupling partner with a sacrificial organometallic moiety, allowing the desired polymer to be synthesized with fewer steps and more atom efficiently (Figure 4b). In addition, the byproduct of DArP is benign, making this polymerization approach an attractive alternative and could help accelerate the



**Figure 4.** Overview of the polymerization methods used to synthesize conjugated polymers from their monomer repeat units (new bonds formed in purple): (a) imine polycondensations, (b) direct arylation polymerization, (c) cross-dehydrogenative coupling, (d) aldol polymerization, and (e) enzymatic oxidative polymerization. (f) Synthetic strategy of a degradable carbazole-*co*-fluorene poly(azomethine) via imine polycondensation. (g) Direct arylation polymerization of degradable branched and linear polyimidazole nanoparticles. (h) Direct arylation polymerization of a degradable conjugated polymer with 1,2,4-oxadiazole linkers. (i) Left: Direct arylation polymerization of a degradable indacenodithiophene-*co*-thiophene-imine-thiophene poly(azomethine). Right: Photos of the polymerization between indacenodithiophene and thiophene-imine-thiophene at 0 and 22 h. Images and synthetic schemes adapted with permission from refs 67, 76, 77, and 78. Copyright 2021 American Chemical Society, 2021 Royal Society of Chemistry, and 2023 American Chemical Society.

commercial feasibility, production, and competitiveness of using  $\pi$ -conjugated polymers. Like other Pd-mediated cross-coupling catalytic cycles which involve oxidative addition and reductive elimination, the C–H bond functionalization proceeds via a pathway facilitated by a carboxylic acid additive. Although one major limitation of DArP is the possibility of undesired C–H activation leading to homocoupling and branching defects, which are detrimental to the performance of the conjugated polymers, much of the research attention in DArP has been dedicated to addressing this challenge. For example, Marks and co-workers<sup>75</sup> have successfully employed

relatively cheap and bulky carboxylic acid derivatives that suppress the formation of undesired C–H activation at beta-sites on monomers, to prepare five known high-performance  $\pi$ -conjugated polymers for photovoltaic applications. The polymers were prepared by DArP in high yields, with similar dispersities, and exhibited molecular weight comparable to that of polymers synthesized by Stille cross-coupling polymerization. Device characterization showed indistinguishable photovoltaic performance and minimal difference in charge transport, charge generation/recombination, and thin-film microstructural properties. These results demonstrated that

high-performing, defect-free  $\pi$ -conjugated polymers for photovoltaic applications can be synthesized via a more atom-efficient and greener polymerization method, yielding polymers with molecular weights equal to or higher than those of Stille copolymers.

Inspired by the development of DArP as an alternative greener polymerization method to synthesize  $\pi$ -conjugated polymers, recent progress has focused on the utilization of DArP for the polymerization of degradable  $\pi$ -conjugated polymers. Kuenhe and co-workers<sup>76</sup> synthesized biodegradable polyimidazole particles via DArP using a Pd-catalyst and adamantylphosphine oxide ligands. Notably, they noticed linear polymer chains were obtained using imidazole-based monomers with the 4-position sterically blocked with a methyl group but cross-linked polymers when leaving the 4-position unblocked (Figure 4g). This shed light on the importance of monomeric design when using DArP as a coupling strategy for degradable polymers. In 2022, Seferos and co-workers<sup>77</sup> synthesized a new class of degradable  $\pi$ -conjugated polymers using oxadiazole as the cleavable  $\pi$ -conjugated monomer via DArP (Figure 4h). In their approach, an asymmetric monomer was synthesized flanking the 1,2,4-oxadiazole linker between two thiophene groups. Two DArP conditions were used to prepare the polymers: phosphine-free conditions, which required a higher catalyst loading, and  $\beta$ -branching suppression conditions, which utilized neo-decanoic acid. Phosphine-free conditions resulted in moderately higher polymerization yields with higher molecular weights compared to those of the  $\beta$ -branching suppression conditions. Interestingly, the authors suggest that the relatively high free energy of activation for the monomers, coupled with the lower temperature and sterically bulky reagents used in the  $\beta$ -branching-suppressing conditions, may be responsible for slowing the polymerization enough for debromination to outcompete and hinder the polymerization of the  $\beta$ -branching-suppressing conditions.<sup>77</sup> More recently, Tran and co-workers<sup>78</sup> have recently demonstrated the first example of a successful optimization of DArP for the synthesis of a degradable imine-based conjugated polymer. They demonstrated a systematic study that focused on optimization DArP conditions with the use of tetramethylethylenediamine as a coligand to synthesize a new polymer, p(IDT-TIT), composed of indacenothiophene (IDT) and thiophene-imine-thiophene (TIT) units (Figure 4i). With the simple monomer preparation and polymerization protocol, this work encourages future high-performing degradable  $\pi$ -conjugated polymers to be synthesized via DArP.

**3.2. Cross-Dehydrogenative Coupling Polymerization.** Although there have been significant research efforts using DArP to synthesize  $\pi$ -conjugated polymers, the method still relies on using a dibrominated monomer as a coupling partner. Similar to Stille and Suzuki cross-coupling polymerization, the use of dibrominated monomer calls for additional synthetic and purification, thus there has been a trend toward investigating polymerization via cross-dehydrogenative-coupling (CDC) reactions,<sup>79</sup> which involves direct  $sp^2$  C–H functionalization between two monomers (Figure 4c). One major challenge with CDC polymerization is maintaining the selectivity of successive C–H metalation between the two monomers while suppressing undesired homocoupling and branching. One of the earliest investigations of CDC polymerization was demonstrated by Kanbara and co-workers,<sup>80</sup> in which a Ag/Pd dual catalytic system was utilized to synthesize an octafluorobiphenyl-bithiophene polymer. While

small amounts of homocoupling defects were still observed in the polymer and the monomer choices, the synthetic methodology demonstrated in this work provides the future promise of moving toward polymerization that does not require any prior preparation or purification of dibrominated or organometallic-based monomers. Toward adopting more atom-efficient polymerization methods, we direct readers to a minireview<sup>81</sup> that highlights in greater detail the development of the CDC polymerization strategy as it becomes an additional polymerization method that can be used to access  $\pi$ -conjugated polymers. Although there has yet to be a reported degradable  $\pi$ -conjugated polymer that uses CDC, we envision that this polymerization method will be widely used in the near future.

Luscombe and co-workers<sup>82</sup> have also investigated CDC polymerization, in which the Ag/Au catalytic system was utilized. This work was inspired by a Ag/Au-catalyzed  $sp^2$  cross-coupling reported by Larrosa and co-workers,<sup>83</sup> where they reported that the cross-coupling was fully selective between the electron-rich and electron-poor arenes, eliminating the need of directing groups or excess of one coupling partner over another. In Luscombe's<sup>82</sup> Ag/Au catalytic system, selectivity between the two monomers was lost during polymerization due to increased reactivity of the oligomer as it grew longer compared to the monomer during small molecule model studies. Further mechanistic studies by DFT revealed that orthogonal control to maintain an alternating conjugated polymer is dictated by the C–H acidity of one monomer and the arene nucleophilicity of the other. Specifically, chemoselectivity in the Ag cycle is controlled by C–H acidity, while chemoselectivity in the Au cycle is dictated by arene nucleophilicity. Since these two chemoselectivity mechanisms are orthogonal, CDC polymerization can be controlled by optimizing the C–H acidity of one monomer and the nucleophilicity of the other such that alternating conjugated polymers can be synthesized.<sup>84</sup> This earlier work motivates the need to further investigate the use of dual catalytic systems to synthesize  $\pi$ -conjugated polymers using a more atom-economical and benign method.

**3.3. Aldol Polymerization.** Traditional polymerization methods, as well as the DArP and CDC polymerization, involve transition-metal-mediated coupling reactions to connect  $\pi$ -conjugated monomers through carbon–carbon single bonds. The use of transition metals to synthesize polymers raises toxicity concerns if these polymers are used in a biological environment, because any remaining metallic residue would affect device operations. Aldol condensation furnishes the backbone with carbon–carbon double bonds and eliminates transition-metal mediated coupling reactions (Figure 4d). They are catalyzed by an acid or base, such as *p*-toluenesulfonic acid (*p*-TsOH), piperidine, or potassium *tert*-butoxide (*t*-BuOK), release water as a byproduct, and can be done in nonhalogenated solvents.<sup>85–87</sup> McCulloch and co-workers,<sup>85</sup> reported the synthesis of five rigid polymers using aldol polymerization between derivatives of bis-oxindole and bis-isatin monomers. By incorporation of phenyl, naphthalene, and thieno[3,2-*b*]thiophene as central aromatic cores, electron mobilities up to  $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{1-}$  can be achieved, and these polymers exhibited near-IR absorption properties with PS exhibiting the longest  $\lambda_{\text{max}}$  of 1128 nm. Since the report of these conjugated polymers that exhibit fully fused backbones, libraries of half-fused backbones have been explored by introducing aldehyde monomers.<sup>88</sup> Instead of exhibiting strict

double bonds between monomers, these half-fused polymers consist of monomers connected through alternating double and single bonds, but through judicious monomer designs by introducing intramolecular noncovalent interactions, coplanarity is still maintained. This approach broadens the scope of the monomers that can undergo aldol polymerization while still maintaining a rigid backbone and opens opportunities to use the aldol reaction to construct degradable  $\pi$ -conjugated polymers.

**3.4. Enzymatic Polymerizations.** In the pursuit of transition-metal free chemistry, biocatalysis has been an evolving technique to synthesize  $\pi$ -conjugated polymers (Figure 4e).<sup>89–91</sup> In 1999, Samuelson and co-workers<sup>92</sup> used horseradish peroxidase (HRP), an oxidoreductase that functions in the presence of hydrogen peroxide, to synthesize a conducting polyaniline/sulfonated polystyrene (SPS) complex. Their approach of using a polyelectrolyte template to enzymatically polymerize aniline circumvented the common drawbacks of previously biocatalyzed polymerization, namely, the production of short oligomers as precipitation out of solution would occur once conductive polymers approached larger molecular weights. Moreover, by templating with sulfonated polystyrene, the synthesis promotes a more para-directed head-to-tail polymerization of aniline and allows the resulting conductive polymer to be soluble in aqueous conditions. However, a large amount of HRP was needed as polymerizations proceeded best under acidic conditions at pH 4.0–4.5, whereas HRP activity performs optimally at pH 6.0–6.5. This prompted Sakharov and co-workers<sup>93</sup> to synthesize conductive, water-soluble SPS-polyaniline complexes using another oxidoreductase, laccase, which optimally catalyzed the reaction at pH 4.0–4.5 in the presence of molecular dioxygen. Since then, numerous other publications have emerged using oxidoreductases such as HRP,<sup>94,95</sup> laccase,<sup>96</sup> glucose oxidase,<sup>97,98</sup> and others,<sup>99,100</sup> to catalyze the synthesis of  $\pi$ -conjugated polymers.

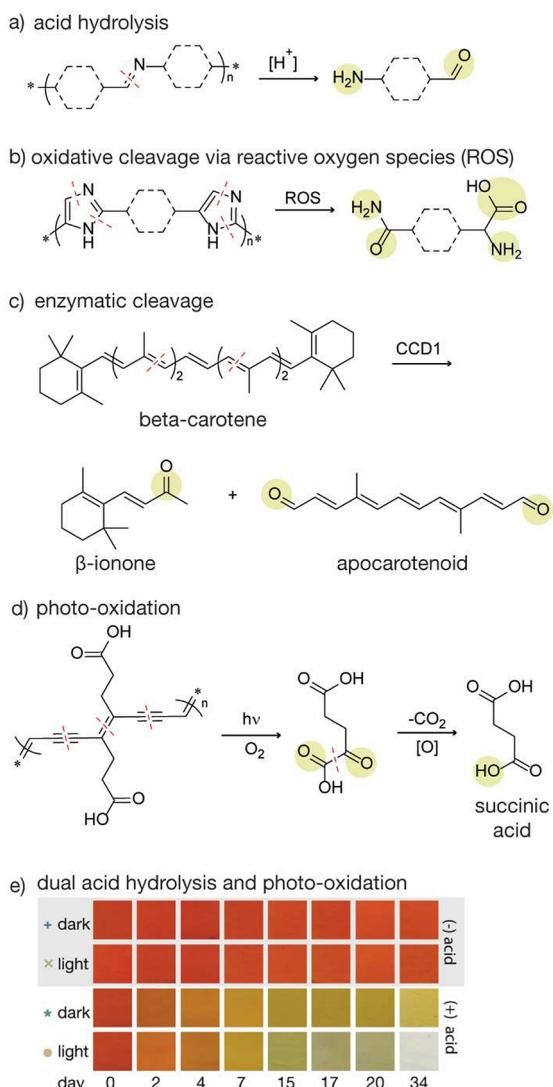
In recent years, an emerging field within the biocatalysis of  $\pi$ -conjugated polymers is *in vivo* enzymatic polymerization. First demonstrated by Berggren, Stavrinidou, and co-workers<sup>101</sup> in the vascular tissues of plants, a poly(3,4-ethylenedioxythiophene) (PEDOT) analogue, p(ETE-S), was synthesized and its *in vivo* polymerization mechanism explored.<sup>102</sup> Peroxidases, such as HRP, occur naturally in high concentrations within plant cell walls, as they play a vital role in lignification. When 4-(2-(2,5-bis(2,3-dihydrothieno[3,4-*b*]-[1,4]dioxin-5-yl)thiophen-3-yl)ethoxy)butane-1-sulfonate (ETE-S) is injected into the vascular tissue of plants, ETE-S enters the plant's peroxidative cycle and polymerizes along the cell wall. This discovery has led to the creation of biohybrid plants with electronic roots<sup>103,104</sup> because of the *in vivo* enzymatic polymerization of conductive polymers. In further pursuits, Xu, Zhu and co-workers<sup>105</sup> demonstrated the first *in vivo* enzymatic polymerization of polyaniline in rat models. In this study, aniline monomers were introduced *in vivo* at a crush injury site of the sciatic nerve in adult male Sprague–Dawley rats. Because of the natural presence of reactive oxygen species (ROS), and catalase at the site, polyaniline was synthesized on microvesicles, creating a conductive environment that enhances the signal transduction of the injured nerve and facilitates nerve reconstruction. Although there is yet to be work on an enzymatically synthesized degradable  $\pi$ -conjugated polymer, the publications highlighted in this section demonstrate the advantages of using enzymes as catalysts for

polymerization, and we foresee this being used to design degradable conductive polymers for temporary bioelectronics soon.

#### 4. DEGRADATION OF $\pi$ -CONJUGATED POLYMERS

The selection of monomer and coupling strategy directly affects what type of labile moiety will or can be incorporated into a polymer backbone. However, it is important to acknowledge that the degradable linker may be introduced in the monomer rather than through the polymerization method. Nevertheless, all three parameters discussed in this perspective complement each other. When thinking about the degradation of  $\pi$ -conjugated polymers, additional aspects must be considered. First, one must select a mechanism (i.e., degradable linker) by which they want their polymer to degrade. Of the many factors that affect which degradable linker is selected, the most prominent is the intended application. For example, a degradable  $\pi$ -conjugated polymer for temporary health monitoring application<sup>23,106</sup> will need to be labile under physiological conditions or triggered by a nontoxic external stimulus. On the contrary, a degradable  $\pi$ -conjugated polymer for environmental monitoring devices<sup>107,108</sup> will need to be cleavable in its native environments, such as soil or marine conditions. The second factor to consider when thinking about the overall degradation of  $\pi$ -conjugated polymers is the degradation kinetics. This area is underexplored, and more is needed to understand how quickly a polymer will degrade as well as factors that affect the kinetics. Lastly, new avenues of  $\pi$ -conjugated polymer degradation, such as enzymatic depolymerization, are needed to better understand the mechanisms by which these polymers degrade with respect to their potential application in the health (*in vivo*) or environmental (enzymes present in nature) monitoring sector.

**4.1. Degradable Linkers and Mechanisms.** We have previously highlighted select examples which utilize the imine bond<sup>56,67,109–111</sup> in the backbone as a cleavable site that maintains  $\pi$ -conjugation (Figure 5a). However, many other degradable linkers which maintain  $\pi$ -conjugation along the polymer backbone may be used such as imidazoles,<sup>112</sup> oxadiazoles,<sup>77</sup> or simple alkene linkages. These linkers are notably cleaved through chemical, UV, or enzymatic degradation. For instance, imidazole is a five-membered heterocyclic compound commonly found in biological systems including the green fluorescent protein, among other fluorescent biomolecules. The moiety has often been used in biodegradable applications *in vivo*, due to its ability to be cleaved by ROS, breaking the aromaticity of imidazole and generating carboxylic and amide byproducts (Figure 5b).<sup>113,114</sup> As a result, incorporating imidazole units into  $\pi$ -conjugated polymer systems has increased in recent years. Kuehne and co-workers<sup>115</sup> incorporated imidazole units into a  $\pi$ -conjugated polymer backbone, allowing the polymer to be degraded by activated macrophages. The imidazole ring was highly susceptible to scission through oxidation. The degradation byproducts produced in this example were water-soluble and nontoxic in small concentrations in cells, although some toxicity was observed upon higher concentrations. The group further demonstrated the versatility of the imidazole unit as a degradable linker in the synthesis of a polyimidazole for theranostic applications.<sup>76</sup> Polyimidazoles can be synthesized using DArP to produce particles that can be degraded through enzymatic oxidation in biological systems, as tested in their report using macrophages and lipopolysaccharides to induce



**Figure 5.** Degradable linkers and mechanisms, with functional groups of degradation products highlighted in yellow. (a) Generic acid hydrolysis mechanism by which an imine bond is cleaved to yield byproducts with amine and aldehyde functionalities. (b) Oxidative cleavage mechanism of imidazole units by reactive oxygen species (ROS). (c) Enzymatic oxidative cleavage of  $\beta$ -carotene using carotenoid cleavage dioxygenase 1 (CCD1), which yields  $\beta$ -ionone and apocarotenoids. (d) Photo-oxidation of PDDA, which generates succinic acid as a byproduct. (e) Photographs illustrating the degradation of p(CP-hexyl), a carotenoid imine-based polymer, in solution via acid hydrolysis and photo-oxidation. Images and schemes adapted with permission from refs 56, 76, and 123. Copyright 2023 American Chemical Society, 2021 American Chemical Society, 2021 American Chemical Society.

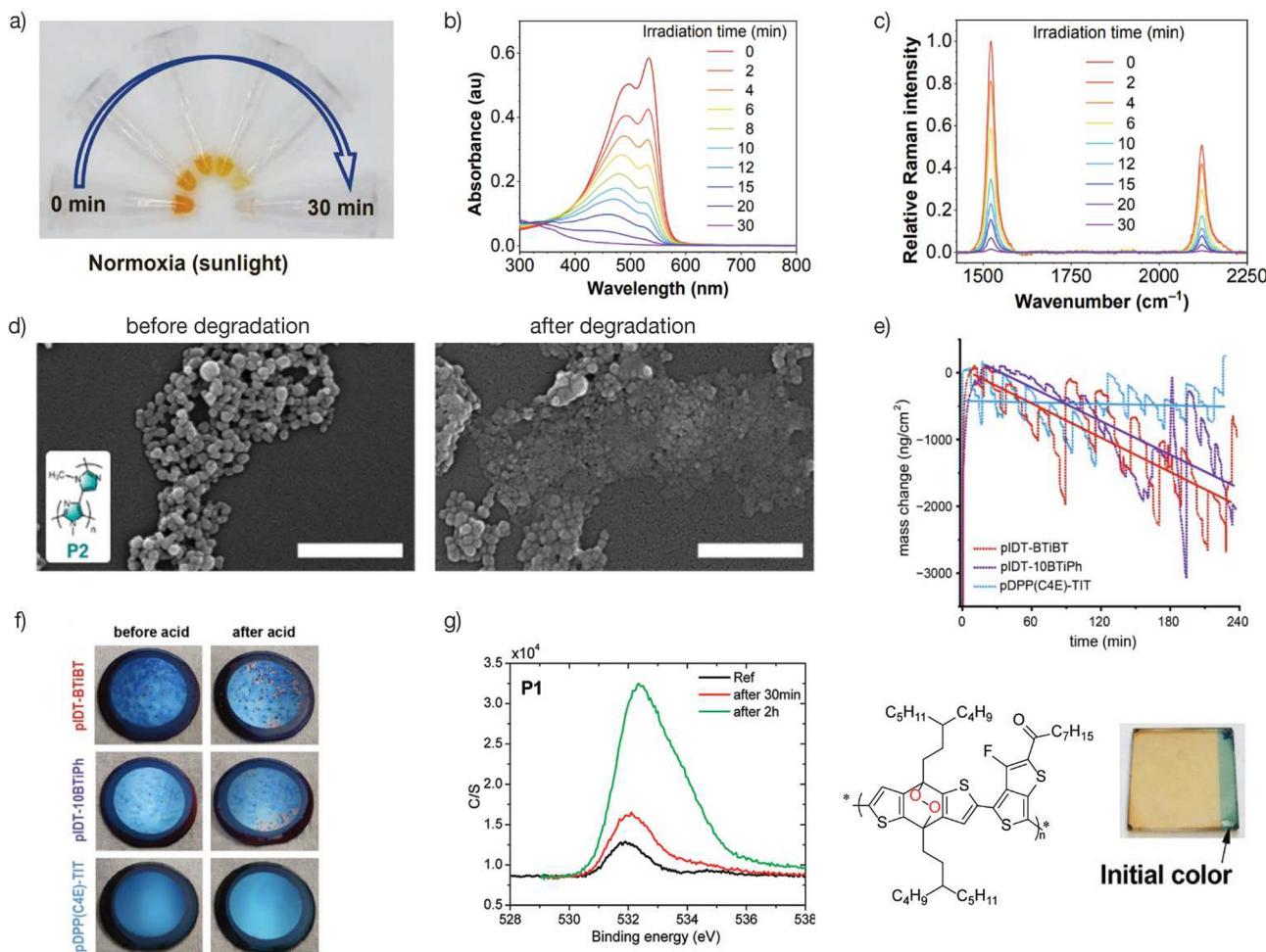
the formation of ROS. Testing the nanoparticle loading and degradation in HeLa cells showed higher cytotoxicity; however, results were inconclusive as to whether the degradation products were causing the cell viability to decrease or if the cells were sensitive to the overloading of nanoparticles. Zhang, Wei, and co-workers<sup>116</sup> have also utilized the degradability of imidazole units in the backbone of a type 1 photosensitizer. Degradation was explored through *in vitro* experiments using hydrogen peroxide and light, as well as *in vivo* experiments using HeLa cells and mice. More importantly, the nanoparticles produced were used as an anticancer agent

by killing cancer cells efficiently upon light irradiation. The cells avoided phototoxicity after photodynamic therapy treatment via self-degradation-induced ROS generation. As a result, imidazole is a versatile conjugated degradable linker suitable for the *in vivo* degradation of bioelectronics.

A common theme across the selected degradable linkers presented thus far is degradation via oxidation. Historically, many researchers have successfully solved the chemical instability of  $\pi$ -conjugated polymers through means of synthetic modifications, additives, or copolymer design.<sup>117</sup> However, for degradable applications, the instability of these materials is highly valued. A common mode of degradation is photooxidation, where the coupling of oxygen and light leads to chain scission of  $\pi$ -conjugated polymers.<sup>118</sup> Most notably, many small molecules, such as carotenoids, degrade via enzymatic oxidative cleavage, resulting in chain scission of unsaturated carbon bonds (Figure 5c). This mechanism is highly accessible, proceeding without intervention from external sources, and is ideal for the autonomous degradation of electronic materials in the environment. The key to utilizing this mechanism is to create an on-demand trigger, where there would be some control to when the materials begin to degrade.

The photooxidative degradation of traditional classes of semiconducting polymers includes poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV), poly(3-hexylthiophene-2,5-diyli) (P3HT), and benzodithiophene-thienopyrrolodione (BDT-TPD) polymers among others, have been extensively studied.<sup>119,120</sup> The overall trend points to illumination intensity and simultaneous exposure to both light and oxygen as the main factors, which accelerate the rate of degradation for semiconducting polymers. For P3HT, fluorescence quenching is observed upon exposure to air and light but the polymer is stable if only subjected to one condition without the other.<sup>121</sup> This has implications for the manufacturing of various electronic devices in which both air and light should be minimized to avoid premature degradation. However, for applications that are actively looking for the degradation of P3HT films, chemical instability can be exploited. A decrease in photoluminescence intensity is also observed in p(BDT-TPD) because emitting sites are converted into luminescence quenchers.<sup>122</sup> Scheblykin and co-workers<sup>122</sup> explored this photodegradation more and noted the presence of H-aggregates in degraded films as a direct result of photoluminescence intensity suppression (absence of non-aggregated chromophores). More recently, Luo and co-workers<sup>123</sup> synthesized a polydiacetylene-based polymer, polymer poly(deca-4,6-diynedioic acid) (PDDA), which was shown to be degradable via photooxidation, degrading into succinic acid as the major byproduct (Figure 5d). PDDA is stable when kept in the dark and in an inert atmosphere, allowing for applications such as a biorthogonal Raman probe for *in-cell* Raman imaging.<sup>124</sup> PDDA is an excellent example of a self-degradable  $\pi$ -conjugated polymer, which utilizes sunlight and air to autonomously degrade into a natural byproduct. The idea to use sunlight as a degradable trigger was further demonstrated by Tran and co-workers,<sup>56</sup> in which their system (p(CP-hexyl)) could degrade via photooxidation alone, acid hydrolysis alone, or combined to increase the rate of degradation in solution (Figure 5e). This example is of particular interest as it means that polymer degradation can be tailored depending on the application it is used for.

The example of photodegradation of p(BDT-TPD), a well-studied donor–acceptor system, points toward the exploration



**Figure 6.** (a) Photo-oxidative degradation of polymer PDPA after being exposed to sunlight for different time periods. (b) A decrease in UV-vis absorption spectra is observed for polymer PDPA after irradiation with sunlight for different time periods. (c) Alkene and alkyne Raman signals decrease upon PDPA degradation being irradiated by sunlight for different time. (d) SEM images of polyimidazole (P2) before and after degradation by exposure to  $\text{H}_2\text{O}_2$  for 24 h. (e) Mass changes of imine-based donor–acceptor based semiconducting polymer thin films monitored by a quartz crystal microbalance. (f) Images of measured imine-based polymers before and after acid hydrolysis. (g) Left: XPS oxygen content on p(BDT-FTT). Right: oxidized structure of polymer P1 and P1 film surface before and after a 2 h exposure to light in air. Images adapted with permission from refs 76, 120, 123, and 136. Copyright 2021 American Chemical Society, 2012 American Chemical Society, 2021 American Chemical Society, and 2023 Royal Society of Chemistry.

of degrading other donor–acceptor systems, as the current trend leverages the use of donor–acceptor motifs to create high electronic performing  $\pi$ -conjugated polymers. Recently, Wang and co-workers<sup>125</sup> have synthesized a degradable donor–acceptor polymer featuring thiophene diketopyrrolopyrrole (TDPP) and benzothiadiazole (Tz) as the donor–acceptor units, respectively. Specifically, the thiophene in the backbone of p(TDPP-Tz) can be cleaved through oxidation via hypochlorite, leading to the overall degradation of the semiconducting polymer nanoparticles. Previously, semiconducting oligomers were shown to be degradable via hypochlorite, a ROS present in high concentrations associated with cardiovascular diseases, neuron degeneration, atherosclerosis, lung injury, arthritis, and cancer.<sup>126</sup> The p(TDPP-Tz) semiconducting polymer nanoparticles were used in mice models, where the polymer degraded in the arthritis environment (hypochlorite present) over 48 h without noticeable damage to organs. Fan and co-workers<sup>127</sup> also demonstrated the degradation of an acceptor unit, ITTC, in the presence of hypochlorite. Their degradable donor–acceptor unit was used

specifically for biomarker-activatable NIR-II fluorescence probes; however, there is potential to design donor–acceptor conjugated polymers that are susceptible to degradation by hypochlorite for use as semiconductors in biomedical-based electronic devices.

Other strategies to impart degradability is to graft susceptible moieties with conductive polymers,<sup>128,129</sup> or include labile nonconjugated moieties,<sup>130,131</sup> such as esters or amide linkages. In these cases, the backbone is not conjugated and is beyond the scope of this perspective; however, we have selected a few key examples that demonstrate notable degradation mechanisms and in-depth studies on degradation byproducts. Liu, Lu, Wang and co-workers<sup>132</sup> synthesized PEDOT grafted with hydrolyzable carboxylic acid pendants, allowing the side chains of the polymer to degrade under aqueous conditions in a pH-dependent manner. This allows for control over degradation kinetics, and their results show that the biodegradation *in vivo* produces nontoxic byproducts in rats. This work is complemented by other strategies to impart degradability in a conjugated system. Although not an example

of a  $\pi$ -conjugated system, Liu, Xiao and co-workers<sup>133</sup> designed a pseudosemiconducting polymer with disulfide linkages in the backbone, which degrade instantly in the presence of cancerous glutathione (GSH). This example is interesting to note as it illustrates a different degradation mechanism that is highly specific to a cancerous environment. Another way to impart degradability was demonstrated by Lutkenhaus, Wooley and co-workers,<sup>134</sup> in which they created degradable redox-active materials, where redox-active pendant groups extend from the backbone of an aliphatic polymer, for battery applications. In their work, the degradable polypeptide-based battery featured viologen and 2,2,6,6-tetramethyl-4-piperidine-1-oxyl (TEMPO) as the redox-active groups. Degradation of the polypeptide polymer proceeded through hydrolysis in either acidic or basic conditions due to the presence of ester linkages in the side chains and amide bonds along the polymer backbone. Specifically, partial degradation of the chains was observed within 24 h under mild acidic conditions, with complete degradation observed with heating at 110 °C. Therefore, there is much interest in incorporating specific linkages into  $\pi$ -conjugated polymers so that they may degrade in environments that are specific to the intended application.

**4.2. Monitoring Degradation Kinetics.** An important factor to discuss is the degradation kinetics for the  $\pi$ -conjugated polymer systems presented thus far. Unfortunately, it is only in the past decade that select reports studied the kinetics of degradable systems. For imine-based systems, we are beginning to better understand strategies to fine-tune degradation for intended applications. Bao and co-workers<sup>135</sup> have found that the aggregation of imine-based polymer chains in solution greatly affects the degradation kinetics, with a decrease in aggregates associated with faster degradation times via acid hydrolysis. Aggregation was found to be solvent-dependent for solution degradation of TIT-based conjugated polymers, with polymers taking longer to degrade in chlorobenzene compared to chloroform. Moreover, branching points along alkyl side chains and  $M_n$  greatly influenced the rate of degradation for these polymers. In thin films, having ordered polymer chains leads to slower device degradation, with disordered chains leading to faster device degradation. In general, the authors found that polymer thin films took longer to degrade compared to solution-based polymer degradation. The Bao group has continued their efforts in studying structure-degradation property relationships with their new class of degradable semiconducting polymers based on IDT units.<sup>136</sup> These polymers degrade more quickly than their DPP counterparts under milder acidic conditions, which more closely resemble biological or environmental pH levels. Thin film degradation studies revealed that a combination of decreased aggregation and increased  $\pi-\pi$  spacing of IDT-based polymers significantly accelerated degradation rates observed for these polymers compared to those of previously studied DPP-based polymers. One step further, Kim and co-workers<sup>111</sup> studied the impact of incorporating imine bonds in the polymer backbone on degradability and electronic performance. Specifically, a naphthalenediimide-based terpolymer was synthesized using imine linkers. This report is unique as it investigates the optimal imine bond composition in the polymer backbone to maximize acid-hydrolyzed degradation and electrical performance, which are features that are simultaneously difficult to achieve. At the optimal condition of 0.45 imine content in the polymer backbone, complete

degradation under acidic conditions and the highest electron mobility were observed. These select examples of kinetic studies are promising for advancing degradable  $\pi$ -conjugated polymers, as these studies deepen our understanding of how these materials will degrade when incorporated into a device.

Many characterization techniques can be used to experimentally monitor the degradation of  $\pi$ -conjugated polymers (Figure 6). Traditional methods to monitor degradation include gel permeation chromatography (GPC), <sup>1</sup>H nuclear magnetic resonance (NMR), mass spectrometry, thermal gravimetric analysis (TGA), and ultraviolet-visible (UV-vis) spectroscopy. GPC provides information about decreases in the molecular weight of polymer samples. However, due to limitations in detection limits for many instruments, GPC is only useful for detecting oligomers greater than 500 Da and is thus unable to provide information on low-molecular-weight degradation products. <sup>1</sup>H NMR may be used to identify specific degradation byproducts, but to do so would require a single predominant degradation product or a purified batch of polymer degradants to easily identify and assign signals. Mass spectrometry techniques are preferred to help identify polymer degradation byproducts, but this method can also be overwhelming depending on the complexity of polymer degradation mechanisms, which can lead to multiple fragmentation patterns, making assignments possible, but tedious. TGA and UV-vis provide qualitative information about the overall polymer degradation, with TGA providing information about thermal degradation and UV-vis providing information about the loss of  $\pi$ -conjugation in the system. UV-vis can also identify byproducts based on new signals that appear if degradation byproducts have unique absorption spectra (Figure 6a,b).<sup>56</sup> Other qualitative techniques that can complement one another when studying the degradation of polymers include infrared (IR) spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). IR and Raman spectroscopy can also provide qualitative information about functional groups that may be unique to degradants and can differentiate between polymers, oligomers, and small molecules (Figure 6c). To further complement the aforementioned techniques, both SEM and XPS provide information about polymer surfaces, with SEM demonstrating visible surface deterioration<sup>137</sup> (Figure 6g), and XPS providing information about chemical changes on the polymer surface,<sup>120,138</sup> making both techniques useful for monitoring the bulk degradation on polymer film surfaces (Figure 6f). For quantitative information on the degradation of polymer films, techniques such as total organic carbon (TOC) analysis to detect the loss in carbon atom,<sup>123</sup> and quartz crystal microbalance (QCM) monitoring may be used. QCM is an increasingly popular technique which relies on the piezoelectric effect to detect differences in the mass of polymer films over time.<sup>139</sup> Bao and co-workers<sup>136</sup> have utilized QCM to illustrate mass changes in acid-labile semiconducting polymer thin films over time when submerged in acidic solutions (Figure 6d, 6e). Therefore, a combination of many analytical techniques described in this section is needed to properly understand how  $\pi$ -conjugated polymers degrade and to identify degradation byproducts.

Although the focus of this perspective so far has been on the synthetic considerations for  $\pi$ -conjugated polymers that may be used as conductors/semiconductors, it is important to consider all the components of an electronic device when designing for degradation as the conductor/semiconductor

only represents a small percentage of the entire device. Therefore, the degradation kinetics of the other components will greatly influence the degradation kinetics of the  $\pi$ -conjugated polymers. For example, the substrate and encapsulant layers of organic field effect transistors (OFETs) comprises up to ~60% of the entire device.<sup>61</sup> As the outermost layers of the devices, their degradation kinetics and mechanisms will dictate how and when the semiconducting layer will begin degrading. Degradation kinetics for these components have been studied more and some recent examples are highlighted in Figure 6.

In 2017, Xu, Yu, and co-workers reported moisture-triggered transient electronics composed of polyanhydride substrates.<sup>140</sup> The anhydride bonds undergo chain scission to produce two carboxylic acids via hydrolysis due to moisture in the air. This allowed for tuning of degradation rates by controlling humidity levels, with lower humidity levels leading to slower degradation. Niederberger, Hwang, and co-workers<sup>141</sup> have recently reported an interesting approach to device degradation using polyanhydrides as the encapsulant layer. The hydrolytic degradation rate at the surface of the encapsulation layers is significantly faster because polyanhydride undergoes surface erosion in aqueous solutions. Degradation times are affected by temperature, pH, and amount of cross-linking agent present in the polyanhydride films. An interesting approach to device degradation has recently been reported by Niederberger, Hwang, and co-workers.<sup>142</sup> A water-soluble polymer composite is used as a packaging material that when dissolved releases a chemical etchant that decomposes aluminum and copper, two metals that are often used in electronic devices. The degradation rate for both metals can be adjusted by varying the amount of FeCl<sub>3</sub> present in the polymer composite. This shows that we can tailor the degradation rates of inorganic components in electronic devices with the possibility of extending this to organic components such as semiconducting polymers.

**4.3. Environmental Depolymerization and Enzymatic Cleavage.** For certain applications, such as biodegradable food packaging with integrated sensors, the complete degradation of  $\pi$ -conjugated polymers in the natural environment without chemical manipulation would be ideal for postconsumer management of electronic waste. Bockstaller and co-workers<sup>143</sup> recently developed a betaine ester-functionalized epoxy resins that completely degraded via hydrolysis in seawater at room temperature in under one month. Although there are currently no reports of a  $\pi$ -conjugated polymer that can degrade in seawater, we can use this example as inspiration to design  $\pi$ -conjugated polymers for environmental depolymerization without needing an external chemical stimulus. Moreover, metrics to assess  $\pi$ -conjugated polymers with low environmental persistence are needed, along with life cycle analyses on devices made with these materials, analogous to metrics and analyses<sup>144–146</sup> developed for commodity plastics.

Another mode of degradation that would be desirable for certain applications is enzymatic cleavage. Degradation triggered by enzymatic cleavage is commonly used in drug delivery, such as the example from Ma, Yu, Wei and co-workers<sup>147</sup> in which they designed a polyfluorene-based bottlebrush polymer with polytyrosine and poly[oligo(ethylene glycol)] methyl ether methacrylate] (POEGMA) side chains for enhanced anticancer drug delivery. Specifically, the polytyrosine side chains can be broken in the presence of proteinase K, a serine protease, allowing for the release of the

anticancer drug. Enzyme-catalyzed degradations often occur on the surface of polymer films as it is difficult for enzymes to access within the bulk of a polymer.<sup>148–150</sup> One example of a  $\pi$ -conjugated polymer designed as a biodegradable electrode material for organic batteries is a polyimidazole nanoparticle developed by Kuehne and co-workers.<sup>151</sup> The authors study the degradation of their polyimidazole via composting bacteria, a mixture of *E. coli*, *P. putida* and *P. aeruginosa* which secrete enzymes and ROS, and demonstrate complete degradation of linear and cross-linked nanoparticles within 72 h in solution. Furthermore, the biodegradation of an electrode composed of their degradable polyimidazole particles, poly(vinylidene fluoride) (PVDF) binder, and Super-P carbon using compostable bacteria was demonstrated. This study is among the first investigations into the bacterial degradation of  $\pi$ -conjugated polymers in solution. With this in mind, there is yet to be a reported study on the degradation of  $\pi$ -conjugated polymers via enzymes alone. Therefore, we envision future research efforts will be directed toward designing  $\pi$ -conjugated polymers with moieties that can be cleaved by naturally occurring enzymes present in humans or the environment.

## 5. SUMMARY AND OUTLOOK

Next-generation organic electronics will feature unique properties that current electronics do not possess, most notably, the feature of programmed or on-demand degradation. Dependable degradable conducting layers are consequently needed for these electronic devices, with  $\pi$ -conjugated polymers being the most promising candidates due to their ability to impart unique properties such as biocompatibility, stretchability, and flexibility. At the precipice of this technology, chemists can design a multitude of  $\pi$ -conjugated materials that contain labile linkages, which can be triggered to break down under specific conditions. Factors such as monomer selection, polymerization conditions, and degradation mechanism have been presented as key design features to consider when specifically synthesizing degradable  $\pi$ -conjugated polymer, with sustainability considerations such as biobased monomers and atom-efficient polymerizations highlighted. However, many questions remain unanswered for the future of  $\pi$ -conjugated polymers. For example, in-depth studies are imperative to assess the toxicity of these materials in the natural environment and *in vivo*. Furthermore, to accelerate the discovery of high-performing  $\pi$ -conjugated polymers with degradable linkages, automation and self-driving laboratories<sup>152,153</sup> may prove to be pivotal. Automation alone would be strategic for monitoring tedious degradation studies under multiple parameters, relieving chemistry from manual repetitive measurements which are prone to error when scaled to 100s to 1000s of measurements. We anticipate that automation coupled with artificial intelligence will streamline the design thinking process, advance the discovery of monomers, optimize polymerization conditions, and help predict depolymerization patterns and degradation byproducts. With increasing efforts and sparked curiosity, degradable  $\pi$ -conjugated polymers will have a defined role in the next-generation of electronics, yielding seamlessly integrated devices into our everyday lives.

## ■ AUTHOR INFORMATION

### Corresponding Author

Helen Tran – Department of Chemistry, Department of Chemical Engineering and Applied Chemistry, and Acceleration Consortium, University of Toronto, Toronto,

Ontario MSS 3H6, Canada; [orcid.org/0000-0002-4041-7340](https://orcid.org/0000-0002-4041-7340); Email: [tran@utoronto.ca](mailto:tran@utoronto.ca)

## Authors

Azalea Uva — Department of Chemistry, University of Toronto, Toronto, Ontario MSS 3H6, Canada; [orcid.org/0001-9661-6413](https://orcid.org/0001-9661-6413)

Sofia Michailovich — Department of Chemistry, University of Toronto, Toronto, Ontario MSS 3H6, Canada

Nathan Sung Yuan Hsu — Department of Chemistry, University of Toronto, Toronto, Ontario MSS 3H6, Canada; [orcid.org/0000-0003-2169-1616](https://orcid.org/0000-0003-2169-1616)

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/jacs.4c03194>

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada (H.T., RGPIN2021-03554; A.U., CGS-D scholarship; N.S.Y.H., CGS-M scholarship), and the University of Toronto's Acceleration Consortium from the Canada First Research Excellence Fund (H.T., CDG13-2023). The authors acknowledge the Department of Chemistry at the University of Toronto for their support.

## REFERENCES

- (1) Lee, D. M.; Rubab, N.; Hyun, I.; Kang, W.; Kim, Y. J.; Kang, M.; Choi, B. O.; Kim, S. W. Ultrasound-Mediated Triboelectric Nanogenerator for Powering on-Demand Transient Electronics. *Sci. Adv.* **2022**, *8* (1), 8423.
- (2) Boutry, C. M.; Beker, L.; Kaizawa, Y.; Vassos, C.; Tran, H.; Hinckley, A. C.; Pfattner, R.; Niu, S.; Li, J.; Claverie, J.; Wang, Z.; Chang, J.; Fox, P. M.; Bao, Z. Biodegradable and Flexible Arterial-Pulse Sensor for the Wireless Monitoring of Blood Flow. *Nat. Biomed. Eng.* **2019**, *3* (1), 47–57.
- (3) Ye, G.; Song, D.; Song, J.; Zhao, Y.; Liu, N. A Fully Biodegradable and Biocompatible Ionotronic Skin for Transient Electronics. *Adv. Funct. Mater.* **2023**, *33*, No. 2303990.
- (4) Jung, Y.; Min, J. K.; Choi, J.; Bang, J.; Jeong, S.; Pyun, K. R.; Ahn, J.; Cho, Y.; Hong, S.; Hong, S.; Lee, J.; Ko, S. H. Smart Paper Electronics by Laser-Induced Graphene for Biodegradable Real-Time Food Spoilage Monitoring. *Appl. Mater. Today* **2022**, *29*, No. 101589.
- (5) Mustafa, F.; Andreeșcu, S. Nanotechnology-Based Approaches for Food Sensing and Packaging Applications. *RSC Adv.* **2020**, *10* (33), 19309–19336.
- (6) Yu, Z.; Boyarkina, V.; Liao, Z.; Lin, M.; Zeng, W.; Lu, X. Boosting Food System Sustainability through Intelligent Packaging: Application of Biodegradable Freshness Indicators. *ACS Food Sci. Technol.* **2023**, *3* (1), 199–212.
- (7) de Oliveira Filho, J. G.; Bertolo, M. R. V.; Fernandes, S. S.; Lemes, A. C.; da Cruz Silva, G.; Junior, S. B.; de Azeredo, H. M. C.; Mattoso, L. H. C.; Egea, M. B. Intelligent and Active Biodegradable Biopolymeric Films Containing Carotenoids. *Food Chem.* **2024**, *434*, No. 137454.
- (8) Yang, Y.; Deng, Z. D. Stretchable Sensors for Environmental Monitoring. *Appl. Phys. Rev.* **2019**, *6* (1), No. 011309.
- (9) Xiang, L.; Xia, F.; Zhang, H.; Liu, Y.; Liu, F.; Liang, X.; Hu, Y.; Xiang, L.; Xia, F.; Zhang, H.; Liu, Y. D.; Liu, F.; Liang, X. L.; Hu, Y. F. Wafer-Scale High-Yield Manufacturing of Degradable Electronics for Environmental Monitoring. *Adv. Funct. Mater.* **2019**, *29* (50), No. 1905518.
- (10) Atreya, M.; Marinick, G.; Baumbauer, C.; Dikshit, K. V.; Liu, S.; Bellerjeau, C.; Nielson, J.; Khorchidian, S.; Palmgren, A.; Sui, Y.; Bardgett, R.; Baumbauer, D.; Bruns, C. J.; Neff, J. C.; Arias, A. C.; Whiting, G. L. Wax Blends as Tunable Encapsulants for Soil-Degradable Electronics. *ACS Appl. Electron. Mater.* **2022**, *4* (10), 4912–4920.
- (11) Jia, X.; Ge, Y.; Shao, L.; Wang, C.; Wallace, G. G. Tunable Conducting Polymers: Toward Sustainable and Versatile Batteries. *ACS Sustain. Chem. Eng.* **2019**, *7* (17), 14321–14340.
- (12) Chae, J. S.; Park, S. K.; Roh, K. C.; Park, H. S. Electrode Materials for Biomedical Patchable and Implantable Energy Storage Devices. *Energy Storage Mater.* **2020**, *24*, 113–128.
- (13) Steiger, C.; Abramson, A.; Nadeau, P.; Chandrasekaran, A. P.; Langer, R.; Traverso, G. Ingestible Electronics for Diagnostics and Therapy. *Nat. Rev. Mater.* **2019**, *4* (2), 83–98.
- (14) Mirvakili, S. M.; Langer, R. Wireless On-Demand Drug Delivery. *Nat. Electron.* **2021**, *4* (7), 464–477.
- (15) Ashton, M. D.; Appen, I. C.; Firlak, M.; Stanhope, N. E.; Schmidt, C. E.; Eisenstadt, W. R.; Hur, B.; Hardy, J. G. Wirelessly Triggered Bioactive Molecule Delivery from Degradable Electroactive Polymer Films. *Polym. Int.* **2021**, *70* (4), 467–474.
- (16) Shahabuddin, M.; Uddin, M. N.; Chowdhury, J. I.; Ahmed, S. F.; Uddin, M. N.; Mofijur, M.; Uddin, M. A. A Review of the Recent Development, Challenges, and Opportunities of Electronic Waste (e-Waste). *Int. J. Environ. Sci. Technol.* **2023**, *20* (4), 4513–4520.
- (17) Kang, S. K.; Yin, L.; Bettinger, C. The Emergence of Transient Electronic Devices. *MRS Bull.* **2020**, *45* (2), 87–95.
- (18) Shim, J. S.; Rogers, J. A.; Kang, S. K. Physically Transient Electronic Materials and Devices. *Mater. Sci. Eng.* **2021**, *145*, No. 100624.
- (19) Zhang, Y.; Lee, G.; Li, S.; Hu, Z.; Zhao, K.; Rogers, J. A. Advances in Bioreversible Materials and Electronics. *Chem. Rev.* **2023**, *123* (19), 11722–11773.
- (20) Fanelli, A.; Ghezzi, D. Transient Electronics: New Opportunities for Implantable Neurotechnology. *Curr. Opin. Biotechnol.* **2021**, *72*, 22–28.
- (21) Tan, M. J.; Owh, C.; Chee, P. L.; Kyaw, A. K. K.; Kai, D.; Loh, X. J. Biodegradable Electronics: Cornerstone for Sustainable Electronics and Transient Applications. *J. Mater. Chem. C* **2016**, *4* (24), 5531–5558.
- (22) Uva, A.; Lin, A.; Babi, J.; Tran, H. Bioderived and Degradable Polymers for Transient Electronics. *J. Chem. Technol. Biotechnol.* **2022**, *97* (4), 801–809.
- (23) Chan, E. W. C.; Sun, X.; Travas-Sejdic, J. Recent Progress and Future Prospects in Transient Polymer Electronics. *Macromolecules* **2023**, *56* (11), 3755–3773.
- (24) Chandramohan Das, B.; Reji, N.; Philip, R. Optical Limiting Behavior of the Natural Dye Extract from Indigofera Tinctoria Leaves. *Opt. Mater. (Amst.)* **2021**, *114*, No. 110925.
- (25) Reali, M.; Gouda, A.; Bellemare, J.; Ménard, D.; Nunzi, J. M.; Soavi, F.; Santato, C. Electronic Transport in the Biopigment Sepia Melanin. *ACS Appl. Bio Mater.* **2020**, *3* (8), 5244–5252.
- (26) Giraud, L.; Grelier, S.; Grau, E.; Hadzioannou, G.; Brochon, C.; Cramail, H.; Cloutet, E. Upgrading the Chemistry of  $\pi$ -Conjugated Polymers toward More Sustainable Materials. *J. Mater. Chem. C* **2020**, *8* (29), 9792–9810.
- (27) Islam, A.; Liu, Z.-y.; Peng, R.-x.; Jiang, W.-g.; Lei, T.; Li, W.; Zhang, L.; Yang, R.-j.; Guan, Q.; Ge, Z.-y. Furan-Containing Conjugated Polymers for Organic Solar Cells. *Chin. J. Polym. Sci.* **2017**, *35* (2), 171–183.
- (28) Lee, S. M.; Lee, H. R.; Han, A.-R. R.; Lee, J.; Oh, J. H.; Yang, C.; Korea, S. High-Performance Furan-Containing Conjugated Polymer for Environmentally Benign Solution Processing. *ACS Appl. Mater. Interfaces* **2017**, *9* (18), 15652–15661.
- (29) Baillargeon, P.; Robidas, R.; Toulemon, O.; Michaud, Z.; Legault, C. Y.; Rahem, T. Crystal Structures of Lignocellulosic Furfuryl Biobased Polydiacetylenes with Hydrogen-Bond Networks: Influencing the Direction of Solid-State Polymerization through Modification of the Spacer Length. *Cryst. Growth Des.* **2022**, *22* (5), 2812–2823.

- (30) Fache, M.; Boutevin, B.; Caillol, S. Vanillin, a Key-Intermediate of Biobased Polymers. *Eur. Polym. J.* **2015**, *68*, 488–502.
- (31) Boivin, L.-P. P.; Dupont, W.; Gendron, D.; Leclerc, M. Biosourced Monomers: Toward Sustainable Conjugated Polymers for Organic Electronics. *Macromol. Chem. Phys.* **2023**, *224* (3), No. 2200378.
- (32) Boivin, L. P.; Dupont, W.; Leclerc, M.; Gendron, D. Biosourced Vanillin-Based Building Blocks for Organic Electronic Materials. *J. Org. Chem.* **2021**, *86* (23), 16548–16557.
- (33) Kayser, L. V.; Hartigan, E. M.; Arndtsen, B. A. Multicomponent Coupling Approach to Cross-Conjugated Polymers from Vanillin-Based Monomers. *ACS Sustain. Chem. Eng.* **2016**, *4* (12), 6263–6267.
- (34) Giraud, L.; Grelier, S.; Grau, E.; Garel, L.; Hadzioannou, G.; Kauffmann, B.; Cloutet, É.; Cramail, H.; Brochon, C. Synthesis and Characterization of Vanillin-Based  $\pi$ -Conjugated Polyazomethines and Their Oligomer Model Compounds. *Molecules* **2022**, *27* (13), 4138.
- (35) Zhu, Y.; Liu, J.; Liao, Y.; Lv, W.; Ma, L.; Wang, C. Degradation of Vanillin During Lignin Valorization Under Alkaline Oxidation. *Top. Curr. Chem.* **2020**, *376*, 33–51.
- (36) Bensaid, F. F.; Wietzerbin, K.; Martin, G. J. Authentication of Natural Vanilla Flavorings: Isotopic Characterization Using Degradation of Vanillin into Guaiacol. *J. Agric. Food Chem.* **2002**, *50* (22), 6271–6275.
- (37) Morales-Cerrada, R.; Molina-Gutierrez, S.; Lacroix-Desmazes, P.; Caillol, S. Eugenol, a Promising Building Block for Biobased Polymers with Cutting-Edge Properties. *Biomacromolecules* **2021**, *22* (9), 3625–3648.
- (38) Molina-Gutiérrez, S.; Manseri, A.; Ladrinal, V.; Bongiovanni, R.; Caillol, S.; Lacroix-Desmazes, P. Eugenol: A Promising Building Block for Synthesis of Radically Polymerizable Monomers. *Macromol. Chem. Phys.* **2019**, *220* (14), No. 1900179.
- (39) Jia, P.; Lamm, M. E.; Sha, Y.; Ma, Y.; Buzoglu Kurnaz, L.; Zhou, Y. Thiol-Ene Eugenol Polymer Networks with Chemical Degradation, Thermal Degradation and Biodegradability. *Chem. Eng. J.* **2023**, *454*, No. 140051.
- (40) Rahim, E. A.; Sanda, F.; Masuda, T. Synthesis and Properties of a Novel Polyacetylene Containing Eugenol Moieties. *J. Macromol. Sci. Part A* **2004**, *41* (2), 133–141.
- (41) Rahim, E. A.; Sanda, F.; Masuda, T. Synthesis and Properties of Optically Active Amino Acid Based Polyacetylenes Bearing Eugenol and Fluorene Moieties. *J. Polym. Sci. Part A Polym. Chem.* **2006**, *44* (2), 810–819.
- (42) Tadasa, K. Degradation of Eugenol by a Microorganism. *Agri. Biol. ChemBiol. Chem.* **1977**, *41* (6), 925–929.
- (43) Chen, P. C.; Zhang, H.; Zheng, P. Direct Biodegradation of Eugenol to Coniferyl Aldehyde and Other Higher Value-Added Products by Gibberella Fujikuroi ZH-34. *Electron. J. Biotechnol.* **2019**, *38*, 32–39.
- (44) Tasior, M.; Kim, D.; Singha, S.; Krzeszewski, M.; Ahn, K. H.; Gryko, D. T.  $\pi$ -Expanded Coumarins: Synthesis, Optical Properties and Applications. *J. Mater. Chem. C* **2015**, *3* (7), 1421–1446.
- (45) Cazin, I.; Rossegger, E.; Guedes de la Cruz, G.; Griesser, T.; Schlögl, S. Recent Advances in Functional Polymers Containing Coumarin Chromophores. *Polymers (Basel)* **2021**, *13* (1), 56.
- (46) Bhaumick, P.; Jana, A.; Choudhury, L. H. Synthesis of Novel Coumarin Containing Conjugated Fluorescent Polymers by Suzuki Cross-Coupling Reactions and Their Chemosensing Studies for Iron and Mercury Ions. *Polymer (Guildf.)* **2021**, *218*, No. 123415.
- (47) Azagarsamy, M. A.; McKinnon, D. D.; Alge, D. L.; Anseth, K. S. Coumarin-Based Photodegradable Hydrogel: Design, Synthesis, Gelation, and Degradation Kinetics. *ACS Macro Lett.* **2014**, *3* (6), 515–519.
- (48) Singh, A.; Mukherjee, T. Application of Carotenoids in Sustainable Energy and Green Electronics. *Mater. Adv.* **2022**, *3* (3), 1341–1358.
- (49) Cazzonelli, C. I.; Cazzonelli, C. I. Carotenoids in Nature: Insights from Plants and Beyond. *Funct. Plant Biol.* **2011**, *38* (11), 833–847.
- (50) Burch, R. R.; Dong, Y. H.; Fincher, C.; Goldfinger, M.; Rouviere, P. E. Electrical Properties of Polyunsaturated Natural Products: Field Effect Mobility of Carotenoid Polyenes. *Synth. Met.* **2004**, *146* (1), 43–46.
- (51) Walter, M. H.; Strack, D. Carotenoids and Their Cleavage Products: Biosynthesis and Functions. *Nat. Prod. Rep.* **2011**, *28* (4), 663–692.
- (52) Irimia-Vladu, M.; Troshin, P. A.; Reisinger, M.; Shmygleva, L.; Kanbur, Y.; Schwabegger, G.; Bodea, M.; Schwödiauer, R.; Mumyatov, A.; Fergus, J. W.; Razumov, V. F.; Sitter, H.; Sariciftci, N. S.; Bauer, S. Biocompatible and Biodegradable Materials for Organic Field-Effect Transistors. *Adv. Funct. Mater.* **2010**, *20* (23), 4069–4076.
- (53) Mogg, T. J.; Burton, G. W. The  $\beta$ -Carotene-Oxygen Copolymer: Its Relationship to Apocarotenoids and  $\beta$ -Carotene Function. *Can. J. Chem.* **2021**, *99* (999), 751–762.
- (54) Johnston, J. B.; Nickerson, J. G.; Daroszewski, J.; Mogg, T. J.; Burton, G. W. Biologically Active Polymers from Spontaneous Carotenoid Oxidation: A New Frontier in Carotenoid Activity. *PLoS One* **2014**, *9* (10), No. e111346.
- (55) Burton, G. W.; Daroszewski, J.; Mogg, T. J.; Nikiforov, G. B.; Nickerson, J. G. Discovery and Characterization of Carotenoid-Oxygen Copolymers in Fruits and Vegetables with Potential Health Benefits. *J. Agric. Food Chem.* **2016**, *64* (19), 3767–3777.
- (56) Uva, A.; Lin, A.; Tran, H. Biobased, Degradable, and Conjugated Poly(Azomethine)S. *J. Am. Chem. Soc.* **2023**, *145* (6), 3606–3614.
- (57) Bartlett, K. A.; Charland-Martin, A.; Lawton, J.; Tomlinson, A. L.; Collier, G. S. Azomethine-Containing Pyrrolo[3,2-b]Pyrrole Copolymers for Simple and Degradable Conjugated Polymers. *Macromol. Rapid Commun.* **2024**, *45*, No. 2300220.
- (58) Lei, T.; Chen, X.; Pitner, G.; Wong, H. S. P.; Bao, Z. Removable and Recyclable Conjugated Polymers for Highly Selective and High-Yield Dispersion and Release of Low-Cost Carbon Nanotubes. *J. Am. Chem. Soc.* **2016**, *138* (3), 802–805.
- (59) Jin, H.; Kim, K. K.; Park, S.; Rhee, J. H.; Ahn, H.; Kim, D. J.; Kim, K. K.; Noh, J. H.; Kim, T. S.; Shin, E. Y.; Son, H. J. Chemically Recyclable Conjugated Polymer and One-Shot Preparation of Thermally Stable and Efficient Bulk-Heterojunction from Recycled Monomer. *Adv. Funct. Mater.* **2023**, *33*, No. 2304930.
- (60) Nozaki, N.; Uva, A.; Matsumoto, H.; Tran, H.; Ashizawa, M. Thienoisobindigo-Based Recyclable Conjugated Polymers for Organic Electronics. *RSC Appl. Polym.* **2024**, *2* (2), 163–171.
- (61) Lei, T.; Guan, M.; Liu, J.; Lin, H. C.; Pfattner, R.; Shaw, L.; McGuire, A. F.; Huang, T. C.; Shao, L.; Cheng, K. T.; Tok, J. B. H.; Bao, Z. Biocompatible and Totally Disintegrable Semiconducting Polymer for Ultrathin and Ultralightweight Transient Electronics. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114* (20), 5107–5112.
- (62) Coates, G. W.; Getzler, Y. D. Y. L. Chemical Recycling to Monomer for an Ideal, Circular Polymer Economy. *Nat. Rev. Mater.* **2020**, *5* (7), 501–516.
- (63) Lohmann, V.; Jones, G. R.; Truong, N. P.; Anastasaki, A. The Thermodynamics and Kinetics of Depolymerization: What Makes Vinyl Monomer Regeneration Feasible? *Chem. Sci.* **2024**, *15* (3), 832–853.
- (64) Deng, Z.; Gillies, E. R. Emerging Trends in the Chemistry of End-to-End Depolymerization. *JACS Au* **2023**, *3* (9), 2436–2450.
- (65) Shelef, O.; Gnaim, S.; Shabat, D. Self-Immollative Polymers: An Emerging Class of Degradable Materials with Distinct Disassembly Profiles. *J. Am. Chem. Soc.* **2021**, *143* (50), 21177–21188.
- (66) Tran, H.; Feig, V. R.; Liu, K.; Wu, H. C.; Chen, R.; Xu, J.; Deisseroth, K.; Bao, Z. Stretchable and Fully Degradable Semiconductors for Transient Electronics. *ACS Cent. Sci.* **2019**, *5* (11), 1884–1891.
- (67) Xu, L.; Valášek, M.; Hennrich, F.; Fischer, R.; Kappes, M. M.; Mayor, M. Degradable Fluorene- And Carbazole-Based Copolymers for Selective Extraction of Semiconducting Single-Walled Carbon Nanotubes. *Macromolecules* **2021**, *54* (9), 4363–4374.

- (68) Matsumoto, T.; Yamada, F.; Kurosaki, T. Fully Conjugated and Soluble Polyazomethines. *Macromolecules* **1997**, *30* (12), 3547–3555.
- (69) Petrus, M. L.; Bouwer, R. K. M.; Lafont, U.; Murthy, D. H. K.; Kist, R. J. P.; Böhm, M. L.; Olivier, Y.; Savenije, T. J.; Siebbeles, L. D. A.; Greenham, N. C.; Dingemans, T. J. Conjugated Poly(Azomethine)s via Simple One-Step Polycondensation Chemistry: Synthesis, Thermal and Optoelectronic Properties. *Polym. Chem.* **2013**, *4* (15), 4182–4191.
- (70) Barik, S.; Bletzacker, T.; Skene, W. G.  $\pi$ -Conjugated Fluorescent Azomethine Copolymers: Opto-Electronic, Halochromic, and Doping Properties. *Macromolecules* **2012**, *45* (3), 1165–1173.
- (71) Li, G.; Yu, K.; Noordijk, J.; Meeusen-Wiertz, M. H. M.; Gebben, B.; Oude Lohuis, P. A. M.; Schotman, A. H. M.; Bernaerts, K. V. Hydrothermal Polymerization towards Fully Biobased Polyazomethines. *Chem. Commun.* **2020**, *56* (64), 9194–9197.
- (72) Pouliot, J. R.; Grenier, F.; Blaskovits, J. T.; Beaupré, S.; Leclerc, M. Direct (Hetero)Arylation Polymerization: Simplicity for Conjugated Polymer Synthesis. *Chem. Rev.* **2016**, *116* (22), 14225–14274.
- (73) Bohra, H.; Wang, M. Direct C–H Arylation: A “Greener” Approach towards Facile Synthesis of Organic Semiconducting Molecules and Polymers. *J. Mater. Chem. A* **2017**, *5* (23), 11550–11571.
- (74) Suraru, S. L.; Lee, J. A.; Luscombe, C. K. C–H Arylation in the Synthesis of  $\pi$ -Conjugated Polymers. *ACS Macro Lett.* **2016**, *5* (6), 724–729.
- (75) Dudnik, A. S.; Aldrich, T. J.; Eastham, N. D.; Chang, R. P. H.; Facchetti, A.; Marks, T. J. Tin-Free Direct C–H Arylation Polymerization for High Photovoltaic Efficiency Conjugated Copolymers. *J. Am. Chem. Soc.* **2016**, *138* (48), 15699–15709.
- (76) Jansen, F.; Schuster, P. A.; Lamla, M.; Trautwein, C.; Kuehne, A. J. C. Biodegradable Polyimidazole Particles as Contrast Agents Produced by Direct Arylation Polymerization. *Biomacromolecules* **2021**, *22* (12), 5065–5073.
- (77) Varju, B. R.; Seferos, D. S. Direct Heteroarylation Polymerization of a  $\pi$ -Conjugated Polymer with Degradable 1,2,4-Oxadiazole Linkers. *Polym. Chem.* **2022**, *13* (46), 6386–6392.
- (78) Hsu, N. S. Y.; Lin, A.; Uva, A.; Huang, S. H.; Tran, H. Direct Arylation Polymerization of Degradable Imine-Based Conjugated Polymers. *Macromolecules* **2023**, *56* (21), 8947–8955.
- (79) Tian, T.; Li, Z.; Li, C. J. Cross-Dehydrogenative Coupling: A Sustainable Reaction for C–C Bond Formations. *Green Chem.* **2021**, *23* (18), 6789–6862.
- (80) Aoki, H.; Saito, H.; Shimoyama, Y.; Kuwabara, J.; Yasuda, T.; Kanbara, T. Synthesis of Conjugated Polymers Containing Octa-fluorobiphenylene Unit via Pd-Catalyzed Cross-Dehydrogenative-Coupling Reaction. *ACS Macro Lett.* **2018**, *7* (1), 90–94.
- (81) Chakraborty, B.; Luscombe, C. K. Cross-Dehydrogenative Coupling Polymerization via C–H Activation for the Synthesis of Conjugated Polymers. *Angew. Chem. Int. Ed.* **2023**, *62* (21), No. e202301247.
- (82) Kang, L. J.; Xing, L.; Luscombe, C. K. Exploration and Development of Gold- and Silver-Catalyzed Cross Dehydrogenative Coupling toward Donor–Acceptor  $\pi$ -Conjugated Polymer Synthesis. *Polym. Chem.* **2019**, *10* (4), 486–493.
- (83) Cambeiro, X. C.; Ahlsten, N.; Larrosa, I. Au-Catalyzed Cross-Coupling of Arenes via Double C–H Activation. *J. Am. Chem. Soc.* **2015**, *137* (50), 15636–15639.
- (84) Liu, J. R.; Duan, Y. Q.; Zhang, S. Q.; Zhu, L. J.; Jiang, Y. Y.; Bi, S.; Hong, X. C–H Acidity and Arene Nucleophilicity as Orthogonal Control of Chemoselectivity in Dual C–H Bond Activation. *Org. Lett.* **2019**, *21* (7), 2360–2364.
- (85) Wang, Y.; Yu, Y.; Liao, H.; Zhou, Y.; McCulloch, I.; Yue, W. The Chemistry and Applications of Heteroisoidindigo Units as Enabling Links for Semiconducting Materials. *Acc. Chem. Res.* **2020**, *53* (12), 2855–2868.
- (86) Zhang, G.; Dai, Y.; Liu, Y.; Liu, J.; Lu, H.; Qiu, L.; Cho, K. Facile Green Synthesis of Isoindigo-Based Conjugated Polymers Using Aldol Polycondensation. *Polym. Chem.* **2017**, *8* (22), 3448–3456.
- (87) Huang, Y. W.; Lin, Y. C.; Li, J. S.; Chen, W. C.; Chueh, C. C. Investigating the Backbone Conformation and Configuration Effects for Donor–Acceptor Conjugated Polymers with Ladder-Type Structures Synthesized through Aldol Polycondensation. *J. Mater. Chem. C* **2021**, *9* (30), 9473–9483.
- (88) Guo, Y.; Yang, X.; Wang, L.; Duan, J.; Zhou, Y.; Nielsen, C. B.; Yu, Y.; Yang, J.; Guo, Y.; Li, Z.; Yue, W.; Liu, Y.; McCulloch, I. Aldol Polymerization to Construct Half-Fused Semiconducting Polymers. *Macromolecules* **2021**, *54* (22), 10312–10320.
- (89) Shoda, S. I.; Uyama, H.; Kadokawa, J. I.; Kimura, S.; Kobayashi, S. Enzymes as Green Catalysts for Precision Macromolecular Synthesis. *Chem. Rev.* **2016**, *116* (4), 2307–2413.
- (90) Behabtu, N.; Kralj, S. Enzymatic Polymerization Routes to Synthetic-Natural Materials: A Review. *ACS Sustain. Chem. Eng.* **2020**, *8* (27), 9947–9954.
- (91) Kobayashi, S.; Uyama, H.; Kimura, S. Enzymatic Polymerization. *Chem. Rev.* **2001**, *101* (12), 3793–3818.
- (92) Liu, W.; Kumar, J.; Tripathy, S.; Senecal, K. J.; Samuelson, L. Enzymatically Synthesized Conducting Polyaniline. *J. Am. Chem. Soc.* **1999**, *121* (1), 71–78.
- (93) Karamyshev, A. V.; Shleev, S. V.; Koroleva, O. V.; Yaropolov, A. I.; Sakharov, I. Y. Laccase-Catalyzed Synthesis of Conducting Polyaniline. *Enzyme Microb. Technol.* **2003**, *33* (5), 556–564.
- (94) Duan, L.; Zhao, Y.; Guo, F.; Liu, W.; Hou, C.; Ni, Z. Enzymatic-Catalyzed Polymerization of Water-Soluble Electrically Conductive Polymer PEDOT:PSS. *Polym. Adv. Technol.* **2014**, *25* (8), 896–899.
- (95) Rumbau, V.; Pomposo, J. A.; Eleta, A.; Rodriguez, J.; Grande, H.; Mecerreyres, D.; Ochoteco, E. First Enzymatic Synthesis of Water-Soluble Conducting Poly(3,4-Ethylenedioxothiophene). *Biomacromolecules* **2007**, *8* (2), 315–317.
- (96) Contaldo, U.; Gentil, S.; Courvoisier-Desord, E.; Rousselot-Pailley, P.; Thomas, F.; Tron, T.; Le Goff, A. Laccase-Catalyzed Functionalization of Phenol-Modified Carbon Nanotubes: From Grafting of Metallocopolyphenols to Enzyme Self-Immobilization. *J. Mater. Chem. A* **2023**, *11* (20), 10850–10856.
- (97) Krikstolaityte, V.; Kuliesius, J.; Ramanaviciene, A.; Mikoliunaite, L.; Kausaite-Minkstimiene, A.; Oztekin, Y.; Ramanavicius, A. Enzymatic Polymerization of Polythiophene by Immobilized Glucose Oxidase. *Polymer (Guildf.)* **2014**, *55* (7), 1613–1620.
- (98) Arnaboldi, S.; Salinas, G.; Bichon, S.; Gounel, S.; Mano, N.; Kuhn, A. Bi-Enzymatic Chemo-Mechanical Feedback Loop for Continuous Self-Sustained Actuation of Conducting Polymers. *Nat. Commun.* **2023**, *14* (1), 1–9.
- (99) Bouldin, R.; Ravichandran, S.; Kokil, A.; Garhwal, R.; Nagarajan, S.; Kumar, J.; Bruno, F. F.; Samuelson, L. A.; Nagarajan, R. Synthesis of Polypyrrole with Fewer Structural Defects Using Enzyme Catalysis. *Synth. Met.* **2011**, *161* (15–16), 1611–1617.
- (100) Cruz-Silva, R.; Romero-García, J.; Angulo-Sánchez, J. L.; Ledezma-Pérez, A.; Arias-Marín, E.; Moggio, I.; Flores-Loyola, E. Template-Free Enzymatic Synthesis of Electrically Conducting Polyaniline Using Soybean Peroxidase. *Eur. Polym. J.* **2005**, *41* (5), 1129–1135.
- (101) Stavriniou, E.; Gabrielsson, R.; Nilsson, K. P. R.; Singh, S. K.; Franco-Gonzalez, J. F.; Volkov, A. V.; Jonsson, M. P.; Grimoldi, A.; Elgland, M.; Zozoulenko, I. V.; Simon, D. T.; Berggren, M. In Vivo Polymerization and Manufacturing of Wires and Supercapacitors in Plants. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114* (11), 2807–2812.
- (102) Dufil, G.; Parker, D.; Gerasimov, J. Y.; Nguyen, T. Q.; Berggren, M.; Stavriniou, E. Enzyme-Assisted in Vivo Polymerisation of Conjugated Oligomer Based Conductors. *J. Mater. Chem. B* **2020**, *8* (19), 4221–4227.
- (103) Dufil, G.; Bernacka-Wojcik, I.; Armada-Moreira, A.; Stavriniou, E. Plant Bioelectronics and Biohybrids: The Growing Contribution of Organic Electronic and Carbon-Based Materials. *Chem. Rev.* **2022**, *122* (4), 4847–4883.
- (104) Parker, D.; Daguerre, Y.; Dufil, G.; Mantione, D.; Solano, E.; Cloutet, E.; Hadzioannou, G.; Näsholm, T.; Berggren, M.,

- Pavlopoulou, E.; Stavriniidou, E. Biohybrid Plants with Electronic Roots via in Vivo Polymerization of Conjugated Oligomers. *Mater. Horizons* **2021**, *8* (12), 3295–3305.
- (105) Qin, Y.; Fan, Y.; Chen, R.; Yin, H.; Zou, H.; Qu, X.; Tan, J.; Xu, Y.; Zhu, C. Harnessing Oxidative Microenvironment for in Vivo Synthesis of Subcellular Conductive Polymer Microesicles Enhances Nerve Reconstruction. *Nano Lett.* **2022**, *22*, 3825–3831.
- (106) Kenry, K.; Liu, B. Recent Advances in Biodegradable Conducting Polymers and Their Biomedical Applications. *Biomacromolecules* **2018**, *19* (6), 1783–1803.
- (107) Elli, G.; Hamed, S.; Petrelli, M.; Ibba, P.; Ciocca, M.; Lugli, P.; Petti, L. Field-Effect Transistor-Based Biosensors for Environmental and Agricultural Monitoring. *Sensors* **2022**, *22* (11), 4178.
- (108) Gopalakrishnan, S.; Waimin, J.; Zareei, A.; Sedaghat, S.; Raghunathan, N.; Shakouri, A.; Rahimi, R. A Biodegradable Chipless Sensor for Wireless Subsoil Health Monitoring. *Sci. Rep.* **2022**, *12* (8011), 1–14.
- (109) Tran, H.; Nikzad, S.; Chiong, J. A.; Schuster, N. J.; Peña-Alcántara, A. E.; Feig, V. R.; Zheng, Y.-Q.; Q.; Bao, Z. Modular Synthesis of Fully Degradable Imine-Based Semiconducting p-Type and n-Type Polymers. *Chem. Mater.* **2021**, *33* (18), 7465–7474.
- (110) Garbay, G.; Giraud, L.; Gali, S. M.; Hadzioannou, G.; Grau, E.; Grelier, S.; Cloutet, E.; Cramail, H.; Brochon, C. Divanillin-Based Polyazomethines: Toward Biobased and Metal-Free  $\pi$ -Conjugated Polymers. *ACS Omega* **2020**, *5* (10), 5176–5181.
- (111) Park, H.; Kim, Y.; Kim, D.; Lee, S.; Kim, F. S.; Kim, B. J. Disintegrable N-Type Electroactive Terpolymers for High-Performance, Transient Organic Electronics. *Adv. Funct. Mater.* **2022**, *32* (2), No. 2106977.
- (112) Liu, J.; Wang, S.; Cai, X.; Zhou, S.; Liu, B. Hydrogen Peroxide Degradable Conjugated Polymer Nanoparticles for Fluorescence and Photoacoustic Bimodal Imaging. *Chem. Commun.* **2018**, *54* (20), 2518–2521.
- (113) Boethling, R. S.; Sommer, E.; DiFiore, D. Designing Small Molecules for Biodegradability. *Chem. Rev.* **2007**, *107* (6), 2207–2227.
- (114) Rorije, E.; Germa, F.; Philipp, B.; Schink, B.; Beimborn, D. B. Prediction of Biodegradability from Structure: Imidazoles. *SAR QSAR Environ. Res.* **2002**, *13* (1), 199–204.
- (115) Repenko, T.; Rix, A.; Ludwanowski, S.; Go, D.; Kiessling, F.; Lederle, W.; Kuehne, A. J. C. Bio-Degradable Highly Fluorescent Conjugated Polymer Nanoparticles for Bio-Medical Imaging Applications. *Nat. Commun.* **2017** *81* **2017**, *8* (1), 1–8.
- (116) Huang, H.; Xie, W.; Wan, Q.; Mao, L.; Hu, D.; Sun, H.; Zhang, X.; Wei, Y. A Self-Degradable Conjugated Polymer for Photodynamic Therapy with Reliable Postoperative Safety. *Adv. Sci.* **2022**, *9* (4), No. 2104101.
- (117) Manceau, M.; Bundgaard, E.; Carlé, J. E.; Hagemann, O.; Helgesen, M.; Søndergaard, R.; Jørgensen, M.; Krebs, F. C. Photochemical Stability of  $\pi$ -Conjugated Polymers for Polymer Solar Cells: A Rule of Thumb. *J. Mater. Chem.* **2011**, *21* (12), 4132–4141.
- (118) Louis, B.; Caubergh, S.; Larsson, P. O.; Tian, Y.; Scheblykin, I. G. Light and Oxygen Induce Chain Scission of Conjugated Polymers in Solution. *Phys. Chem. Chem. Phys.* **2018**, *20* (3), 1829–1837.
- (119) Tromholt, T.; Manceau, M.; Helgesen, M.; Carlé, J. E.; Krebs, F. C. Degradation of Semiconducting Polymers by Concentrated Sunlight. *Sol. Energy Mater. Sol. Cells* **2011**, *95* (5), 1308–1314.
- (120) Alem, S.; Wakim, S.; Lu, J.; Robertson, G.; Ding, J.; Tao, Y. Degradation Mechanism of Benzodithiophene-Based Conjugated Polymers When Exposed to Light in Air. *ACS Appl. Mater. Interfaces* **2012**, *4* (6), 2993–2998.
- (121) Cook, S.; Furube, A.; Katoh, R. Matter of Minutes Degradation of Poly(3-Hexylthiophene) under Illumination in Air. *J. Mater. Chem.* **2012**, *22* (10), 4282–4289.
- (122) Shi, J.; Xu, X.; Xia, Y.; Chen, R.; Hawash, Z.; Deribew, D.; Moons, E.; Inganäs, O.; Scheblykin, I. G. Photo-Oxidation Reveals H-Aggregates Hidden in Spin-Cast-Conjugated Polymer Films as Observed by Two-Dimensional Polarization Imaging. *Chem. Mater.* **2019**, *31* (21), 8927–8936.
- (123) Tian, S.; Yue, Q.; Liu, C.; Li, M.; Yin, M.; Gao, Y.; Meng, F.; Tang, B. Z.; Luo, L. Complete Degradation of a Conjugated Polymer into Green Upcycling Products by Sunlight in Air. *J. Am. Chem. Soc.* **2021**, *143* (27), 10054–10058.
- (124) Tian, S.; Li, H.; Li, Z.; Tang, H.; Yin, M.; Chen, Y.; Wang, S.; Gao, Y.; Yang, X.; Meng, F.; Lauher, J. W.; Wang, P.; Luo, L. Polydiacetylene-Based Ultrastrong Bioorthogonal Raman Probes for Targeted Live-Cell Raman Imaging. *Nat. Commun.* **2020**, *11* (1), 1–9.
- (125) Ma, L.; Cai, Y.; Li, S.; Li, J.; Chen, P.; Zyryanov, G. V.; Kopchuk, D. S.; Kovalev, I. S.; Wang, Z. New Degradable Semiconducting Polymers for Photoacoustic Imaging of  $\lambda$ -Carrageenan-Induced Arthritis Mouse Model. *Anal. Chem.* **2022**, *94* (41), 14322–14330.
- (126) Yin, C.; Zhen, X.; Fan, Q.; Huang, W.; Pu, K. Degradable Semiconducting Oligomer Amphiphile for Ratiometric Photoacoustic Imaging of Hypochlorite. *ACS Nano* **2017**, *11* (4), 4174–4182.
- (127) Tang, Y.; Li, Y.; Lu, X.; Hu, X.; Zhao, H.; Hu, W.; Lu, F.; Fan, Q.; Huang, W. Bio-Erasable Intermolecular Donor–Acceptor Interaction of Organic Semiconducting Nanoprobes for Activatable NIR-II Fluorescence Imaging. *Adv. Funct. Mater.* **2019**, *29* (10), No. 1807376.
- (128) Da Silva, A. C.; Semeano, A. T. S.; Dourado, A. H. B.; Ulrich, H.; Cordoba De Torresi, S. I. Novel Conducting and Biodegradable Copolymers with Noncytotoxic Properties toward Embryonic Stem Cells. *ACS Omega* **2018**, *3* (5), 5593–5604.
- (129) Maity, N.; Dawn, A. Conducting Polymer Grafting: Recent and Key Developments. *Polymers (Basel)* **2020**, *12* (3), 709.
- (130) Sugiyama, F.; Kleinschmidt, A. T.; Kayser, L. V.; Alkhadra, M. A.; Wan, J. M. H.; Chiang, A. S. C.; Rodriguez, D.; Root, S. E.; Savagatrup, S.; Lipomi, D. J. Stretchable and Degradable Semiconducting Block Copolymers. *Macromolecules* **2018**, *51* (15), 5944–5949.
- (131) Chen, D.; Hickner, M. A. Degradation of Imidazolium- and Quaternary Ammonium-Functionalized Poly(Fluorenyl Ether Ketone Sulfone) Anion Exchange Membranes. *ACS Appl. Mater. Interfaces* **2012**, *4* (11), 5775–5781.
- (132) Jia, X.; Ma, X.; Zhao, L.; Xin, M.; Hao, Y.; Sun, P.; Wang, C.; Chao, D.; Liu, F.; Wang, C.; Lu, G.; Wallace, G. A Biocompatible and Fully Erodible Conducting Polymer Enables Implanted Rechargeable Zn Batteries. *Chem. Sci.* **2023**, *14* (8), 2123–2130.
- (133) Tang, D.; Yu, Y.; Zhang, J.; Dong, X.; Liu, C.; Xiao, H. Self-Sacrificially Degradable Pseudo-Semiconducting Polymer Nanoparticles That Integrate NIR-II Fluorescence Bioimaging, Photodynamic Immunotherapy, and Photo-Activated Chemotherapy. *Adv. Mater.* **2022**, *34* (34), No. 2203820.
- (134) Nguyen, T. P.; Easley, A. D.; Kang, N.; Khan, S.; Lim, S. M.; Rezenom, Y. H.; Wang, S.; Tran, D. K.; Fan, J.; Letteri, R. A.; He, X.; Su, L.; Yu, C. H.; Lutkenhaus, J. L.; Wooley, K. L. Polypeptide Organic Radical Batteries. *Nature* **2021**, *593* (7857), 61–66.
- (135) Chiong, J. A.; Zheng, Y.; Zhang, S.; Ma, G.; Wu, Y.; Ngaruka, G.; Lin, Y.; Gu, X.; Bao, Z. Impact of Molecular Design on Degradation Lifetimes of Degradable Imine-Based Semiconducting Polymers. *J. Am. Chem. Soc.* **2022**, *144* (8), 3717–3726.
- (136) Chiong, J. A.; Michalek, L.; Peña-Alcántara, A. E.; Ji, X.; Schuster, N. J.; Bao, Z.; Mater, J.; Chem, C.; Chiong, J. A.; Michalek, L.; Peña-Alcántara, A. E.; Ji, X.; Schuster, N. J.; Bao, Z. Degradable Semiconducting Polymers without Long-Range Order for on-Demand Degradation of Transient Electronics. *J. Mater. Chem. C* **2023**, *11* (43), 15205–15214.
- (137) Baidurah, S. Methods of Analyses for Biodegradable Polymers: A Review. *Polymers (Basel)* **2022**, *14* (22), 4928.
- (138) Manceau, M.; Gaume, J.; Rivaton, A.; Gardette, J. L.; Monier, G.; Bideux, L. Further Insights into the Photodegradation of Poly(3-Hexylthiophene) by Means of X-Ray Photoelectron Spectroscopy. *Thin Solid Films* **2010**, *518* (23), 7113–7118.
- (139) Marx, K. A. Quartz Crystal Microbalance: A Useful Tool for Studying Thin Polymer Films and Complex Biomolecular Systems at

- the Solution - Surface Interface. *Biomacromolecules*. **2003**, *4* (5), 1099–1120.
- (140) Gao, Y.; Zhang, Y.; Wang, X.; Sim, K.; Liu, J.; Chen, J.; Feng, X.; Xu, H.; Yu, C. Moisture-Triggered Physically Transient Electronics. *Sci. Adv.* **2017**, *3* (9), 1–9.
- (141) Choi, Y. S.; Koo, J.; Lee, Y. J.; Lee, G.; Avila, R.; Ying, H.; Reeder, J.; Hambitzer, L.; Im, K.; Kim, J.; Lee, K. M.; Cheng, J.; Huang, Y.; Kang, S. K.; Rogers, J. A. Biodegradable Polyanhydrides as Encapsulation Layers for Transient Electronics. *Adv. Funct. Mater.* **2020**, *30* (31), No. 2000941.
- (142) Mittal, N.; Jang, T. M.; Hwang, S. W.; Niederberger, M. PVA–FeCl<sub>3</sub> Composites as Substrate and Packaging Materials for the Controlled Degradation of Non-Degradable Metals in Transient Electronics. *J. Mater. Chem. A* **2023**, *11* (24), 12999–13006.
- (143) Han, J.; Chen, Q.; Feng, Y.; Shen, Y.; Wu, D.; Zhong, M.; Zhang, Q.; Zhao, Z.; Zhai, Y.; Bockstaller, M. R. Seawater-Degradable and Antibacterial Epoxy Thermosets Employing Betaine Ester Linkages. *ACS Appl. Polym. Mater.* **2023**, *5* (5), 3298–3305.
- (144) Chamas, A.; Moon, H.; Zheng, J.; Qiu, Y.; Tabassum, T.; Jang, J. H.; Abu-Omar, M.; Scott, S. L.; Suh, S. Degradation Rates of Plastics in the Environment. *ACS Sustain. Chem. Eng.* **2020**, *8* (9), 3494–3511.
- (145) James, B. D.; Ward, C. P.; Hahn, M. E.; Thorpe, S. J.; Reddy, C. M. Minimizing the Environmental Impacts of Plastic Pollution through Ecodesign of Products with Low Environmental Persistence. *ACS Sustain. Chem. Eng.* **2024**, *12* (3), 1185–1194.
- (146) Law, K. L.; Narayan, R. Reducing Environmental Plastic Pollution by Designing Polymer Materials for Managed End-of-Life. *Nat. Rev. Mater.* **2021** *72* **2022**, *7* (2), 104–116.
- (147) Liu, F.; Wang, D.; Zhang, M.; Ma, L.; Yu, C. Y.; Wei, H. Synthesis of Enzyme-Responsive Theranostic Amphiphilic Conjugated Bottlebrush Copolymers for Enhanced Anticancer Drug Delivery. *Acta Biomater.* **2022**, *144*, 15–31.
- (148) Feig, V. R.; Tran, H.; Bao, Z. Biodegradable Polymeric Materials in Degradable Electronic Devices. *ACS Cent. Sci.* **2018**, *4* (3), 337–348.
- (149) Gazvoda, L.; Višić, B.; Spreitzer, M.; Vukomanović, M. Hydrophilicity Affecting the Enzyme-Driven Degradation of Piezoelectric Poly-l-Lactide Films. *Polymers (Basel)* **2021**, *13* (11), 1719.
- (150) Rivers, T. J.; Hudson, T. W.; Schmidt, C. E. Synthesis of a Novel, Biodegradable Electrically Conducting Polymer for Biomedical Applications. *Adv. Funct. Mater.* **2002**, *12*, 33–37.
- (151) Schuster, P. A.; Uhl, M.; Kissmann, A.-K. K. A.-K.; Jansen, F.; Geng, T.; Ceblin, M. U.; Spiewok, S.; Rosenau, F.; Jacob, T.; Kuehne, A. J. C. Conjugated Polyimidazole Nanoparticles as Biodegradable Electrode Materials for Organic Batteries. *Adv. Electron. Mater.* **2024**, *10*, No. 2300464.
- (152) Vriza, A.; Chan, H.; Xu, J. Self-Driving Laboratory for Polymer Electronics. *Chem. Mater.* **2023**, *35* (8), 3046–3056.
- (153) Abolhasani, M.; Kumacheva, E. The Rise of Self-Driving Labs in Chemical and Materials Sciences. *Nat. Synth.* **2023**, *2* (6), 483–492.
- (154) Balachandran, V.; Parimala, K. Vanillin and Isovanillin: Comparative Vibrational Spectroscopic Studies, Conformational Stability and NLO Properties by Density Functional Theory Calculations. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2012**, *95*, 354–368.
- (155) Glowacki, E. D.; Leonat, L.; Voss, G.; Bodea, M.; Bozkurt, Z.; Irimia-Vladu, M.; Bauer, S.; Sariciftci, N. S. Natural and Nature-Inspired Semiconductors for Organic Electronics. *Org. Semicond. Sensors Bioelectron. IV* **2011**, *8118*, 78–87.
- (156) Siddiqui, S. A. In Silico Investigation of the Coumarin-Based Organic Semiconductors for the Possible Use in Organic Electronic Devices. *J. Phys. Org. Chem.* **2019**, *32* (3), No. e3905.
- (157) Niyonkuru, D.; Carrière, A.; Ambrose, R.; Gouda, A.; Reali, M.; Camus, A.; Pezzella, A.; Hill, I.; Santato, C. Locating the Bandgap Edges of Eumelanin Thin Films for Applications in Organic Electronics. *J. Chem. Technol. Biotechnol.* **2022**, *97* (4), 837–843.
- (158) Konar, S.; Samanta, D.; Mandal, S.; Das, S.; Mahto, M. K.; Shaw, M.; Mandal, M.; Pathak, A. Selective and Sensitive Detection of Cinnamaldehyde by Nitrogen and Sulphur Co-Doped Carbon Dots: A Detailed Systematic Study. *RSC Adv.* **2018**, *8* (74), 42361–42373.