

## Organic NIR Photodetectors: Pushing Photodiodes Beyond 1000 nm

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**Abstract** Advances in the synthesis of low bandgap ( $E_g < 1.5$  eV) conjugated polymers has produced organic materials capable of absorbing near-infrared (NIR) light (800–2500 nm), with these materials first applied to photodiode NIR detectors in 2007 as an alternative to more traditional inorganic devices. Although the development of organic NIR photodetectors has continued to advance, their ability to effectively detect wavelengths in the low-energy portion of the NIR spectrum is still limited. Efforts to date concerning the production of photodiode-based devices capable of detecting light beyond 1000 nm are reviewed.

**Keywords** conjugated polymers, low bandgap polymers, NIR photodetectors, photodiodes, organic electronics

### Introduction

Organic materials have grown to represent a lasting aspect of modern society such that organic plastics have become more ubiquitous than other common materials (e.g., metals, glass, or ceramics). While commonly associated with structural applications (e.g., plastics, resins, etc.), organic materials have grown to also include species for a range of optical and electronic applications, with conjugated organic materials playing a dominant role.<sup>[1–7]</sup> As such conjugated materials combine the properties of organic plastics with the electronic properties of classical inorganic semiconductors, they are typically viewed as quite modern materials. In reality, however, conjugated organic polymers date back to the early 19th century,<sup>[8,9]</sup> although interest in their electronic properties did not really manifest until the early 1960s.<sup>[8–10]</sup> Reports of conductivities in the metallic regime then brought specific focus to these materials in the 1970s,<sup>[8,9,11]</sup> resulting in the addition of doped conjugated polymers to the growing class of *synthetic metals*.<sup>[12,13]</sup> Before long, a broad interdisciplinary field had developed, ultimately leading to various technological applications and the current field of organic electronics, common examples of which include organic photovoltaics (OPVs), organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), electrochromic devices, and chemical sensors.<sup>[1–7]</sup>

One limitation of organic materials is the inability to effectively absorb light deep into the near-infrared (NIR) spectrum (800–2500 nm). This has changed, however, with the ongoing development of low bandgap ( $E_g < 1.5$  eV) polymers,<sup>[14–16]</sup> which allows the realistic possibility of organic devices able to act as optical sensors for the detection of NIR light. While several reviews on organic NIR photodetectors have already been reported, these have either included photodetectors as a subset of larger topics<sup>[17–19]</sup> or tend to focus on devices capable of sensing the higher energy edge of the NIR spectrum (800–1000 nm).<sup>[20–22]</sup> Due to the inherent difficulties in producing materials capable of effectively absorbing light at energies below 1000 nm, photodetectors able to operate in this low-energy portion of the NIR spectrum are much less common. As such, the current review will summarize the progress to date on photodiode-based devices capable of detecting light beyond

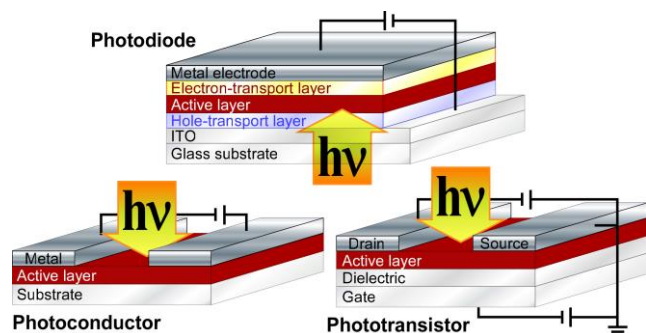
1000 nm, while highlighting the current difficulties and limitations associated with their development.

### NIR Photodetectors

Sensing NIR light plays a critical role in various applications. As such, NIR photodetector applications include optical communication, remote control, chemical sensing, nighttime surveillance, spectroscopy instrumentation, and medical monitoring devices for photodynamic therapy.<sup>[16–21]</sup> Perhaps the most widespread of these uses lies in telecommunications, which transmit large amounts of data in the form of light through fiber-optic cables at wavelengths of 1150, 1350, and 1550 nm.<sup>[16]</sup>

Commercial NIR sensors utilize inorganic materials (GaAs, InGaAs, etc.) due to their excellent charge-carrier mobility, small exciton binding energy, and high stability.<sup>[18,20,21]</sup> However, such inorganic devices have inherent drawbacks including complex and costly manufacturing, mechanical inflexibility, high driving voltage, low operating temperatures, and limited tunability of the spectral response range, all of which restrict their application to large-area, flexible, or portable devices.<sup>[17,20,21]</sup> In contrast, organic photodetectors offer the potential of low-cost manufacturing, facile processing methods, light weight forms, high flexibility, and large-area scalability, while also providing tunable bandgaps, high quantum efficiency, and high sensitivity, thus making them promising alternatives to current commercial devices.<sup>[18,20,22]</sup>

Current approaches to organic NIR photodetectors include photoconductor,<sup>[21,22]</sup> photodiode,<sup>[17–23]</sup> and phototransistor<sup>[21,23]</sup> devices (Figure 1), of which photodiodes were the first to be developed and are still the most commonly studied. In addition, photodetectors can be classified as broadband (panchromatic) or narrowband (wavelength selective), depending on the width of their spectral response window.<sup>[20]</sup> The general device structure for most photodiode-based organic NIR photodetectors is essentially identical to conventional bulk heterojunction organic photovoltaic (BHJ OPV) devices.<sup>[19,20]</sup> The performance of these devices, however, is typically characterized by somewhat different figure-of-merit parameters associated with the efficiency, noise, and speed of detection at a given wavelength ( $\lambda$ ).<sup>[19,20]</sup> Like BHJ OPV devices, this includes the external quantum efficiency (EQE( $\lambda$ )), which is related to the device



**Figure 1** Primary types of organic NIR photodetector devices.

responsivity ( $R(\lambda)$ ) at the wavelength in question.<sup>[18–20]</sup> However, it is the specific detectivity ( $D^*(\lambda)$ ) that is considered the most critical parameter.<sup>[17–20]</sup> This value is expressed in units of  $\text{cm Hz}^{1/2} \text{W}^{-1}$ , which is equal to the more commonly cited unit of 1 Jones, with values  $>10^{11}$  Jones considered satisfactory. Thus,  $D^*(\lambda)$  is used to measure the ability to detect signals of weak irradiation intensity and can be improved by increasing  $R(\lambda)$  and suppressing the dark current.<sup>[20]</sup> Additional figures-of-merit include the noise equivalent power ( $\text{NEP}(\lambda)$ ), linear dynamic range ( $\text{LDR}(\lambda)$ ), temporal response time ( $\tau$ ),  $-3$  dB bandwidth ( $f_{-3\text{dB}}$ ), and spectral response range.<sup>[18–20]</sup>

### Low Bandgap Conjugated Polymers and the First Organic Materials with Photoresponse $>1000$ nm

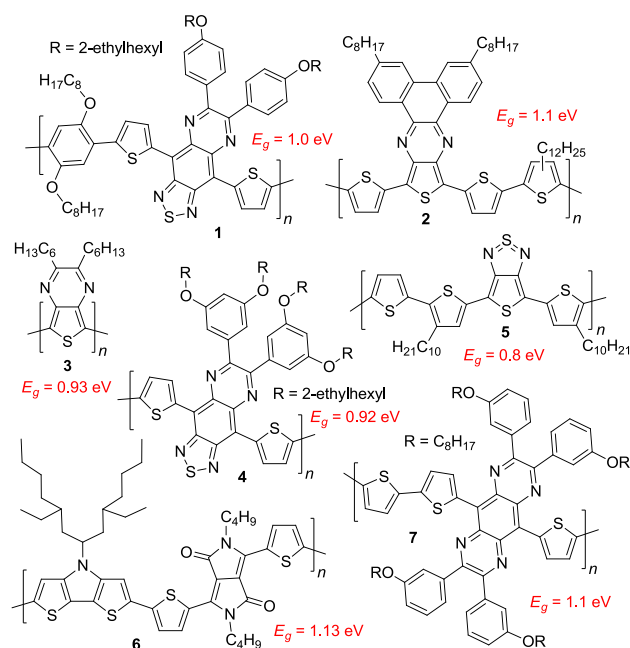
The ability to absorb sufficient NIR light requires an  $E_g$  of ca. 1.5 eV or lower and thus the design and synthesis of low  $E_g$  polymers is integral to the development of organic NIR photodetectors. In terms of design, various structure-function principles have been shown to contribute to lowered  $E_g$  values. These include both the degree of bond length alternation and planarity along the polymer backbone, as well as monomer aromaticity, the heteroatom of any heterocyclic units, and interchain coupling in the solid state.<sup>[14–16]</sup> Although all of these factors play a role in the resulting  $E_g$ , two general design approaches are largely responsible for the successful generation of low  $E_g$  polymers. The earliest of these was the application of fused-ring thiophenes that enhances the quinoidal nature of the polymer backbone, thus resulting in lower bandgaps. However, it is the application of “donor-acceptor” (D-A) frameworks that has become the prevalent design criteria for most low  $E_g$  materials.<sup>[16]</sup>

Although these design principles have resulted in a wide variety of low bandgap polymers dating back to 1984,<sup>[14–16]</sup> the  $E_g$  value alone does not ensure successful application to electronic devices. Thus, by 2010, only 7 examples (Figure 2) provided the necessary combination of  $E_g$ , suitable frontier energy levels, and blend morphology to allow photoresponse at wavelengths greater than 1000 nm in BHJ OPV devices.<sup>[24–30]</sup> With the exception of **3**, all of these are copolymeric materials that utilize a combination of fused-ring quinoidal units and D-A frameworks to give  $E_g$  values of 0.8–1.13 eV. Of the polymers given in Figure 2, polymer **5** provided the lowest energy onset at ca. 1450 nm.<sup>[28]</sup> Not surprisingly, it was from this initial set of materials that early organic NIR photodetectors were developed.

### Photodiode-Based Organic NIR Photodetectors

#### Polymer-based devices

The first material to successfully exhibit photoresponse beyond 1000 nm was **1** (Figure 2) reported by Andersson and coworkers in 2007, with a spectral edge at 1200 nm.<sup>[24]</sup> Perhaps of little surprise, the authors recognized the potential application to NIR photodetectors and determined a peak NIR



**Figure 2** Initial materials capable of photoresponse  $>1000$  nm.

**Table 1** Select parameters of polymer NIR photodetectors

Active layer <sup>a</sup>	Spectral Region/nm	$\lambda_{\text{det}}$ (nm)/ $V_{\text{app}}$ (V)	$\text{EQE}(\lambda)$ (%)	$D^*(\lambda)$ (Jones) <sup>b</sup>	Ref.
1:PCBM	320–1200	950/0	12.5	$5 \times 10^{9c}$	[24]
5:PCBM	300–1450	800/–0.1		$2.3 \times 10^{13}$	[28]
8:PCBM	400–1100	1000/–5	28.9		[32]
9:PCBM	400–1100	800/–1	12.5	$2.3 \times 10^{10}$	[33]
5:PCBM <sup>d,e</sup>	300–1450	800/0	27.0	$2 \times 10^{11}$	[34]
3:PCBM	380–1250	950/0	2.6		[35]
10:PCBM	400–1100	800/0	16.0	$1.75 \times 10^{13}$	[36]
11:PCBM	400–1200	800/–0.1		$1.4 \times 10^{12}$	[37]
10:PCBM <sup>d</sup>	350–1100	800/0	18.2	$4.01 \times 10^{13}$	[38]
12:PCBM	300–1200	800/–0.1		$4.1 \times 10^{11}$	[39]
13:PCBM	300–1200	800/–0.1		$1.0 \times 10^{11}$	[39]
14:PC <sub>71</sub> BM	400–1200	900/0	5.8	$1.04 \times 10^{12}$	[40]
15:PCBM	300–1600	900/–0.1		$2.6 \times 10^{12}$	[41]
16:PC <sub>71</sub> BM	500–1800	1800/0	$<0.01$	$1.2 \times 10^{8c}$	[42]
17:PC <sub>71</sub> BM	300–1700	1200/–2	7.8	$>10^{13}$	[43]
18:triPCBM	350–2500	1500/–0.5	13.4	$2.2 \times 10^{11}$	[44]
19:PC <sub>71</sub> BM	300–1100	1100/–2	30	$10^{12}$	[45]

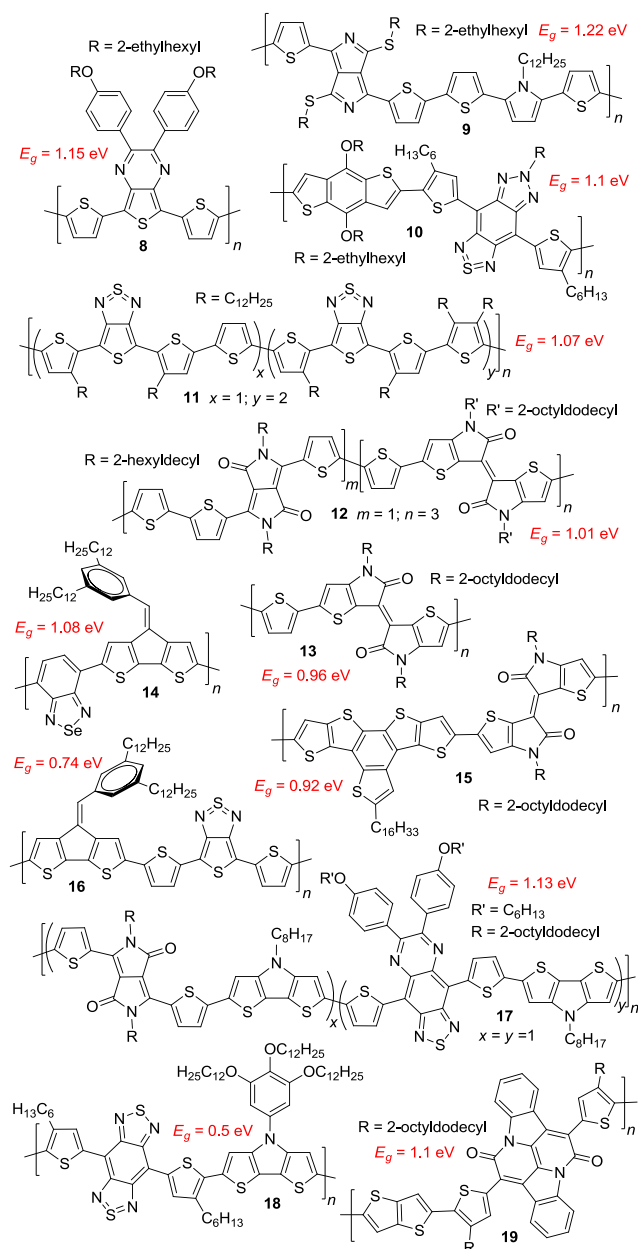
<sup>a</sup> PCBM = [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester; PC<sub>71</sub>BM = [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester; triPCBM = triphenyl-C<sub>61</sub>-butyric acid methyl ester. <sup>b</sup> Determined from dark current, unless otherwise noted. <sup>c</sup> From noise current. <sup>d</sup> Inverted device. <sup>e</sup> With a ZnO nanowire array.

sensitivity at 950 nm. From the reported  $\text{NEP}(\lambda)$  ( $2 \times 10^{-9} \text{ W}$ ) and the device area ( $5 \text{ mm}^2$ ), this gives a  $D^*(\lambda)$  of  $5 \times 10^9$  Jones (Table 1). A month later, another NIR photodetector was also reported by Yu, Yang, and coworkers, but this utilized a polymer with a higher  $E_g$  and thus its spectral region did not extend beyond 970 nm.<sup>[31]</sup>

This was then followed up two years later by the more high-profile report of Heeger and coworkers on devices of **5** in 2009.<sup>[28]</sup> Due to the lower  $E_g$  of **5** in comparison to **1**, this later

work was able to extend the spectral region out to ca. 1450 nm, although the peak sensitivity was blue-shifted to ca. 850 nm. Still, the calculated  $D^*(\lambda)$  at 800 nm was  $2.3 \times 10^{13}$  Jones, significantly improved in comparison to the previous devices of **1**.

It was then another two years before a third example to extend beyond 1000 nm was reported by Meng, Chen, and co-workers in 2011.<sup>[32]</sup> This was also the first report that utilized a new polymer that was not one of the original seven materials given in Figure 2. As shown in Figure 3, **8** was of similar design to the previous materials, exhibiting an  $E_g$  of 1.15 eV and yielding devices with a spectral range out to 1100 nm.



**Figure 3** Additional NIR photodetector materials after 2010.

From 2012 onward, reports of photodetectors capable of extending beyond 1000 nm become more common, with roughly two or more appearing each year.<sup>[33–46]</sup> Of the devices given in Table 1, the next real advancement came in 2014, with devices of **10** (Figure 3) exhibiting a  $D^*(\lambda)$  at 800 nm of  $4.01 \times 10^{13}$  Jones,<sup>[38]</sup> roughly twice that reported by Heeger and coworkers in 2009.<sup>[28]</sup> Of course, this improvement was offset by a much narrower spectral region, only extending as far as 1100 nm.

Further extension beyond the limit of 1450 nm set by Heeger and coworkers had to wait until 2017, when Qiao, Wang, and coworkers reported a photodetector with a spectral region out to 1600 nm.<sup>[41]</sup> This device utilized **15**, with an  $E_g$  of 0.92 eV, thus significantly extending its ability to absorb lower energy NIR wavelengths. Although the maximum  $D^*(\lambda)$  near 900 nm was a factor of 10 times lower than the previous devices of **5**<sup>[28]</sup> and **10**,<sup>[38]</sup> it still exhibited a detectivity  $>10^{11}$  Jones at 1300 nm and  $>10^{10}$  Jones at 1600 nm, thus showing great promise as a detector at lower energy wavelengths not previously possible.

The spectral region was further broadened that same year by Azoulay and coworkers, who reported a photodetector based on **16**.<sup>[42]</sup> As its bandgap ( $E_g = 0.74$  eV) was the lowest applied to NIR photodetectors to date, the resulting devices were now capable of response down to 1800 nm. This extension of the spectral region was offset by significantly lower  $D^*(\lambda)$  values, although still providing a detectivity of ca.  $10^8$  Jones at 1800 nm.

By far the greatest advancement, however, came in 2018 when Wudl and coworkers successfully extended the spectral region down to 2500 nm.<sup>[44]</sup> Again, this was achieved by further reducing the bandgap, with **18** exhibiting one of the lowest known bandgaps ( $E_g = 0.5$  eV) for a soluble, processible material. This allowed an especially broad photoresponse with a reasonable  $D^*(\lambda)$  at 800 nm ( $1.4 \times 10^{11}$  Jones) and remaining above  $10^{11}$  Jones out to ca. 2200 nm.

Finally, an alternate approach was introduced in 2018 that moved the emphasis from the donor polymer of the BHJ to the acceptor material.<sup>[46]</sup> Here, the fullerene component was replaced with small-molecule acceptors capable of NIR absorption. While early reports were limited to photoresponse below 1000 nm, more recent efforts have led to spectral regions extending to 1100 nm with detectivities as high as  $1.5 \times 10^{12}$  Jones.<sup>[47]</sup>

### Small molecule-based devices

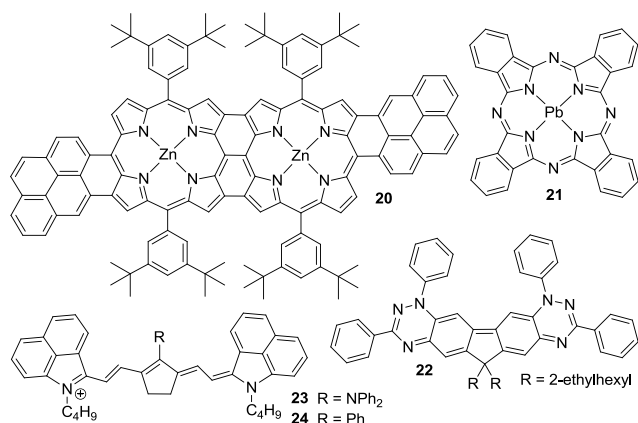
In addition to the polymer-based devices discussed above, alternate approaches have included various small molecule species capable of NIR absorption (Figure 4).<sup>[48–55]</sup> While such species utilize the same design principles as low  $E_g$  polymers, they are constrained by the shorter conjugation lengths of small molecules and thus typically rely on additional factors. The earliest such example was the application of porphyrin-tapes as reported by Forrest and coworkers in 2010.<sup>[48]</sup> The most successful of these was **20**, which provided photoresponse over 400–1600 nm and a  $D^*(\lambda)$  at 1350 nm of  $2.3 \times 10^{10}$  Jones (Table 2). In a follow-up study, it was found that additives could improve device response. Thus, the addition of 4,4-bipyridine to a **20**:PCBM device raised the  $D^*(\lambda)$  at 1400 nm to  $8.2 \times 10^{10}$

**Table 2** Select parameters of small molecule photodetectors

Active layer <sup>a</sup>	Spectral region (nm)	$\lambda_{\text{det}}$ (nm)/ $V_{\text{appl}}$ (V)	EQE( $\lambda$ ) (%)	$D^*(\lambda)$ (Jones)	Ref.
<b>20</b> :C <sub>60</sub>	400–1600	1350/0	6.5	$2.3 \times 10^{10}$	[48]
<b>20</b> :PCBM:bpy	400–1600	1400/0	10.5	$8.2 \times 10^{10}$	[49]
<b>21</b> :C <sub>60</sub>	300–1100	900/0	18.0	$2.34 \times 10^{11}$	[50]
<b>21</b> :C <sub>70</sub>	300–1100	890/0	32.5	$4.2 \times 10^{12}$	[51]
<b>22</b> :PCBM	300–1200	1200/0		$> 10^{11}$	[52]
<b>23</b> :C <sub>60</sub>	400–1400	1140/0	1.1	$5.3 \times 10^{10}$	[53]
<b>24</b> :C <sub>60</sub>	400–1500	1390/0	0.8	$1.7 \times 10^{10}$	[53]
<b>23</b> :perovskite	500–1600	1500/0		$2 \times 10^7$	[54]
<b>21</b> :C <sub>60</sub> <sup>b</sup>	300–1100	970/0	6.3	$9.01 \times 10^{12}$	[55]

<sup>a</sup> PCBM = [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester; bpy = 4,4'-bipyridine. <sup>b</sup> Inverted device.





**Figure 4** Small molecules giving photoresponse >1000 nm.

Jones.<sup>[49]</sup>

While none of the remaining small-molecule devices were able to extend the response beyond 1600 nm, the phthalocyanine **21** did result in higher detectivity (ca.  $10^{12}$  Jones).<sup>[50,51,55]</sup> The next best system for broad spectral response was the heptamethine  $B(C_6F_5)_4$  salts **23** and **24**.<sup>[53,54]</sup> These provide similar detectivity to **20**, with response to 1500 nm. It was also found that **23**:perovskite composites could extend this to 1600 nm, although with a significant decrease in  $D^*(\lambda)$ .<sup>[54]</sup>

## Conclusions and Perspectives

As illustrated by the discussion above, strides have been made in extending the spectral region of organic NIR photodetectors, with devices of **18** exhibiting photoresponse across the full NIR spectrum (800–2500 nm).<sup>[44]</sup> While such achievements in organic NIR photodetectors are remarkable, it also needs to be pointed out that after 13 years of development, there are still only six polymers capable of photoresponse at energies lower than 1200 nm.<sup>[28,34,35,41–44]</sup> If we add in the more successful small-molecule devices,<sup>[48,49,53,54]</sup> that brings us up to nine materials for applications beyond 1200 nm. Thus, while further advances can be made through efforts in film morphological control and interfacial reengineering,<sup>[18]</sup> thus improving EQE or  $D^*(\lambda)$ , the real need is the further development of new low  $E_g$  materials capable of effective NIR absorption.

Of course, successfully producing conjugated materials that effectively combine low bandgaps, suitable solubility, and good film formation properties can still be a challenge. As seen in Figures 2 & 3, low  $E_g$  materials generally incorporate various fused-ring units, which by their rigid nature tend to reduce polymer solubility. While this limitation can be overcome, it often requires bulky, branched sidechains that can inhibit interchain coupling, thus working against further  $E_g$  reduction. Even if the desired combination of properties can be achieved, most really low bandgaps are achieved by destabilizing the material HOMO, often to the point that the orbital energies are incompatible with typical device configurations. In this respect, newer approaches to low  $E_g$  materials *via* stabilization of the polymer LUMO may be the key to future advances in NIR photodetectors.<sup>[56]</sup>

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## Author Contributions

S. C. R. organized and wrote the initial manuscript, with the

remaining authors collecting relevant literature and contributing to manuscript editing and revision.

## Conflict of Interest

The authors declare no conflict of interest.

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