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Published in:
ACS Applied Materials and Interfaces

DOI:
[10.1021/acsami.1c03411](https://doi.org/10.1021/acsami.1c03411)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2021

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Liu, J., Van Der Zee, B., Villava, D. R., Ye, G., Kahmann, S., Kamperman, M., Dong, J., Qiu, L., Portale, G., Loi, M. A., Hummelen, J. C., Chiechi, R. C., Baran, D., & Koster, L. J. A. (2021). Molecular Doping Directed by a Neutral Radical. *ACS Applied Materials and Interfaces*, 13(25), 29858–29865.
<https://doi.org/10.1021/acsami.1c03411>

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Molecular Doping Directed by a Neutral Radical

Jian Liu,* Bas Van der Zee, Diego R. Villava, Gang Ye, Simon Kahmann, Max Kamperman, Jingjin Dong, Li Qiu, Giuseppe Portale, Maria Antonietta Loi, Jan C. Hummelen, Ryan C. Chiechi, Derya Baran, and L. Jan Anton Koster*

Cite This: *ACS Appl. Mater. Interfaces* 2021, 13, 29858–29865

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ABSTRACT: Molecular doping makes possible tunable electronic properties of organic semiconductors, yet a lack of control of the doping process narrows its scope for advancing organic electronics. Here, we demonstrate that the molecular doping process can be improved by introducing a neutral radical molecule, namely nitroxyl radical (2,2,6,6-tetramethylpiperidin-1-yl) oxyl (TEMPO). Fullerene derivatives are used as the host and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazoles (DMBI-H) as the n-type dopant. TEMPO can abstract a hydrogen atom from DMBI-H and transform the latter into a much stronger reducing agent DMBI•, which efficiently dopes the fullerene derivative to yield an electrical conductivity of 4.4 S cm^{-1} . However, without TEMPO, the fullerene derivative is only weakly doped likely by a hydride transfer following by an inefficient electron transfer. This work unambiguously identifies the doping pathway in fullerene derivative/DMBI-H systems in the presence of TEMPO as the transfer of a hydrogen atom accompanied by electron transfer. In the absence of TEMPO, the doping process inevitably leads to the formation of less symmetrical hydrogenated fullerene derivative anions or radicals, which adversely affect the molecular packing. By adding TEMPO we can exclude the formation of such species and, thus, improve charge transport. In addition, a lower temperature is sufficient to meet an efficient doping process in the presence of TEMPO. Thereby, we provide an extra control of the doping process, enabling enhanced thermoelectric performance at a low processing temperature.

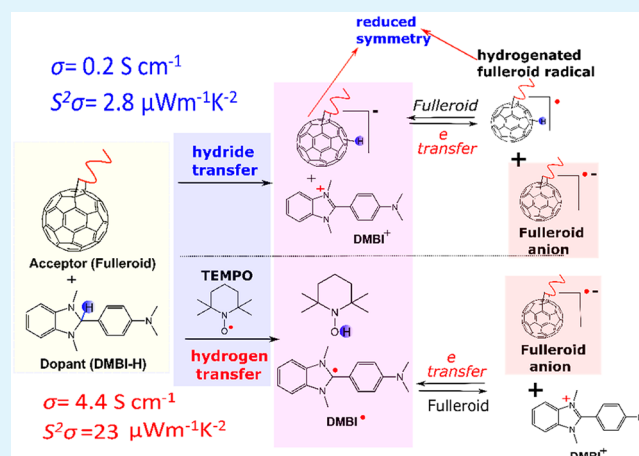
KEYWORDS: organic thermoelectrics, molecular doping, fullerene derivatives, neutral radical, electrical conductivity, Seebeck coefficient

INTRODUCTION

Semiconducting organic materials have the potential to deliver low-cost, scalable, and mechanically flexible electronic devices including organic light-emitting diodes, organic photovoltaics, organic transistors and organic thermoelectrics.^{1–5} The development of both efficient p-type and n-type doping strategies for organic materials is vital to success of those organic electronic devices.^{6,7} P-doping of organic materials has proved very stable in ambient conditions and has been extensively investigated.^{8,9} However, developing n-type dopants that have sufficiently low ionization energies for enabling both efficient electrical doping and good ambient stability is particularly challenging. Leo and co-workers reported the use of air-stable precursors of n-type dopants.^{10,11} Upon heating or illumination, these precursors decompose in situ into stronger reducing organic radicals to enable n-doping. Bao et al. developed air-stable n-type dopants based on reduced 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazoles (DMBI-H) or dimers of benzimidazoline radicals.^{12,13} It is

proposed that DMBI-H undergoes a C–H bond homolysis driven by thermal activation, and the resulting imidazoline radical DMBI• functions as a single-electron donor to efficiently dope organic semiconductors.¹² So far, most reported efficient n-type organic thermoelectric materials employ DMBI-H as the dopant.^{14–16} Therefore, to understand the underlying doping mechanism of DMBI-H and the ability of precisely controlling the doping process are significant for further development.

Fullerenes and fullerene derivatives have been widely used in organic electronic devices,¹⁷ and special interest is given to their recent applications in organic thermoelectrics and



Received: February 21, 2021

Accepted: June 1, 2021

Published: June 16, 2021



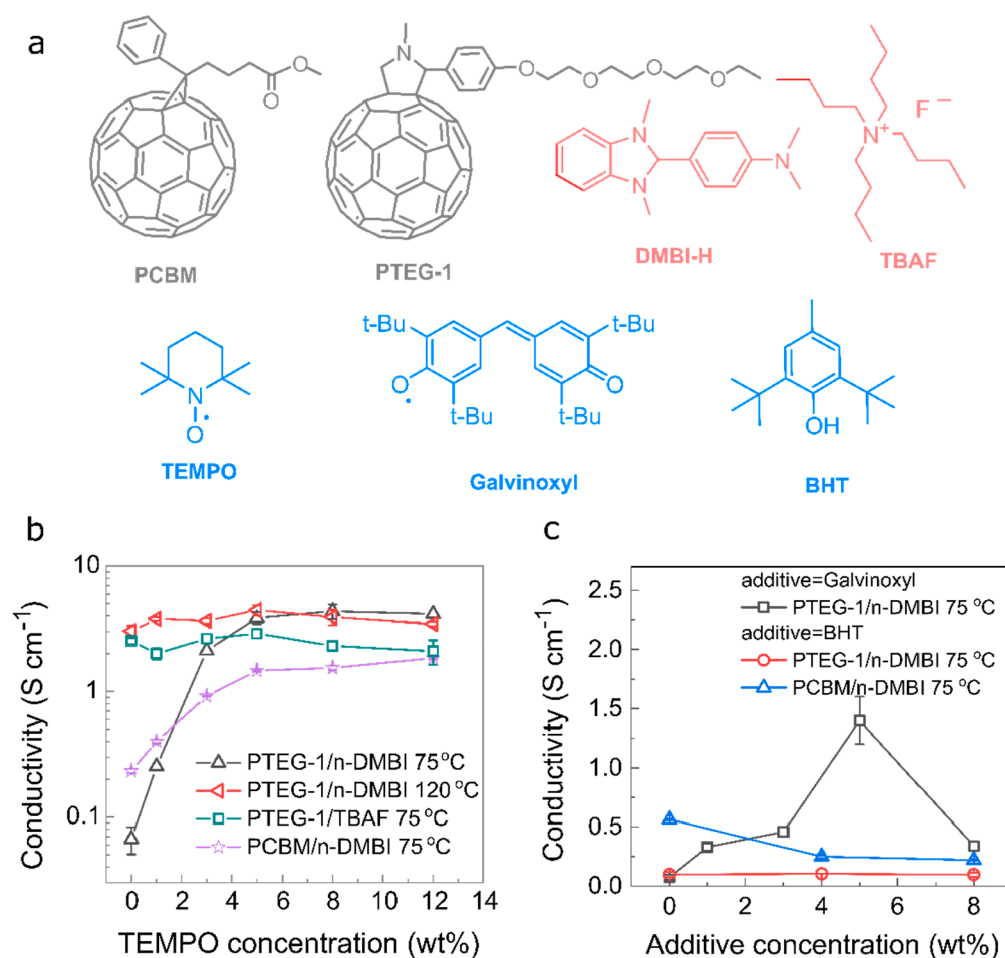
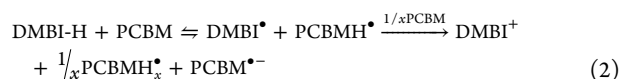
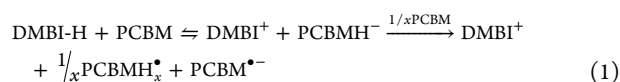


Figure 1. Effects of small molecule additives on n-doping of fullerene derivatives. (a) Chemical structures of fullerene derivatives, n-type dopants, and small molecule additives. Electrical conductivity as a function of the amount of (b) TEMPO and (c) galvinoxyl or BHT in doped PTEG-1 and PCBM films treated with different annealing temperatures.

molecular electronics.^{18–20} C60 was reported to react with a wide variety of electron donors to form either poorly conducting or insulating charge transfer complexes (CTCs).^{21,22} In the case of using tetrakis(dimethylamino)-ethylene (TDAE) as the donor, the CTC was identified to be fully ionic but being electrically insulating.²³ A few studies focused on n-type doping of the fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) with either anionic salts or DMBI-H as the dopant.^{24,25} Naab et al. studied the doping mechanism of PCBM/DMBI-H system.²⁶ They suggested two possible operative doping pathways:



Electron transfer is coupled with a hydride transfer in pathway (1) or a hydrogen-atom transfer in pathway (2) in the course of n-doping. Naab et al. deemed pathway (1) the most likely mechanism in the rate-determining step, but do not rule out pathway (2). Therefore, it is still an open question which mechanism is actually operative. Furthermore, lacking control of the doping process largely limits the scope of the doping strategy toward advancing organic electronics.

In this contribution, we introduce a neutral radical molecule, namely nitroxyl radical (2,2,6,6-tetramethylpiperidin-1-yl) oxyl (TEMPO). Fulleropyrrolidine PTEG-1, with a triethylene glycol side chain, and PCBM are employed as the host and DMBI-H as the dopant. TEMPO reacts with DMBI-H at lower temperatures than fullerenes and directly forms TEMPOH and DMBI[•]. The resultant DMBI[•] radical is more reactive than DMBI-H toward fullerene derivatives, enabling efficient n-doping. Our work unambiguously identifies hydrogen-atom transfer (pathway 2) as the main doping mechanism of fullerene derivatives by DMBI-H in the presence of TEMPO. Thereby, we provide extra control of the doping process, which enables enhanced thermoelectric performance.

EXPERIMENTAL SECTION

Materials. PTEG-1 was synthesized according to a previously reported procedure.²⁷ PCBM was purchased from Solenne. TBAF, DMBI-H, BHT, and TEMPO were purchased from Sigma-Aldrich.

Device Fabrication and Thermoelectric Characterization. Clean borosilicate glass substrates were treated with UV-ozone for 20 min. A fullerene derivative solution (10 mg/mL in chloroform) was mixed with different amounts of dopant solution (20 mg/mL in chloroform), which was followed by spin-coating to prepare the fullerene derivative-based samples without TEMPO in a glovebox with a nitrogen atmosphere. The resultant films were annealed at either 75 or 120 °C for 1 h. Similarly, a fullerene derivative solution (10 mg/mL in chloroform) was first mixed with different amounts of

dopant solution (20 mg/mL in chloroform). The resultant solutions were then mixed with a solution of TEMPO in chloroform keeping a weight ratio 1:1 of TEMPO to DMBI-H. The resultant solutions were spin-coated to prepare the films with TEMPO in a glovebox with a nitrogen atmosphere. The resultant films were annealed at either 75 or 120 °C for 1 h. Standard four-point probe method was used to measure the conductivity of the doped PTEG-1 and doped PCBM thin films. The electrical conductivity measurements were performed in an inert environment (see details in the [Supporting Information, SI](#)).

Photoluminescence Spectroscopy. Pristine PTEG-1 film and various PTEG-1-based films were excited at 3.1 eV (400 nm) using the second harmonic of a mode-locked Ti:sapphire laser (Mira 900, coherent) emitting at a repetition rate of 76 MHz. Steady-state spectra were recorded with a Hamamatsu EM-CCD camera that was spectrally calibrated. The excitation beam was spatially limited by an iris and focused with a lens of 150 mm focal length. The fluence was adjusted using gray filters and spectra were taken in reflection geometry. Time-resolved traces were taken with a Hamamatsu streak camera working in synchroscan mode.

RESULTS

The most widely used strategy for controlling doping is to tune the composition of host/dopant systems. Instead, we explored the effects of additives on the n-doping of fullerene derivatives. We varied the host, the type of dopant and the additive (their chemical structures are shown in [Figure 1](#)). TEMPO is a radical initiator widely used in chemical reactions.^{28–30} To introduce TEMPO into the doping process, we blended it with the host and the dopant in chloroform solution. The weight percentage of dopants relative to the host was kept at 8 wt %, while varying the amount of TEMPO. The solutions were spin-cast onto glass substrates (covered with an electrode). Next, the films were annealed at either 75 or 120 °C, respectively. Adding TEMPO into pristine PTEG-1 film caused negligible changes in (two-probe) electrical conductivity and both samples exhibited values of $\times 10^{-7}$ S cm⁻¹. To explore the effects of TEMPO on the DMBI-H involved n-doping, we measured the electrical conductivities of doped fullerene derivatives films by using the standard four-probe method (see details in the [SI](#)). The corresponding results are shown in [Figure 1b](#). In the PTEG-1/DMBI-H system annealed at 75 °C, we observed that the electrical conductivity of the doped film increases with the loading of TEMPO from 0.07 ± 0.02 S cm⁻¹ to 3.9 ± 0.4 S cm⁻¹ at 5 wt %. Note that 5 wt % TEMPO represents a molar ratio of approximately 1:1 to 8 wt % DMBI-H. In contrast, the electrical conductivity of the doped PTEG-1 film annealed at 120 °C shows a relatively weak dependence on the loading of TEMPO (from 3.0 ± 0.4 S cm⁻¹ at 0 wt % to 4.4 ± 0.4 S cm⁻¹ at 5 wt %).

The same phenomenon was also seen in the PCBM/DMBI-H system, suggesting the effects of TEMPO on the n-doping of fullerene derivatives are independent of the type of the side chain. Similarly, we examined the effects of TEMPO when a different type of dopant (i.e., TBAF, structure in [Figure 1a](#)) is used. It is noted that TBAF involved doping does not depend on the annealing temperature, and 75 °C was used in this context. It appears that TEMPO does not affect doping with TBAF (see [Figure 1b](#)). Therefore, the way TEMPO is involved in the doping process is most likely associated with the DMBI-H molecule. In addition, we used another radical additive, galvinoxyl, instead of TEMPO in the PTEG-1/DMBI-H system. As shown in [Figure 1c](#), the electrical conductivity increases with the loading of galvinoxyl and reaches a peak of 1.4 ± 0.2 S cm⁻¹ at 5 wt %. The lower conductivity achieved

with galvinoxyl relative to that with TEMPO could be explained either by differences in reactivity or by the larger molecule size of the former, which is more likely to disrupt the morphology and to degrade the charge transport. As such, we assume that the radical nature of additives plays the key role in the doping process. Butylhydroxytoluene (BHT) is a commonly used radical scavenger, meaning it is not a radical itself, but it forms stable radicals. Clearly, BHT exerts negligible effect on the doping process of fullerene derivative/DMBI-H systems ([Figure 1c](#)). This result further supports our hypothesis that free radicals enhance the n-doping.

Apparently, the effectiveness of TEMPO in enhancing n-doping relies on the specific dopant (DMBI-H). A previous study suggested that DMBI-H undergoes C–H bond homolysis above 90 °C.¹⁵ This point was further verified by the thermogravimetric analysis (TGA) of DMBI-H ([SI Figure S1](#)). DMBI-H is air stable and renders constant weight when the sample temperature is below 90 °C. After C–H bond homolysis, DMBI-H becomes DMBI•, which is a much stronger reducing agent and expected to be easily oxidized in air. The oxidation process was evidenced by the weight gain in the TGA curve above 90 °C, which confirms the thermal activation of DMBI-H at the same temperature. Therefore, the traditional protocol of preparing doped samples often includes a postannealing step above 90 °C. Interestingly, TEMPO appears to boost the n-doping of fullerene derivatives without the thermal activation to be even more efficient than that for samples prepared by the traditional protocol (as shown in [Figure 1b](#)). Indeed, that is the role of radical initiators; TEMPO abstracts a hydrogen from DMBI-H directly, altering the reaction pathway and effectively lowering the thermal barrier to the formation of DMBI•.

In order to verify this point, we measured Fourier transform infrared spectroscopy (FTIR) spectra of DMBI-H, TEMPO and a mixture of DMBI-H/TEMPO (molar ratio of 1:1) powders treated by annealing at 75 °C (as shown in [Figure 2](#)).

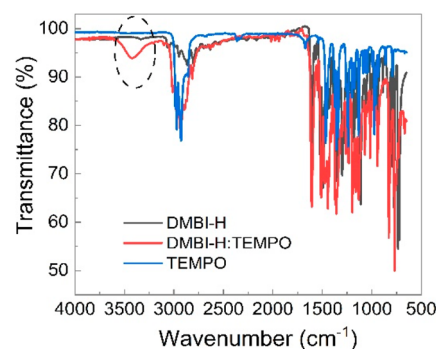


Figure 2. Fourier transform infrared spectroscopy (FTIR) spectra of DMBI-H, TEMPO, and mixture of DMBI-H and TEMPO with a molar ratio of 1:1.

We observed a clear peak at 3420 cm^{-1} for the mixture sample, which is attributed to the characteristic vibration of an –OH but not seen for the individual neat samples. It indicates that DMBI-H transfers a hydrogen atom to TEMPO, converting it to an hydroxylamine with a characteristic broad vibration band around 3420 cm^{-1} .^{31,32} These results explain the roles of TEMPO in the course of n-doping: the activation barrier for forming DMBI• by reacting with TEMPO is lower than direct

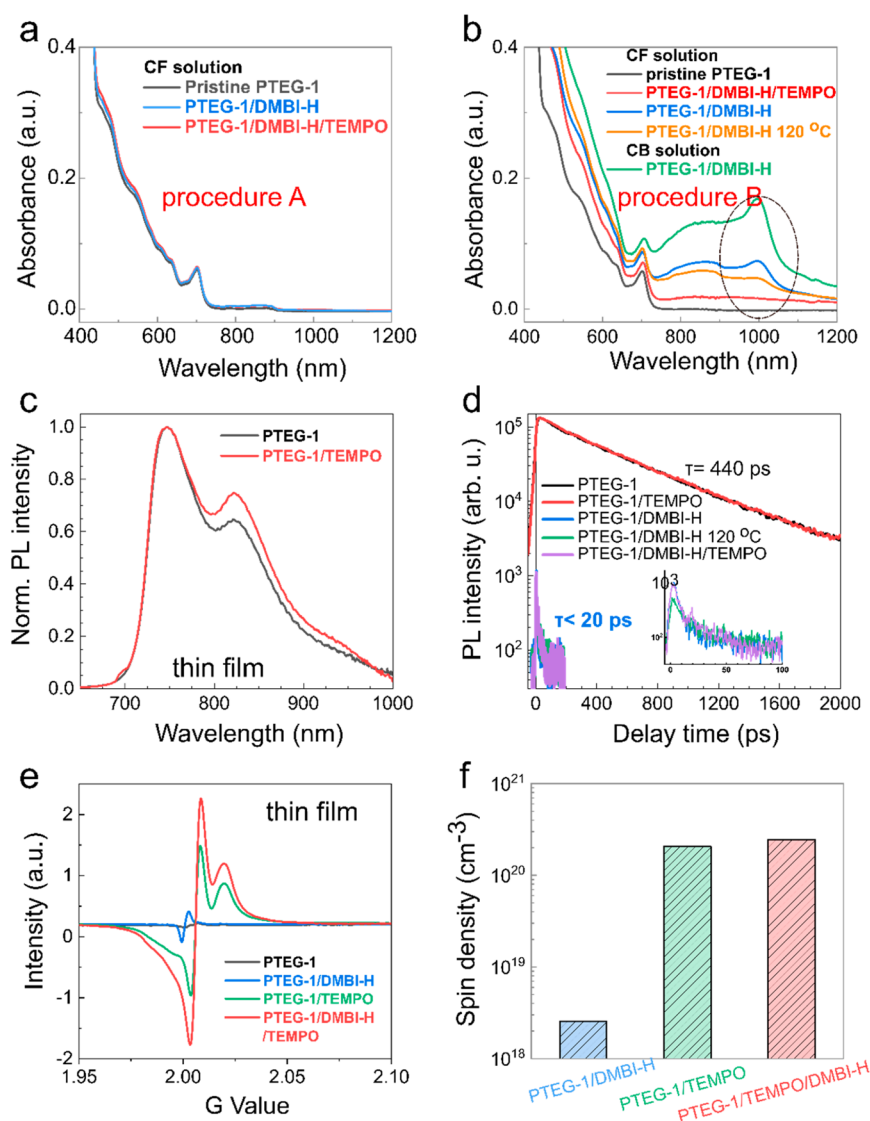
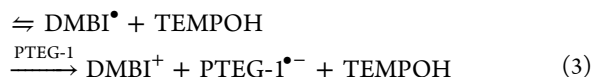


Figure 3. UV-vis-NIR absorption spectra of pristine PTEG-1, binary blend of PTEG-1 and DMBI-H, and ternary blend of PTEG-1, DMBI-H, and TEMPO solution prepared based on (a) the procedure A and (b) the procedure B, CF: chloroform, CB: chlorobenzene; (c) Photoluminescence spectra of pristine PTEG-1 and PTEG-1/TEMPO films and (d) the time-resolved photoluminescence of various PTEG-1-based films; and (e) the EPR and (f) calculated spin density of various PTEG-1-based thin films.

thermolysis or reacting with fullerene derivatives directly. Since DMBI \cdot is the active species responsible for doping, the net effect is more efficient doping at lower temperature.

DMBI-H + TEMPO



It should be noted that doping fullerene derivatives with DMBI-H (i.e., without TEMPO) inevitably generates side products like PCBM-H \cdot or PTEG-1-H \cdot , which are less symmetrical and, therefore, could be detrimental to the molecular packing and charge transport. Importantly, these products do not form in the presence of TEMPO because, at 75 °C, it reacts much faster with DMBI-H than the fullerene derivatives. As such, n-doping in the system with TEMPO is more efficient than that in those prepared by the traditional protocol, highlighting the importance of precisely controlling the n-doping process.

The n-doping of fullerene derivatives by DMBI-H either with or without TEMPO generates fulleroid anions, which can be detected in optical absorption spectra. In order to probe the formation of fulleroid anions, we measured UV-vis-NIR absorption spectra of pristine and various doped solution samples encapsulated under inert atmosphere. We used two different procedures (A and B) to prepare the samples. In the procedure A, the host, dopant, and TEMPO were separately dissolved in chloroform and we blended those solutions based on the required combination for each specific doping condition. The UV-vis-NIR absorption spectra of PTEG-1-based samples prepared by following the procedure A are displayed in Figure 3a. There are no apparent differences among neat PTEG-1, PTEG-1/DMBI-H binary and PTEG-1/DMBI-H/TEMPO ternary. It indicates that the doping process did not occur in the solution state. In the procedure B, we prepared the samples by mimicking the spin-coating process. The prepared solution samples after the procedure A were dried in vacuum, then thermally annealed at 75 or 120 °C and

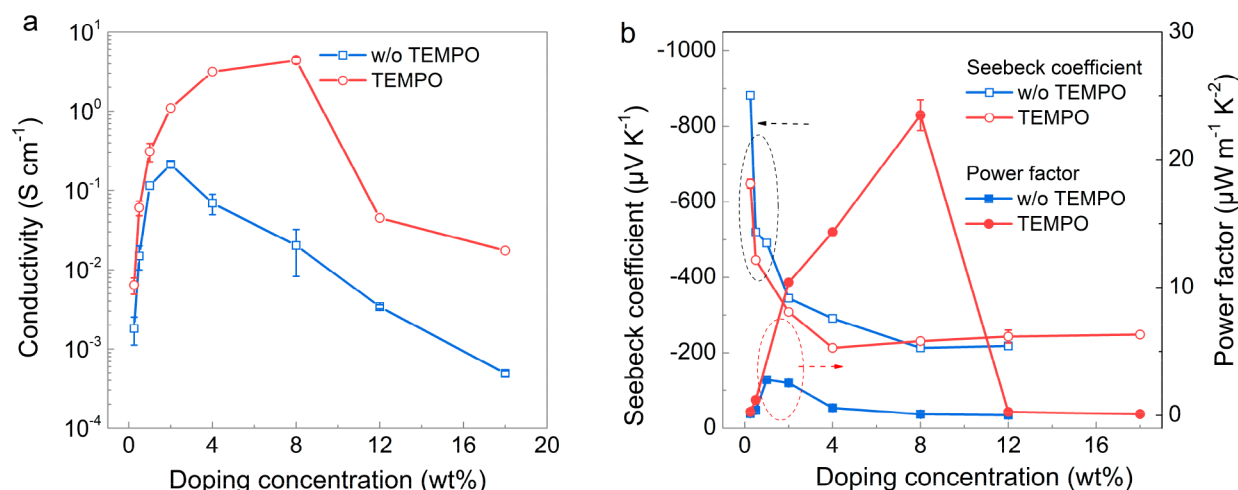


Figure 4. Effects of TEMPO on thermoelectric parameters of doped PTEG-1. (a) Electrical conductivity and (b) Seebeck coefficient and power factor as a function of doping concentration in doped PTEG-1 films with or w/o TEMPO. The annealing temperature is 75 °C.

finally redissolved in chloroform or chlorobenzene for absorption measurements. Note that all the solutions have a constant concentration of 1 mg/mL for PTEG-1 and the loading with DMBI-H or TEMPO is kept at 8 wt % relative to PTEG-1.

Figure 3b shows the UV–vis–NIR absorption spectra of the samples prepared following procedure B. For the PTEG-1/DMBI-H blend annealed at 75 °C before redissolving in chloroform, we observed a sharp peak at 998 nm and a broad absorption band between 750 and 950 nm. These sub-bandgap absorption features become more pronounced when using a less polar solvent (chlorobenzene). Similar features (with a sharp peak at 1030 nm and a broad band between 800 and 980 nm) for the PCBM/DMBI-H blend prepared under the same condition were seen as well (SI Figure S3). The strong intensity of the newly formed absorption features is attributed to either a large amount of fulleroid anions being generated or the reduced symmetry of fulleroid anions that leads to an increase of the probability of the forbidden transitions.^{33,34} In contrast, for the PTEG-1/DMBI-H/TEMPO ternary sample and PTEG-1/DMBI-H binary annealed at 120 °C, the characteristic absorption features for fulleroid anions are much weaker. Note that we do not exclude the possibility of poor solubility of fulleroid anions in the organic solvent, which could also cause the weak anion absorption.

Due to the poor donor ability of the DMBI-H, no charge transfer is expected to occur between DMBI-H and the semiconductors to form partial charge-transfer complexes. However, recent calculations indicate that the hydride transfer process may occur when DMBI-H is in the vicinity of organic semiconductors with suitable electron affinities.³⁵ Thus, we argue that without thermal activation and TEMPO additive, the doping of the fullerene derivative likely happens via hydride transfer, that is the pathway (1). The resultant hydrogenated fulleroid anions (PCBM- H^- or PTEG-1- H^-) are expected to have a reduced symmetry than fulleroid anions and cause the broad absorption band as observed in Figure 3b. We also suspect that hydrogenated fulleroid anions form charge transfer complexes with DMBI $^+$, analogous to the case of C60/TDAE CTC system,³⁶ which further reduces the symmetry of fullerene derivatives. The formation of those CTCs may compromise the reaction of the second step (in the pathway 1), leading to a limited generation of fulleroid anions. While

for systems with TEMPO added or after the thermal activation, DMBI-H becomes the very reactive DMBI $^+$ radical, which formally reduces the fullerene derivatives rather than forming CTCs. The charges residing on fulleroid anions are expected to be more delocalized, contributing to the charge transport.

Lowering the molecular symmetry of fullerene derivatives is deleterious to the molecular packing. This was confirmed by the two-dimensional grazing incidence wide-angle X-ray scattering (2D-GIWAXS) results (SI Figure S4): the molecular packing of the PTEG-1/DMBI-H binary film is more disordered than that of the PTEG-1/DMBI-H/TEMPO ternary film at the same annealing temperature (75 °C). The poor molecular packing is another factor causing the low electrical conductivity for the fullerene derivative/DMBI-H binary film. The changes in the electrical conductivity originate from differences in the doping mechanism due to the incorporation of TEMPO, regardless of the underlying causes (charge density and/or mobility).

Figure 3c shows the photoluminescence (PL) spectra of pristine PTEG-1 and PTEG-1/TEMPO films, and Figure 3d displays the time-resolved PL of various PTEG-1-based films, showing that TEMPO barely interacts with PTEG-1, as evidenced by the nearly unchanged PL spectra and PL lifetime ($t = 440$ ps). The PL of PTEG-1 molecules was completely quenched with merely a faint signal (<20 ps) detectable in the transient measurement upon DMBI-H loading for all doped fulleroid based films. Fullerene derivatives typically have an exciton diffusion length of ~ 5 nm.^{37,38} The strong PL quenching indicates a uniform doping with a spatial resolution down to a scale of several nm.

The electron paramagnetic resonance spectra of various PTEG-1-based thin-film samples were measured in an N_2 atmosphere and the corresponding results are displayed in Figure 3f. The PTEG-1/DMBI-H binary film after the thermal annealing at 75 °C exhibits a spin density of $2.6 \times 10^{18} \text{ cm}^{-3}$. The PTEG-1/TEMPO binary and PTEG-1/DMBI-H/TEMPO ternary films show spin density of $2.06 \times 10^{20} \text{ cm}^{-3}$ and $2.45 \times 10^{20} \text{ cm}^{-3}$, respectively. The net spin density contributed by DMBI-H doping in the ternary blend was calculated to be $3.9 \times 10^{19} \text{ cm}^{-3}$, which is more than 1 order of magnitude higher than that of PTEG-1/DMBI-H binary film. We expect a similar density for the PTEG-1 film to that (1.5 g/cm^3) of the PCBM film.³⁹ Accordingly, the spin number is 2.9

$\times 10^{-3}$ per bucky ball and 4.3×10^{-2} per bucky ball for before and after adding TEMPO, respectively. This result indicates the n-doping of PTEG-1 by DMBI-H was largely improved by the TEMPO additive, which agrees with the enhanced electrical conductivity after incorporating TEMPO. It is noteworthy that hydrogenated fulleroid anions resulting from the hydride transfer process are spinless, and only contribute to EPR signal when they transfer electrons to adjacent fulleroid molecules. Therefore, the low spin density of the binary film may suggest an inefficient process of the second step of pathway (1).

We tuned the loading of DMBI-H and probed the changes of thermoelectric properties in cases with or without TEMPO, and the corresponding results are displayed in Figure 4 and Figures S5 and S6. The electrical conductivity of doped PTEG-1 film without TEMPO exhibits a peak value of 0.2 S cm^{-1} at a doping concentration of 2 wt %. In contrast, the doped PTEG-1 film with TEMPO shows the best electrical conductivity of 4.4 S cm^{-1} at a much higher doping concentration of 8 wt %. Electrical conductivity enhancement of doped PCBM by TEMPO additive was observed as well (SI Figure S7). Regardless of the strong impact on the electrical conductivity, TEMPO merely slightly influenced the Seebeck coefficient of doped PTEG-1 film at doping concentrations (Figure 4b). At a doping concentration of 8 wt %, the doped PTEG-1 films without and with TEMPO exhibit comparable Seebeck coefficient of -213 and $-231 \text{ } \mu\text{V K}^{-1}$, respectively. This suggests that the TEMPO additive may provide an opportunity to overcome the trade-off between Seebeck coefficient and electrical conductivity by improving the molecular packing order or modifying the doping mechanism. As a result, the doped PTEG-1 with TEMPO additive exhibits an optimized power factor of $23.5 \pm 1.2 \text{ } \mu\text{Wm}^{-1}\text{K}^{-2}$, much higher than that ($2.8 \text{ } \mu\text{Wm}^{-1}\text{K}^{-2}$) of the doped film without TEMPO. It should be noted that the power factor of doped PTEG-1 with TEMPO is higher than that ($17 \text{ } \mu\text{Wm}^{-1}\text{K}^{-2}$) of the doped film prepared in the conventional way.^{40,41} This highlights the importance of an extra control of doping process on the organic thermoelectric performance.

CONCLUSIONS

In summary, we first introduced a neutral radical molecule TEMPO as an additive into DMBI-H involved doping systems. Fullerene derivatives (PTEG-1 and PCBM) are used as the host. It appears that TEMPO can react directly with DMBI-H to form DMBI \cdot and TEMPOH. The resultant DMBI \cdot is a strong reducing agent, enabling efficient doping of fullerene derivatives by formal reduction. Our work identifies the doping pathway for fullerene derivative/DMBI-H systems in the presence of TEMPO as being the transfer of a hydrogen atom accompanied by electron transfer. It should be noted that the exact doping mechanism in the absence of TEMPO is still an open question. More importantly, we provide extra control over the doping process by using the radical additive, leading to enhanced thermoelectric performance at a lower process temperature. This work introduces a new strategy for engineering the doping of organic materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.1c03411>.

Experimental section; Figure S1, TGA plots; Figure S2, schematic reaction; Figure S3, UV-vis-NIR absorption spectra; Figure S4, GIWAXS; Figures S5 and S6, raw data for thermoelectric measurement; and Figure S7, electrical conductivity vs doping concentration of doped PCBM films (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was supported by a grant from STW/NWO (VIDI 13476). This study is part of the research program of the Foundation of Fundamental Research on Matter (FOM), which is part of The Netherlands Organization for Scientific Research (NWO). This is a publication by the FOM Focus Group “Next Generation Organic Photovoltaics”, participating in the Dutch Institute for Fundamental Energy Research (DIFFER). J.D. acknowledge financial support from the China Scholarship Council. S.K. acknowledges the Deutsche Forschungsgemeinschaft (DFG) for a postdoctoral research fellowship (grant no. 408012143). L.Q. thanks National Natural Science Foundation of China (Grant No. 51962036) for financial support. G.Y. acknowledges the China Postdoctoral Science Foundation Funded Project (grant 2020M672771). D.B. and D.R. acknowledge King Abdullah University of Science and Technology (KAUST) Office of Sponsored Research (OSR) under award no. OSRCRG2018-3737 for the completion of this work. J.L. thanks Xuwen Yang for the help in preparing PL samples.

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