Metal Residues in Semiconducting Polymers: Impact on the Performance of Organic Electronic Devices

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S Supporting Information

ABSTRACT: The effect of impurities on the optoelectronic and charge transport properties of semiconducting polymers was investigated through the performance of organic photovoltaics (OPVs) and organic field effect transistors (OFETs), respectively. A model representative semiconducting polymer, i.e., poly(3-hexylthiophene) (P3HT), was synthesized and purified using different methods such as precipitation, metals' complexation, and Soxhlet extraction. After the purification processes, each fraction was analyzed to determine its composition in metals (impurities) by various techniques. OFETs and OPVs fabricated from these purified polymer fractions were found to show different charge carrier properties and photovoltaic behaviors. The purest fraction which was obtained after Soxhlet extraction complemented by metals' complexation with the help of ethylenediamine and 15-crown-5 ether showed the best performance in both OPVs and OFETs.
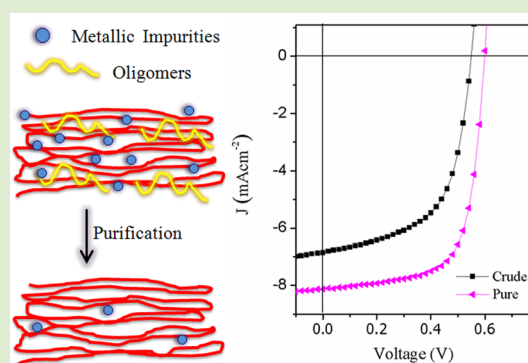
Semiconducting polymers have been extensively investigated over the last few decades due to their potential applications in organic photovoltaic cells (OPVs),[1,2] organic light emitting diodes (OLEDs),[3,4] organic field-effect transistors (OFETs),[5,6] and sensors.[7] The synthesis of the π-conjugated polymers mainly dealing with cross-coupling reaction routes (e.g., Suzuki, Stille, Yamamoto, Kumada, Negishi, Sonogashira, Heck, etc.) or oxidative polymerizations often involves transition-metal-based materials as catalysts.[8] After polymerization, depending on the reactions and purification procedures, different types of metals such as Ni, Pd, Fe, Sn, Pt, Cd, Mg, Na, and K, etc., may remain in the final raw material. Residual catalysts and other organic or inorganic impurities present in the polymers may act as charge carrier traps or photoquenchers affecting strongly their intrinsic properties, consequently reducing the performance of the optoelectronic devices.[9−13] Residual metal ions in the π-conjugated polymer can also cause a leakage current in the optoelectronic devices and reduce device efficiency and stability. Finally, impurities can also affect the solubility of π-conjugated polymers by causing aggregation.[14]

Procedures have been reported to remove metallic residues from polymers. Washing with polar solvents and/or selective organic solvents via Soxhlet extraction is a common purification method. Metal chelating agents, crown ethers, and ionic complexing agents are also used to remove metallic residues from conducting polymers.[15,16] Metal chelating agents are ligands known to bind a metal at two or more sites. The most widely used chelating agents are those that coordinate to metal ions through oxygen or nitrogen donor atoms, or both. For instance, ethylenediamine, ethylenediamine tetraacetic acid, and dimethylglyoxime were used as chelating agents.[17] Crown ethers are cyclic chemical compounds that consist of a ring containing several ether groups that can also be used as metal chelating agents. Crown ether molecules can trap metal ions by forming ion−dipole bonds with them. The ring size as well as the number and the type of heteroatoms are very important parameters for the connection with the metal ions. For instance, 18-crown-6 has high selectivity for K^+, 15-crown-5 for Na^+, and 12-crown-4 for Li^+.[18]

The effects of organic dopants on the performance of OPVs[19] and OFETs,[20] along with the effect of doping with a metal complex on OPV devices, have recently been investigated.[21] Nevertheless, a study on the impact of residual metals, left from different purification processes, for both OFET and OPV devices has yet to be systematically carried out, and a suitable purification process in achieving a polymer fraction which works best for devices should be identified.

In this work, the influence of metal residues and purification process of P3HT, used as a semiconducting polymer model, on OFET characteristics and OPV device performance was investigated in order to identify the optimal purification procedure suited to the best performing polymer fraction in
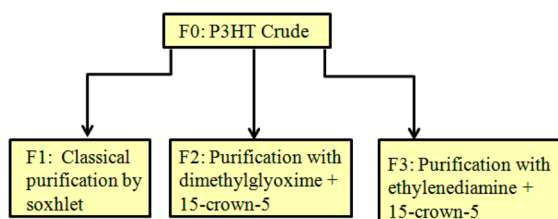
both devices and to explore the intrinsic properties of the semiconducting polymers. P3HT polymer samples were synthesized via a nickel complex catalyst transfer chain-growth polymerization route and purified using various procedures. The latter combined precipitation, metals' complexation using metals' scavengers, and chelating agents such as dimethylglyoxime, ethylenediamine, and crown ether derivatives, and finally Soxhlet extraction with different ultrapure solvents (such as hexane, methanol, and chloroform). After each purification process, all polymer fractions were characterized and analyzed to determine their structure as well as their composition in metallic residues by various techniques. The performance of the various purified semiconducting polymer fractions in OPV and OFET devices was studied. The best purified fraction in terms of metallic residues was found to show high power conversion efficiency (PCE) in OPVs and low hysteresis together with a high on/off current ratio in OFETs.

The synthesis of poly(3-hexylthiophene) (P3HT) polymers was conducted following a well-established procedure which uses the Grignard metathesis method (GRIM) also called transition-metal-catalyzed chain-growth polymerization.[22] The polymers were purified by using metal complexing agents and consecutive washings using the Soxhlet technique with methanol, hexane, and chloroform, respectively (Scheme 1).

Scheme 1. Purification Methods of P3HT

F0: P3HT Crude

F1: Classical purification by soxhlet

F2: Purification with dimethylglyoxime + 15-crown-5

F3: Purification with ethylenediamine + 15-crown-5

After each purification method, polymer fractions were analyzed with SEC, ^{1}H NMR, and ICP−MS. ^{1}H NMR spectra were recorded for each fraction of P3HT. There was no significant difference among the NMR spectra of P3HT fractions (see in Supporting Information Figure S1).

Results obtained from SEC characterization (in CHCl$_3$, RI detector, polystyrene standards calibration) are provided in Table 1.

The macromolecular features of all P3HT fractions are consistent with the different purification stages achieved from the raw **F0** fraction. In fact, high dispersity values arise from the initial **F0** fraction which was around 1.8, and the Soxhlet procedure usually results in an increase in molecular weight together with a decrease in the dispersity of the semiconductor polymer when going from bad to good solvents (see Supporting Information Figure S2).
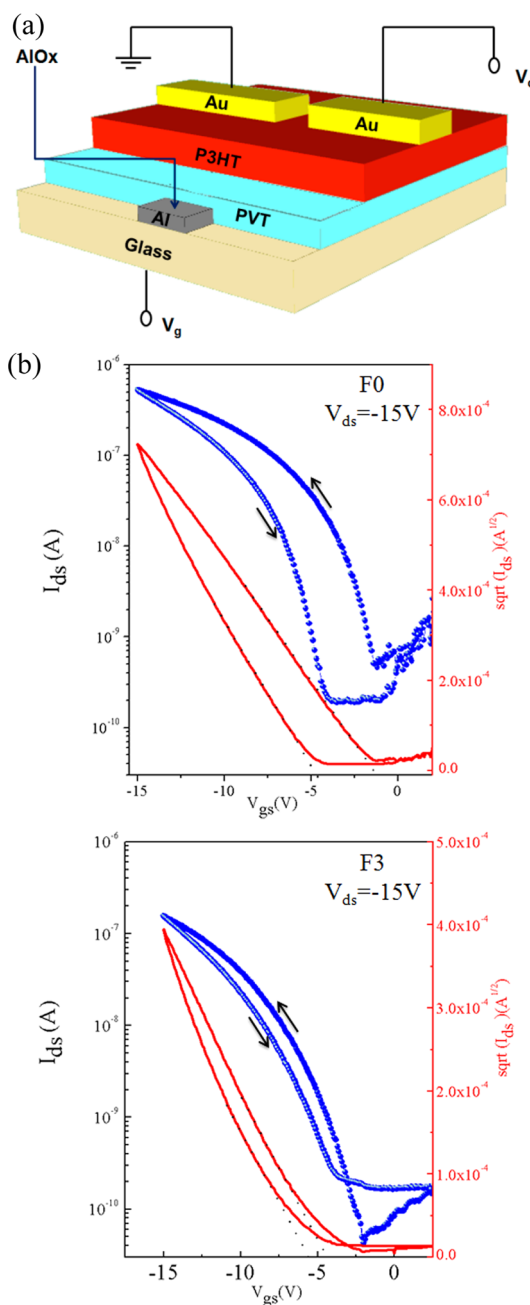

Figure 1. (a) Bottom gate, top-contact field-effect transistor device used in this work and (b) transfer characteristics of the OFET devices in saturation regime with **F0** and **F3** as the active layer. Threshold voltage was determined by extrapolating $\sqrt{(I_{ds})}$ to zero current. Hysteresis was quantified by the difference in the threshold voltages (ΔV_{th}) of forward and backward scan as shown in the figure as dashed lines.

Table 1. Macromolecular Characteristics of P3HT Fractions Obtained from SEC Analysis (in CHCl$_3$, PS Calibration) and ICP-MS Data for All Fractions of P3HT Polymers According to the Purification Stage

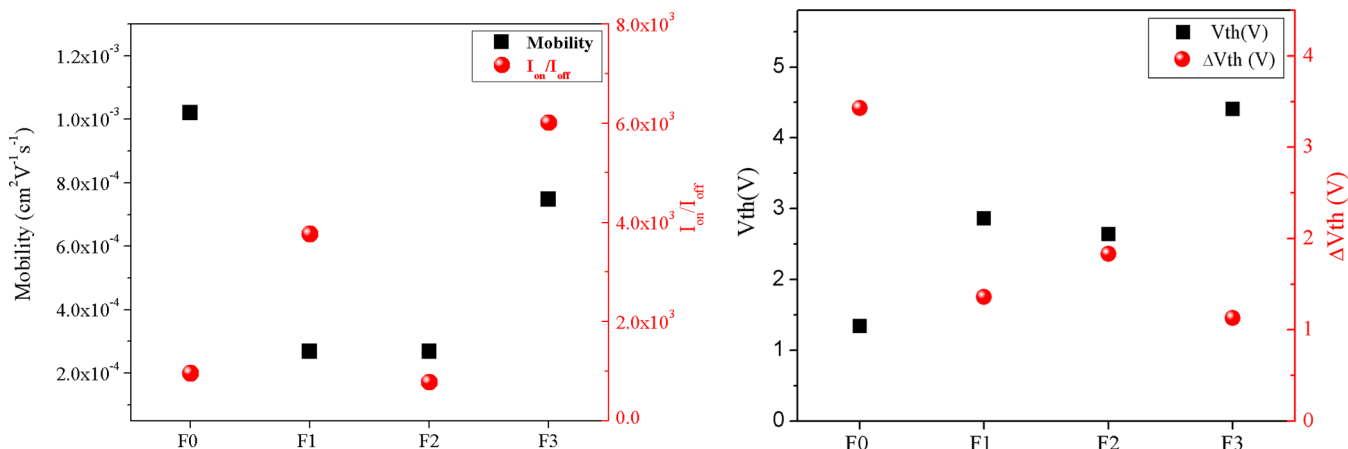|	SEC results			analyte concentration (ppm)							
sample	Mn [g mol^{-1}]	Mw [g mol^{-1}]	Đ	Ni	Fe	K	Mg	Cu	Ca	Na	Zn
F0	13080	23730	1.8	0.61	4.28	5.54	1.81	0.57	4.08	16.39	0.98
F1	23650	37050	1.6	0.13	2.20	0.7	0.36	0.10	1.4	3.74	0.15
F2	24420	40140	1.6	0.13	2.50	2.58	0.46	0.29	2.80	6.94	0.18
F3	32390	44940	1.4	0.02	2.05	0.53	0.04	0.23	0.40	1.69	0.13

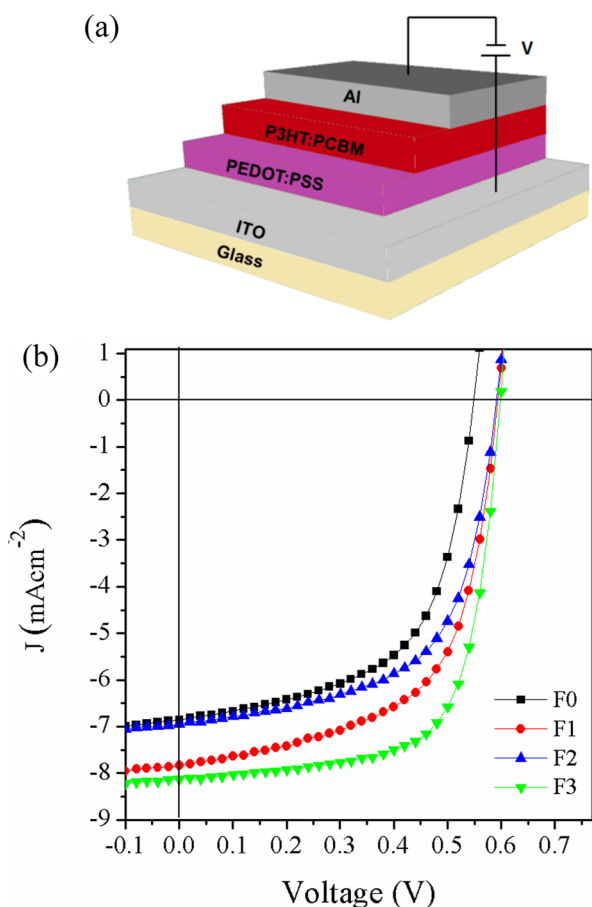**Figure 2.** OFET device parameters for all P3HT fractions.

Figure 3. (a) Bulk heterojunction solar cell device architecture used in this work and (b) *J*−*V* curves of solar cells utilizing P3HT:PCBM blends (1:0.7 weight ratio).

The amount of residues in each fraction of P3HT was determined by ICP-MS, and all data for several elements are shown in Table 1. ICP-MS analyses clearly show a variation of the composition depending on the purification methods. Ni, Mg, and Na were introduced during the monomer and polymer synthesis multistep process, with reagents, catalysts, or even drying agent (Na_2SO_4). The other metals Fe, K, Cu, Ca, and Zn might come from reagents and solvents, which were used as-received without further purification. According to ICP-MS data, **F0** fraction (crude product) has the highest level of

contamination. After classical purification (**F1**, Soxhlet extraction with methanol, hexane, and chloroform) most of the metallic residues have been removed from the polymers. Purification by using dimethylglyoxime supplemented with 15-crown-5 ether (**F2**) does not decrease the level of metal residues in regard to the classical purification (**F1**). The purification consisting of the combination of ethylenediamine and crown ether as chelating agents (**F3**) seems more efficient than purification associating dimethylglyoxime and crown ethers (**F2**). This is particularly the case for the reduction of alkali ions (e.g., Na^+ and K^+). It is noteworthy that the purest P3HT fractions are recovered in chloroform after several purification stages including metal scavengers and Soxhlet extraction. All fractions were therefore collected and studied in organic field effect transistor and solar cell devices in order to correlate the "purity" of the semiconducting polymer or the purification methodology to their performance in organic electronic devices.

When it comes to the quality of OFET devices, hysteresis and on/off current ratio are the prime parameters, as they concern the stability and sensitivity of the device, essential for OFETs as active components in circuits and sensors. Among six devices fabricated for each fraction of polymer as active layers, the devices with the minimum hysteresis were chosen as the best performing ones. When hysteresis was similar, the highest on/off current ratio was used as the second criterion. A typical transfer characteristic in the saturation regime of the OFET device with **F0** (crude product) and **F3** (purest) fraction as active layers is shown in Figure 1b. Derived device parameters such as threshold voltage (V_{th}), hysteresis (ΔV_{th}), and on/off current ratio could be extracted from Figure 1b. Mobilities were estimated from the maximum of the gate voltage dependent mobility curves. The comparison of these parameters for the different fractions is displayed in Figure 2.

Molecular weight and dispersity ($Đ = M_w/M_n$) of P3HT are known to have a significant effect on the charge carrier mobility. While smaller molecular weight polymer thin films tend to crystallize better with enhanced grain boundaries, high molecular weight polymer thin films show more amorphous but interconnected network character. Higher macromolecular dispersity allows for the combination of these two cases with crystalline zones efficiently connected by amorphous zones leading to higher charge carrier mobility.[23] Therefore, in our different fractions through various purification processes, the resultant differences in molecular weight and dispersity are
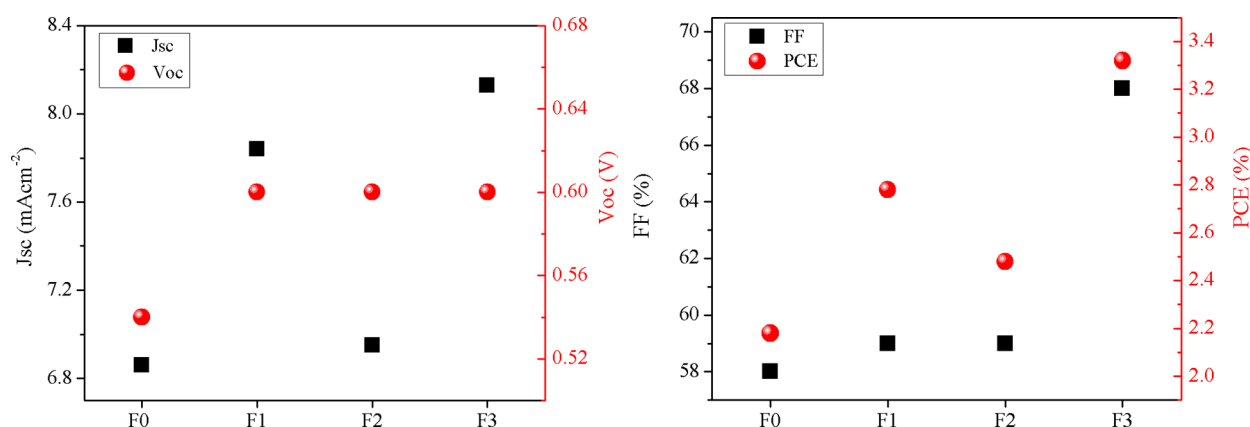
Figure 4. Photovoltaic device performance parameters of the solar cells fabricated from each fraction of P3HT:PCBM blends.

important parameters affecting device performance, especially the mobility.

While having the lowest molecular weight and the higher level of metallic contamination, the crude product (**F0**) shows relatively high mobility (1×10^{-3} cm^2 V s^{-1}). In that specific case, not only the purity plays a role but also the high dispersity value (i.e., $Đ \sim 1.8$) which facilitates interconnection between crystal domains.[9] When classical purification was used (**F1**), the obtained high molecular weight (i.e., Mw $\sim$ 37k) together with a relatively lower dispersity value (i.e., $Đ \sim 1.6$) can be the causes of the decreased mobility (2.7×10^{-4} cm^2 V s^{-1}) in regard to the crude product. Polymer fraction issued from purifications with dimethylglyoxime plus 15-crown-5 (**F2**), despite showing quite different degrees of ionic impurity content, exhibits comparable mobilities to that of **F1**, as their molecular weight and dispersity values are similar. The purification method consisting of combining ethylenediamine and 15-crown-5 ether (**F3**) led to a higher mobility (7.5×10^{-4} cm^2 V s^{-1}). This is caused by a significantly higher molecular weight (Mw $\sim$ 45k) overweighing the role of lower dispersity (i.e., $Đ \sim 1.4$). Therefore, when it comes to the mobilities of different polymer fractions, molecular weight and dispersity play a determining role compared to the amount of metal residues, as positive ions do not act as trapping species for hole charge transport in the p-channel layer. They do, however, contribute to the current: notably high concentration results in elevated I_{off} and early switching on of the channel through filling hole trapping sites, thus leading to lower threshold voltage (V_{th}).[24] A general trend of increased V_{th} was observed, when ionic impurities were decreased. The **F3** fraction as the purest fraction evidenced the highest V_{th}.

Ionic impurities should have a strong effect on the hysteresis behavior of the device, as the ion transport is much slower than charge transport. Indeed we have observed the biggest hysteresis (ΔV_{th} = 3.4 V) in the crude product (**F0**) (see Figure 2). The **F1** fraction with classical purification process led to a remarkable decrease in hysteresis. However, the **F2** fraction again shows enlarged hysteresis, which can be attributed to the fact that the addition of dimethylglyoxime together with 15-crown-5 ether was not as efficient as classical purification in eliminating the ionic impurities. Hysteresis decreased to the minimum in the case of **F3** fraction owing to the lowest amount of contamination level when compared to all other fractions.

Finally, on/off current ratio also strongly depends on the effect of ionic residues as shown in Figure 2. High concentration of ionic impurities leads to elevated I_{off}, thus resulting in low on/off current ratio, as in the case of the crude product (**F0**). Evidently, we have achieved the highest on/off current ratio from the **F3** fraction, which contains the lowest amount of metals, notwithstanding its moderate mobility.

In this respect, we can claim that by decreasing the ionic impurities to the lowest amount we managed to achieve the best performing OFET devices. In the following we have investigated the role of P3HT contamination when integrated within a common bulk heterojunction organic solar cell architecture in the presence of PCBM acceptor even though the purity of the latter was not checked.

In order to investigate the effect of impurities in P3HT on photovoltaic performance, bulk heterojunction solar cell devices were fabricated and tested with all P3HT fractions issued from the different purification methods. The devices with the highest power conversion efficiency (PCE) were chosen among eight devices for each fraction. Figure 3b shows the $J-V$ curves of the fabricated solar cells. Figure 4 shows the photovoltaic parameters under AM1.5 illumination for the best solar cell device of each fraction of P3HT:PCBM blend.

The effect of mobility variation due to the difference in the molecular weight and dispersity of the polymers on the OPV device performance is not substantial, as proved by the **F1** fraction which yields higher power conversion efficiency (2.78%) than **F0** (2.18%) even though the former has relatively lower mobility than the latter. This allows us to observe the direct effect of ionic impurities on OPV device performance. As both holes and electrons are transported in the active layer, any type of ion can act as a recombination center for the two types of charges. For instance, it can be observed that increased recombination deteriorates the short-circuit current density (J_{sc}) and open-circuit voltage. Indeed, we have detected very good agreement between J_{sc} values and the amount of metallic residues in the different fractions. The J_{sc} increased from the lowest value of 6.86 mA cm^{-2} in the crude product (**F0**) to the highest one being 8.13 mA cm^{-2} in the purest fraction (**F3**). Besides, the open-circuit voltage (V_{oc}) can consistently decline when trap-assisted recombination is significant enough in regard to high ionic impurity concentration. This could be the reason for the low V_{oc} (0.54 V) we obtained in the case of crude product (**F0**). If concentrations of metal residues are decreased to a certain level, intrinsic recombination mechanisms dominate in the devices and yield rather similar V_{oc} values for the other fractions. Added to charge trapping, the presence of ions can also lead to greater leakage current from the diode, effectively decreasing shunt resistance. This can

eventually cause fill factor (FF) compensation. While crude product (**F0**) yielded only 58% of FF, we obtained the highest FF (68%) for the purest fraction (**F3**), one of the highest values reported for P3HT:PCBM-based OPV devices. Thus, the fraction bearing the lowest ionic impurity concentration evidenced the best device performance parameters with a PCE of 3.32% compared to 2.18% for the crude product.

In summary, we have studied the effect of ionic metal residues present in freshly synthesized and purified P3HT polymer on OFETs and OPVs. Importantly, different purification methodologies were developed so as to evaluate the best one. Classical purification (**F1**, Soxhlet extraction with methanol, hexane, and chloroform) proved to be quite efficient in removing most of the ionic impurities. Among the various systems studied in this work it appears that the combination of metal scavengers based on polyamine and cyclic polyether derivatives (i.e., ethylenediamine plus 15-crown-5 ether) gives rise to the lower level of metallic contamination within the semiconducting poly(3-hexylthiophene) (P3HT). For instance, we have achieved the best operating OFET device with the lowest hysteresis and the highest I_{on}/I_{off} ratio from the device based on the purest fraction (**F3**). This fraction also showed the best performance in OPV devices with PCE of 3.32% in regard to 2.18% using the crude product. This work will bring a deeper understanding on how impurities affect the electrical properties of organic electronic devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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