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**Charge Delocalization in Oligomers of
Poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-*b*]thiophene), PBTtT**

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ABSTRACT

We investigate theoretically charge delocalization in radical-cations, *i.e.*, positive polarons, formed on oligomer chains of poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-*b*]thiophene), PBTTT. We use non-empirically tuned range-separated density functionals (TRS-DFT), including LC- ω PBE, LC-BLYP, and ω B97XD. We consider the evolution with oligomer length of the molecular geometric and electronic structures, optical absorption features, and spin densities. The TRS-DFT results indicate that a positive polaron can delocalize ideally over some 10 thiophene rings when the backbone is non-planar and up to 14 rings for a backbone forced to be completely planar. Interestingly, up to six polarons can co-exist side-by-side in a hexamer (which contains 24 thiophene rings), which is consistent with the highest degrees of doping (oxidation) experimentally achievable in polythiophene derivatives.

I. INTRODUCTION

The potential for low-cost, solution-based, high-throughput device fabrication makes π -conjugated polymers attractive materials as components of active layers in organic-based electronics applications, including organic light-emitting diodes (OLED),^{1,2} thin-film transistors (OTFTs),^{3,4} or photovoltaic devices (OPVs).⁵⁻⁷ Charge delocalization is one important factor influencing the performance of organic semiconductor devices; this is, *e.g.*, the case for OPV as the extent of charge delocalization has been reported to directly influence the charge separation process on fast time scales.⁸ The polymer 2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophene (PBTtT, see Figure 1) has recently shown promise as an active-layer component for organic-based electronics applications due to its large hole mobility up to $1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.⁹⁻¹² At this point in time, however, OPV devices based on PBTtT show rather low power conversion efficiencies, on the order of 2.3%.^{13,14} In the present work, our main goal is to characterize the extent of charge (hole) delocalization on PBTtT chains from a theoretical point of view.

PBTtT

Figure 1. Chemical structure of PBTtT with dodecyl side-chains.

Due to the great significance of charge delocalization in organic semiconductor devices, many efforts have been made to describe its extent using both experimental and theoretical techniques. Experimentally, charge delocalization in positive [negative] polarons on a π -conjugated system (corresponding to radical cations [radical anions]) has been studied by high-resolution electron paramagnetic resonance (EPR) and light-induced pulsed electron-nuclear double resonance spectroscopy (ENDOR), which allows the determination of the ^1H hyperfine coupling constants of photo-generated charge carriers.^{7,15-17} Alternatively, the extent of charge delocalization can also be evaluated at the theoretical level by calculating the geometric and electronic structure in the ionized state of the polymer. However, many earlier theoretical investigations have exploited standard hybrid density functionals such as B3LYP, which tend to greatly overestimate delocalization as a result of the large self-electron interaction (SEI) error associated with these functionals.^{7,18}

Here, we study the extent of charge delocalization in the oxidized form of a series of PBTTT oligomers containing from one to six repeat units ($n=1-6$, BTTT1-BTTT6). We use non-empirically tuned range-separated density functionals (TRS-DFT), which are known to largely alleviate the SEI error and to provide a good balance between localization and delocalization effects. Using TRS-DFT functionals, we examine: (i) the molecular geometric structures; (ii) the electronic structures and optical absorption features; and (iii) the spin densities. We also discuss the delocalization behavior in chains with completely planar backbones and in the presence of multiple charges.

II. COMPUTATIONAL METHODOLOGY

As stated in the Introduction, in order to be able to properly characterize charge delocalization, it is necessary to exploit a methodology that reduces the SEI (and thus the delocalization) error present in traditional density functionals such as B3LYP. A coupled cluster approach using both single and double substitutions from the Hartree-Fock determinant (CCSD)¹⁹⁻²² is often used as a benchmark.²³ Here, we choose the geometry of BTTT1 optimized at the CCSD/6-31G* level as a reference in order to compare the accuracy of the TRS-DFT functionals; for the sake of comparison, we also include results with B3LYP.^{24,25} In addition, the BTTT1 geometry is also optimized at the B3LYP/6-31+G(d,p) levels to better assess basis set vs. functional effects.

All the neutral molecules and cations are assumed to have C_i symmetry (which we have checked does not impact the results to any significant extent but reduces greatly the computational costs) and the alkyl side-chains are simplified to ethyl groups. We consider three optimally tuned range-separation (TRS) DFT methods, LC- ω PBE,²⁶⁻²⁹ LC-BLYP,³⁰ and ω B97XD³¹. It is important to bear in mind that the default ω values of range-separated DFT functions are generally too large when considering extended π -conjugated systems, which thus require ω tuning.^{18,32-35} The optimal ω values are obtained by minimizing $J(\omega)^2 = [\epsilon_H(N) + IP(N)]^2$ (where ϵ_H is the (negative) energy of the highest occupied molecular orbital (HOMO) and IP is the vertical ionization potential) for a given N-electron system.³² The minimization proceeds in the following way: A first ω value is obtained based on the initial geometry; the geometry is then re-optimized with this ω value and a new ω value is optimized from the new geometry; this process is repeated until the ω value converges (within a threshold of 0.0001 Bohr⁻¹), which usually occurs after 3-4 iteration steps. We note that earlier works³³⁻³⁵ sometimes used geometries

optimized with the B3LYP functional; thus, one can expect that the geometries obtained with this self-consistent procedure are more reliable (Figure S1). In order to keep the same functional for a given oligomer, optimizations of the cations are performed with the tuned ω value of the neutral molecule (and the 6-31G(d) basis set). The ω values of the fully coplanar models of the BTTT1-BTTT6 oligomers (obtained by replacing the $-\text{CH}_2\text{CH}_3$ substituents with $-\text{H}$, and constraining all the atoms in the same plane) are optimized using the same procedure. Also, the calculations on the multiply oxidized systems, including dications on BTTT1-BTTT6 and BTTT6 chains containing from 1 to 6 polarons, are carried out with the same ω values as for the neutral molecules. However, the geometries of multiply oxidized systems are fully optimized with an initial guess introduced by using a fragment wavefunction approach. The IP values (at the TRS- ω B97XD/6-31G(d) level) and optical gap values (at the Time-Dependent (TD)-TRS- ω B97XD/6-31G(d) level) are calculated using the integral equation formalism of the polarizable continuum model (IEF-PCM),³⁶ taking into account the dielectric constant of chloroform ($\epsilon = 4.7113$) and a tuned ω value of 0.0047 Bohr^{-1} . This ω value is obtained from the optimized geometries of BTTT1-BTTT6 *in vacuo* at the TRS- ω B97XD/6-31G(d) level by minimizing the sum of the $J(\omega)^2$ values then calculated with IEF-PCM across the whole BTTT1-BTTT6 oligomer series. All calculations were carried out with the Gaussian 09 package.³⁷

III RESULTS AND DISCUSSION

1. Molecular Geometric Structures

The minimum of the potential energy surface of BTTT1 corresponds to a geometry where the backbone is twisted and the side-chains are not co-planar with respect to the thiophene rings they are attached to. This is in line with previous works that show that thiophene-based polymers and

oligomers are flexible, with the thiophene rings being able to rotate easily along the inter-ring bonds.³⁸⁻⁴² As a consequence, both cis-like and trans-like configurations can form. This feature has been reported in the case of crystals of thiophene-based oligomers, for example, didodecylquaterthiophenes (DDQT).⁴³⁻⁴⁵ In the case of available single-crystal structures of BTTT1 and BTTT2, only trans configurations have been observed to date.⁴⁶ As a result, we have chosen to focus here on the trans isomers.

Figure 2 illustrates the molecular structure of BTTT1 and its cation. A comparison between the CCSD optimized geometry of BTTT1 and those from a series of DFT methods including B3LYP, B2PLYPD, TRS-LC- ω PBE, TRS-LC-BLYP, and TRS- ω B97XD, is given in Figure S1 of the Supporting Information. The TRS functionals are found to provide geometries in much better agreement with CCSD (bond length deviations from CCSD results lower than 0.015 Å) and are expected to be more reliable than the B3LYP geometries. In particular, the TRS- ω B97XD functional gives the best comparison with the CCSD geometries. (We give in Table S1 a comparison of the calculated IP and EA values as well as the geometry of BTTT1 among all three TRS-DFTs (ω B97XD, LC- ω PBE, and LC-BLYP), taking into account both default and optimized ω values). We also note that going from the 6-31G(d) basis set to 6-31+G(d,p) with the B3LYP functional shows negligible variations in bond lengths (<0.003 Å), bond angles (<0.5°), and dihedral angles (<6°); these results underline that the basis set effect is much smaller than the influence of the nature of the functional.

Figure 2. Optimized molecular structures of (a) BTTT1 and (b) BTTT1⁺, at the TRS- ω B97XD ($\omega=0.1565$ Bohr⁻¹) level of theory with the 6-31G(d) basis set. In each case, two different views of the backbone are presented. Dihedral angles between the thiophene (T) and thienothiophene (TT) units as well as between a side-chain and T are given in red and highlighted with black arrows.

The significant differences between the neutral and cation geometries can be used to study the extent of charge delocalization in all the oligomers. We will especially refer, as a good index for delocalization, to the dihedral angles between consecutive thiophene (T) and thienothiophene (TT) units, denoted $\theta(\text{T-TT})$, or between two consecutive thiophene rings, denoted $\theta(\text{T-T})$. Note that, as a threshold to define the extent of delocalization, we consider that deviations in dihedral

angle have to be at least 10° (see Figure S2). Figure 3 compares the T-TT and T-T dihedral angles in the BTTT5 and BTTT6 neutral molecules and their cations, as calculated with TRS- ω B97XD. A comparison of the dihedral-angle values for the oligomer series with all the functionals can be found in Table S2. We stress that B3LYP indicates that the charge would be delocalized over the whole BTTT5⁺ or BTTT6⁺ backbone except for the very terminal T units. In contrast, the TRS- ω B97XD/6-31G(d) results point to a charge delocalization extent over some 10 thiophene rings, that is over 3TT-4T (out of a total of 5TT-10T) units and 2TT-6T (out of 6TT-12T) units in BTTT5⁺ and BTTT6⁺, respectively. (Since the comparison of the B3LYP results with the TRS-functional results clearly confirms the significant delocalization error of B3LYP, B3LYP will not be further discussed in the remainder of this work). Charge delocalization in BTTT3⁺ and BTTT4⁺ also occurs over some 10 thiophene rings, *i.e.*, 3TT-4T or 2TT-6T units. In the cases of BTTT1⁺ and BTTT2⁺, the charge is found to be delocalized throughout the backbone as the total numbers of thiophene rings in these two oligomers are equal to 4 and 8, respectively. In general, the impact of oxidization in the BTTT oligomers is to increase the planarity of the central units, where the polaron resides, more significantly than the terminal units.

Figure 3. Dihedral angles in the optimized geometries of BTTT5 and BTTT6 and their cations BTTT5⁺ and BTTT6⁺, at the TRS- ω B97XD/6-31G(d) level of theory. The 1.5 value on the *x*-axis corresponds to the dihedral angle between the first T unit (labeled as #1) and the first TT unit (labeled as #2) from one end of the molecules (see labels in Figure S2).

Overall, it is found from this analysis of the dihedral angles that in long BTTT chains, polarons tend to delocalize optimally over some 10 thiophene rings, be them fused or not (3TT-4T or 2TT-6T units). This conclusion based on the dihedral angles is fully confirmed by an analysis of the bond-length modifications upon oxidation, see Figures S3-S5.

2. Electronic Structure

Figure 4 shows the evolutions, as a function of oligomer length, of the ionization potentials and optical gaps, calculated at the TRS-(TD)- ω B97XD/PCM/6-31G(d) level, in comparison to experimental results. The evolution of the calculated IPs matches very well that of the experimental IPs for BTTT1-BTTT5 derived from the oxidation potentials measured by cyclic voltammetry (CV) in THF solution (deviations of 0.12 eV for BTTT5 and less than 0.06 eV for the others).⁴⁶ The TRS- ω B97XD/PCM/6-31G(d) calculated optical gaps (energy of the lowest excited state with significant oscillator strengths in the TDDFT calculations) also follow very well the values estimated from the maximum absorption wavelengths in chloroform (with maximum deviations of less than 0.09 eV). While the IP of BTTT2 is about 0.3-0.4 eV smaller than that of BTTT1, the decrease in IP when going from BTTT4 to BTTT6 is less than 0.03 eV, which indicates saturation of the π -conjugation in long BTTT chains beyond some four repeat units. A similar conclusion can be drawn from an analysis of the optical gaps. Though no experimental electronic affinity (EA) values are available, the calculated EA saturates at 1.63 eV for BTTT4. We note that the deviations between computed and experimental IP values are larger in the longer oligomers than the deviations for the calculated optical gaps; it must be borne in mind that the IP values are measured by CV in THF solutions while the absorption spectra come from chloroform solutions, pointing to differences in the surrounding media not explicitly considered in the calculations (see also the SI of Ref. 46).

Figure 4. Change in calculated ionization potential (IPc, red filled square) and optical gap (OGc, red filled triangle) as a function of $1/n$ (n =number of T-TT-T repeat units) at the TRS-(TD)- ω B97XD/6-31G(d) level ($\omega=0.0047$ Bohr⁻¹) in a dielectric medium ($\epsilon=4.7113$) corresponding to chloroform). Comparison with the experimental IPs (IPe, black filled circle) derived from oxidation potential values measured by cyclic voltammetry (CV) in THF solution and with the experimental optical gaps (OGe, black filled diamond) from absorption spectra measured in chloroform (Ref. 46). The two points at the 0.1 value for the $1/n$ axis correspond to experimental IP and optical gap of the polymer (referred to as BTTT-C in Ref. 46).

We also studied the optical gaps of the BTTT cations. The first excitation energy of BTTT1⁺ (calculated at the TD-TRS- ω B97XD/PCM/6-31G(d) level) is 1.58 eV and decreases rapidly to 0.84 eV for BTTT3⁺ and BTTT5⁺. There occurs an odd-even effect as the optical-gap value in BTTT2⁺ is 0.83 eV while that in BTTT4⁺ and BTTT6⁺ is 0.64 eV. This odd-even effect (which we have confirmed is not simply due to the imposition of C_i symmetry) can be understood on the basis of the somewhat different geometries for the BTTTs with odd and even repeat units (since the molecular center is a thienothiophene unit for the BTTTs with an odd number of repeat units

and an inter-ring bond between two thiophenes for the BTTTs with an even number of repeat units), which leads to slight differences in electronic structures and optical gaps.

3. Spin Densities

Another direct reflection of the charge delocalization extent can be found in the evolution of the spin density corresponding to the formation of the radical-cation upon oxidation. The spin density on each T or TT unit in the cations of BTTT1-BTTT6 has been calculated at the TRS- ω B97XD/6-31G(d) level using the Natural Population Analysis (NPA) phase of a full Natural Bond Orbital analysis (NBO). The results are given in Table S3 together with the calculated Mulliken spin densities for all functionals (Figures S6 and S7). Here, we have chosen a spin density threshold on each T or TT unit of 0.01 e (where e is the elementary charge); that is, we consider that the charge effectively delocalizes over a T or TT unit only if the spin density on the unit is larger than 0.01 e. For all the cations, the spin density generally increases from end to center, which is consistent with the fact that the polaron occupies the center of the molecule. According to the NPA spin density calculated at the TRS- ω B97XD/6-31G(d) level, the spin density on every T or TT unit for the BTTT1 and BTTT2 cations is larger than 0.04 e, indicating that the polaron is delocalized over the whole molecule. In contrast, the charge delocalization region is confined to 3TT-4T units for BTTT3⁺ and BTTT5⁺ and 2TT-6T units for BTTT4⁺ and BTTT6⁺, which is fully in line with the conclusions drawn from the analysis of the geometries. The spin density map (with isovalue of 0.0004 e·Å⁻³) is illustrated in Figure 5 for BTTT2⁺, BTTT4⁺, and BTTT6⁺. Figure 5 clearly demonstrates the saturation of the polaron delocalization beyond 3 T-TT-T repeat units. We note that the Mulliken spin density shows a slightly lower degree of delocalization than NPA, with the spin density on the central T/TT units slightly

increased and that on the end T/TT units decreased; however, the difference is not significant and a similar delocalization extent is revealed when using the same threshold cut-off value of 0.01 e, see Table S3.

Figure 5. Spin density map (with isovalue of $0.0004 \text{ e}\cdot\text{\AA}^{-3}$) for the BTTT2^+ , BTTT4^+ , and BTTT6^+ radical-cations, calculated at the TRS- ω B97XD/6-31G(d) level of theory. The red lines mark the region with spin density on a T/TT unit of more than 0.01 e.

4. Influence of Coplanarity

We now turn to an examination of the impact of coplanarity, which can be induced in the solid state due to packing effects, on the charge delocalization in the BTTT1-BTTT6 cations. We considered fully coplanar models of the BTTT1-BTTT6 cations by replacing the $-\text{CH}_2\text{CH}_3$ substituents with H, and constraining all the atoms in the same plane. The results are shown in

Figures S8 and S9 and Table S4 of the Supporting Information. Due to the increase in π -conjugation associated with the planar structure, the charge delocalization region increases in comparison to that in the non-planar cations of BTTT1-BTTT6. According to the TRS- ω B97XD results, the charge delocalization reaches some 14 thiophene rings (4TT-6T units for BTTT4²⁺ and BTTT6²⁺ and 3TT-8T units in BTTT5²⁺). Overall, with respect to cations that are not constrained to be fully coplanar, charge delocalization increases by about one full repeat unit, from *ca.* 2.5-3 T-TT-T units to 3.5-4 T-TT-T units. Again, the results from geometric structure, electronic structure, and spin density analysis are all internally consistent.

5. Delocalization in Multiply Oxidized Systems: Bipolarons vs. Separated Polarons

When two positive charges appear on a single oligomer, there are two possible configurations for the dication. One is to have the two charges coupled and associated to a stronger geometry relaxation, that is to form a bipolaron; the other is to have two separated (side-by-side) polarons.⁴⁷ Whether the dication ends up as a bipolaron or two polarons depends on a subtle balance between the charge pairing effects (two charges sharing the same region of space) and the geometry relaxation effects.

Figure 6 compares the spin density values in the dications of BTTT2, BTTT4, and BTTT6 (Figure S10 shows the spin density of BTTT6²⁺ with the spin density value on each T/TT unit as well as the dihedral angles and T-TT/T bond distances). From Figure 6, it is seen that BTTT6²⁺ corresponds to two separated polarons with almost no overlap between them; indeed, there is hardly any spin density (<0.001 e) on the two terminal T units and the two center T units. Each polaron is delocalized over a total of 3TT-4T units, which is similar to the situation for the

BTTT3 and BTTT5 cations. From this view point, BTTT6^{2+} can be seen as two BTTT3^+ cations connected together. The total spin density of the left half of BTTT6^{2+} is almost 1 e (0.9989 e), confirming the negligible overlap between the two polarons. The dihedral angle between one of the two central T units and the neighboring TT unit is 133° , similar to the value in the BTTT6 neutral molecule, which points out that charge delocalization does not extend there. Due to the negligible overlap between the two polaron wave functions, the triplet and (spin polarized) singlet BTTT6^{2+} dications have the same geometry, total energy, and spin distribution. In contrast, the BTTT6^{2+} bipolaron configuration is about 1.18 eV less stable than the two-polaron triplet configuration. When forcing the system to keep the bipolaron geometry, separating the bipolaron into two side-by-side polarons reduces the total energy by 0.81 eV, confirming the greater stability of separated polarons in BTTT6^{2+} . It must be borne in mind, however, that these results do not take into account the presence of counter-ions (as would be the case upon chemical doping) and possible solid-state effects.

Figure 6. Comparison of the spin densities on the dications of BTTT2, BTTT4, and BTTT6 calculated at the TRS- ω B97XD/6-31G(d) level.

Decreasing the chain length from BTTT6^{2+} to BTTT1^{2+} triggers overlap between the two polarons. For BTTT1^{2+} , the singlet bipolaron is 1.72 eV more stable than the triplet configuration (while a side-by-side spin-polarized singlet configuration cannot be obtained). Thus, the confinement in BTTT1^{2+} leads to bipolaron formation. However, as soon as the chain length increases to BTTT2 , the divalent cations correspond to side-by-side polaron configurations (Figures 6 and S11). The sum of spin density on one-half of BTTT2^{2+} - BTTT5^{2+} increases from 0.8440 e to 0.9677, 0.9913, and 0.9972 e, respectively, indicating the decrease in wave function overlap between the two polarons. BTTT5^{2+} and BTTT6^{2+} have long enough backbones for the two polarons to be fully delocalized as in the cation case, while the delocalization distance in BTTT2^{2+} - BTTT4^{2+} is compressed to only 3-5 T/TT units. The total energy difference between the singlet bipolaron and the spin-polarized singlet two-polaron case decreases from 1.18 eV in BTTT6^{2+} to 0.25 eV in BTTT2^{2+} , as a result of the increase in overlap of the polarons.

Finally, we have studied the evolution of the charge distribution on a BTTT6 chain as a function of increasing the number of polarons from 1 to 6 (Figure S12 and Table S5, Supporting Information). We note that maximum chemical doping (oxidation) levels on the order of 25-33% per thiophene ring have been reported in polythiophene derivatives,^{47,48} which is in line with our consideration of up to one charge per four rings. For each BTTT6^{n+} ($n=1-6$) cation, all the possible spin multiplicity and antiferromagnetic couplings have been considered in order to obtain the most stable geometry. Table S5 collects the spin density and corresponding geometry of the most stable configuration for each cation. For the BTTT6^{n+} ($n=2-6$) systems, the most stable species is the one having the smallest total spin multiplicity, with the alpha and beta electrons alternating along the oligomer chain; when 3 to 6 positive charges co-exist, the alpha

and beta electrons cannot separate fully since there is not enough space for each of the polarons to completely delocalize. For example, while in BTTT6^{2+} the alpha electron distributes on one half (0.9994 e) of the molecule and the beta electron on the other, in the case of BTTT6^{4+} , the second and fourth T units from the end carry comparable and significant alpha and beta electrons, 0.13 vs 0.16 e and 0.12 vs 0.12 e, respectively, indicative of the overlap between consecutive polarons. Comparing the first to third ionization energies shows that the second IP is 0.37 eV larger than the first and the third IP is 0.99 eV larger than the second; such charging effects can be expected to reduce considerably in the presence of counter-ions and in the solid state.

IV. CONCLUSIONS

We have systematically studied the delocalization of cations on PBTTT chains using optimally tuned range-separated DFT methodologies. Through an analysis of the evolution with oligomer length of the molecular geometric and electronic structures, optical gaps, and spin densities of the singly oxidized species, it is found that:

- (i) Oxidation leads to significant dihedral-angle and bond-length modifications that extend optimally over some 10 thiophene units. The evolutions of the spin density distributions fully match the geometry results.
- (ii) The evolutions of the ionization potentials and optical gaps with oligomer length, which fit well with the experimental evolutions, saturate at the level of BTTT4.
- (iii) When forcing the backbones to be fully coplanar (as can be largely the case for the polymer in the solid state), the polaron tends to delocalize optimally over one more full repeat unit, that is over some 14 thiophene rings.

When considering dications, two-polaron configurations become more favorable than bipolaron configurations as soon as the oligomer is at least two repeat unit-long (8 thiophene rings). In the case of the longest oligomer we considered, *i.e.*, the hexamer, up to six polarons can co-exist side-by-side; this corresponds to an oxidation level of 25% per thiophene ring, which is consistent with the highest doping levels reported for polythiophene derivatives.

Overall, our computational work provides a reliable framework to analyze charge delocalization in π -conjugated systems. We are currently extending it to analyze the extent of hole delocalization along PBTTT oligomers in the mixed polymer-fullerene phases present in the bulk heterojunction layers of OPV devices.

ASSOCIATED CONTENT

Supporting Information. Detailed descriptions and corresponding figures for the geometries and electronic structures of the neutral and cations of the BTTT1-BTTT6 series, and spin densities for the cations of BTTT1-BTTT6, as well as spin densities in the planar unsubstituted species BTTT1'-BTTT6' and the multiply oxidized systems [BTTT1²⁺-BTTT6²⁺, and BTTT6ⁿ⁺ (n=1-6)] at the TRS-DFT (LC-wPBE, LC-BLYP, wB97XD) and B3LYP levels. 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 interests.

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