Impact of Electron Acceptor on Three-Photon Absorption Cross-Section of the Fluorene Derivatives

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Supporting Information

ABSTRACT: Small three-photon absorption (3PA) cross-section values of present nonlinear organic molecules limit their practical applications. Although electron donors and electron acceptors have a great effect on 3PA cross-section, little is known about how the strength and situation of electron acceptors influence the 3PA cross-section value of a compound. The present work reports 3PA effects of two fluorene derivatives with symmetric D-\pi-A (D-\pi-D) archetype, which are named as 2,7-bis(4-methoxyphenylacetylene)-9-fluorenone (FATT) and 2,7-bis(4-methoxyphenylacetylene)-9-thione-fluorene (TSATL). Large 3PA cross-section and ideal 3PA-induced optical limiting effects have been found in the two fluorene derivatives. The two molecules both have a different electron acceptor on the fluorene core, by which the 3PA cross-section value for FATT is enhanced by nearly 3-fold compared with that for TSATL. The mechanism of this significant enhancement in 3PA cross-section has been investigated by density functional theory (DFT) and configuration interaction singles (CIS) method with use of 6-311+G basis set in combination with conductor polarizable continuum model (CPCM). The theoretical results show that increase of electronegative character of the electron acceptor on the core is responsible for the increase of 3PA cross-section values of the two molecules.

INTRODUCTION

Three-photon absorption (3PA) is based on the simultaneous absorption of three photons in a single event. Novel organic compounds with large 3PA cross-section have been of particular interest since many attractive applications exploiting high-order nonlinearity of media’s response to the exciting light have been suggested. The applicability of three-photon absorption processes is based on several key advantages: (1) improvement in penetration depth when working in the living organism transparency windows in the near-IR; (2) minimization of losses due to scattering when longer wavelengths are used; and (3) enhancement of the spatial resolution. Consequently, molecules with large 3PA cross-section can be widely used in the fields of ultra-high-resolution biological imaging (three-photon confocal microscopy), high-efficiency up-converted stimulated emission, optical limiting, biomedical, light-activated therapy fields, and so on. However, the relatively small 3PA cross-section values of present organic molecules have hampered their practical applications. Until now, only a few systematic experimental and theoretical studies on 3PA have been reported. The design criteria for the molecules with large 3PA cross-section have not been developed yet. Therefore, it is desirable to investigate the structure/3PA property relationship and study the prospect of any enhancement behavior, which are important for the design and synthesis of molecules with large 3PA cross-section.

Fluorene derivatives used as 3PA materials have many potential applications. Recently, Hernández et al. investigated some compounds with different electron-donor and electron-acceptor groups, such as D-\pi-D, A-\pi-A, D-\pi-A archetype. Their results demonstrated that symmetric intramolecular charge transfer favors 3PA in the fluorene derivatives and enlarged \pi-conjugated system can also enhance 3PA cross-section. Parasad et al. reported an enhanced 3PA cross-section by two-dimensional \pi-delocalization. We also showed 3PA enhancement in two symmetrical molecules with 2D-\pi-2D and 2D-D-\pi-D-2D archetype. D and A stand for electron donor and electron acceptor groups, respectively, and \pi refers the conjugated \pi-electron bridge. These studies assisted researchers in identifying some of the structure-property relationships. However, the strength of the acceptor has great influence on nonlinear optical chromophores. Few researches are about effect of the strength of electron acceptor substituents on the property of 3PA materials. On the other hand, electroacceptor substituents on different C sites of fluorene may also influence the 3PA property of the fluorene-type molecules.

To protect optical detectors, human eyes, and sensors against high-intensity laser-irradiation-induced damage, materials with excellent optical limiting behaviors are in great need. Optical
limiting is that the optical transmissivity decreases when the input signal intensity increases. In multiphoton absorption-based optical limiting, using materials with a larger 3PA cross-section value will result in a better limiting behavior. 3PA-based optical limiting has several salient features: (i) there is no linear absorption at the working wavelength range, so that the medium is highly transparent for weak input light signals; (ii) there is a very fast temporal response of nonlinear transmission changes following the intensity change of the input signals; and (iii) the materials may produce a very sharp change of nonlinear transmission with respect to the input intensity change because of the cubic dependence of the nonlinear absorption on the local light intensity. In the recent decade, several kinds of 3PA materials have been developed for optical limiting purposes, such as organic materials,10,13,17 organic metals,15 semiconductor materials,21,22 and nanoparticle activated materials.23,24

Recently, we designed and synthesized two fluorene derivatives with different electron acceptors on the core, which can affect deeply the conjugated π-electron bridges. The two compounds both have symmetric D-π-A-D-π-D archetype, which are named as 2,7-bis(4-methoxyphenylacetylene)-9-fluorenone (FATT) and 2,7-bis(4-methoxyphenylacetylene)-9-thiofluorene (TSATL). The molecular structures of the two compounds are shown in Figure 1. The synthesis route is shown in Scheme 1. The only difference between FATT and TSATL is the electron acceptor that is directly connected to the fluorene core (C9 site) by a double bond: one is oxygen and the other is sulfur. The attachment of electron-withdrawing groups to the fluorene was expected to favor the charge transport as being excited. Carbon—carbon triple bond units were utilized as π-electron bridge and connecting spacers between the central core and the electron donor, in order to ensure effective electronic conjugation between end groups and the core moiety, and allow large intramolecular charge transfer to take place within the chromophore. To provide useful information for the design of large 3PA materials, we focus on gaining insight into the effect of strength and site of electron acceptor groups on the 3PA properties of these fluorene-based molecules.

### EXPERIMENTAL SECTION

Linear absorption and steady state fluorescence spectra of FATT (3.3 × 10⁻⁶ mol/L in CHCL₃) and TSATL (7.9 × 10⁻⁶ mol/L in CHCL₃) were recorded on a UV−vis−NIR spectrophotometer (Cary 5000, Varian) and a steady-state fluorescence spectrometer (FluoroSENS, Gilden), respectively. The optical pathlengths of sample solutions for these measurements were 10 mm.

The experimental setup for 3PA-induced fluorescence and nonlinear absorption effects is presented in Figure 2. In measurement of upconversion fluorescence of the two compounds, the incident laser was provided by a Q-switched Mode-locked Nd:YAG pulsed laser system (Continuum, PY61-10). The pulse duration, wavelength, and repetition rate of this pump beam were 38 ps, 1064 nm, and 10 Hz, respectively. In
measurement of nonlinear transmission of the two compounds, the same laser was used.

After spatial filtering (lenses L1 and L2, and the pinhole (PH)), the laser beam was directed to the sample and focused inside the 10 mm cell filled with dye solution by using lens L3 (focal length 25.6 cm). The beam waist at the focal plane was 26 μm. The upconversion fluorescence light from the dyes (1.0 × 10⁻³ mol/L in CHCl₃) was collected with lens L4 perpendicular to the cell, and then coupled into a monochromator connected with a photomultiplier (D3). The laser beam was separated into two beams with use of a beam splitter. J3-05 probes (Molelectron Co.), i.e., D1 and D2, were used to monitor the incident and transmitted laser pulse energy simultaneously, respectively. To validate the experimental setup, a compound, which is named 2,7-bis(4-methoxystyryl)-9,9-bis(2-ethylhexyl)-9H-fluorene has been reported by W. Ma et al., was chosen to measure the 3PA cross-section in the same experimental condition. Within allowable error, the obtained result ([(64 ± 6) × 10⁻⁷ cm² s²] with the same fitting method is consistent with theirs ([(70 × 10⁻⁷ cm² s²]².

**Synthesis of FATT.** A solution of Pd(OAc)₂ (225 mg, 1 mmol) and PPh₃ (530 mg, 2 mmol) in 25 mL of H₂O–CH₂CN (1/10) in a Schlenk tube under argon was added to be a well-stirred mixture of the 4-methoxyphenylacetylene (1.335 g, 10 mmol), 2,7-dibromo-9-fluorene (1.39 g, 4 mmol), Et₃N (3.5 mL 25 mmol), and Bu₄NHSO₄ (3.24 g, 10 mmol) in 25 mL of H₂O–CH₂CN (1/10). Stirring was continued at room temperature for 10 h. The mixture was then hydrolyzed with 30 mL of H₂O and extracted with 3 × 100 mL of diethyl ether. Removing the solvent in vacuo was followed by column chromatography on silica gel, using as eluent a mixture of CHCl₃ and petroleum ether (1:1) to give red needles of FATT (500 mg, 1.2 mmol) under an inert atmosphere. The mixture was refluxed overnight and the cooled solution was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with as eluent a mixture of CHCl₃ and petroleum ether (1:1) to give deep-blue crystals of TSATL (62 mg, 30%).

**Synthesis of TSATL.** To a toluene solution (3 mL) of 2,7-bis-(4-methoxyphenylacetylene)-9-fluorenone (200 mg, 0.45 mmol) was added Lawesson’s reagent (500 mg, 1.2 mmol) under an inert atmosphere. The mixture was refluxed overnight and the cooled solution was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with as eluent a mixture of CHCl₃ and petroleum ether (2:1) to give deep-blue crystals of TSATL (62 mg, 30%).

**RESULTS AND DISCUSSION**

**Linear Absorption and Steady-State Fluorescence Emission Spectra.** Linear absorption and steady-state fluorescence spectra of FATT and TSATL are shown in Figure 3. In comparison with FATT, the fluorescence emission peaks for TSATL show a red-shift of 28 nm and two new fluorescence emission peaks appear at 457 and 580 nm, which are attributed to its weak electronacceptivity of the S atom on the core. It should be noted that the two molecules show strong UV absorption in the spectral ranges of 280–390 nm for FATT and 280–450 nm for TSATL, but scarcely any absorption in the spectral ranges of 500–1100 nm. This indicates that excitation in the longer wavelength range can occur only through multiphoton absorption processes.

**Three-Photon-Absorption-Induced Upconversion Fluorescence.** Upconversion fluorescence emission could be easily observed by the naked eye when the incident intensity reached 10⁶ W/cm². Cubic dependence of the fluorescence intensity on the incident laser intensity is characteristic of the 3PA-induced fluorescence emission. To confirm the order of the excitation process, we measured the fluorescence emission intensity vs incident intensity at 405 nm for TSATL and 430 nm for FATT. Parts a and b of Figure 4 show the measured relative intensities of 3PA-induced fluorescence as a function of the pumping intensities for FATT and TSATL at a concentration of 1 × 10⁻³ mol/L, respectively. The measured data are in good agreement with the best-fitting curve (solid lines) following the cubic laws. Excited state absorption can be discarded for three reasons: (1) the absence of one-photon (1064 nm) and two-photon (532 nm) absorption; (2) quantum chemistry computations have been carried out by means of the CIS/6-311+G method and the sophisticated polarized continuum model (CPCM), the results indicate that the compounds have no stepwise absorption (excited state absorption) channels such as the 1 + 1 + 1, 2 + 1, or 1 + 2 photons absorption process, only one single-step transition matches the 3PA rules for 1064 nm wavelength laser; and (3) the upconversion fluorescence intensity exhibits a cubic dependence on incident intensity, which is characteristic of the three-photon process. The shapes of the steady-state and upconversion fluorescence are similar (data not included). One can be confident that the excitation process is induced by the simultaneous absorption of three photons.

**Three-Photon Absorption Cross-Section and Optical Limiting.** Intensity-dependent transmittance measurements of the two compounds in CHCl₃ solution were done in a 10-mm-long quartz cell. Assuming a laser beam traveling within a nonlinear sample along the +z direction and neglecting linear absorption and two-photon absorption at pump wavelength, the light beam propagation through a thin sample is governed by the following equation:

\[
df(z, r, t)/dz = -\gamma I(z, r, t)^3
\]  

(1)

**Figure 3. Linear absorption spectra of FATT (green) and TSATL (cyan), and fluorescence spectra of FATT (blue) and TSATL (red).**
Here $\gamma$ is the 3PA coefficient of the sample at the pump wavelength. $z$, $r$, and $t$ are the propagation length inside the sample, the transverse coordinate, and the time, respectively. $I(z, r, t)$ is the irradiance that depends on the propagation distance.

The solution of eq 1 is

$$I(z, r, t) = \frac{I(z = 0, r, t)}{1 + 2\gamma L_i z(z = 0, r, t)}$$

(2)

where $I(z = 0, r, t)$ is the incident irradiance of the excitation beam and $L$ is the thickness of sample.

The sample passed by the laser is averagely divided into $m$ cylinders along the $z$ direction, and every cylinder is averagely divided into $n$ annuluses along the $r$ direction, hence there are $m \times n$ annuluses in the sample. The light intensity in a given annulus is deemed homogeneous along the $r$ direction and parallel along the $z$ direction, therefore eq 2 can be used for all the annuluses.

$$I'(i, j, t) = \frac{I'(i, j, t)}{1 + 2\gamma L_i z(i, j, t)}$$

(3)

Here $L' = L/m$ is the thickness of every annulus, $L$ is the distance traveled by the beam through the sample, and $t_p$ is the pulse width. $I'(i, j, t)$ is the incident irradiance at the front side of the $(i, j)$ annulus, $I''(i, j, t)$ is the transmitted irradiance of the same annulus, and $S'^{(i, j)}$ and $S'(i, j + 1)$ are the area of the exit plane of the annulus and the area of the incident plane of the next annulus, respectively. After fitting the experimental curves with the given $i$ and $j$ values, the 3PA coefficients $\gamma$ can be obtained. The larger the $i$ and $j$ values are, the more accurate the $\gamma$ value we obtain. By this method, one can obtain the light intensity $I$ at any position in the samples.

Figure 5 shows the transmitted on-axis intensity versus input on-axis intensity curves for each of the two compounds. The solid lines represent the theoretical fittings. The best-fit parameters were $\gamma = 17.1 \times 10^{-20}$ cm$^3$/W$^2$ and $\gamma = 3.4 \times 10^{-20}$ cm$^3$/W$^2$.
cm$^3$/W$^2$ for FATT and TSATL using eq 3, respectively. The 3PA coefficient can be correlated to the 3PA cross-section by

$$
\sigma_{3PA} \propto \left( \frac{hc}{\lambda} \right)^2 \cdot N_A \cdot d_0 \times 10^{-3}
$$

where $N_A$ is Avogadro’s number, $d_0$ (mol/L) is the solution concentration, and $hc/\lambda$ is the energy of the incident photons. By using eq 4, the intrinsic molecular 3PA cross-section can be evaluated to be $(7.5 \pm 0.8) \times 10^{-76}$ cm$^6$/s/photon$^2$ and $(2.5 \pm 0.3) \times 10^{-76}$ cm$^6$/s/photon$^2$ for FATT and TSATL, respectively. The intrinsic molecular 3PA cross-section is high.

As shown in Figure 5a, FATT show ideal optical limiting behavior. When the incident intensity increased from 0.1 to 1.4 GW/cm$^2$ ($\sim$14 times increase) for FATT, the transmitted intensity changed from 0.1 to 0.4 GW/cm$^2$ ($\sim$4 times increase). This is a typical optical limiting behavior based on the 3PA mechanism. It permits high linear transmittance at low input light levels. Meanwhile, for higher inputs it can clamp the transmitted energy below some maximum value. This means that this compound has promise for optical-limiting applications induced by 3PA.

As comparison, it can be easily found that the 3PA cross-section value is strongly related to the chemical structures. The only difference between the two molecules is the electron acceptor on the core, because of which the 3PA cross-section value for FATT is enhanced by 3-fold compared with that for TSATL. It is significant to clarify the influence of electron acceptor on the 3PA cross-section, so as to offer more useful information for further synthesis of new materials with large 3PA cross-section values.

Ground- and Excited-State Geometries and Electronic Excitations Processes. All calculations for the two molecules were carried out with use of Gaussian 03 software. Since the experimental data are obtained in CHCl$_3$ solution, the conductor polarizable continuum model (CPCM) was used to obtain a valid approximation of chemical environment. Initial geometries of the two molecules are obtained with the PM3 method. The optimized geometries at the B3LYP/6-31G level were taken as the input structures for the calculations at the B3LYP/6-311G level. Similarly, the optimized geometries at the B3LYP/6-311G level were used as the input structures for the calculations at the B3LYP/6-311+G level. Finally, the geometries and electronic structures of the excited state of the molecules were evaluated by the configuration interaction singles (CIS) method at the 6-311+G level.

The optimized configurations of the two molecules in the ground states are shown in Figure 6. It should be noted that for each molecule, all atoms except three hydrogens in each methyl are coplanar (see Figure 6, parts b and d). The good coplanarity in molecules can produce the greatest degree of overlap of p electron orbits, which should be a beneficial factor for communication among the acceptor, donor, and conjugated π-bridge, and hence result in more efficient intramolecular charge transfer. The calculated molecular frontier orbitals of the ground states in Figure 7 support this standpoint. So we suggest that good coplanarity in molecules can enhance the 3PA cross-section. On the other hand, whether the good coplanarity will favor the coupling effect between the molecules and the linearly polarized exciting beam needs further investigation.

Optimized structure parameters of the two molecules are obtained at the B3LYP/6-311+G level (see the Supporting Information). It can be seen that the geometries of the two optimized molecules show large differences in the fluorene core. The bonds C9–C10, C9–C13, and C11–C12 in FATT are calculated to be lengthened as compared to those in TSATL by 0.015, 0.015, and 0.006 Å, respectively. On the other hand,
the bonds C8–C13, C1–C10, C10–C11, and C12–C13 in FATT are shortened as compared to those in TSATL by 0.004, 0.004, 0.005, and 0.005 Å, respectively. As a result, the bond angles in the central fluorene also show corresponding variation. The results indicate that oxygen and sulfur near the carbon C9 site both exert a strong but different impact on the fluorene cores, which are attributed to that their high but different electronegative character pulls the electronic charge from the fluorene core toward itself and results in the change of configurations and electronic structures of the two molecules. Consequently, different energy levels and excitation properties between the two molecules may appear.

Recently, theoretical investigation revealed that there are several possible transition paths from ground S0 to final states Sf involved in a three-photon process, such as (I) S0 → S1 → Sf, (II) S0 → S1 → S2 → Sf, (III) S0 → S1 → S2 → Sf, (IV) S0 → S1 → S2 → Sf, and (V) S0 → S1 → S2 → Sf. Among them, path I will play an important role in the excited state absorption process. Path II is present in both symmetrical and asymmetrical systems and is also the most important contributor for the two compounds. The calculated excitation energy, transition electric dipole moments, and oscillator strength of the two compounds. The calculated excitation energy, transition electric dipole moments, and oscillator strength of 3PA transitions (see Figure 7). The occupied molecular orbitals (HOMO) and the unoccupied molecular orbitals (LUMO) are helpful for understanding the change of absorption properties. Theoretically, the energy gap is the orbital energy difference between HOMO and LUMO. Experimentally, the most-used band gap (i.e., optical band gap) can be obtained from the absorption spectra, which is the lowest excitation energy from the ground state to the first dipole-allowed excited state. The 3PA excitation corresponds to the promotion of the electron from the HOMO to the LUMO. The electronic transitions are attributed to ππ* transition type. As can be seen, for the two molecules, in the HOMO, electrons are delocalized over almost the whole molecules, while in the LUMO, electrons are delocalized only over the fluorene core and electron acceptor (S or O). Substantial contribution from the electron acceptor (S or O) can be seen in the LUMO orbital plots of the two molecules. It is noteworthy that the LUMO orbitals of the two molecules show an antibonding interaction between the acceptor and the fluorene core. It is known that the 3PA properties of organic molecules are mainly influenced from the conjugated delocalized π-electrons. In the 3PA process, upon absorbing three photons simultaneously, electron transition is excited from the HOMOs to the LUMOs and at the same time, large intramolecular charge transfer may easily take place from the electron donors to the electron acceptors.

Much research has shown that the efficient intramolecular charge transfer played a key role in increasing the molecular 3PA cross-section value. The transition electric dipole moment along the X axis (μ = 2.8789) of the S0 → S1 transition for FATT is ~2 times that of the S0 → S2 transition for TSATL, which shows that more efficient intramolecular charge transfer may occur in FATT. However, the electron acceptors (C=O) on the fluorene core are the only difference between FATT and TSATL, and they have different strength of withdrawing electrons. Consequently, we suggest that the high electronegative character of the electron acceptor on the core can strongly improve the capability of accepting the excited electron by pulling the electronic charge from the core and the branches toward itself.

### Table 1. Electronic Transition Data Obtained by the CIS/6-311+G Level for the Two Molecules

<table>
<thead>
<tr>
<th>electronic transition</th>
<th>excitation energy (eV)</th>
<th>calcd absorption wavelength (nm)</th>
<th>oscillator strength (f)</th>
<th>transition electric dipole moments (au)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>FATT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S0 → S1</td>
<td>3.6533</td>
<td>339.37</td>
<td>0.7419</td>
<td>2.8789</td>
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<tr>
<td>S0 → S2</td>
<td>4.029</td>
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<td>−0.0099</td>
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<tr>
<td>S0 → S3</td>
<td>4.6646</td>
<td>265.80</td>
<td>1.5917</td>
<td>3.7320</td>
</tr>
<tr>
<td>S0 → S4</td>
<td>4.8756</td>
<td>254.30</td>
<td>0.1487</td>
<td>−0.0096</td>
</tr>
<tr>
<td>S0 → S5</td>
<td>5.2097</td>
<td>237.99</td>
<td>1.3894</td>
<td>3.2991</td>
</tr>
<tr>
<td>TSATL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S0 → S1</td>
<td>2.8676</td>
<td>432.36</td>
<td>0.0000</td>
<td>0.0009</td>
</tr>
<tr>
<td>S0 → S2</td>
<td>3.0430</td>
<td>407.44</td>
<td>0.1566</td>
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<tr>
<td>S0 → S3</td>
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<td>S0 → S4</td>
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<tr>
<td>S0 → S5</td>
<td>4.6848</td>
<td>264.65</td>
<td>2.5340</td>
<td>−4.6987</td>
</tr>
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</table>
and therefore increase the intramolecular charge transfer between the core and the branches. As a result we can conclude that for the system the strong electron acceptors on the fluorine core increase the efficiency of intramolecular charge transfer and thus increase the 3PA cross-section value.

## CONCLUSIONS

In conclusion, we designed and synthesized two fluorine derivatives with symmetric D-$\pi$-$\pi$(A)-$\pi$-D archetype. Through the intensity-dependent transmittance measurements and an accurate fitting method which can be used for a focused Gaussian beam, high 3PA cross-section values in the two molecules have been evaluated to be $7.53 \times 10^{-76}$ cm$^6$ s$^2$/photon$^2$ and $2.53 \times 10^{-76}$ cm$^6$ s$^2$/photon$^2$ for FATT and TSATL, respectively. Obvious optical limiting effects have been shown. The 3PA cross-section value is enhanced by nearly 3-fold through increasing the electronegative character for electron acceptor on the fluorine core (C9 site). The optimized configurations of the two molecules in the ground states show good coplanarity and the intramolecular charge transfer is increased. The 3PA-induced electron transition processes in the two molecules have been assigned. The analysis of ground state molecular 3PA cross-section values by changing the strength of two molecules have been assigned. The analysis of ground state molecules, and to a large extent increase the efficiency of intramolecular charge transfer. The increased intramolecular charge associated with large transition dipole moments of the molecules is responsible for systematic increase of the 3PA cross-section value. It would be a new way to increase the molecular 3PA cross-section value by changing the strength of the electron acceptor linked to the fluorine core.

## ASSOCIATED CONTENT

### Supporting Information

Table of optimized structure parameters of the two molecules. 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.

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