



# The aggregation-induced emission of Methyl-bis-(4-triphenylvinyl-benzyl)-amine in solution with torsional and locked stacking effects

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## ABSTRACT

Herein, we designed and synthesized a compound, Di-TPE, which has the torsional, locked stacking effect in aggregation with aggregation-induced emission properties in solution. The carbon chain of Di-TPE molecule centered on the nitrogen atom acts as a linker to connect two tetraphenylethylene groups. Di-TPE has a torsional stacking effect in the aggregation state, which is very different from the face-to-face stacking mode of TPE. Under the torsional stacking effect, Di-TPE aggregates will also form intra-locked conformation, resulting in the electron cloud distribution of Di-TPE aggregates with the sandwich biscuit shape. This is completely different from TPE and has a profound effect on the spectral properties of Di-TPE. Di-TPE with aggregation-induced emission properties under torsional stacking effect may provide a beneficial help for researchers to expand the field of fluorescent molecules, luminescent devices and biological fluorescent probes.

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## 1. Introduction

Fluorescent molecules have a wide range of applications in the fields of biological fluorescent probes, light-emitting devices [1–8] and fluorescent chemical sensors due to their advantages of high fluorescence intensity, long fluorescence lifetime, and high sensitivity [9–17]. However, the emission of traditional fluorophores tends to be quenched by aggregation at high concentration or aggregation [13–15]. This phenomenon greatly limits the application concentration of fluorescent molecules, resulting in a very limited application range of fluorescent molecules, which cannot be well utilized and developed [18–21].

In order to solve the problem of aggregation quenching or concentration quenching of traditional fluorescent molecules, in recent years, researchers have discovered a series of compounds that are nonemissive when molecularly dissolved but highly emissive when aggregated [22–25]. This phenomenon is called aggregation-induced emission (AIE), and compounds with the property are called AIEgenes [25–29]. The aggregation-induced emission (AIE) properties solve the problem of quenching caused by the aggregation of traditional fluorescent molecules, and expand the application of fluorescent molecules in the fields of biological probes and fluorescent chemical sensors [29–32]. The fluo-

rescence emission of molecules with aggregation-induced emission (AIE) properties is weak in the single-molecule state or molecular dissolved state, and strong in the aggregate state. The limitation of intramolecular rotation is the main reason for the increase of fluorescence emission in aggregate state [13,26–27].

In addition, a typical compound with aggregation-induced emission properties is tetraphenylethylene (TPE), which is nonemissive in a good solvent such as a tetrahydrofuran solution, but has emissivity in a tetrahydrofuran/water mixed solution with a high water content fraction (fw). Its simple structure is widely used in the design of fluorescent biological probes and fluorescent sensors [33–35]. The aggregation-induced emission property is the most prominent property of tetraphenylethylene (TPE). The stacking mode of tetraphenylethylene is face-to-face stacking, but the stacking mode of tetraphenylethylene (TPE) compounds is single, which cannot meet the various needs of researchers for luminescent groups [35–42]. Therefore, it is of great significance to develop molecules with aggregation-induced emission properties with different stacking modes. Herein, we designed and synthesized a compound named methyl-bis-(4-triphenylvinyl-benzyl)-amine (Di-TPE) by using a carbon chain centered on the nitrogen atom as the linker. Di-TPE has aggregation-induced emission properties. Interestingly, the stacking mode of Di-TPE in the aggregate state is different from TPE which is called torsional stacking. The stacking mode makes the electron cloud in the Di-TPE aggregate state present a molecular layer spacing distribution. These findings would

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have important guiding significance for the molecular design and application expansion of AIEgenes.

## 2. Experimental Section

### 2.1. Synthesis of TPE-CH<sub>3</sub>

Bromotri styrene (4.0 g, 11.95 mmol, 1.00 eq), p-methylphenylboric acid (2.43 g, 17.93 mmol, 1.50 eq) and tetramethylammonium bromide (384.5 mg, 1.2 mmol, 0.10 eq) were placed in a 250ml round bottom flask under the protection of argon gas, and toluene (50ml) and 2 mol/L K<sub>2</sub>CO<sub>3</sub> (20ml) were added. Stirring at 90°C for 10 minutes, four (triphenylphosphine) palladium (477.0 mg, 0.4 mmol, 0.03 eq) was added, and the reaction continued for 11 hours. After the reaction, ethyl acetate was used for extraction three times, and Na<sub>2</sub>SO<sub>4</sub> was dried without water. The crude product was separated by silica gel column chromatography. After the experiment, the white solid TPE-CH<sub>3</sub> 2.64 g was obtained and the yield was 66%. TPE-CH<sub>3</sub>: <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.19 – 6.96 (m, 15H), 6.90 (d, J = 2.1 Hz, 4H), 2.25 (d, J = 2.1 Hz, 3H).

### 2.2. Synthesis of TPE-CH<sub>2</sub>-Br

Under the protection of argon, compound TPE-CH<sub>3</sub> (2.64 g, 7.612 mmol, 1.00 eq), N-bromosuccinimide (1.436 g, 8.069 mmol, 1.06 eq) and benzoyl peroxide (18.43 mg, 0.0761 mmol, 0.01 eq) were placed in a 50 ml round bottom flask, and carbon tetrachloride (35 ml) was added. After refluxing at 100 °C for 8 hours, the reactants were cooled to room temperature and added with a few drops of water for stirring. The crude solvent was removed by vacuum distillation and separated by silica gel column chromatography (petroleum ether) to obtain white solid B. After the experiment, 1.08 g white solid was obtained and the yield was 41%. TPE-CH<sub>2</sub>-Br: <sup>1</sup>H-NMR (400 MHz, Chloroform-d) δ 7.19 – 7.05 (m, 15H), 7.01 (d, J = 9.7 Hz, 4H), 4.42 (d, J = 12.0 Hz, 2H).

### 2.3. Synthesis of the Di-TPE

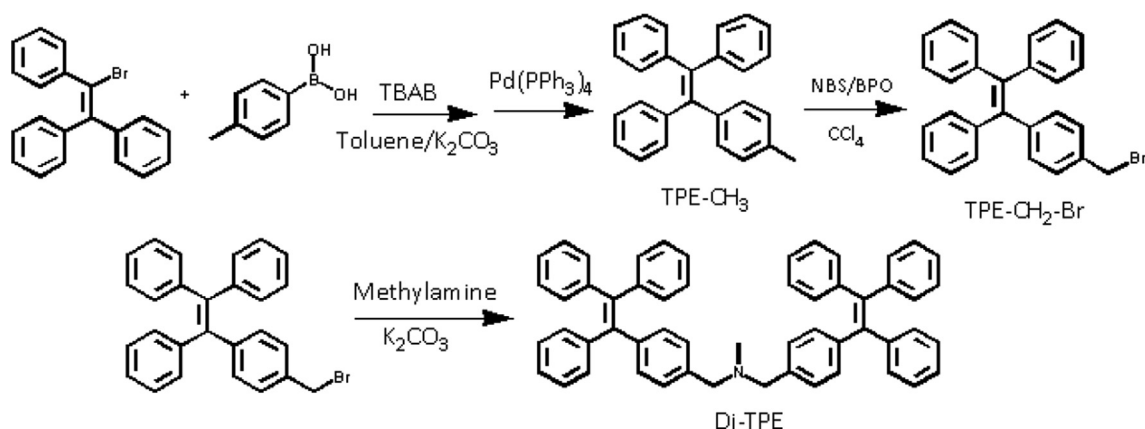
TPE-CH<sub>2</sub>-Br (150 mg, 0.354 mmol), methylamine ethanol solution (56μL, 0.550 mmol), K<sub>2</sub>CO<sub>3</sub> (333.35 mg, 2.412 mmol) were refluxed overnight in acetonitrile (50ml), and the refluxing temperature was set to 84 °C. At the end of the experiment, silica gel column chromatography was used to separate the white solid 0.0502 g, and the yield was 33.5%. Di-TPE: <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.16 – 6.92 (m, 38H), 3.35 (s, 4H), 2.10 (s, 3H).

HRMS (ESI): m/z [M+H]<sup>+</sup> calcd for C<sub>55</sub>H<sub>46</sub>N 720.3552; found 720.3696. [Scheme 1](#).

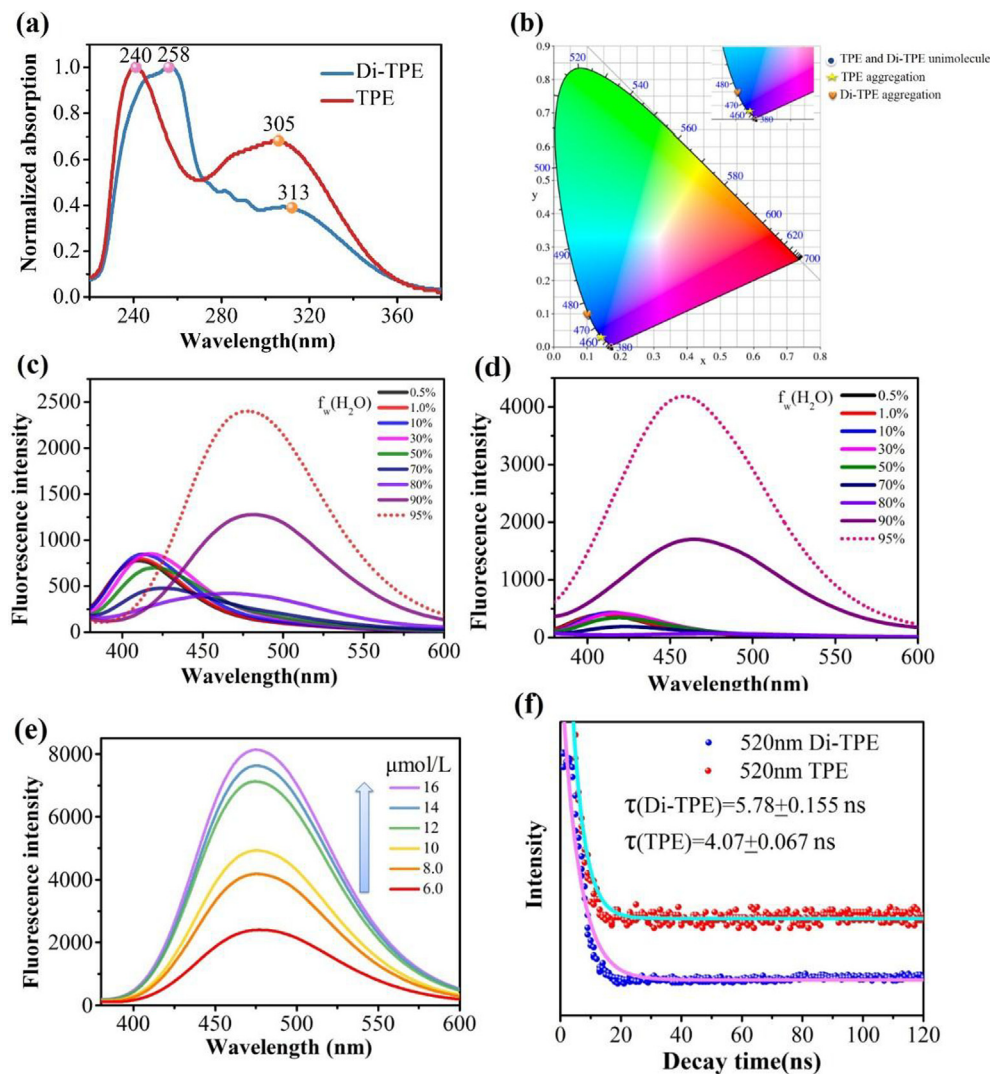
## 3. Results and Discussion

We investigated the UV-vis absorption of Di-TPE ([Figure 1a](#)). Both Di-TPE and TPE have two absorption peaks, which are due to the conjugated structure of the molecules. Both molecules have π – π\* transition and local excitation. The absorption peaks of TPE molecule appear at 240 nm and 305 nm, and the absorption peaks of Di-TPE appear at 258 nm and 313 nm. Compared with TPE, Di-TPE has a red shift of 18 nm. This is due to the fact that there are two conjugated structures in the Di-TPE molecule. The two tetraphenylvinyl groups in the molecule have intramolecular interactions. In addition, the conjugated structure of the lone pair electron on the N atom and the conjugated structure of the tetraphenylethylene group in the Di-TPE molecule have the hyperconjugation effect, which leads to the absorption of Di-TPE red shift.

In order to study the aggregation-induced emission properties of Di-TPE molecules, we measured the emission of Di-TPE in different proportions of THF/H<sub>2</sub>O. As shown in [Figure 1c](#), with the increase of water content in the mixed solution system, the fluorescence emission intensity of Di-TPE gradually increases, especially when the water content increases to 90%, the fluorescence emission intensity will increase sharply. Di-TPE has large solubility in tetrahydrofuran, but very small solubility in water, so THF is a good solvent for Di-TPE, and water is a poor solvent. In the mixed solution of THF/H<sub>2</sub>O with different proportions, the gradual increase of water ratio will cause Di-TPE to aggregate in the solution, the molecular packing will become more and more tight, the π-π interaction between molecules will become more and more intense, so that the emission intensity will increase rapidly. When TPE does not aggregate, the difference between the emission wavelength and intensity and Di-TPE is very small, the emission wavelength of Di-TPE is slightly red-shifted, and the emission intensity increases slightly ([Figure 1d](#)). In the aggregation state, the emission wavelengths of Di-TPE and TPE are quite different. The emission wavelength of TPE is red-shifted to 457 nm, and the emission wavelength of Di-TPE is red-shifted to 478 nm. The emission intensity of Di-TPE is slightly smaller than that of TPE. It is related to the molecular stacking mode and the molecular conformation after stacking, which we will discuss in detail below. In the meantime, we analysed the variation of the emission intensity of Di-TPE molecules with the concentration in the THF/H<sub>2</sub>O mixed solution system with 95% water content ([Figure 1e](#)). With the increase of molecular concentration, the fluorescence emission intensity also gradually increases. Because when the content of



**Scheme 1.** Synthesis route of Methyl-bis-(4-triphenylvinyl-benzyl)-amine (Di-TPE)



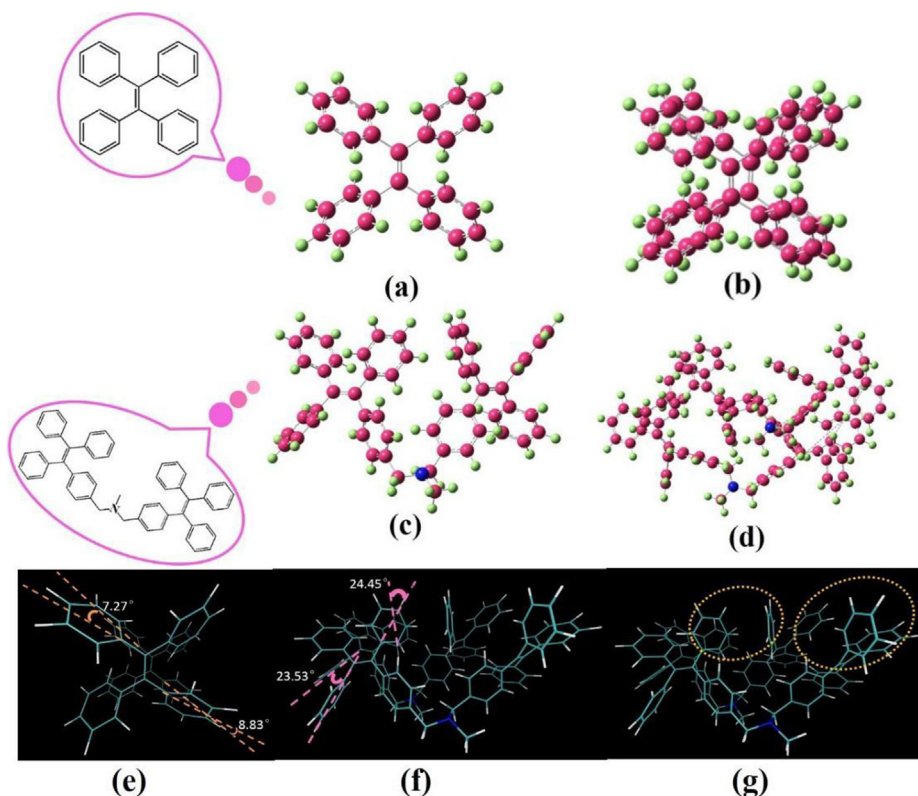
**Fig. 1.** (a) The UV-Vis absorption of Di-TPE and TPE molecule (the solid ball indicates the absorption wavelength). (b) Chromaticity diagrams of TPE and Di-TPE unimolecules and dimers. Fluorescence spectra of the Di-TPE (c) and the TPE molecule (d) in THF/H<sub>2</sub>O mixture ( $6 \times 10^{-6}$  mol/L, fraction of water,  $f_w$ : 0.5–95%,  $\lambda_{ex}$ =316 nm). (e) Fluorescence spectra of Di-TPE at different concentrations in THF/H<sub>2</sub>O mixture (fraction of water,  $f_w$ : 95%,  $\lambda_{ex}$ =316 nm). (f) Time-resolved decay profiles of Di-TPE and TPE molecule ( $6 \times 10^{-6}$  mol/L,  $\lambda_{ex}$ =355 nm).

poor solvent water reaches 95%, the higher the molecular concentration, the closer the aggregation between molecules, and the emission intensity will increase. In order to more directly and vividly highlight the difference in fluorescence emission between TPE and Di-TPE single molecule state and aggregation state, Figure 1b shows the position of the TPE and Di-TPE single molecule state and aggregation state on the chromaticity diagram. Among them, the change between Di-TPE single molecule state and aggregation state is obvious. In addition, we used nanosecond transient spectroscopy to analyze the fluorescence emission lifetimes of Di-TPE and TPE molecules. It can be obtained that the lifetime of Di-TPE molecule is 5.78 ns, and the lifetime of TPE molecule is 4.07 ns (Figure 1f). The Di-TPE molecule contains a bond bridge centered on the nitrogen atom, the molecular configuration is more distorted, the tetraphenyl vinyl groups on both sides have intra-locked conformation, and the molecular vibration is restricted, which leads to the longer lifetime of Di-TPE than TPE.

Figure 2 shows the molecular structure of Di-TPE and the geometrically optimized conformation of its dimer. For better comparison, we also calculated the optimized geometric conformation of the TPE molecule and its dimer. It can be clearly seen that the

Di-TPE molecule contains a bond bridge centered on the nitrogen atom, and the molecular structure is very large, which makes the molecular conformation of Di-TPE twist during aggregation, while the stacking mode of TPE is face-to-face stacking, and the molecular configuration hardly changes. We calculated that the dihedral angles between the corresponding benzene with  $\pi$ - $\pi$  stacking between TPE molecules were  $7.27^\circ$  and  $8.83^\circ$  (Figure 2e). The twisting degree of TPE is very small when stacking, and the stacking mode is face-to-face stacking. For Di-TPE, the dihedral angles between the corresponding benzene that undergo  $\pi$ - $\pi$  stacking are  $23.53^\circ$  and  $24.45^\circ$  (Figure 2f), and the degree of molecular conformation torsion is greater. The stacking mode of Di-TPE is torsional stacking. Interestingly, we also found a locked stacking effect in the dimer of Di-TPE. Two angled benzene planes will lock the adjacent third benzene (Figure 2g). In other words, the torsional stacking effect and the locked stacking effect increase the intermolecular interaction, which has a fixed effect on the molecular configuration, thus leading to the red shift of the aggregation emission wavelength of Di-TPE (Figure 1c).

To better reveal the stacking mode of molecules in the aggregation state, we studied the frontier orbitals of Di-TPE and TPE



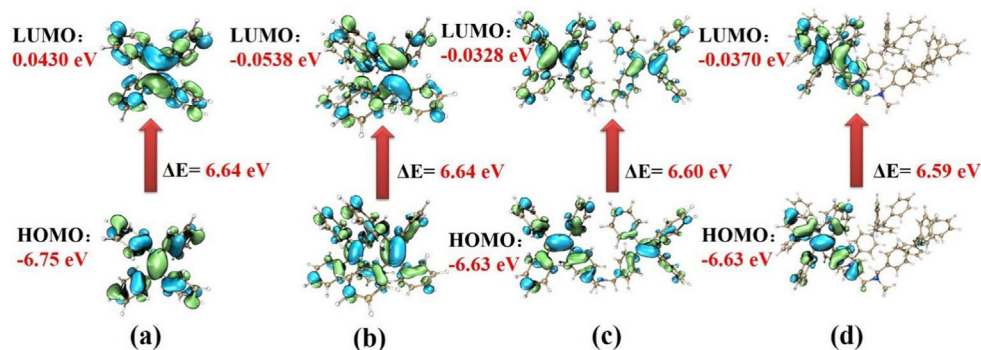
**Fig. 2.** Optimized geometric conformations of TPE (a), TPE Dimer (b), Di-TPE (c) and Di-TPE Dimer (d). (e) Dihedral angle of benzene plane corresponding to  $\pi$  -  $\pi$  stacking between TPE (e) and Di-TPE (f) dimers, dotted line represents the benzene plane. (g) Schematic diagram of the locked stacking effect formed between the three benzene rings of Di-TPE dimer.

molecules by DFT / TDDFT theoretical calculation, and explored the properties of excited states. In the absence of aggregation, the electron clouds of HOMO and LUMO orbitals of TPE molecule are uniformly distributed over the whole molecular group (Figure 3a). There is a bond bridge centered on nitrogen atom in Di-TPE molecule, which makes the electron cloud no longer evenly distributed on the whole molecule. The electron cloud on one tetraphenylethylene group is relatively dense, and the other is relatively sparse (Figure 3c). However, it is worth noting that the electron clouds of the HOMO and LUMO orbitals of the TPE dimer are also uniform on the two TPE molecules, and the electron clouds on the two TPE molecules are almost the same (Figure 3b). In the Di-TPE dimer, the electron cloud is only localized on a tetraphenylvinyl group in a Di-TPE molecule (Figure 3d). It indicates that the face-to-face stacking mode of TPE is beneficial to electron delocalization, and the torsional stacking of Di-TPE is beneficial to the local distribution of

electrons. In addition, what is more interesting is that the Di-TPE molecule contains a bond bridge centered on the nitrogen atom, which has a certain barrier effect on the two tetraphenylethylene conjugated groups and limits the electron transport. The torsional stacking of Di-TPE can block the electron transmission between molecules to a certain extent, resulting in the distribution of the electron cloud in the state of Di-TPE aggregation in a sandwich biscuit shape. The torsional stacking and electron cloud distribution like sandwich biscuit would be of great significance for the development of new AIEgens.

#### 4. Conclusions

In summary, we designed and synthesized a compound, Di-TPE, which has aggregation-induced emission properties under the control of torsional stacking effect. Di-TPE molecules are linked by two



**Fig. 3.** Frontier molecular orbitals (FMOs) of (a) TPE, (b) TPE Dimer, (c) Di-TPE and (d) Di-TPE Dimer.

tetraphenylethylene groups with a nitrogen centered bond bridge as linker. The stacking mode of the traditional aggregation-induced emission molecule TPE is face-to-face stacking, which is conducive to the delocalization of electrons, and the electron cloud of TPE is evenly distributed over the entire molecule in both unimolecular state and aggregated states. The stacking mode of Di-TPE aggregation is torsional stacking. The torsional stacking effect will induce the locked stacking effect. The stacking mode will not only have a profound impact on fluorescence emission and fluorescence lifetime, but also lead to the electron cloud of Di-TPE dimer localized on a tetraphenyl vinyl group of a Di-TPE molecule. The unique torsional stacking effect and electron cloud distribution of Di-TPE molecules may provide researchers with new thoughts for designing AIEgenes, and provide new options for the use of fluorescent probe methods to explore the detection and imaging of substances, organic light-emitting materials and other application fields.

### CRedit authorship contribution statement

**Mengmei Qin:** Conceptualization, Formal analysis, Investigation, Software, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Zibo Wu:** Methodology, Software, Data curation, Visualization. **Jingran Zhang:** Investigation, Data curation, Validation, Resources, Methodology. **Xinyi Xing:** Validation, Resources. **Lina Zhu:** Conceptualization, Writing - review & editing. **Yingqian Zhong:** Supervision, Methodology. **Yurong Guo:** Project administration, Visualization. **Guangjiu Zhao:** Conceptualization, Writing - original draft, Writing - review & editing.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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