Rationalizing the Molecular Design of Hole-Selective Contacts to Improve Charge Extraction in Perovskite Solar Cells

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1. Introduction

Lead halide perovskites present some outstanding photo-physical properties as well as structural flexibility.\(^1\) Perovskite solar cells (PSCs) in particular have shown great potential as the alternative, highly efficient photovoltaics (PVs) to the well-established PV technology.\(^2\) The solution-processed perovskite films show a low density of bulk trap states,\(^3\) which enriches the possible architectures of PSCs.\(^4-6\) Moreover, monolithic films can be easily formed between the electron selective contact (ESC) and the hole selective contact (HSC).\(^6,7\) This further benefits the charge transport inside the bulk perovskite film.\(^8,9\) To further promote the power conversion efficiency (PCE) of PSCs, researchers emphasize the optimization of the interface between perovskite film and ESC/HSC.\(^10\) Tan et al.\(^11\) modified the TiO\(_2\) compact layer with chlorine and they found that the Cl-doped TiO\(_2\) can improve charge extraction efficiency.

Two new hole selective materials (HSMs) based on dangling methylsulfanyl groups connected to the C-9 position of the fluorene core are synthesized and applied in perovskite solar cells. Being structurally similar to a half of Spiro-OMeTAD molecule, these HSMs (referred as FS and DFS) share similar redox potentials but are endowed with slightly higher hole mobility, due to the planarity and large extension of their structure. Competitive power conversion efficiency (up to 18.6%) is achieved by using the new HSMs in suitable perovskite solar cells. Time-resolved photoluminescence decay measurements and electrochemical impedance spectroscopy show more efficient charge extraction at the HSM/perovskite interface with respect to Spiro-OMeTAD, which is reflected in higher photocurrents exhibited by DFS/FS-integrated perovskite solar cells. Density functional theory simulations reveal that the interactions of methylammonium with methylsulfanyl groups in DFS/FS strengthen their electrostatic attraction with the perovskite surface, providing an additional path for hole extraction compared to the sole presence of methoxy groups in Spiro-OMeTAD. Importantly, the low-cost synthesis of FS makes it significantly attractive for the future commercialization of perovskite solar cells.

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form stronger Pb-Cl binding at the surface of perovskite film, as predicted by theory,[12] which delivered an improved PSCs photovoltaic performance and stability. Meanwhile, more works are conducted on the optimization of the perovskite/HSC interface, because there is more room to play with the organic hole selective materials (HSMs) compared to the limited options with the inorganic electron selective counterparts.[13] Therefore, new HSMs have been reported with the main effort to replace the most commonly used but expensive $2,2',7,7'$-tetrakis(N,N-di-$p$-methoxyphenylamine)-9,9'$-spirobi fluorene (Spiro-OMeTAD).[14] Another important section of the fundamental research around the HSM optimization moves toward the improvement of the device stability.[15] For example, Joen et al.[16] synthesized a fluorene-terminated HSM with a fine-tuned energy level and a high glass transition temperature, which resulted in a high efficiency of 23.2% with robust thermal stability.

At the nanometric level, the passivation of the perovskite film under the assistance of Lewis bases could play a crucial role in the charge transfer dynamics at the perovskite/HSM interface.[17] In particular, electron donating thiophene groups bind to the lead ions (Pb$^{2+}$) coordinatively showing excellent defect passivation effect of perovskite film and resulting in enhanced PCE in devices.[18] Later, Saliba et al.[19] reported the synthesis of (2$'$-bis[bis(4-methoxyphenyl)amino]spiroyl[cyclopenta[2,1-b:3,4-b']dithiophene-4,9'$'$-fluorene] (commonly known as FDT) that contains two thiophene groups as the π-linker one of the Spiro-OMeTAD fluorenes. They observed a slightly higher efficiency in devices using FDT than their control cells using Spiro-OMeTAD, which was explained by the interaction between the thiophene group in FDT and the perovskite film. Other studies suggested that the presence of thiophene[20] or phenothiazine[21] is beneficial for charge extraction due to the potential trap passivation via Pb–S interactions. In another work, Hu et al.[22] introduced three new spirofluorene-based HSMs by replacing the para-methoxy substituent in Spiro-OMeTAD with methylsulfanyl, N,N-dimethylamino, and ethyl groups. They found that the methylsulfonyl substituted spirofluorene gave a higher efficiency than the other two HSMs, also outperforming Spiro-OMeTAD. Time-resolved photoluminescence (PL) measurements showed that such compounds had a better hole extraction compared to Spiro-OMeTAD. However, the reason behind the enhanced hole extraction efficiency was not further investigated.

Here, we designed two new HSMs with the aim to connect the methylsulfonyl groups with the C-9 position of the fluorene scaffold characterizing the Spiro-OMeTAD reference. The advantage of these two materials (denoted as DFS and FS) over those previously reported[22] is that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies of these two materials resemble those of Spiro-OMeTAD. Employing molecules with matched energy levels may elucidate additional interactions and exclude the influence on the photovoltaic performance of PSCs brought by the energy alignment differences in HSMs. We carried out time-resolved photoluminescence and electrochemical impedance measurements to quantify the hole extraction efficiency by our HSMs. Supported by density functional theory (DFT) calculations, we attribute the enhanced hole extraction at the perovskite interface to the additive electrostatic attraction between the methylsulfonyl groups of DFS/FS and surface methylammonium of the perovskite film, thus creating a new pathway for charge transfer. In perspective, this study paves the way for new concepts in the molecular design of novel HSMs.

2. Results and Discussion

2.1. Synthesis and Characterization

The synthetic sequences for obtaining FS and DFS are reported in Scheme 1. The sulphur-containing fluorene-based core of these HSMs was obtained in a straightforward manner from

![Scheme 1](image-url)

Scheme 1. Synthetic sequence for the obtainment of FS and DFS: i) tert-BuONa, CS$_2$, methyl iodide, DMSO (95% yield); ii) $p$-methoxy-diphenylamine, Pd$_2$(dba)$_3$/Bu$_3$P, tert-BuONa, toluene, 100 °C (81% yield); iii) $p$-methoxy-diphenylamine, Pd(AcO)$_2$/dppf, tert-BuONa, toluene, 100 °C (34% yield); iv) $p$-anisidine, Pd$_2$(dba)$_3$/Bu$_3$P, tert-BuONa, toluene, 100 °C (65% yield).
commercially available 2,7-dibromofluorene. The synthetic details, nuclear magnetic resonance (NMR) spectra as well as cost estimate[23] are reported in the Supporting Information. (Schemes S1–S4 and Figures S1–S4, Supporting Information)

The stability and thermal behavior of FS and DFS were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements in comparison with the thermal properties of Spiro-OMeTAD reference. (Figure S5a,b, Supporting Information) Both in the case of FS and DFS, the 5% weight loss of the sample commonly accepted as the event associated with the material decomposition, was observed at 347 °C, indicating satisfactory thermal stability, although lower than that of Spiro-OMeTAD (424 °C). The relatively lower decomposition and glass transition temperatures exhibited by FS and DFS are due to the peculiar functionalization of fluorene C-9 position, which is traditionally considered as the weakness point of the aromatic structure and introduces dangling groups endowed with higher degrees of ro-vibrational freedom.[24] The normalized UV–vis absorption spectra of FS and DFS in CH2Cl2 are shown in Figure S5c, Supporting Information. It shows that the two absorption profiles are very similar with an absorption maximum at 380 nm and a shoulder at longer wavelength. The absorption maximum recorded for Spiro-OMeTAD in the same experimental conditions was observed at 386 nm. The optical band gap of FS and DFS determined from the absorption onset (417 and 426 nm for FS and DFS, respectively) are consistent with the different conjugation extension of the two molecules. The main difference in the optical properties concerning that of Spiro-OMeTAD concerns the presence of a broad and weak absorption feature in the wavelength ranging from 450 to 600 nm. According to our previous work,[25] this absorption feature can be ascribed to the sulphur atoms involved n→π* transition. To further clarify this aspect, we theoretically investigated the absorption spectra and the electronic properties of FS and DFS and compared them with those of Spiro-OMeTAD. As it can be deduced from inspection of Table 1, the absorption maxima calculated by time-dependent DFT (TDDFT) are in good agreement with the experimental measurements.

The calculated UV–vis absorption spectra in comparison with the experimental data are given in Figure 1a. Based on calculations, we assign the weak absorption band above 500 nm for FS to the HOMO→LUMO transition (Figure 1b), involving the -S-CH3 groups as final states. The main signal at around 380 nm is related to the HOMO→LUMO+1 transition, mainly involving the molecular core, and higher-lying transition at 365 nm is associated to excitation within the fluorene–S-CH3 groups (Figure 1b). Similar behavior is found for DFS where the low-intensity signal is found at 508 nm. The oxidation potentials of FS and DFS were determined by cyclic voltammograms (CVs) (Figure S5d, Supporting Information). By the electrochemical data, the HOMOs of FS and DFS are estimated to be −5.05 and −5.06 eV, respectively. Meanwhile, Spiro-OMeTAD exhibits a value of −5.09 eV as calculated from Figure S5d, Supporting Information. We also calculated the oxidation potential by DFT calculations, which resulted in the values of −5.11, −4.92, and −4.98 eV, for FS, DFS, and Spiro-OMeTAD, respectively, in line with the electrochemical measurements. The energy levels of FS, DFS, and Spiro-OMeTAD are aligned with ESMs and perovskite layer in Figure 2a, which shows high similarity in energy levels of the studied HSMs in this work. Hole mobility of pristine FS and DFS are characterized using space-charge-limited current (SCLC) method with details given in the Supporting Information (Figure S6, Supporting Information). Pristine DFS and FS show hole mobility of 2.5 × 10−4 and 2.1 × 10−4 cm2 V−1 s−1, slightly higher than that of pristine Spiro-OMeTAD (1.3 × 10−4 cm2 V−1 s−1).[26] 2.2. Device Characterization

DFS and FS have been applied in PSCs where planar SnO2 deposited from chemical bath deposition[27] is used as the

Table 1. Measured UV–vis absorption maxima (CH2Cl2) along with the calculated values of the strongest transitions calculated by Time-Dependent DFT.

|          | Exp. | Calc. |
|----------|------|-------|
| Spiro-OMeTAD | 386  | 387   |
| FS       | 380  | 379   |
| DFS      | 380  | 397   |

Figure 1. a) Absorption spectra for FS (red), DFS (blue), and Spiro-OMeTAD (black). The experimental data are given with solid lines while the calculated spectra are reported with dashed lines. b) Electronic transitions calculated by TDDFT for the FS molecule.
Figure 2. a) Scheme of energy level alignment for each component of PSCs. Note: the energy level of SnO$_2$, CsFAMA, and Au were extracted from the literature data. b) Photovoltaic characterization of DFS (blue line) and FS (red line) in comparison with Spiro-OMeTAD (black line) as the control. Measured under 1 Sun (AM 1.5G, 100 mW cm$^{-2}$) illumination. Scan rate: 100 mV s$^{-1}$. Reverse scan (referred as “re” in the inset table): scanning from high potential to low potential (solid line). Forward scan (referred as “fw” in the inset table): scanning from low potential to high potential (dash line).

ESC, and Cs$_{0.05}$(FA$_{0.87}$MA$_{0.13}$)$_{0.95}$Pb(I$_{0.87}$Br$_{0.13}$)$_3$ triple cation perovskite is used as the light absorber. The cross-sectional scanning electron microscopy (SEM) images of the devices are given in Figure S7, Supporting Information. It shows that a monolithic perovskite film is deposited between the SnO$_2$ ESM and the HSM. A similar perovskite film thickness of around 550 nm is observed for all devices. The light current-voltage ($JV$) curve of the champion device is given in Figure 2b. The photovoltaic parameters are summarized in Table S6, Supporting Information. It shows that devices using DFS and FS as HSMs can achieve efficiencies of 18.4% and 18.6%, respectively, which is competitive to that of the standard, highly optimized, Spiro-OMeTAD (19.0%). The external quantum efficiency (EQE) spectra were measured, as given in Figure S8, Supporting Information. The integrated short-circuit current density ($J_s$) from EQE measurement matches well with the value measured from the $JV$ scan. Dark $JV$ given in Figure S9, Supporting Information shows a better suppression of dark current for devices using DFS and FS as HSMs than that of Spiro-OMeTAD. The box charts of photovoltaic parameters of 18 devices are given in Figure S10, Supporting Information. Particularly, we notice that there is a general enhancement in photocurrent for devices with DFS/FS compared to those of Spiro-OMeTAD based devices, on a par with the champion $JV$ curves given in Figure 2. To gain a better understanding of the interaction between DFS/FS and perovskite at the interface, we conducted steady state and time-resolved PL (TRPL) spectroscopy measurement and electrochemical impedance spectroscopy measurement.

The TRPL spectroscopy measurement of perovskite films with and without ESMs/HSMs have been the subject of several studies mainly conducted by Stranks et al. as well as others. Following absorption of a photon, an electron and hole pair is generated. Charge carriers can either recombine radiatively or be trapped by defects in the bulk and at the surface of the sample. Most of these trap states are shallow in lead-halide perovskites, which means the captured electrons and holes can be released in a short time scale in the range of nanoseconds. This explains the long electron-hole lifetime in perovskite film. Radiative recombination happens in a very short time, and normally appears as a power-law decay in the TRPL measurement, whereas the non-radiative recombination by monomolecular shows a monoexponential decay in the TRPL measurement. It should be noted that the actual TRPL data of the same perovskite sample is highly influenced by the pulse fluence.

When the perovskite film is deposited adjacent to an ESM or HSM, the interpretation of TRPL data can be more complicated. First, electrons or holes can be extracted by the ESM or HSM and then lead to a decrease in PL intensity. The more efficient in charge extraction, the more efficient in quenching of PL intensity. Second, the ESM/HSM may bring some defects at the interface with the perovskite, which results in non-radiative recombination and leading to drops in PL intensity. The second role played by ESM/HSM has been confirmed by Stolterfoht et al. who compared a range of ESMs and HSMs using the TRPL and absolute PL spectra measurement. However, it should be noted that these two roles played by ESMs/HSMs both involve a monomolecular process that leads to a monoexponential decay in PL intensity. Moreover, these two processes happen simultaneously and are connected. As a result, when we fit the TRPL curve with a monoexponential curve, the PL lifetime calculated from the fitting contains the charge transfer process as well as the non-radiative recombination process. The reciprocal of the PL lifetime refers to the overall rate constant of these two processes. A faster charge transfer process or increased non-radiative recombination will both lead to a shorter PL lifetime.

Figure 3a shows the PL decay of perovskite film with and without top layers. We can observe a faster decrease in the PL intensity of the three HSMs compared to pristine perovskite film. In particular, the PL decay of perovskite films coated with...
either DFS or FS, lead to a stronger quenching effect of the PL intensity compared to Spiro-OMeTAD. Steady-state PL spectra were given in Figure S11, Supporting Information. It shows a clear decrease in the absolute PL intensity in samples: neat perovskite > Spiro-OMeTAD > DFS > FS, which agrees well with what is observed in TRPL measurement. Based on the previous work,[30–32] we fit the PL decay curve with the monoexponential decay function given in Equation (1).[34,35]

$$I_t = I_0 \exp \left(-\frac{t}{\tau}\right)$$  

where $I_t$ and $I_0$ refer to the PL intensity at time $t$ and zero, and $\tau$ is the PL lifetime. It measures the decay rate of PL intensity. For perovskite films without any ESMs/HSMs, $\tau$ is the reciprocal of the rate constant of non-radiative recombination process. For perovskite films coated with ESMs/HSMs, $\tau$ takes into account the rate constant of charge transfer and non-radiative recombination. Figure 3b shows the PL lifetime, $\tau_{PL}$ of perovskite films with and without HSMs. The pristine perovskite films show a slightly longer lifetime than that of perovskite films coated by a thin layer of poly(methyl methacrylate) (PMMA), which indicates the robustness of triple-cation perovskite films during the TRPL measurement conducted in ambient atmosphere. DFS and FS as HSMs show a similar value of 26.2 and 24.4 ns, respectively, which is about one quarter of that of Spiro-OMeTAD (103.5 ns). As previously discussed, the short PL lifetime indicates a faster charge transfer process or a faster non-radiative recombination process. To investigate which process dominates we conducted electrochemical impedance spectroscopy measurements.

Impedance spectra of the devices were conducted at open-circuit at a low light intensity equivalent to 0.1 Sun to study the recombination information inside the system. Figure 4a shows the Nyquist plot of the devices. Based on Bisquert and Garcia-Belmonte’s work,[36,37] the first semi-circle appeared at high frequency range at $10^{3}$–$10^{5}$ Hz correlates to the dielectric property of bulk perovskite film, and the second semi-circle presented at low-frequency range at $10^{0}$–$10^{1}$ Hz correlates to the surface charge recombination at the interface of perovskite and electron/HSC layers. The equivalent circuit used to analyze the impedance data is given in Figure S13, Supporting Information. The diameter of the high frequency semicircle ($R_1$) and low frequency semicircle ($R_3$) correlates to the recombination
resistance in the bulk and at the interface of perovskite film, respectively. Both relate to the surface recombination current flux.[37,38] The frequency where the imaginary part of impedance, $-\frac{Z}{\pi}$ reaches the maximum can be referred to as the maximum frequency, $f_{\text{max}}$. The reciprocal of $f_{\text{max}}$ correlates to a time constant.[39] In particular, $(f_{\text{max}})^{-1}$ of the second semi-circle corresponds to the recombination lifetime. To distinguish this recombination lifetime from the non-radiative recombination lifetime extracted from TRPL measurement, it is noted as $\tau_2$. It should be noted that the recombination lifetime extracted from impedance spectra contain different meanings from the non-radiative recombination lifetime and they were measured under different conditions. One would expect, $\tau_2 > \tau_{\text{rel}}$. It can be seen from Figure 4a that the diameter of the first semi-circle and the second semi-circle in devices of DFS is larger than that of FS and the latter is larger than that of Spiro-OMeTAD ($R_1 > R_2$). This information further correlates to the capacitance or charge carrier density at the interface. Figure 4b shows the dependence of capacitance as a function of frequency, calculated from the equation $C = 1/(2\pi f Z)$, where $f$ is the frequency and $Z$ is the impedance. It can be seen that the chemical capacitance, $C_p$, at low frequency of the devices of DFS is lower than that of FS and lower than that of Spiro-OMeTAD ($C_p$: DFS $>$ FS $>$ Spiro-OMeTAD). In other words, the charge carrier density at the interface for devices of DFS is less than that of FS and less than that of Spiro-OMeTAD. It means that at the same quantity of photo-generated electron and holes in the bulk of perovskite film, devices with DFS and FS is more efficient in charge extraction and thus less charges are accumulated at the interface.[39,40] This conclusion supports that the shorter PL lifetime observed in TRPL measurement is attributed to the faster charge transfer. In addition, it is also noted that the bulk capacitance at high frequency range is identical the same for these devices because the bulk capacitance is mainly related to the film thickness and area of the bulk perovskite film. As we explained in the experimental section in the Supporting Information, the devices were prepared under the same condition. Also, the film thickness of the perovskite layer can be measured from the cross-sectional SEM image given in Figure S7. Supporting Information. The fast extraction of holes at the interface of perovskite/HSMs in devices of DFS/FS also results in an effective suppression of bulk recombination inside the perovskite film as $R_2$ is found to be higher than that of Spiro-OMeTAD based devices.

Meanwhile, we also notice that there is a general trend in the $V_{\text{oc}}$: Spiro-OMeTAD > DFS > FS. It would be quite interesting to study the origin for the difference in $V_{\text{oc}}$ of these HSMs. Indeed, $V_{\text{oc}}$ of a PSC can be influenced by many factors, such as bulk non-radiative recombination inside the perovskite film and the interfacial non-radiative recombination at the interface between perovskite and HSMs. As we used the same device architecture for all the HSMs in this work, one would expect the bulk recombination in the perovskite film to be the same. From the TRPL measurement, the impedance spectroscopy and the dark current measurement, we believe that interfacial recombination for FS and DFS was more suppressed than that of Spiro-OMeTAD. One possible reason for the relative low $V_{\text{oc}}$ in FS and DFS based regular structured PSCs can be the migration of gold from the metal electrode.[41] Figure S7, Supporting Information shows that FS and DFS have a slightly low film thickness compared to Spiro-OMeTAD. This is resulted from the relatively low molecular weight of FS and DFS that are deposited at the same concentration and spin-coating speed as that of Spiro-OMeTAD. A thinner film thickness of HSM is not beneficial for n-i-p devices because the gold migration underlines the potential $V_{\text{oc}}$, which explains what we have observed for FS and DFS based PSCs. The relatively high $J_{\text{sc}}$ but low $V_{\text{oc}}$ together with comparable $FF$ in FS and DFS based PSCs finally make them of similar photovoltaic performance to Spiro-OMeTAD based devices.

Comparing the molecular structure of FS with that of Spiro-OMeTAD, it is clear how, let alone the spiro-structure, the main difference resides in the presence of a methylsulfanyl group at the fluorene C-9 position. In a simulation study on surface interaction between methoxy anchors and lead iodide perovskite by Torres et al.[42] they reported that the methoxy group adsorbed to the surface of perovskite via the interaction with methylammonium cation governed by electrostatic interaction. To further investigate the interface interaction between DFS/FS and perovskite, we conducted the DFT simulations. In particular, we modeled the interface of the more stable MAI-terminated perovskite slab exposing (001) facet with FS and Spiro-OMeTAD. Notice that this is an idealized surface, since we use a fully passivated MAI-terminated surface, while disorder and surface reconstruction may alter the exact nature of the interface. Still, by performing a direct comparison between the HSMs interacting with the same perovskite surface, we may extract useful information on the fundamental interactions ruling the functioning of such interface. The optimized geometries and the electronic properties of the two HSM/perovskite interfaces are shown in Figure 5. As suggested by Torres et al.[42] Spiro-OMeTAD interacts via hydrogen bonding methoxy oxygen with the MA$^+$ cations of the perovskite surface, as highlighted by the blue circle in Figure 5c. In the FS HSM case, we found that in addition to the MA$^+$—O-CH$_3$ hydrogen bond (highlighted by the blue circle in Figure 5a), a stabilizing interaction was formed between the sulfur atoms and the surface MA$^+$ cations (highlighted by the red circle in Figure 5a). We then calculated the energy ($\Delta E$) associated with the interface formation. We found that the FS molecule has a strongly favored interaction energy ($\Delta E = -1.52$ eV) compared to that of Spiro-OMeTAD ($\Delta E = -0.11$ eV). This underlines that the additional specific hydrogen bond interaction between MA$^+$ and methylsulfanyl group in FS significantly increases the stability of the perovskite/FS interface. The electronic properties of the perovskite/HSM interface presented in terms of the interface density of states (DOS) are given in Figure 5b,d. FS shows more positive HOMO energy concerning Spiro-OMeTAD when interacting with the MAI-terminated perovskite slab. This more positive energy level of the FS HSM and the related energy alignment at the perovskite valence band leads to the higher driving force for the hole extraction, and thus a faster charge transfer as observed in the TRPL and the impedance measurements. The overall picture extracted from the theoretical
simulation suggest that i) the electrostatic effect between the methylsulfanyl and MA$^+$ brings about an extra interaction path for DFS/FS compared to the methoxy group bound with MA$^+$ in the case of Spiro-OMeTAD; and ii) the electronic properties and relative energy alignment at the valence band between the FS and perovskite provides a higher driving force for the hole injection process upon photoexcitation.

3. Conclusions

In this work, we reported two new HSMs (DFS and FS) that exhibit similar LUMO and HOMO positions to that of Spiro-OMeTAD. The TRPL measurement together with impedance spectra revealed a more efficient hole extraction in DFS and FS than that of Spiro-OMeTAD. DFT calculations revealed that the fast charge extraction was partially originated from the formation of an additional path for charge extraction, that is, the electrostatic effect between methylsulfanyl in FS/DFS and MA$^+$ at perovskite surface, compared to the hydrogen bond between methoxy group and MA$^+$. The optical and electrochemical measurements in line with DFT calculations show that the preferred energy alignment at the interface of FS/DFS and perovskite also contributes to the better charge extraction. As a result, this work reveals the reasons for the better charge transfer for FS/DFS that contain a methylsulfanyl group. More importantly, these findings pave the way to innovative ideas regarding the molecular design of the next generation of HSMs for application in efficient PSCs.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
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