High Photon Upconversion Efficiency with Hybrid Triplet Sensitizers by Ultrafast Hole-Routing in Electronic-Doped Nanocrystals

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Low-power photon upconversion (UC) based on sensitized triplet–triplet annihilation (sTTA) is considered as the most promising upward wavelength-shifting technique to enhance the light-harvesting capability of solar devices. Colloidal nanocrystals (NCs) with conjugated organic ligands have been recently proposed to extend the limited light-harvesting capability of molecular absorbers. Key to their functioning is efficient energy transfer (ET) from the NC to the triplet state of the ligands that sensitize free annihilator moieties responsible for the upconverted luminescence. The ET efficiency is typically limited by parasitic processes, above all nonradiative hole-transfer to the ligand highest occupied molecular orbital (HOMO). Here, a new exciton-manipulation approach is demonstrated that enables loss-free ET by electronically doping CdSe NCs with gold impurities that introduce a hole-accepting intragap state above the HOMO energy of 9-anthracene acid ligands. Upon photoexcitation, the NC photoholes are rapidly routed to the Au-level, producing a long-lived bound exciton in perfect resonance with the ligand triplet. This hinders hole-transfer leading to ≈100% efficient ET that translates into an upconversion quantum yield as high as ≈12% (≈24% in the normalized definition), which is the highest performance for NC-based upconverters based on sTTA to date and approaches the record efficiency of optimized organic systems.

Despite this promise, the application of sTTA-UC is still hindered by the limited choice of organic moieties with optically accessible long-lived triplet states (i.e., sufficiently efficient intersystem crossing) necessary to act as triplet sensitizers and by their typically narrow absorption bandwidth, which caps their spectral-harvesting capability of solar light. To overcome this issue, several strategies have been introduced, such as the use of multicomponent or multilayer systems exploiting sensitizers with complementary absorption properties.[11–13] More recently, colloidal semiconductor nanocrystals (NCs)[14,15] have been proposed as broadband-absorbing component of hybrid sTTA-UC sensitizers.[16–19] NCs offer several advantages over molecular photosensitizers, including facile preparative synthesis via scalable colloidal methods, photostability, size-tunable electronic and photophysical properties,[15] large molar extinction coefficients, and broadband optical absorption extendable from the UV to the near-infrared spectral region,[20–22] which is key for coupling sTTA-UC with silicon-based devices. Furthermore, NCs feature a versatile surface chemistry that enables their postsynthesis functionalization with a variety of molecular species, including suitable derivatives of conjugated organic dyes.[23] As a result, as sketched in Figure 1A for the upconverted photons are generated by the radiative decay of fluorescent singlet states obtained through the fusion after collision of optically dark triplets of two annihilator molecules (often referred to also as emitters). Such triplet states are populated via Dexter energy transfer (ET) from a low-energy light-harvesting moiety, commonly referred to as the sensitizer.[5,6,7] With optimized organic sensitizer/annihilator pairs UC quantum yields (QYuc) as high as 30% have been obtained at excitation intensities comparable to solar irradiance, not far from energy-conservation limit of QYuc = 50%.[8] Crucially, the sTTA-UC process is activated upon absorption of noncoherent photons and its efficiency at solar irradiance levels is orders of magnitude higher than typical noncoherent light upconverters based on lanthanide ions.[9] For this reason, sTTA-UC is considered as the most promising upward wavelength-shifting approach to recover the sub-bandgap portion of the solar spectrum of most photovoltaic or photocatalytic devices.[5,10,11]
case of CdSe NCs functionalized with 9-anthracencarboxylic acid (9-ACA), NCs and conjugated dyes can be rationally combined so as to create hybrid sensitizers,[16–18,24] in which the NC absorbs and transfers the luminous energy via Dexter ET (ET′ in Figure 1A) to the triplet state of a surface-attached organic moiety (hereafter referred to as triplet acceptor). The resulting excited triplet state acts as an energy bridge to populate, via a second Dexter-type ET process (ET″), the long-lived triplet state of a free emitter, whose fusion with the excited triplet state of a second emitter (generated through an identical multistep process) finally generates a highly emissive singlet responsible for the upconverted luminescence.[4,6,7]

Over the years, tremendous progress in the design of such NC-organic hybrid sensitizers has enabled a substantial growth of the sTTA-UC performance, as highlighted in Figure 1B, where we report the chronological evolution of the QYuc since their appearance in 2015. White circle, ref. [21]; black circle, ref. [25]; white diamond, ref. [23]; black diamond, ref. [26]; white triangle, ref. [22]; black reversed triangle, ref. [27]; white reversed triangle, ref. [27]; black triangle, ref. [28]; black hexagon, ref. [24]. The red star marks the efficiency obtained in this work. The QYuc values are reported according to the standard convention (Supporting Information). C) Energy diagram and mechanistic picture of the hole-transfer process that outcompetes ET′ in CdSe NCs functionalized with 9-ACA. D) In CdSe NCs with Au⁺ dopants, hole-transfer is outpaced by the ultrafast localization of the photohole in the intragap states (∼100 ps) associated with the d-levels of Au⁺, leading to the formation of a bound exciton perfectly resonant with the triplet state of 9-ACA. As a result, the ET′ step reaches 100% efficiency.

Figure 1. Sensitized sTTA-UC in hybrid NC-based systems and hole rerouting strategy using electronic-doped NCs. A) Energy flux in sTTA-UC. Upon absorption of a green photon by the NC, the exciton energy is transferred via energy transfer (ET′) to the triplet acceptor ligand that then populates the triplet state of the emitter via ET″. The annihilation of two emitter triplets (TTA) results in the formation of a high-energy fluorescent singlet state responsible for the upconverted blue luminescence. B) Chronological evolution of the sTTA-UC quantum yield QYuc in hybrid systems since their appearance in 2015. White circle, ref. [21]; black circle, ref. [25]; white diamond, ref. [23]; black diamond, ref. [26]; white triangle, ref. [22]; black reversed triangle, ref. [27]; white reversed triangle, ref. [27]; black triangle, ref. [28]; black hexagon, ref. [24]. The red star marks the efficiency obtained in this work. The QYuc values are reported according to the standard convention (Supporting Information). C) Energy diagram and mechanistic picture of the hole-transfer process that outcompetes ET′ in CdSe NCs functionalized with 9-ACA. D) In CdSe NCs with Au⁺ dopants, hole-transfer is outpaced by the ultrafast localization of the photohole in the intragap states (∼100 ps) associated with the d-levels of Au⁺, leading to the formation of a bound exciton perfectly resonant with the triplet state of 9-ACA. As a result, the ET′ step reaches 100% efficiency.

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carrier transfer from core/shell NCs to surface ligands, but the increased donor–acceptor distance between the NC core and the triplet acceptor lowers the ET\(^+\) rate in favour of radiative exciton decay, as shown for PbS/CdS and CdS/ZnS NCs functionalized with (5-carboxylic acid tetracene)\(^{[28,32]}\) or 2,5-diphenylloxazole molecules.\(^{[38]}\)

A strategy for suppressing efficiency losses associated to hole-transfer/trapping, that has not been explored so far, would be to employ NCs with an engineered intragap hole-accepting state lying above the HOMO energy of the triplet acceptor and featuring a higher hole-capturing rate. For this scheme to be effective, upon photoexcitation, ultrafast rerouting of the BE hole into such an intragap state should generate a bound exciton—featuring a CB electron orbiting within the Coulomb potential of a localized photohole—with energy matching the triplet state of the triplet acceptor. Such a design would provide multiple benefits for the upconversion process: the intragap photohole would be unaffected by transfer to the triplet acceptor HOMO (or trapping) and, owing to the reduced spatial overlap between the electron and hole wavefunctions, the exciton radiative recombination rate would be significantly lowered with respect to the BE exciton, thus favoring Dexter ET\(^+\) over radiative decay.\(^{[18]}\) Also crucially, by manipulating the energetics of the hole-related process, this scheme does not require heterostructuring with thick wide-bandgap shells and would thus impose no limitation to ET\(^+\) due to increased donor–acceptor distance.

In this work, we realize this regime for the first time by exploiting the ultrafast hole dynamics in CdSe NCs electronically doped with Au\(^+\) cations. In these systems, similar to Cu\(^+\)- or Ag\(^+\)-doped NCs,\(^{[36,37]}\) the d-electrons of Au\(^+\) impurities (in 5d\(^{10}\) electronic configuration) introduce intragap hole acceptor states at \(\Delta E_{\text{VB-Au}} \approx 0.6\) eV above the VB maximum that localize the photohole in \(-1-2\) ps.\(^{[36]}\) This gives rise to a bound exciton with the delocalized CB electron, whose radiative decay yields the characteristic long-lived, Stokes-shifted photoluminescence (PL). Importantly, since the Au\(^+\) states are pinned to the host VB, the energy of the bound excitons can be tuned by control of the particle size so as to maximize the energy resonance with the triplet acceptor moiety of choice, 9-ACA. This represents the best candidate for validating our hole-routing concept in the triplet state of the triplet acceptor.

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cdSe NCs doped with Au\(^+\) impurities were synthesized following the method reported in ref. \([36]\) using oleic acid (OA) as surface ligands. The particle size is 2.3 nm (Figure S1, Supporting Information) so as to maximize the spectral resonance between the emission energy of the doped NCs and the triplet state of the ligand. After purification, the native OA ligands were replaced by 9-ACA moieties. Details of the synthesis procedure and structural characterization of the NCs are reported as the Supporting Information. To quantitatively evaluate the effectiveness of the hole routing strategy, we performed side-by-side spectroscopic investigations of toluene dispersions (with identical absorbance of 0.13 OD at 532 nm) of undoped and Au-doped CdSe NCs before and after ligand exchange with 9-ACA molecules. Figure 2A,B shows the optical absorption and PL spectra of CdSe and Au:CdSe NCs both as-synthesized (OA-capped) and functionalized with 9-ACA; the corresponding PL decay curves are shown in Figure 2C,D, respectively. Both doped and undoped NCs show a well-defined 1S absorption peak confirming the good size dispersion of the NCs and that the incorporation of Au\(^+\) impurities does not perturb the electronic structure of the NC host, in agreement with previous studies.\(^{[36]}\) The as-synthesized undoped NCs feature the typically narrow band-edge PL of CdSe NCs (Stokes shifted of \(-80\) meV from the respective 1S absorption peak) and a weak broadband emission at lower energies commonly ascribed to surface traps.\(^{[39]}\) The time decay of the band-edge PL (Figure 2C) is multiexponential consistent with the core-only nature of the NCs and features an effective lifetime \(\tau_{\text{band edge}} = 40\) ns (Table 1, Supporting Information). Doping with Au\(^+\) drastically modifies the PL spectrum and dynamics of the NCs, with the suppression of the band-edge PL in favor of a broad, long-lived emission centered at \(\approx 670\) nm (1.85 eV). In agreement with the mechanistic scheme drawn in Figure 1D and in the inset of Figure 2B, as well as with previous reports on NCs doped with group 11 metals,\(^{[36,37]}\) this intragap emission, hereafter referred to as Au-PL, is ascribed to the radiative decay of the CB electron in the d-states of gold following the transient oxidation of Au\(^+\) to Au\(^{2+}\) upon ultrafast localization of the VB hole according to the reaction \(\text{Au}^+ + \text{h}_{\text{VB}} \rightarrow \text{Au}^{2+}\).

The large Stokes-shift, \(\Delta E_{\text{VB-Au}} = 650\) meV, separating the Au-PL from the respective 1S absorption peak corresponds to the energy difference between theVB and the t-states of the Au dopants resulting from the splitting of the d-manifold by the crystal-field. The residual band-edge PL observed for the Au:CdSe NCs is due to a minor population of undoped CdSe NCs in the ensemble. Consistent with the reduced wavefunction spatial overlap between the CB electron and the Au-localized hole with respect to the intrinsic band-edge exciton,\(^{[36]}\) the Au-PL in as-sensitized Au:CdSe NCs features a slower kinetics (Figure 2D and Figure S3, Supporting Information). Specifically, the decay is multiexponential with faster components ascribed to nonradiative losses likely associated to trapping in surface defects (notice that neither the doped NCs are passivated with wide bandgap shells) and a slower dominant tail due to the decay of bound excitons. The effective lifetime of the Au-PL extracted as the weighted average between the decay components is \(\tau_{\text{Au-PL}} = 153\) ns.

To estimate the efficiency of the ET\(^+\) channel and thereby to assess the effective suppression of nonradiative losses by
hole-transfer to the triplet acceptor in Au-doped CdSe NCs, we monitored the relative PL intensity and dynamics of undoped and doped NCs upon replacing the native OA ligands with 9-ACA. As shown in Figure 2A,B, in both cases the functionalization with 9-ACA leads to the essentially complete suppression of the cw PL. Crucially, however, the corresponding time-resolved PL measurements reported in Figure 2C,D—also confirmed by the UC efficiency measurements reported in Figure 3—reveal that the photophysical process underpinning the observed PL quenching is drastically different in doped versus undoped NCs. Specifically, upon replacing OA with 9-ACA, the undoped NCs show a dramatic drop of the zero-delay PL intensity (I₀) accompanied by the substantial acceleration of their PL lifetime (estimated as the time after which the PL intensity has dropped by a factor e). Consistent with previous reports, the zero-delay drop is ascribed to ultrafast exciton dissociation by hole-transfer to 9-ACA—with some minor contribution by hole trapping in surface defects due to incomplete surface coverage by 9-ACA molecules—occurring on a timescale faster than our experimental resolution and affecting the vast majority (>95%) of the NC population. The accelerated PL decay, on the other hand, is caused by ET to 9-ACA in the complementary minor fraction (<5%) of the NC ensemble, in which hole-transfer is inefficient. From the acceleration of the PL lifetime (∆τ/τ₀ ~ 5 ns vs ∆τ/τ₀ ~ 40 ns), we estimate that, in such a subpopulation of NCs, ΦET = 1 − τᵦ₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋˓→  

A strikingly different behavior is found for the PL decay of Au: CdSe NCs (Figure 2D). Specifically, upon replacing OA with 9-ACA, the Au-PL undergoes exclusively a substantial acceleration of its kinetics, with no drop of its zero-delay intensity (η = 1). This behavior strongly suggests that the hole-routing process in Au: CdSe NCs is effective in preventing the ultrafast hole-transfer to the HOMO level of 9-ACA in the whole NC ensemble. Consistently, the ET process shortens the PL decay time from τᵦ₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋˓→
upconverting mixture of DPA and the 9-ACA-functionalized Au: CdSe NCs under increasing cw laser excitation fluence at 532 nm (that is, below the energy gap of DPA) are reported in Figure 3A, showing the characteristic emission profile of DPA peaked at 440 nm (the spectra for the solution featuring the undoped NCs are shown in Figure S5 in the Supporting Information). The corresponding time decay curve measured using pulsed 532 nm laser excitation at high intensity (10 W cm$^{-2}$) is shown in Figure 3B. Consistent with previous reports, the decay kinetics of the delayed fluorescence intensity ($I_{\text{uc}}$) excited via sTTA-UC is orders of magnitude slower than the DPA prompt fluorescence ($\tau = 8$ ns$^{[40]}$) and it is described by the relation $I_{\text{uc}}(t) \propto \left( 1 - \Phi_{\text{TTA}} \right)^2 / \left( e^{-\gamma_T t} - \Phi_{\text{TTA}} \right)^2$, where $k_T$ is the spontaneous decay rate of the DPA triplet and $\Phi_{\text{TTA}}$ is the TTA yield.$^{[41]}$ The fit of the experimental data yields $k_T = 6.8$ kHz, in agreement with the literature, and $\Phi_{\text{TTA}}$ as large as 0.90 (i.e., 90%), which is consistent with the high excitation intensity employed (vide infra).$^{[42]}$ Finally, in Figure 3C we compare the evolution of the global sTTA-UC quantum yield ($\Phi_{\text{UC}}$ as expressed as the ratio between the number of upconverted photons emitted by DPA and the number of incident photons absorbed by the NC sensitizers) with the absorbed excitation intensity ($I_{\text{exc}}$), see the Supporting Information) in upconverting solutions of DPA with either 9-ACA-functionalized undoped or Au-doped CdSe NCs. Both samples behave according to the bimolecular nature of the TTA process in which the triplet annihilation rate ($k_{\text{TTA}}$) is proportional to the density of emitter triplets $T$ by $k_{\text{TTA}} = \gamma_T T$, where $\gamma_T$ is the second order rate constant that characterize the TTA.$^{[43]}$ Specifically, in the low excitation regime, where $k_{\text{TTA}} \ll k_F \Phi_{\text{UC}}$ (as well as $\Phi_{\text{TTA}}$) grows linearly with increasing $I_{\text{exc}}$ and gradually plateaus to its maximum value in the high excitation regime, when the triplet density is so large that TTA becomes the dominant deactivation channel for the emitter triplets. The excitation intensity at which $\Phi_{\text{UC}}$ is half of its saturation value is typically referred to as the excitation threshold for TTA, and is a relevant figure of merit that marks the beginning of the high excitation regime.$^{[35,44]}$ It is worth noting that, as detailed in the Supporting Information, both $\Phi_{\text{UC}}$ and the excitation threshold $I_{\text{ex}}$ depend on the efficiency of the ET$^+$ step by which the NC sensitizes the 9-ACA triplet: the first grows linearly with $\Phi_{\text{ET}^+}$ whereas the latter scales with $(\Phi_{\text{ET}^+})^{-2}$. As a result, owing to the effective suppression of nonradiative losses due to hole-transfer that boosts $\Phi_{\text{ET}+}$ from the Au:CdSe NCs to their 9-ACA ligands, the upconversion efficiency saturates at the unprecedented value of $\Phi_{\text{UC}} = 12 \pm 1\%$ (24 $\pm$ 2% in the normalized convention), which is nearly 40 times higher than for the standard undoped NCs ($\Phi_{\text{UC}} = 0.3\%$) in good agreement with the observed enhancement of $\Phi_{\text{ET}+}$. This result represents the highest upconversion efficiency value reported to date for hybrid sensitizers for sTTA, and unambiguously confirms the validity of the proposed exciton manipulation approach to efficiently drive the energy migration across from NCs to conjugated organic ligands. As a further demonstration it should be noted that, as highlighted in Figure 3C, through the use of Au-doped NCs the upconversion excitation threshold is lowered by nearly one order of magnitude with respect to the control solution (from 1.8 to 0.2 W cm$^{-2}$), thus enabling efficient UC at substantially lower illumination densities thanks to their enhanced triplet sensitization ability.
In summary, we have demonstrated a novel strategy to boost the efficiency of hybrid sTTA upconversion systems by using electronic-doped semiconductor NCs as light harvesters to populate the long-lived triplet states of surface-attached conjugated organic moieties. The key aspect of our design is the controlled introduction of a hole-accepting state associated with the electronic dopant within the forbidden gap of the NC that rapidly routes the photohole to an energy above the HOMO level of the organic ligand. This enables us to completely suppress excitation losses by nonradiative hole-transfer that is a detrimental parasitic process strongly limiting the efficiency of conventional NC-organic sensitizers for sTTA-UC. Owing to their nearly 100% efficient ET yield from the NC exciton to the ligand triplets, our surface functionalized doped-NCs enabled us to obtain photon upconversion yield as high as 12% (24%), representing a record performance for hybrid upconverters based on sTTA. We highlight that the strategy proposed here is not limited to the reported material system, but it could be readily applied to any hybrid architecture which requires tuning of the band alignment between its constituents. As such, our approach can be translated to engineer narrower bandgap NCs for upward as well as for downconversion photonic applications based on sTTA. We highlight that the strategy proposed here is not limited to the reported material system, but it could be readily applied to any hybrid architecture which requires tuning of the band alignment between its constituents. As such, our approach can be translated to engineer narrower bandgap NCs for upward as well as for downconversion photonic applications based on sTTA. We highlight that the principle be adapted to rationally design multicomponent systems to recover sub-bandgap photons, thus further pushing these technologies. Indeed, the nanocrystal size, composition, shape, and dopant species, as well as the energy-receiving moiety (either organic ligands or other inorganic nanoparticles) can in principle be adapted to rationally design multicomponent systems for upward as well as for downconversion photonic applications that require efficient energy transport across any nanointerface without incurring into losses due to ultrafast carrier transfer, including photochemical synthesis, photoredox catalysis, photostimulation of biologic and metabolic processes, and singlet oxygen generation for photodynamic therapy.

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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