Access to Multiblock Copolymers via Supramolecular Host−Guest Chemistry and Photochemical Ligation

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S *Supporting Information*

ABSTRACT: We combine supramolecular host−guest interactions of β-cyclodextrin (CD) with light-induced Diels−Alder reactions of 2-methoxy-6-methylbenzaldehyde (photoenol, PE) for the formation of multiblock copolymers. Via the synthesis of a new bifunctional chain transfer agent (CTA) and subsequent reversible addition−fragmentation chain transfer (RAFT) polymerization, we introduce a supramolecular recognition unit (*tert*-butyl phenyl) and a photoactive unit (photoenol) to a polymer chain in order to obtain an α,ω-functionalized polymeric center block, having orthogonal recognition units at each chain end. Multiblock copolymers are formed via the light-induced reaction of the photoenol with a maleimide-functionalized polymer chain and the supramolecular self-assembly of the *tert*-butyl phenyl group with the β-CD end group of a third polymer chain. By employing the fast and efficient photoinduced Diels−Alder reaction in combination with supramolecular host−guest interactions, a novel method for macromolecular modular ligation is introduced.
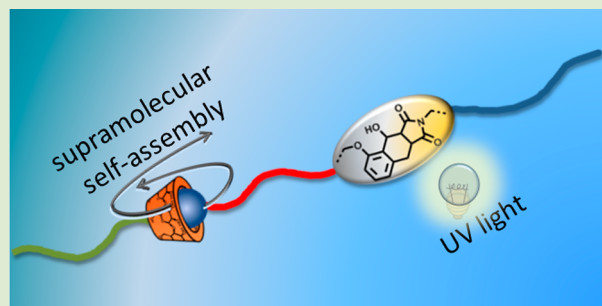
The demand for modular ligation techniques to generate complex macromolecular architectures is constantly increasing. In fundamental research and industrial applications, block copolymers consisting of polymer chains with varying features, such as crystallinity or flexibility, are mandatory to develop innovative and advanced materials. Especially the formation of diverse topologies of diblock and triblock copolymers via the functionalization of polymer termini with active moieties is an intensely investigated field.[1−4] Such copolymers are often applied for the generation of micelles or nanoparticles for drug delivery purposes.[5−7] For example, Yuan and co-workers constructed a triblock copolymer for micelle formation by thiol−ene Michael addition and host−guest interactions, employing atom transfer radical polymerization (ATRP), ring-opening polymerization (ROP), and reversible addition−fragmentation chain transfer (RAFT) polymerization to synthesize functional polymer chains.[8] The utilization of small molecule chemistry concepts has led to a broad variety of macromolecular designs.[9] Click chemistry especially is a versatile strategy to synthesize tailor-made polymer architectures[10,11] in a very mild and sometimes ultrarapid fashion.[12] In order to form a triblock copolymer via the modular ligation of three polymer building blocks, at least one polymer block has

to carry specific functionalities on both chain ends. RAFT polymerization is an efficient tool to introduce such specific end groups to a polymer chain and to obtain well-defined polymers with narrow weight distributions.[13]
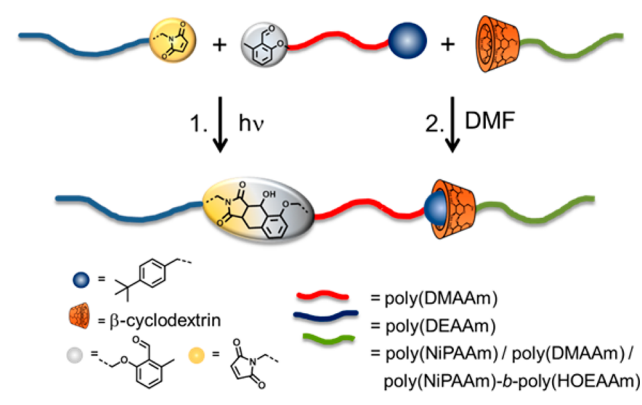
In the present contribution, RAFT polymerization was employed to introduce defined end groups to polymer chains and demonstrate the formation of multiblock copolymers via the combination of β-cyclodextrin (CD) host−guest interactions and light-induced chemistry. The overall strategy is depicted in Scheme 1. Initially, a diblock copolymer is formed in the reaction of a maleimide-functionalized poly(*N,N*-diethylacrylamide) (poly(DEAAm)-Mal) and an α-*tert*-butyl-benzyl-ω-photoenol-poly(*N,N*-dimethylacrylamide) (poly(DMAAm)-*t*BuBnPE) via irradiation with UV light. Subsequently, a β-CD functionalized poly(*N*-isopropylacrylamide) (poly(NiPAAm)-β-CD) chain is introduced as a third block via complexation of its β-CD terminus with the *t*BuBn guest located at the α-chain end of the diblock. Furthermore, we employed two alternative β-CD functionalized polymer chains, poly(DMAAm) and

Scheme 1. Outline of the Multiblock Copolymer Synthesis Described in the Present Study

Scheme 2. Reaction Sequence for the Synthesis of the Bifunctional CTA 3 Featuring Complexation and Photoreactive Groups


poly(NiPAAm)-*b*-poly(*N*-hydroxyethylacrylamide) (poly-(HOEAAm)), to demonstrate the modular nature of our synthetic approach. Both the light-induced Diels−Alder reaction and the supramolecular self-assembly of *β*-CD with a guest molecule are highly attractive orthogonal conjugation techniques since no additives such as initiators or coupling compounds are necessary. Thus, no further purification steps have to be performed after the ligation reaction between stoichiometric amounts of the polymeric building blocks, resulting in half covalent and half supramolecularly connected triblock or multiblock copolymers.

Individual applications of light-induced ligation of polymer blocks[4,14−17] as well as the supramolecular di- and triblock formation with *β*-CD[18−23] have been reported before. In a recent publication, we even demonstrated the successful formation of thermoresponsive nanoparticles by use of supramolecular diblock formation and photoinduced cross-linking and evidenced the efficiency of these ligation techniques.[24] However, it is for the first time that the features of *β*-CD host−guest and light-induced chemistry are united in one chain transfer agent (CTA) and transferred to the center polymer block of our triblock copolymer via controlled polymerization, which leads to a broad variety of possible multiblock copolymer materials via modular covalent and supramolecular ligation.

In order to obtain an *α,ω*-functionalized center polymer block, a novel bifunctional CTA was synthesized. The new CTA 3 was equipped with a *tert*-butyl phenyl guest molecule and a photoactive 2-methoxy-6-methylbenzaldehyde (photo-enol, PE) unit. The *tert*-butyl phenyl group was chosen due to its high association constant with *β*-CD (18000−25000 L mol⁻¹).[25,26] Scheme 2 depicts the synthetic route to CTA 3. The trithiocarbonate precursor 1 was synthesized by mixing 4-*tert*-butyl benzyl mercaptan, 3-bromopropanoic acid, CS$_2$, and K$_3$PO$_4$ in acetone and stirring the mixture overnight.[27] After purification of the crude product 1 via column chromatography, the PE derivative 2-((11-hydroxyundecyl)oxy)-6-methylbenzal-dehyde 2 was esterified with the trithiocarbonate 1 under Steglich conditions. The freshly synthesized RAFT agent was characterized via ¹H and ¹³C NMR (Figures S5 and S6), as well as UV−vis spectroscopy (Figure S26), revealing an absorption maximum at 309 nm.

Individual polymer blocks for the tri- and tetrablock formation were synthesized in RAFT polymerizations with different CTAs and functionalities. The *α-tBuBn-ω*-PE functionalized center block 4 was obtained via polymerization
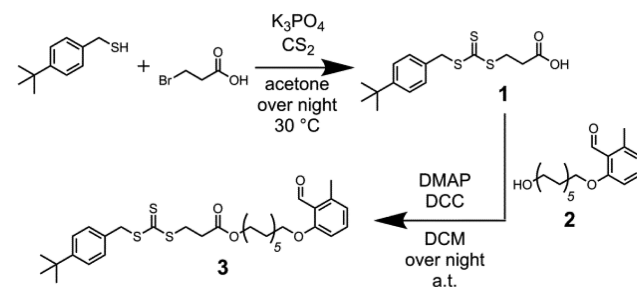
of DMAAm employing the novel CTA 3 and AIBN at 60 °C in 1,4-dioxane. After dialysis of the reaction mixture and lyophilization, poly(DMAAm)-*tBuBnPE* 4 was obtained as a yellowish powder. The SEC trace of the center block 4 ($M_{n,SEC}$ = 7300 g mol⁻¹, Đ = 1.1) is shown in Figure 1A (red trace) and also shown in the SI (Figure S8), along with the ¹H NMR spectrum (Figure S7) and the ESI-MS spectrum (Figure S9). The narrow distribution of the SEC trace and the low Đ indicate the controlled nature of the polymerization. In addition, the mass spectrum (Figure S9) reveals the single, double, and triple charged mass peaks of 4, indicating that no disturbing side reactions occurred during the polymerization. DEAAm was utilized to synthesize the second block, which carries a maleimide end-group for the light-induced reaction with the PE unit of the center block. A trithiocarbonate CTA 5i (Mal-trithiocarbonate) (which is depicted in Scheme S2 and Figure S12, ¹H NMR; and Figure S13, ¹³C NMR), equipped with a protected maleimide functionality, was employed for the controlled polymerization of DEAAm.[28,29] Following the polymerization with the protected Mal-trithiocarbonate 5i, the furan protecting group was removed by heating the poly(DEAAm)-Mal-protc 5a at 120 °C in vacuo overnight. The successful deprotection was verified via ¹H NMR spectroscopy (Figure S14) by means of the disappearance of the furan proton resonances at 6.51 and 5.26 ppm and the appearance of the maleimide protons at 6.70 ppm. Further, the SEC traces of the protected (5a) and the deprotected poly(DEAAm)-Mal 5 are illustrated in Figure S15 (5a, M_n = 5400 g mol⁻¹, Đ = 1.2; 5, M_n = 5600 g mol⁻¹, Đ = 1.2). Figure S17 depicts the ESI-MS spectrum of 5, also confirming the complete removal of the furan protecting group (compare to Figure S16, ESI-MS spectrum of 5a).

After the successful synthesis of both polymeric building blocks, poly(DMAAm)-*tBuBnPE* 4 and poly(DEAAm)-Mal 5 were added in stoichiometric amounts into a headspace vial, dissolved in acetonitrile, and crimped airtight with a SBR seal with a PTFE inlet. Oxygen was removed from the solution by purging with nitrogen for 15 min. Subsequently, the sample was placed in a custom-built photoreactor, depicted in Figure S27 and irradiated with a compact low-pressure fluorescent lamp (Arimed B6, 36 W) at 320 nm for 40 min (Figure 1).

Next, the sample was directly analyzed via SEC and ESI-MS, shown in Figure 1 as blue traces, as well as NMR spectroscopy (Figure S28). The graph depicted in Figure 1A illustrates the SEC traces of poly(DEAAm)-Mal 5 (black line), poly-(DMAAm)-*tBuBnPE* 4 (red line), and the resulting diblock copolymer *tBuBn*-poly(DMAAm)-*b*-poly(DEAAM) 6 (blue line; $M_{n,SEC}$ = 10000 g mol⁻¹, Đ = 1.3). The clear shift to lower retention time of the SEC trace of 6 and the
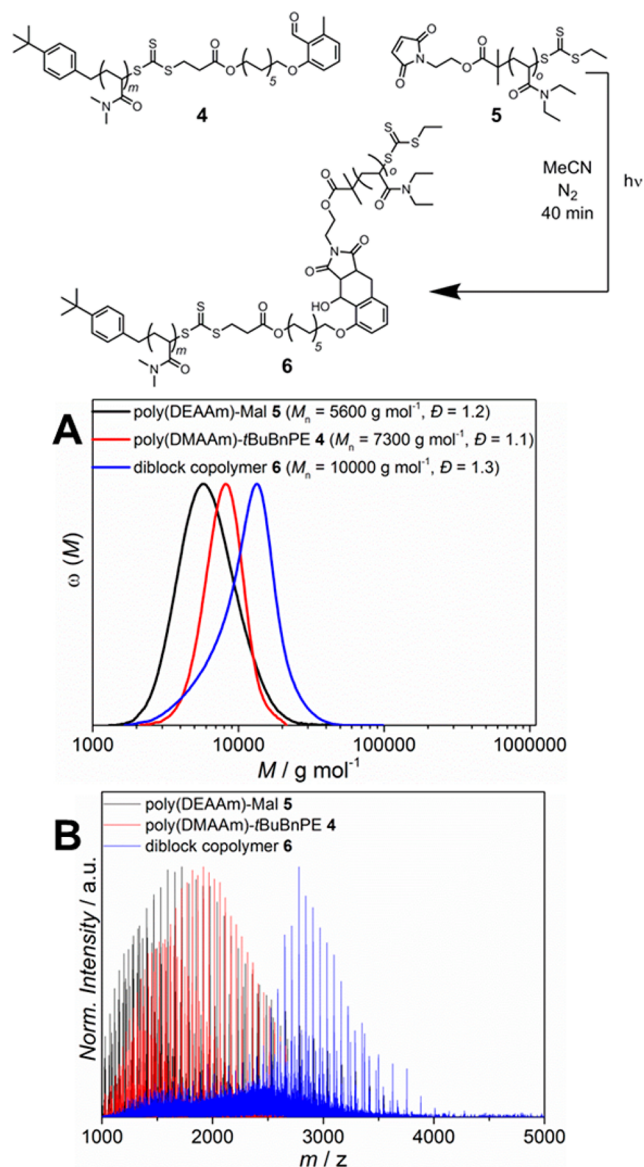
Figure 1. Synthetic strategy for the formation of the diblock copolymer **6** via photoinduced Diels−Alder reaction. (A) SEC traces recorded in DMAC at 50 °C of poly(DEAAm)-Mal **5**, poly-(DMAAm)-*t*BuBnPE **4**, and the diblock copolymer **6**. (B) ESI-MS spectra of poly(DEAAm)-Mal **5** (black), poly(DMAAm)-*t*BuBnPE **4** (red), and the diblock copolymer **6** (blue). A detailed analysis of the ESI-MS can be found in Figure S29.

disappearance of the SEC traces of **5** and **4** indicate the successful formation of the diblock copolymer. Yet, a slight shoulder remains in the SEC trace of **6**, which is due to the loss of end-group fidelity during RAFT polymerization. During the polymerization process, the decomposition of the AIBN initiator is rather slow and can replace the RAFT end-group of some polymer chains.[30,31] In addition to the SEC, the ESI-MS spectrum (Figure 1B) indicates a clear shift to higher *m*/*z*, confirming the diblock formation. Small traces of the starting materials **4** and **5** are detected in the mass spectrum of **6** as well, analogous with the SEC trace. Specific mass peak assignments of all three compounds **4**, **5**, and **6** are summarized in the SI (Tables S1−S3 and S7). Moreover, DLS measurements were performed that showed a clear shift to higher

hydrodynamic diameter (D_h) after the diblock copolymer formation (Figure S30).

Extensive kinetic studies addressing the reaction rate of the photochemical ligation have already been performed by our group. One study reports the synthesis of a monofunctional PE CTA in order to obtain a polymer with a PE end-group, which was utilized in the diblock formation with a maleimide-bearing PEG chain, as well as for the functionalization of microspheres.[15] Another study investigates the kinetics of the maleimide molecule with a PE-functionalized polymer, which is then employed in λ-orthogonal block building reactions.[32] Both studies find that full conversion is achieved after an irradiation time of 30 min at the selected irradiation conditions.

Host−guest interactions of β-cyclodextrins (CD) with specific guest molecules constitute a versatile ligation technique.[18] The supramolecular inclusion complex of the guest molecule in β-CD creates a dynamic bond that is responsive to external triggers such as light,[19,33] temperature,[19] redox,[34] or pH.[35,22] Thus, the supramolecularly bonded macromolecule can be exchanged or completely removed from the covalently formed diblock copolymer **6**. Three different β-CD bearing polymer blocks were employed for the formation of the supramolecular triblock copolymer to prove that any β-CD functionalized polymer chain can be attached to the covalently bound diblock copolymer **6**. The individual blocks consisting of poly(NiPAAm) **7a** (M_n = 8800 g mol^{-1}, *Đ* = 1.2), poly(DMAAm) **7b** (M_n = 10700 g mol^{-1}, *Đ* = 1.3) and even a diblock copolymer of poly(NiPAAm)-*b*-poly(HOEAAm) **7c** (M_n = 16400 g mol^{-1}, *Đ* = 1.3), leading to the formation of a tetrablock copolymer were synthesized via RAFT polymerizations with CTA **7i** (Scheme S3), carrying an alkyne group. Subsequent to the polymerization, the trithiocarbonate was cleaved from the polymer chain in a radical transformation reaction of the trithiocarbonate group into a hydroxyl function (refer to Scheme S5). The trithiocarbonate had to be removed in order to efficiently click an azide-functionalized β-CD to the alkyne polymer end-group.[36] The success of the CuAAC click reaction (Scheme S6) was verified via ¹H NMR, which is shown in the SI along with the corresponding SEC traces for each polymer chain in every reaction step (Figures S20−S25). According to the SEC traces (Figures S21, S23, and S25), a slight shoulder toward higher molecular weight is formed after the trithiocarbonate removal, which is due to heating the alkyne polymer in the presence of AIBN, resulting in small amounts of coupling products. Additionally, the chain extension of poly(NiPAAm)-alkyne (**7iia**) to poly(NiPAAm)-*b*-poly(HOEAAm) (**7iic**; Scheme S4 and Figures S18 and S19) is shown in the SI.

The supramolecular triblock formation of the Diels−Alder product **6** and the β-CD functionalized poly(NiPAAm) **7a**, poly(DMAAm) **7b**, and poly(NiPAAm)-*b*-poly(HOEAAm) **7c**, depicted in Figure 2, was performed via dialysis of an equimolar mixture of the building blocks **6** and **7a** (**7b**, **7c**) in DMF against deionized water. In DMF the guest-group has improved accessibility since it is a nonselective solvent for the chosen polymers. With the subsequent dialysis against deionized water and the slow exchange of solvent, the triblock copolymer is formed. Finally, the supramolecular triblock copolymer poly-(NiPAAm)-*b*-poly(DMAAm)-*b*-poly(DEAAm) **8a** (**8b**, **8c**) was analyzed via DLS and NOESY NMR. Figure 2A illustrates the number-weighted size distribution of the Diels−Alder diblock copolymer **6**, the poly(NiPAAm)-β-CD polymer chain **7a**, and the resulting supramolecular triblock copolymer **8a**. In Figure 2,
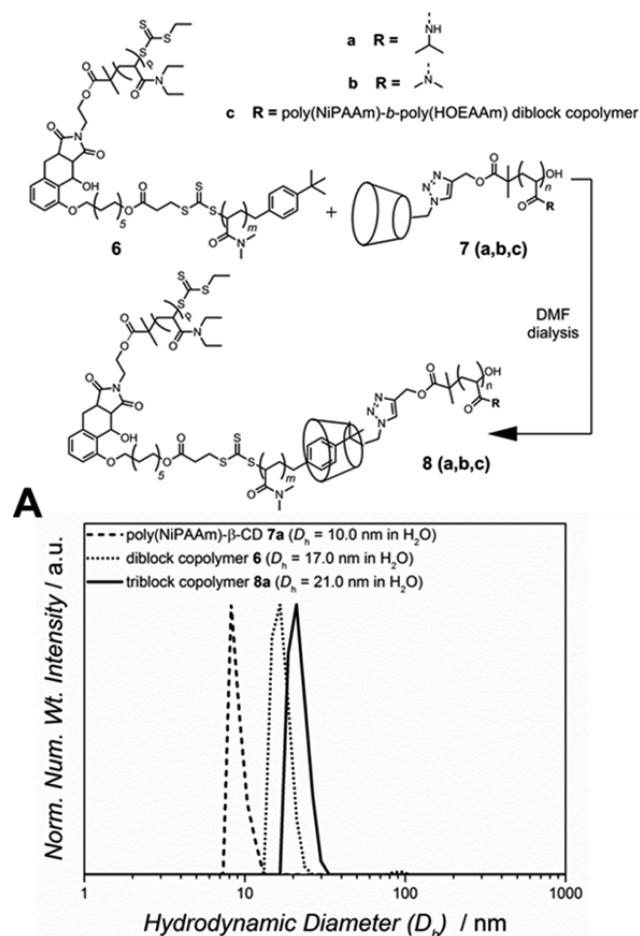
Figure 2. Formation of the supramolecular triblock copolymer **8a** (**8b**, **8c**) in DMF and subsequent dialysis against deionized water. (A) DLS measurements at 25 °C in Milli Q water, showing the number-weighted size distribution of the β-CD functionalized poly(NiPAAm) block **7a**, the Diels−Alder ligated diblock copolymer **6**, and the supramolecular ligated triblock copolymer **8a** with a polymer concentration of 0.06 mmol L^{-1}.

the shift to higher hydrodynamic radii indicates the successful triblock copolymer formation. The associated autocorrelation functions along with the number-weighted distribution of all polymer building blocks and products are collated in the SI (Figures S33−S44).

In addition, a 2D NOESY NMR experiment of the triblock copolymer **8a** (**8b**, **8c**) was performed as depicted in Figure 3. The spectrum reveals cross-correlation peaks between the inner protons of the β-CD (3.10, 3.34, and 3.60 ppm) and the proton resonances of the *tert*-butyl phenyl group (6.90 and 7.10 ppm) further evidencing the formation of the supramolecular inclusion complex. Supplementary, correlation between the methyl protons of the *tert*-butyl group (1.86 ppm) and the phenyl ring (6.90 and 7.10 ppm) are observed as well.

The DLS data and NOESY spectra for the supramolecular triblock copolymer with poly(DMAAm) **8b** and the tetrablock copolymer **8c** are presented in the SI (Figures S34−S42), also showing cross-correlation peaks between the host- and the guest-molecule, as well as a shift to higher hydrodynamic radii in the DLS measurement after the supramolecular triblock formation.
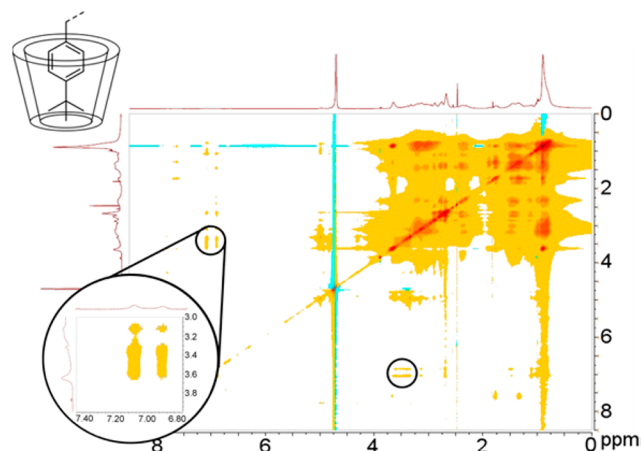
Figure 3. 2D NOESY NMR spectrum of the supramolecular triblock copolymer poly(NiPAAm)-*b*-poly(DMAAm)-*b*-poly(DEAAm) **8a** in D$_2$O at 25 °C. The close proximity of the inner protons of β-CD and the *tert*-butyl phenyl protons is evidenced by the cross-correlation peaks highlighted in the spectrum. Additionally, an illustration of the inclusion complex of the *tert*-butyl phenyl guest and the β-CD host is shown.

In summary, we introduce the synthesis of a novel bifunctional CTA, carrying a guest molecule for β-CD host−guest interactions and a photoenol unit, which can undergo light induced Diels−Alder reactions. An α-*t*BuBn-ω-PE-functionalized poly(DMAAm) center block was synthesized via RAFT polymerization with the bifunctional CTA, thus, transferring the functionalities onto a polymer chain and creating orthogonal ligation points for block copolymer formation. Several additional polymer blocks equipped with a β-CD host molecule along with a maleimide-functionalized polymer chain were prepared via RAFT in order to form triblock and tetrablock copolymers. The success of the light-induced diblock formation was evidenced by SEC and ESI-MS measurements. Furthermore, NOESY NMR and DLS were employed to verify the supramolecular triblock and tetrablock copolymer formation. The combination of light-induced Diels−Alder chemistry with the supramolecular host−guest inter-actions of β-CD generates an effective tool for the formation of multiblock copolymers, offering new possibilities for the modular ligation of polymer blocks.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.5b00485.

> Contains all syntheses, experimental characterization methods and instrument data, and the spectra that where referred to in the main text (Schemes S1−S6 and Figures S1−S43) (PDF)

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Notes

The authors declare no competing financial interest.

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