Accumulation of the photonic energy of the deep-red part of the terrestrial sun irradiation by rare-earth metal-free E-Z photoisomerization

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Large scale solar energy storage in form of E-Z photoisomerisable organic materials requires avoiding of application of rare earths metals at any stage of the process used. Here we report on drastically shortening of the synthetic route of crown ether functionalized hemicyanine dyes, able for efficient E-Z photoisomerization under extremely low excitation light intensities – comparable with not concentrated sunlight. The higher energetic form was successfully stabilized by rare earth free cations – in this case by styryl dye-Ba\textsuperscript{2+} complexes. For the first time was demonstrated E-Z-photoisomerization observed directly by excitation with light substantially red-shifted regarding the absorption spectrum of the trans-to-cis active moieties via the process of triplet-triplet annihilation upconversion.

Introduction

Initially the idea of storing solar energy in molecular systems via valence isomerisation dates back to the late 50'ies. In the last two decades a number of molecular organic solar-thermal (MOST) energy storage systems based on stilbene, azobenzene, anthracene, tetracarbonyl-fulvalene-diruthenium and dihydroazulene have been explored [1, 2]. It was successfully demonstrated an laboratory “closed cycle” continuous flow MOST-device [4], based on Ru\textsubscript{2}Fv (3,3’-Bis(1,1-dimethyltridecyl)fulvalene)dirutheniumtetracarbonyl).

The favoured MOST system have to fulfil simultaneously a chain of material requirements: (1) having in mind the global shortage in precious- and rare-earths- metals, the identified MOST-system must avoid or reduce strongly their usage; (2) the absorption band of the parent compound must overlap optimally with the most intense terrestrial solar spectral part (i.e. the VIS-spectrum); (3) should demonstrate high photoisomerization quantum yield, realized at low excitation intensity; (4) the spectral overlap between the parent compound and the photoisomer must be as small as possible; (5) having a highly endergonic reaction profile together with a high activation energy for the reverse reaction [3] will ensure long lifetime of the stored optical energy; (6) last, but no least, the MOST-system should have as low as possible molecular weight of the parent compounds in order to maximize the sunlight storage density [3].

Merging the technologies of low molecular weight & precious / rare-earths metal-free MOST systems with the triplet-triplet annihilation photon energy upconversion (TTA-UC) opens new perspectives for realistic industrial applications of the proposed sunlight energy storage schema. In this work, the synthetic route, together with the optical characteristics and energy storage parameters, including lifetime and cycling properties of the precous / rare-earths metal-free MOST systems excited directly by TTA-UC device will be reported in details.

Results and discussion

Synthesis

In a recently published work [5], it was described one of the possible strategies for the synthesis of target dyes 4a-4d (Scheme 1). In the published procedure [5], the first reaction step is quaternization of benzoazoles with the corresponding alkanesultons. The reaction being carried out in the absence of a solvent. Such reaction conditions have their advantages, but a major drawback is the accumulation of an insoluble product in the reaction volume, which after a certain point makes difficult the quaternization to be completed. The addition of small amounts of the highly boiling N-Methyl-2-pyrrolidone (NMP) to the mixture (Scheme 1A) ensures a good solubility during the entire process and the prolonged reaction time (half an hour) provides almost quantitative reaction yields (Scheme 1A).

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In the same work [5] on the synthesis of 4-(aza-15-crown-5)bencocarbaldehyde (3) was described the use of a modified four step synthetic procedure [6]. Led by the willing to create an economical, reproducible and simple synthetic scheme through the combination of few known methods [5-8], here we have created a new, more robust, easy-to-implement and cost-effective (only) two steps procedure for the preparation of intermediate 3 (Scheme 1 B). Our crucial optimisation in this procedure is the neutralization of the reaction mixture after the Vilsmeier-Haack-Arnold reaction with the milder reagent sodium acetate instead the aggressive sodium hydroxide [8] which in the reported case causes ring opening and damages of the crown functionality (TLC monitoring, NMR). Another seminal advancement is the conversion of the target crown ether-aldehyde 3 (Scheme 1 B) into a corresponding sodium perchlorate complex-salt, which allows for easy and successful recrystallization of the product instead of the expensive chromatographic purification methods used up to now. These optimisations pave the possibility for straightforward up-scale synthesis of these type precious and rare-earths metal-free MOST-dyes.

**Scheme 1.** A) Quaternization of 2-methylbenzothiazoles with alkane sultones; B) Synthesis of 4-(aza-15-crown-5)bencocarbaldehyde (3); C) Synthesis of dyes 4a-4d [5].

**Z-Photoisomerization of dyes 4a-4c performed by extremely low intensity VIS-light**

In order to reveal the temporal evolution of the process of E - Z photoisomerization the pump-probe experimental setup shown in Figure 1 was realized. The pump-channel uses as excitation sources temperature & current stabilized, single mode diode lasers, mounted on laser heads (TCLDM9, Thorlabs Inc.) and operating either at \( \lambda = 450 \text{ nm} \) (for direct E - Z photoisomerization), or at \( \lambda = 635 \text{ nm} \) (for indirect E - Z photoisomerization via the process of TTA-UC). Both lasers are collimated to a mutually uniform spot with aspect ratio of ~ 1:2 by applying cylindrical telescopes. The temperature & current control of all diode lasers is performed by PRO8000 / 8-Slot Modular Rack Chassis (Thorlabs Inc.), supporting laser current control units LDC8002 / LDC8010 and laser diode temperature controller modules TED8040 (Thorlabs Inc.). The probe channel consist of “white light source” (LED flood lights, SL 20W 5500K) with current & temperature stabilized power supply and adjustable light intensity. Additionally, a band-pass filter (03 FIV 044 Melles Griot) with central wavelength of \( \lambda = 550 \text{ nm} \) and the spectral width of \( \Delta \lambda = 40 \text{ nm} \) (FWHM) modify the spectrum of the probe channel (Figure 3a, the grey line). For all measurement the intensity (less than 1 \( \mu \text{W} \times \text{cm}^{-2} \)) of the probe...
beam was kept constant, thus its E-Z photoisomerization activity is negligible.

**Figure 1:** Experimental setup for real time observation of E-Z photoisomerization.

The emission spectra were registered by Optical Multichannel Analyser (OMA, PMA-50 Hamamatsu Inc.) with absolute wavelength calibration and corrected spectral response. Since E-Z photoisomerization is relatively slow process, the integration time of Δt = 100 ms was more than sufficient. Using edge filter, designed for $\lambda = 455$ nm (HQ455LP, Chroma Tech. Corp.), or notch filter for $\lambda = 633$ nm (NF 03-633E-25, Semrock Inc.) it is possible to suppress more than $10^4$ times the intensity of the excitation laser.

All measurements were performed in fluorescent quartz cuvette (Q 23-3.45, Starna Scientific GmbH) with optical - quality base (dimensions 3×3×40 mm, four windows and base polished.). In order to reduce the convection of the MOST-fluid the cuvette was placed horizontally. As shown in Figure 1, the pump and probe beams are mutually perpendicular. Complete spatial overlapping of the pump and the probe beams with the studied sample was achieved by placing of the cuvette (including the temperature modulation unit) on a double-row ball micropositioning XYZ-stage (M-UMR5.16, Newport Corp.). This fact ensures that the probe beam will travel only through optically-excited medium. The temperature of the sample was actively controlled by Peltier-based temperature control module (TCM, Electron Dynamics Limited). It is important to mention explicitly that only after reaching of stationary temperature signal from the Pt-100 sensor placed on top of the quartz cuvette the optical measurements were performed.

A typical experimental procedure for determination of the time-resolved dependence of the E-Z photoisomerization on the excitation intensity, temperature and sample composition is shown in Figure 2 (for instance, for the structure 4b). The absorption of a neat 4b in acetonitrile (ACN) is shown in Figure 2a (the green line). Further, the addition of Ba(ClO$_4$)$_2$ to the ACN solution of 4b-dye induces a significant decrease of the local absorption maximum (at $\lambda = 523$ nm) and a substantial hypsochromic shift of the absorption maximum (at $\lambda_{\text{max}} = 438$ nm). These changes in the absorption spectra of the 4b under addition of Ba$^{2+}$-ion reveal an extensive ion-complexation by the azacrown ether group of the chromo-ionophore. The absorption spectrum in Figure 2a (the blue line) refers to the formation of the trans-dye-Ba$^{2+}$ complex [5].

As it is shown in Figure 2b, formation of cis-dye-Ba$^{2+}$ isomers causes monotonic decrease of the visible sample absorption. It is important to mention that this is an integral response on the optical excitation, predetermined by the excitation intensity, light dose and/or sample temperature and material composition. To distinguish the importance of these experimental factors was a partial objective of this work.

The pump wavelength ($\lambda_{\text{pump}} = 450$ nm) performing trans-to-cis photoisomerization excites predominantly the trans-dye-Ba$^{2+}$ complex (Figure 3a, the blue line) represents the absorption of trans-4b-Ba$^{2+}$ complex. As an experimental measure, referring to the degree of cis-dye-Ba$^{2+}$ isomerisation the transmittance of the probe beam (Figure 3a, the grey line) was used. In figure 3a (the red line) demonstrate the fluorescence spectrum of 4b with a maximum at $\lambda_{\text{pump}} = 602$ nm.

The probe beam has vanishing intensity of $I_{\text{probe}} = 1 \mu$W×cm$^{-2}$, therefore for the specific excitation times (in order of 100s) the isomerisation activity of the probe beam can be neglected. The maximum of the probe beam spectrum is $\lambda_{\text{probe}} = 532$ nm, therefore the temporal evolution of this wavelength reports for the trans-to-cis status of the sample, shown in Figure 4a (the green line).
Figure 3: (a) – Optical signal obtained from trans-dye–Ba\textsuperscript{2+} complex excited simultaneously with pumping beam (\(\lambda_\text{exc} = 450\) nm) and probe beam (\(\lambda_\text{probe} = 532\) nm), \(cw\) – registration (multicolour line); (b) – Dependence of sample transmittance and fluorescence on the intensity of the pump beam; \textbf{Conditions}: Intensity of the probe beam is constant, 1 \(\mu\)W•cm\(^{-2}\); Sample temperature \(T = 22^\circ\)C; Excitation duration \(\Delta t = 90\)s; 4b (\(1\times10^{-4}\)M) / a concentration of Ba\textsuperscript{2+} ions 2\(\times\)10\(^{-1}\)M.

Figure 4: (a) – Temporal evolution of the trans-transmittance (the green line) and trans-fluorescence for the 4b at sample temperature \(T=35^\circ\)C; (b) – Temperature dependence of the temporal evolution of the trans-transmittance for the 4b compound at \(T=15^\circ\)C (the blue line) and \(T=35^\circ\)C; \textbf{Conditions}: Intensity of the probe beam is constant, 1 \(\mu\)W•cm\(^{-2}\); Excitation duration \(\Delta t = 90\)s; dye (\(1\times10^{-4}\)M) / at concentration of Ba\textsuperscript{2+} ions 2\(\times\)10\(^{-1}\)M; Pump beam intently \(I_\text{pump} = 4\) mW•cm\(^{-2}\). The vertical black line is a guide to the eye.

Additionally, the studied crown ether containing styryl dye core with non-zero fluorescence quantum yield and this fact is used as a second measure revealing the cis-dye-Ba\textsuperscript{2+} isomers formation (Figure 4a, the red line). Since the evolution of the trans-transmittance represents simultaneously measure for the degree of E-Z-photoisomerization and the stability parameters of the cis-form all further optical experiments will use this process.
As shown in Figure 5, the structure 4b demonstrates better ability for cis-state formation, together with longer cis-life time. A probable reason for the observed phenomenon with dye 4b is due to the combination of the optimum spacer length separating the anchor group from the chromophore on the one hand and the presence of a methyl group directing the spacer and the anchor sulfo-group to the Ba2+-crown ether complex from another. During the excitation, E-Z-photoisomerization leads to increase of the trans-state transmittance and simultaneously to decrease of the trans-state fluorescence.

Figure 5: Temporal evolution of the trans-transmittance for the 4a - 4d compounds at constant temperature of T=15°C; Conditions: Intensity of the probe beam is constant, 1 µW/cm²; Excitation duration Δt = 90s; dye (1×10⁻⁴M) / at concentration of Ba2+ ions 2×10⁻¹M; Pump beam intensity Ipump = 4 mW/cm². The vertical black line is a guide to the eye.

Nevertheless, at given Ba2+ concentration the concentration of cis-forms depends substantially on the excitation intensity and sample temperature – importance of these parameters will be revealed on the example of 4b-compound. As shown in Figure 6a, excitation intensity increase causes substantial growth the degree of E-Z-photoisomerization, simultaneously the life-time of the cis-form is not strongly affected. In contrary, relative moderate increase of the sample temperature strongly affects the stability of the dye-metal ion complex in the cis-state and leads to remarkable decrease (more than 6 times) of the life-time of the cis-form (Figure 6b).

It is important to emphasize that E-Z photoisomerization is realized at extremely low excitation intensities (as low as 40µW/cm² and moderate excitation time). Such excitation intensities are much lower than the intensity of 15un (AM1.5). The unusual sensitivity of the studied photochemical reaction will be further demonstrated by direct E-Z photoisomerization of the trans-styryl dye–Ba2+ complex via the process of Triplet-Triplet Annihilation Upconversion (TTA-UC).

Triplet-triplet annihilation photon energy upconversion driven E-Z-Photoisomerization of dyes 4a-4d.

The process of TTA-UC is the only upconversion process realized up to now with non-coherent, ultra-low intensity sunlight [9]. The TTA-UC based upconveror can effectively harvest the sub-band gap terrestrial sunlight photons and transfers their energy to a photon flux with optimal spectrum toward the optically coupled MOST-device. A key advantage of the TTA-UC using techniques is that the conversion processes and devices can be considered and optimized independently, without affecting the particular properties of the operating photochemical material or device architectures.
The TTA-UC takes place in multi-chromophore systems consisting of energetically optimized pairs of emitter molecules (typically aromatic hydrocarbons) and sensitizer molecules (usually, metalled macrocycles, such as porphyrins and phthalocyanines), as shown in Figure 7a. Shortly, the photon energy absorbed by a sensitizer is stored in its metastable triplet state, formed in the process of intersystem crossing (ISC). Further, this energy is transferred to an emitter triplet state via the process of triplet-triplet transfer (TTT). Next, the excited triplet states of two emitter molecules undergo triplet-triplet
annihilation (TTA), in which one emitter molecule returns back to its singlet ground state and the other molecule gains the energy of both triplet states and is excited to the higher singlet state. As the singlet state emitter decays radiatively back to the ground state, a delayed fluorescence photon (the blue arrow, Figure 7a) bearing higher energy than that of the excitation photons is emitted.

Merging the technologies for E2Z-photoisomerization, stabilized by complexation with precious metal-free cations (direct excitation of the MOST-dyes: ΔHΔH = 400 – 530 nm and the triplet-triplet annihilation upconversion (indirect excitation of the MOST-dyes via the TTA-UC process, ΔHΔH = 580 – 730 nm [11]) allows to broaden substantially the solar spectrum available for effective energy storage. The emission spectrum of the standard perylene emitter molecule coincide optimally with the absorption spectrum of the trans-dye–Ba2⁺ complex (Figure 3a), therefore the well-studied PdTBP / perylene / organophosphate was applied as UC-system. The experimental data are well approximated with a power law (Figure 8a), the section marked with 1 (Figure 8b). At the reported experiment the focusing and collection of the TTA-UC light was only by excitation with upconverted light. To our knowledge this (Figure 8b), the section marked with 1 (Figure 8b). At the reported experiment the focusing and collection of the TTA-UC light was only by excitation with upconverted light. To our knowledge this

The experimental data are well approximated with a power law

\[ I_{\text{TTA-UC}} = a \times I_{\text{exc}}^b \]

where the parameter \( b = 1.18 \).

The acceptance angle for the upconversion light is relatively small – less than \( \pi/8 \) (Figure 8a, the section marked with 1), therefore only a tiny part of the generated UC-fluorescence can be launched to the interaction zone of the MOST-materials (Figure 8a, the section marked with 2). At the reported experiment the focusing and collection of the TTA-UC light was not optimized, therefore nearly 1% of the generated UC-fluorescence was guided to the MOST-interaction zone: the intensity of the UC-fluorescence at the MOST-interaction zone is estimated to be 25\( W/cm^2 \). In figure 8b is shown the temporal evolution of the trans-transmittance for dyes 4a – 4d, obtained only by excitation with upconverted light. To our knowledge this is the first experimental demonstration of E2Z-photoisomerization observed directly by excitation with light substantially red-shifted regarding the absorption spectrum of the trans-to-cis active moieties.

**Experimental**

All solvents used in the present work were commercially available (HPLC grade). The starting materials 1a, 1b, 2a, and 2b were commercially available and were used as supplied. Melting points were determined on a Kofler apparatus and are uncorrected. NMR spectra were obtained on a Bruker Avance III 500 DRX 600 MHz spectrometer in DMSO-d6. The MALDI–TOF/TOF spectra were measured at Bruker “RapifeX” at MIP, Mainz, Germany. UV–VIS spectra were measured on a Unicam 530 UV–VIS spectrophotometer in conventional quartz cells of 1 cm path length. The spectral bandwidth and the scan rate were \( \Delta \lambda = 1 \ nm \) and \( \Delta \lambda = 140 \ nm \ min^{-1} \), respectively. Stock solutions of each compound were prepared in spectroscopic grade acetonitrile (ACN) and all experiments were carried out in red light and at room temperature. Complex formation of dyes with Ba(ClO4)2 was studied by spectrophotometric titration. In the experiment aliquots of a solution containing known concentrations of dyes and of Ba(ClO4)2 were added to a solution of dyes alone at the same concentration. So the absorption spectra were recorded for solutions with identical total dye concentration (1×10^{-5} M) and variable total Ba(ClO4)2 concentration ranging from 1×10^{-4} M to 5×10^{-1} M in ACN. Emission spectra were recorded on Fluorolog 3-221 HORIBA Jobin Yvon GmbH, spectrophuorometer with Quanta-ϕ accessory having a large 150 mm integrating sphere for the quantum yield measurements. All spectra we recorded using quartz cells of 1 cm path length. The solution concentrations were chosen to give an absorbance A ≤ 0.05 at the excitation wavelength of \( \lambda = 440 \ nm \) and \( \lambda = 488 \ nm \).

**Synthesis of quaternary benzothiazolium salts 2a-2d**

The appropriate 2-methylbenzothiazole 1a or 1b (0.01 mol) and 0.01 mol 1,3-propansultone (1c) or 0.01 mol 1,4-butansultone (1d) were dissolved in 3 ml NMP and heated in a argon atmosphere at 145°C for 3 h. After cooling to room temperature the reaction work-up was performed as already has been described [5].

3-[2-Methylbenzol[d][thiazol-3-ium-3-yl]propane-1-sulfonate (2a): Yield 93%. 1H-NMR (500 MHz, DMSO-d6, δ (ppm)): 2.16 - 2.19 m (2H, CH2), 2.65 t (2H, J = 6.6 Hz, CH2SO3), 3.21 s (3H, CH3), 4.93 t (2H, J3 ZZ = 8.1 Hz, CH3N), 7.78-7.82 m (1H, Ar), 7.88-7.91 m (1H, Ar), 8.44 d (1H, J3 HH = 8.8 Hz, Ar), 8.46 d (1H, J3 HH = 8.7 Hz, Ar). 3-[2,5-Dimethylbenzol[d][thiazol-3-ium-3-yl]propane-1-sulfonate (2b): Yield: 94%. 1H-NMR (500 MHz, DMSO-d6, δ (ppm)): 2.09-2.16 m (2H, CH2), 2.4 t (2H, J3 HH = 6.3 Hz, CH3SO3), 2.51 s (3H, CH3), 2.65 s (3H, CH3), 4.87 t (2H, J3 HH = 8.0 Hz, CH3N), 7.64 s (1H, Ar), 8.25-8.29 m (2H, Ar).

4-[2-Methylbenzol[d][thiazol-3-ium-3-yl]butane-1-sulfonate (2c): Yield 93%. 1H-NMR (500 MHz, DMSO-d6, δ (ppm)): 1.75 - 1.83 m (2H, CH2), 1.95-2.02 m (2H, CH2), 2.54 t (2H, J3 HH = 7.2 Hz, CH3SO3), 3.23 s (3H, CH3), 4.75 t (2H, J3 HH = 8.1 Hz, CH3N), 7.78-7.82 m (1H, Ar), 7.88-7.91 m (1H, Ar), 8.42-8.44 m (2H, Ar).

4-[2,5-Dimethylbenzol[d][thiazol-3-ium-3-yl]butane-1-sulfonate (2d): Yield 97%. 1H-NMR (500 MHz, DMSO-d6, δ (ppm)): 1.75-1.77 m (2H, CH2), 1.79-1.97 m (2H, CH2), 2.57 t (2H, J3 HH = 7.2 Hz, CH3SO3), 3.23 s (3H, CH3), 3.26 s (3H, CH3), 4.67 t (2H, J3 HH = 8.1 Hz, CH3N), 7.62 d (1H, J3 HH = 6.5 Hz, Ar), 8.25 - 8.27 m (2H, Ar).

**Synthesis of N-phenylaza-15-crown-5 (2g)**

In a 500 ml three-neck round-bottom flask, equipped with an electromagnetic stirrer, a reflux condenser and two dropping funnels a solution of 1.81g (0.01 mol) of N-phenyldietanolamine in 100 ml THF and a solution of 4.59g (0.01 mol) of triethylene glycol ditosylate in 100 ml of THF were added simultaneously drop wise to a solution of 1 g of sodium hydride, NaH (0.036 mol of 60% suspension) in 150 ml of THF for three hours. After the addition completed, the reaction...
mixture was refluxed for a further 4 hours, cooled to room temperature and filtered. The filtrate was concentrated to dryness and 1.36 g (0.01 mol) of sodium perchlorate in 50 ml of methanol was added. The mixture was refluxed for 10 minutes. 100 ml of ethyl acetate were added and the mixture concentrated to a 10 ml volume. The resulting white precipitate was filtered off, washed with ethyl acetate and dried. Yield 70%; dryness and 1.36 g (0.01 mol) of sodium perchlorate in 50 ml of methanol was added. The mixture was refluxed for a further 4 hours, cooled to room temperature and for four hours at 70 °C. The reaction mixture was cooled and poured onto ice, neutralized with 2M HCl, extracted with dichloromethane: water = 1:1. The organic layer was dried with calcium dichloride and evaporated to dryness. Tm = 44-45°C (lit. 44-45 °C) [7].

Synthesis of 4-aza-15-crown-5-benzaldehyde (3)

2 g (0.0068 mol) of N-phenylaza-15-crown-5 (2g) were dissolved in 6 ml of dimethylformamide. After cooling to -10 °C, 1.04 g (0.026 ml, 0.0068 mol) of phosphinoxy chloride are added dropwise and the reaction mixture is stirred for one hour at room temperature and for four hours at 70 °C. The reaction mixture was cooled and poured onto ice, neutralized with 2M sodium acetate and extracted with dichloromethane. The extract was washed with water, dried with sodium sulfate and evaporated to dryness. The resulting white precipitate is filtered off and dried. The aldehyde sodium complex is developed as described above. Yield 67%. Tm = 85-87° C (lit. 86-87° C [8]). 1H NMR (500 MHz, CDCl3, TMS, δ ppm)): 3.52-3.72 m (16H, CH2O), 3.78-3.80 t (4H, NCH2), 6.71 d (2H, J1H,1H = 8.7 Hz, Ar), 7.70 d (2H, J1H,1H = 8.5 Hz, Ar), 9.73 s (1H, CHO).

Synthesis of dyes 4a-4d

The dyes 4a-4d were prepared by the described procedure [5]. All analytical data completely correspond to the already published.

Conclusions

Sustainable and cost-effective synthetic protocol for the preparation of the valuable crown ether functionalized styryl hemicyanine dyes 4a-4d avoiding the complete step of chromatographic purification was developed. It was experimentally demonstrated accumulation of the photonic energy of the deep-red part of the terrestrial solar irradiation applying E-Z photoisomerization realized at extremely low excitation light intensities, lower than 4 Sun (AM1.5). The higher energetic form was successfully stabilized by precious- and rare earth metal-free cations. The temporal evolution of the sample transmittance as function of the excitation intensity and sample temperature was measured in real time regime. For the first time E-Z-photoisomerization observed directly by excitation with light substantially red-shifted regarding the absorption spectrum of the trans-to-cis active moieties via the process of triplet-triplet annihilation upconversion was demonstrated experimentally.

Author Contributions

The authors participate equally to this work.

Conflicts of interest

The authors declare no competing financial interests or other potential conflict of interests.

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