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COLOURFUL PATTERNS IN CELLULOSE-BASED LIQUID CRYSTALS

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Abstract. *Cellulose-based thermotropic and lyotropic liquid crystals can be obtained from macromolecules or colloidal particles, such as cellulose nanocrystals. Thermotropic liquid crystals are produced by the effect of temperature, while lyotropic liquid crystals occur in solution for a given range of concentration, pressure, and temperature. Cellulose liquid crystals can form chiral nematic phases characterized by Bragg-type reflections of circularly polarized light. This characteristic is related to a helical structure formed by pseudo nematic layers twisted around an optical axis. The helical structure is characterized by the values of pitch and helicity. The later can be right- (R) or left- (L) handed. Cellulose liquid crystals are well described in literature. They are a source of materials for many applications, including the production of photonic chiral materials. Although many questions remain unanswered such as the origin of helicity of cellulosic chiral structures and those related to out-of-equilibrium systems. In this paper, we are focused at the out-of-equilibrium systems obtained from lyotropic cellulose-based liquid crystals. The development of colorful patterns involving the pitch variation in space and time of self-organized cellulose cholesteric structures is revised.*

Key words: *liquid crystals, cellulose, cellulose-based lyotropic systems, self-organized chiral nematic, open thermodynamic systems, reaction-diffusion mechanisms*

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ЦВЕТНЫЕ ИЗОБРАЖЕНИЯ В ЖИДКИХ КРИСТАЛЛАХ НА ОСНОВЕ ЦЕЛЛЮЛОЗЫ

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Аннотация. *Термотропные и лиотропные жидкие кристаллы на основе целлюлозы могут быть получены из макромолекул или из коллоидных частиц, таких как нанокристаллы целлюлозы. Термотропные жидкие кристаллы образуются под действием температуры, в то время как лиотропные жидкие кристаллы формируются в растворе при заданном диапазоне концентраций, давления и температуры. Жидкие кристаллы целлюлозы могут образовывать хиральные нематические фазы, характеризующиеся брэгговскими отражениями циркулярно поляризованного света. Эта характеристика связана со спиральной структурой, образованной псевдонематическими слоями, закрученными вокруг оптической оси. Закрученная структура характеризуется величиной шага и спиральностью, которая может быть право (R) или лево (L) вращающей. Жидкие кристаллы целлюлозы хорошо описаны в литературе и являются*

источником материалов для многих приложений, включая производство фотонных хиральных материалов. Хотя еще предстоит ответить на многие вопросы, такие как происхождение спиральности целлюлозных хиральных структур и изучение неравновесных систем. В этой статье рассматриваются неравновесные системы, полученные на основе лиотропных жидких кристаллов целлюлозы. Пересмотрено развитие цветных узоров, включающее вариацию шага спирали в пространстве и времени, самоорганизаванных холестерических структур целлюлозы.

Ключевые слова: *жидкие кристаллы, целлюлоза, лиотропные системы на основе целлюлозы, самоорганизованный хиральный нематик, открытые термодинамические системы, механизмы реакции-диффузии*

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Inspiring spatial and temporal evolving colourful patterns in Nature

The spatiotemporal evolution of patterns in nature is an inspiration to develop materials with different functionalities from the same starting formulation.

One example is the eyespots on feathers of adult peacocks. The eyespots, along their radius, present a repetition of colours changing from blue at the centre to green, bronze, green, bronze, to green at the periphery [1]. The formation of the eyespot colours comprises different stages that appear progressively, starting with the appearance of a dark brown at the middle in young peacocks, changing to the sequence of vivid colours observed in the adult eyespot [2]. The colours formation in the eyespots evolves over approximately 3 years [1, 2] (Fig. 1).

Fig. 1. Handmade sketches that illustrate the patterns exhibited by the feathers of a young (two sketches on the left) and an adult peacock (sketch on the right)

Other designs involve the sequence of concentric coloured circles, which are blue, green and red from the centre to the periphery as the spots observed on *Pachyrrhynchus congestus pavonius* [3]. Reaction-diffusion models, firstly evidenced by Belousov–Zhabotinsky reaction [4, 5] and addressed later by Turing [6], were suggested to describe the patterns formation of eyespot [7] as well as the spots exhibited by the *Pachyrrhynchus congestus pavonius* [3]. Strong coloration associate to living systems was also found in fossils with 40 million-years [8], as those of the leaf of the beetle *Chrysomelidae* found in Eckfeld (Germany) [9]. This is an indication that this type of natural coloration does not easily bleach or suffer from discoloration like conventional pigments. These colors are usually referred as structural colors and are associated with the interference of light reflected from structures exhibiting periodicity on scales in the range of visible wavelengths [2].

Structural colors can be obtained from biocompatible and environmentally friendly materials and have attracted much attention because they represent an alternative to the use of fossil fuel-based materials [10, 11]. Cellulose is one of these friendly materials that can develop structural colors if prepared from liquid crystalline phases.

Cellulose structural colours

Cellulosic chains are considered as semirigid molecules and in this brief note we are interested in lyotropic systems. The formation of lyotropic liquid crystalline phases from cellulose derivatives involves the stiffness of the polymer, which is well described by the persistence length ($\boldsymbol{q}$) of the polymeric chain. To determine the critical volume fraction ($C^*(v/v)$) of polymer for the appearance of cellulosic liquid crystalline phase, the theory of Flory for a semirigid chain is commonly used [12]. According to Flory, $C^*(v/v)$ is given by the expression:

$$\boldsymbol{C}^*\left(\frac{\boldsymbol{v}}{\boldsymbol{v}}\right)=\left(\mathbf{1}-\frac{\mathbf{2}}{\boldsymbol{x}}\right),$$

where $x = \mathbf{2}\boldsymbol{q}/\boldsymbol{D}$, and $\boldsymbol{D}$ is the hydrodynamic diameter of polymeric chain. One of the most striking features of cellulose liquid crystalline systems is the development of coloured structures for a range of concentrations above $C^*(v/v)$. The observed colouration is due to the self-assembling of molecules in a helicoidal arrangement existing in chiral nematic liquid crystal organisation. At wavelengths matching the pitch of the supramolecular helicoidal structure, circularly polarized light is reflected. This reflection is selective being right-circularly polarized light reflected by right-handed chiral nematic structures, while left-circularly polarized light is reflected by left-handed helicoidal structures. According to de Vries theory [13], the maximum selective reflection (λ_0) of the reflectance spectra, taken at normal incidence, is related to the pitch value (P) by the expression: $\lambda_0 = \bar{\boldsymbol{n}}P$, where $\bar{\boldsymbol{n}}$ is the average refraction index of the material. The bandwidth values measured at half height of the reflectance spectra are given by $\Delta\lambda = P\Delta n$, where Δn is the birefringence of sample.

The optical as well as the chiroptical behaviour of cellulosic liquid crystalline systems have been well addressed in literature by different reviews published over the years (some examples are in [14–16]). It was reported that many parameters influence the pitch and handedness of chiral nematic structure. Among them are polymer molecular weight, structure and substitution degree of side chains covalently attached along cellulose main chain, temperature, pressure and in lyotropic phases – type and concentration of solvent.

In addition to cellulose-based macromolecular liquid crystalline phases, colloidal suspensions of cellulose nanocrystals (CNCs) are also known to originate lyotropic phases. Cellulose nanocrystals are obtained from different sources that include filter paper, cotton, and wood pulps. More usually, sulfuric acid is used to hydrolyse cellulose fibres resulting in sulphated CNCs, which makes CNCs stable in aqueous suspensions. Above a certain critical concentration of CNCs, the suspension separates into an isotropic low-density phase atop of an anisotropic phase [17]. The anisotropic phase is chiral nematic with the pitch above the visible range, while dried films can show iridescence [18, 19]. Perpendicular and oblique cross sections of CNCs solid films (Fig. 2) show characteristic Bouligand plywood structures [20].

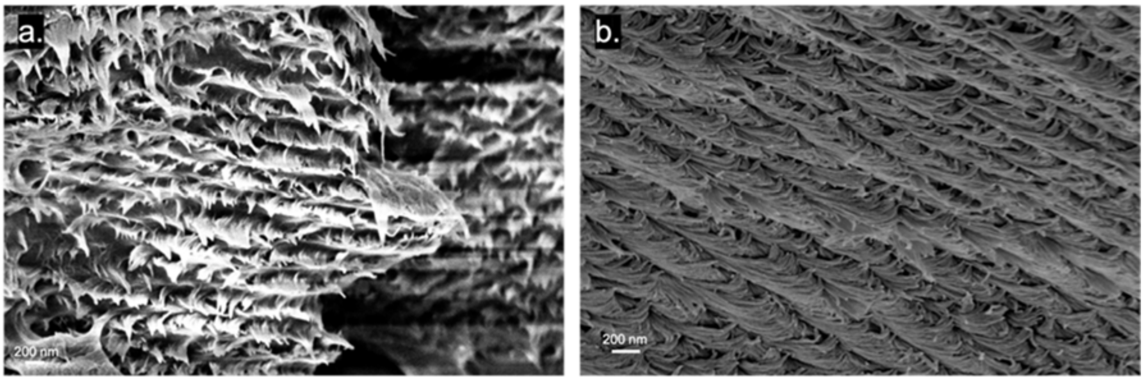

Fig. 2. Scanning electron microscopy (SEM) photos showing the cross section of a solid film obtained from an aqueous suspension of CNCs: *a* – Superimposed parallel planes forming the twisted cellulosic structure. From plane to plane the nanostructures rotate by a small and constant angle. The pitch of the helicoidal structure is the distance that corresponds to a 360° rotation. *b* – Oblique section to the planes define that the helicoidal structure appears as nested arcs

Colours arising from the chiral nematic structure of cellulose-based liquid crystals are well known and firmly recognised in literature. However, the study of open thermodynamic cellulose liquid crystalline systems and the evolution of moving colourful patterns was less addressed. The out-of-equilibrium systems rely in 2D-preparations and droplets obtained from cellulose-based liquid crystalline solutions in which the solvent was allowed to evaporate. All these systems form cellulose-based chiral mesophases and coloured ring patterns, but quite different mechanisms for their formation are involved. Some examples described in literature include the development of Liesegang-type structures in non-equilibrium suspensions of cellulose nanocrystals and *l*-(+)-tartaric acid (*l*-(+)-TA) [21], the coloured "coffee ring effect" observed in dried CNCs droplets [22] and the moving colourful concentric rings radiating in-wards from the periphery of quasi 2D-preparations observed in liquid crystalline solutions of hydroxy propyl methyl cellulose (HPMC) in trifluoroacetic acid (TFA) [23].

For Liesegang-type structures in non-equilibrium suspensions of CNCs and *l*-(+)-TA, the segregation between tartaric acid molecules and the cellulose nanorods associated with the solvent evaporation was found to promote the development of concentric rings from the centre to the border of the sample [21].

The "coffee ring effect" observed in dried droplets of CNC suspensions consists of periodic ring patterns appearing near the periphery of the dried sample. The deposition of CNCs occurs periodically during solvent evaporation for droplets with pinned contact lines [22].

In this paper, the self-organization of HPMC/TFA lyotropic nematic chiral solutions under non-equilibrium conditions is revised. Emphases is given to the formation of spatial and temporal evolving colourful patterns. Chemical reaction – diffusion mechanisms with the evaporation of solvents at the boundaries in quasi-2D and 1D cellulosic systems are considered.

Lyotropic liquid crystalline solutions of cellulose derivatives in trifluoroacetic acid

To address the recent results related to HPMC/TFA system, we must go back to works, where TFA was first used to obtain lyotropic cellulose-based liquid crystals.

It was during the eighties that intense work was made with cellulose lyotropic systems in the presence of trifluoroacetic acid. The work in these systems started after the investigation by Panar and Willcox [24] that showed the formation of a liquid crystalline phase of cellulose triacetate (CTA) in the presence of a mixture of TFA and chlorinated alkanes. Other investigations were dedicated to the study of cellulose acetate and triacetate in TFA. The influence of the solvent acidity upon the mesophase formation and the pitch value was also tested using TFA-CH_2Cl_2, TFA-$ClCH_2CH_2Cl$, TFA-$CHCl_2$. Sixou et al. [25] showed the influence of the polymer molecular weight upon the chiroptical characteristics of the liquid crystalline phase. Meeten and Navard [26] added water to TFA and proofed that besides a CTA/TFA+H_2O mesophase, a gel formed. The gel formation was attributed to crosslinks due to hydrogen bonding.

Some interesting experimental results were obtained when the solutions were observed in time. The ageing of the solutions was found to produce: (i) an exponential increase of the pitch [27–29], (ii) a reversal of the handedness of the nematic chiral supramolecular helicoidal structure [30], and (iii) the development of an isotropic phase [27, 28]. The authors referred that mesophase optical properties were studied as thin samples prepared between glass plates, but no allusion was made related to the solvent evaporation at boundaries.

The characteristics (i), (ii) and (iii) of the system were attributed to different factors, which included a chemical modification of the cellulose derivative in the presence of TFA and a relaxation of strains accumulated during sample preparation. The chemical reaction between the acid and the main chain of the cellulose derivative was found responsible for the appearance of isotropic phase due to the hydrolysis of glycosidic linkages [27, 28]. The optical and chiroptical properties of the solutions were associated with the acetylation of the free hydroxyl groups of cellulose side chain substituents by TFA [30, 31].

Moving colourful waves in cellulosic systems

Recently, the formation of oscillating "travelling" coloured patterns in cellulose-based lyotropic liquid crystals was reported [23]. The unexpected behaviour was attributed to chemical reaction-diffusion mechanisms and solvent evaporation at boundaries. The investigated liquid crystalline system, hydroxy propyl methylcellulose in TFA (HPMC/TFA), developed coloured solutions for a given range of TFA concentrations, pressure, and temperature. The authors reported that the pitch increased with solvent concentration, as expected for most cellulose-based lyotropic systems. The liquid crystalline system investigated showed iridescence and coloration in vials changed from red to blue with polymer concentration. The spatiotemporal evolution of the system was investigated in closed vials and in samples collected from the vials and pressed between two glass plates [23] and inside capillaries [31]. In time, the samples constrained in different geometries were shown to develop completely different optical and chiroptical behaviours (Fig. 3).

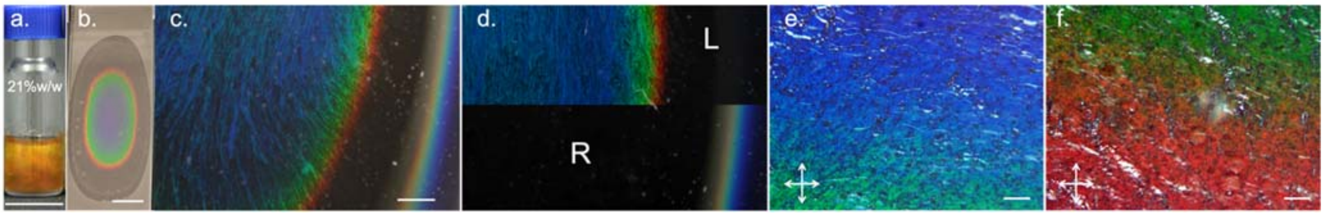

Fig. 3. HPMC/TFA liquid crystalline system: *a* – Liquid crystalline solution in the vial, 2 days after sample preparation; *b* – Quasi-2D geometry; *c* – Quasi-2D geometry between crossed polarizers; *d* – the same sample as in (*c*) under circularly polarized light in reflection mode. [At the centre of the sample, the sequence of colours results from reflection of the left-handed circularly polarized light (LCP) (upper image), while at the periphery, the reflected colours are due to the right-handed circularly polarized light (RCP) (bottom image)]; *e* and *f* – POM pictures between crossed polarizers, taken in transmission. The samples were prepared between two glass plates and the anchoring of molecules near the substrates is planar. The colour variation from up to bottom (blue to green in *e* and green to red in *f*) is due to different pitch values of helical structure. The textures in *e* and *f* present oil streaks characteristic of planar nematic chiral structures. Scale bars in *a* and *b* – 1 cm, *c* – 1 mm, *e* and *f* – 50 µm

The authors referred that inside the vials the pitch of the solutions decreased (all solutions became blue), and after some days similar as for CA in TFA, isotropic solutions developed [23].

The samples enclosed between two glass plates with open boundaries presented a very peculiar behaviour. The initial coloured quasi 2D-preparations developed a series of concentric circular-coloured rings with higher pitch values at the centre of the sample.

However, the sequences of new coloured rings, which appear always at the border and move in-wards until disappearance in the centre of preparation, and the reappearance of new ones at the border were reported. A reversal of the handedness of nematic chiral phase was also observed. The inversion of helix handedness involved variation from positive to negative values of the helix wave vector $\mathbf{q} = \mathbf{2\pi}/\boldsymbol{P}$ from sample centre to its periphery [23].

The authors considered the chemical reaction between the cellulose derivative (cell-OH) and TFA:

$$\mathbf{cell - OH + TFA \rightarrow Cell - OCOCF_3 + H_2O},$$

the diffusion and evaporation of TFA and water at boundaries to explain the observed “travelling colours” (Fig. 4). According to reference [23], the concentrations [cell-OH], [cell-OCOCF$_3$], [TFA] and [H$_2$O] change in space and time due to the chemical reaction, diffusion and evaporation. To simulate the behavior observed, the authors considered the following chemical reactions and diffusion equations:

$$\frac{d[cell-OH]}{dt} = D_{cell-OH}\nabla^2[Cell-OH] + g([TFA],[Cell-OH]) \quad (1)$$

$$\frac{d[cell-OCOCF_3]}{dt} = D_{celll-OCOCF_3}\nabla^2[cell-OCOCF_3] + j([H_2O],[cell-OCOCF_3]) \quad (2)$$

$$\frac{d[TFA]}{dt} = D_{TFA}\nabla^2[TFA] + f([TFA],[cell-OH]) \quad (3)$$

$$\frac{d[H_2O]}{dt} = D_{H_2O}\nabla^2[H_2O] + h([H_2O],[Cell-OCOCF_3]), \quad (4)$$

where D_{HPMC}, $D_{HPMC-COOCF_3}$, D_{TFA} and D_{H_2O} represent the values of diffusion rate constants of initial HPMC, ester ($\mathrm{HPMC}-\mathrm{COOCF_3}$), trifluoracetic acid (TFA) and water, respectively.

To explain the reverse of the handedness of the chiral nematic supramolecular helicoidal structure a conformational self-arrangement of the cellulosic chain was considered [23]. Similar behaviour was observed for samples encapsulated in capillaries [32].

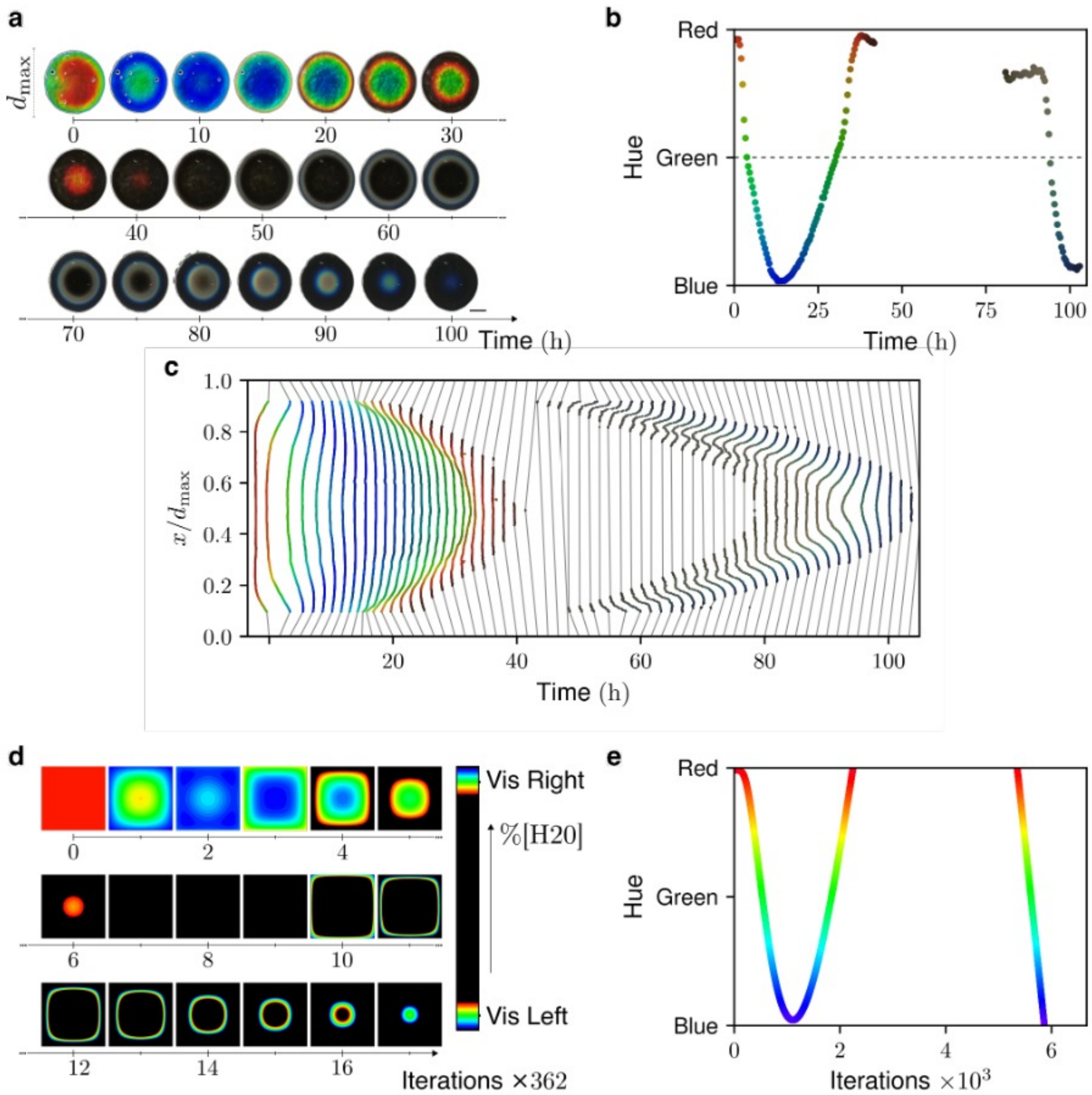

Fig. 4. Travelling cellulose-structural colors in a quasi-2D geometry: *a* – example of a quasi-2D liquid crystalline sample evolution, *b* – color evolution at the center of sample, *c* – same as in *b* but along a line that passes through the center of sample, *d* – numerical simulations of travelling colors with square geometry, *e* – color evolution at the center of simulated square. Reprinted with permission from [23] under the terms of the Creative Commons CC BY license Copyright © 2021, The Author(s)

Conclusions

The topic of this note is not closed. New experimental protocols and computational tools are needed to understand and control the production of novel interactive cellulosic structures with self-oscillating-colourfull patterns. The "fossilization" of these coloured patterns, obtained by reaction/diffusion mechanisms, into different shaped materials (spheres, cylinders and flakes) is one of the main targets that can be achieved by crosslinking and/or solvent evaporation. The materials prepared will provide a toolbox of self-assembled (soft and solid) structures, which will be at the geneses of natural-coloured particles for water-based inks, including aquarelles, which can replace pigments produced by plastics. The production of structural patterns in the liquid state from cellulose, by reaction-diffusion mechanisms, and their "fossilization" will represent a great contribute to the production of materials with low impact on the environment and made by a sustainnable resource.

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Contribution of the authors:
Godinho M.H. supervised and directed this project. Drew the handmade sketches in Fig. 1 and wrote the manuscript. ***All the authors*** contributed equally to the design, assembling of the figures, experimental results, improvement and editing of the manuscript.

The authors declare no conflicts of interests.

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