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Generating Circularly Polarized Light from Clustering-Triggered Emission Using Solid Phase Molecular Self-Assembly

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Abstract

Clustering-triggered emission (CTE) has displayed promising abilities in bioimaging, chemical sensing, and multicolor luminescence. However, it remains absent in the field of circularly polarized emission (CPL) due to the difficulties in well-aligning the nonconventional luminogens. We report the first case of CPL generated with CTE using the solid phase molecular self-assembly (SPMSA) of poly-L-lysine (PLL) and sodium oleate (OL). Under mechanical pressure, the electrostatic complex of PLL/OL form supramolecular film in which the OL ions self-assemble into lamellar mesophases bridged by the PLL chains. Since the OL mesophases are very alike giant

2D rigid supramolecular polymers with well-defined surface charge distribution, the PLL chains are forced to fold regularly as a requirement of optimal electrostatic interaction. Further facilitated by hydrogen bonding, the O and N atoms that form through space conjugation aligned orderly on the 2D surface, leading to CTE-based CPL. The CTE-based CPL is in analogy with conventional emission, which is capable to transfer its energy to a donor via a FRET process, making it possible to develop environmental friendly and economic CPL from sustained and renewable materials.

Key Words: Clustering-Triggered Emission; Solid Phase Molecular Self-Assembly; Circularly Polarized Light;

Introduction

It has long been recognized that the generation of fluorescence requires conjugated groups¹⁻³. The dislocation of electrons in a conjugated system allows decreasing the energy gap between the electronic ground and excited states, leading to emission of visible light⁴. However, recently a large number of molecules without conjugated groups were found to give considerable emission⁵⁻⁸. These molecules generally contain abundant electron-rich atoms, such as N, O, S, P, Si. Tang and Yuan et al revealed when these atoms cluster together, extended delocalization of the lone pair electrons would occur through-space conjugation (TSC), which results in conformation rigidification and leads to clustering-triggered emission(CTE)^{9,10}. Because CTE does not require conjugated groups, it has many advantages over emission from traditional

aromatic conjugated molecules, such as facile synthesis, good water solubility, and low biological toxicity^{9,11-14}. For this reason, CTE has become the potent alternative for the conventional one in many fields, such as color tunable light-emitting¹⁵⁻²⁰, room-temperature phosphorescence^{11-14,21-26}, as well as bioimaging and chemical sensing^{13,22-24,27-30}. It would be very promising if CTE is able to replace traditional emission in an even vast number of fields.

Circularly polarized emission (CPL) is attracting intensive interest in recent years owing to its significant importance in photoelectronics^{31,32}, nonlinear optics^{33,34}, three-dimensional displays³⁵, biological probes³⁶⁻³⁸ and data recording^{39,40}. However, so far it is still impossible to create CPL from CTE. A crucial requirement for the occurrence of CPL is the alignment of the chromophores in chiral environment⁴¹⁻⁴³. Unfortunately, the clustering states of the electron-rich atoms are heterogeneous in a CTE system^{9,10} and the luminescent clusters can hardly align orderly. It still remains an insurmountable challenge to align the clusteroluminogens in a CTE system.

Herein, we report the first case of CPL generated from CTE using the strategy of solid phase molecular self-assembly (SPMSA) proposed by us⁴⁴⁻⁴⁶. In this strategy, a precipitate composed of a pair of oppositely charged polyelectrolyte and amphiphile was first generated in water, which was further subjected to mild mechanical pressure to facilitate merging of the nanometer-sized hydrophobic domains into mesophases. As such, a free-standing supramolecular film came into formation owing to the bridging of these mesophases with polyelectrolyte chains. Considering the hydrophobic mesophases are very alike giant 2D rigid supramolecular polymers with well-defined

surface charge distribution, we therefore hypothesis that this unique structural feature is able to induce well-defined folding of polyelectrolytes composed of chiral units, thus leading to CTE-based CPL.

For that to occur, we chose the cationic α -poly-L-lysine (PLL) and sodium oleate (OL) in this work to build supramolecular films through the strategy of SPMSA. Amino acids are well-known chiral molecules. Poly-amino acids have been verified to display CTE^{14,23,24,47-50}. In this work we show that the ionic interaction between PLL and OL in water results in cross-linked vesicles at charge balancing ratio. PLL displays characteristic CTE which is CPL silent in the vesicle networks. However, upon centrifugation, the vesicle networks precipitated, which would transform into planar bilayers under a mild mechanical pressure (Fig. 1a). Up to our expectation, PLL folded into a well-defined structure on the surface of the bilayers formed with oleate ions. As a result, alignment of the clusteroluminogens (O and N atoms) occurred in the process of through-space conjugation, and the chirality of the amino groups is expressed in the CTE, leading to significant CPL. Through Förster resonance energy transfer (FRET), chirality transfer and magnification for the CTE-based CPL would occur, in analogy to conventional CPL. We envision that the current work would open a new paradigm in the study of CTE, making it possible to generate environment friendly CPL through economic pathway.

83

84 **Figure 1. Solid Phase Molecular Self-Assembly (SPMSA) of PLL-OL. a** The schematic illustration

85 of the Solid Phase Molecular Self-Assembly (SPMSA) of PLL-OL. **b** Turbidity of PLL-OL aqueous

86 suspension at different Lys: OL ratio ([Lys]=10 mM). **c** TEM image for the structures formed in the

87 PLL-OL suspension (Lys:OL=1:1, [OL]=[Lys]=10 mM). **d** Emission spectra of PLL-OL aqueous

suspension at different excitation wavelengths (Lys:OL=1:1, [OL]=[Lys]=50 mM). **e** The film obtained by pressing the precipitate. **f** The photo of the film under daylight (upper) and 365 nm UV light (lower), respectively. **g** Emission spectra of PLL-OL film at different excitation wavelengths.

Results

Solid Phase Molecular Self-Assembly(SPMSA) of PLL-OL

Fig. 1a shows the schematic process of the solid phase molecular self-assembly (SPMSA) with PLL and OL. As a nonaromatic poly(amino acids), PLL displays typical CTE character at pH 6~8, including concentration dependent emission strength, excitation dependent emission maximum and silence in CPL(Fig. S1). TEM and DLS study (Fig. S2) reveals that the CTE of PLL is originated from the heterogeneous clustering states of PLL chains. The electrostatic complexation of PLL with oppositely charged sodium oleate (NaOL) in water changed the aggregation of PLL but had no impact on the CTE nature(Fig. S3). With increasing the fraction of sodium oleate (NaOL), the turbidity of the mixed system increases drastically, and becomes whitish as the molar ratio between the lysine unit(Lys) and oleate ions(OL) reached 1:1 (Fig. 1b). Microscopic observation reveals that the addition of NaOL to the PLL solution leads to the formation of vesicles(Fig. 1c), and the vesicles are highly cross-linked as the concentration of NaOL reached 50 mM (Fig. S4). Figure 1d shows the excitation dependent emission for the 1:1 complexed PLL/NaOL at 50 mM. These vesicular clusters are CPL silence (Fig. S3c), and their CTE quantum yield (QY) at 365 nm is 4.56%. Lifetime measurements also indicates the presence of excitation

dependent emission species (Fig. S3d). Clearly, the formation of vesicles is not helpful to obtain well-defined folding of the PLL chains, and consequently, no CPL can be detected.

The cross-linked vesicles precipitate out after centrifuging under 12000 rpm. Under mechanical pressures beyond 5 Mpa, the fresh precipitates transform into a whitish film, which gradually becomes transparent within 1 hour (Figure 1e). This PLL-OL film is self-supporting and gives blue emission under 365 nm ultraviolet light (Fig. 1f). Elemental analysis reveal that the ratio of oleate ion (OL) to Lys is around 1.4:1 (Table S1), indicating part of the NaOL have underwent hydrolysis, and the molar ratio between oleic acid (HOL) and OL is roughly 0.4:1, which is further confirmed by XPS measurement⁵¹⁻⁵⁵ (Fig. S5). Strikingly, the emission maximum remains constant at 462 nm regardless the excitation (Fig. 1g). This λ_{ex} -independent CTE indicates that the clustering state of the clusteroluminogens (O and N atoms) in PLL becomes well-defined in the film. In line with this, only one λ_{ex} -independent fluorescence lifetime around 5.76 ns is obtained (Fig. S6). Meanwhile, the CTE quantum yield is up to 5.56%, suggesting that the alignment of the O and N atoms is advantageous for the CTE.

Figure 2. The multilayer ordered structure of the PLL-OL film. **a** small-angle XRD patterns, **b** 2D SAXS image, **c** azimuthal angle (ϕ) plot, and **d** TEM image of the PLL-OL films. **e** Schematic illustrations of PLL-OL self-assembled multilayer ordered structure. **f** Exemplified through space electronic communications among N...O and O...O units in PLL-OL film. **g** Exemplified intermolecular interaction between PLL chains.

In order to reveal the molecular packing mode in the PLL-OL film, X-ray diffraction (XRD) measurement and Wide-angle X-ray scattering (WAXS) (Fig. S7a)

were performed. The XRD pattern in Fig. 2a reveals 3 diffractions with a spacing ratio of 1: 2: 3, corresponding to the (100), (200) and (300) Miller Indices of a 2D lamellar mesostructure^{56,57}. The distance between the bilayers is estimated with Bragg equation to be 3.43 nm. This is 0.2 nm smaller than twice the extending length of the oleate molecule (Fig. S7b), indicating the presence of staggered surfactant bilayer domains in the film. Furthermore, the 2D SAXS pattern of the PLL-OL film shows two obvious dark arcs in the equatorial direction (Fig. 2b). The corresponding azimuthal angle (φ) plot features two sharp peaks at $\varphi = 90^\circ$ and 270° . The calculated orientation order parameter (f) is 0.24(Fig. 2c), indicating that the OL bilayers are well-aligned in the film. On the meanwhile, the TEM image for the cross section of the PLL-OL film shows light and dark stripes with a spacing of 0.355 nm (Fig. 2d and Fig. S7d). Since the dark stripes are generated from the scattering of the electron beam by electron-rich atoms, it reveals the region of clustered O and N atoms. In addition, the 0.355 nm is characteristics for the distance of π - π stacking^{58,59}, indicating the PLL chains have folded in such a way that all the O and N have aligned in a row, and these through-space conjugated O and N further undergo π - π stacking in the film, as illustrated in Fig. 2e. Fig. 2f and g demonstrates the possible chain alignment and the through space conjugation between the N and O atoms in neighboring chains. Owing to the electrostatic interaction between the amide groups and the oleate groups, the aligned PLL chains lay on the surface of the bilayers formed by the oleate, as shown in Fig. 2e.

Figure 3. Humidity responsiveness of the CTE-based CPL. **a** CD and UV-Vis spectra and **b** CPL spectra ($\lambda_{\text{ex}} = 330$ nm) of PLL-OL film (RH: 11.30%). **c** g_{lum} value, **d** CPL spectra ($\lambda_{\text{ex}} = 330$ nm), **e** XRD patterns, and **f** FT-IR spectra of the PLL-OL film at different relative humidity.

The well-defined clustering of PLL chains in the film have resulted in significant chiroptical signal. Fig. 3a shows that an exciton chiral signal featuring davydov splitting⁶⁰ occurs at 375 nm, with the first Cotton Effect($\Delta\epsilon_1$, longer wavelength) value being -40 at 425 nm and the second Cotton Effect($\Delta\epsilon_2$, shorter wavelength) being 69 at 325 nm. This chiroptical signal suggests that the negative excitation chirality has been generated, and the amplitude of the couplet A (defined as $\Delta\epsilon_1 - \Delta\epsilon_2$) and $\Delta\lambda$ (nm) value is 109 and 50, respectively. It is noticed that the CD signal is not

originated from LD(Linear Dichroism), since the CD signal remains nearly constant at varying angle measurements, whereas the LD spectrum is angular dependent (Fig. S8). In line with the reliable CD, right-handed CPL was observed. As shown in Figure 3b, the maximum polarized emission wavelength of PLL-OL film is 454 nm, which coincides with the maximum emission of fluorescence (462 nm). The g_{lum} value, as defined as $2(I_L - I_R)/(I_L + I_R)$, with I_L and I_R denoting the emission intensities of left-handed CPL (*l*-CPL) and right-handed CPL (*r*-CPL) component, respectively^{61,62} is -0.016 (Fig. S9), which is comparable to, and even higher than CPL generated from many conventional conjugated organic emitters⁶³⁻⁶⁵. To the best of our knowledge, this is the first CTE based CPL ever reported, indicating it is very promising in creating CPL with green and sustainable materials.

The CPL intensity reduces significantly with increasing humidity. The g_{lum} value decreases rapidly from -0.016 at RH 11.30% to -0.0033 at RH 32.78% and -0.0018 at RH 52.89% (Fig. 3c). A much higher humidity than 52.89% results in almost complete vanishment of the CPL signal(Fig. 3d), although the fluorescence intensity remains basically unchanged (Fig. S10a). The reduction of the CPL is a manifest of the reduced supramolecular chirality in the film. Fig. S10b reveals that the CD signal decreases drastically as the humidity increases, and disappears completely as the humidity exceeds 75.29%.

The XRD pattern in Fig. 3e suggests that the interlayer spacings increase from 3.43 nm to 4.42 nm as the relative humidity (RH) increases from 11.30% to 93.58%. On the meanwhile, the second-order diffraction peak is significantly weakened (Inset in

Fig. 3e and Table S2), manifesting a less ordered long range stacking of the bilayers in the PLL-OL film. It is noticed that the distance of 4.42 nm is about 0.8 nm larger than two folds of the extending length of the OL chains, indicating that the folding state of the PLL chains has changed drastically with increasing humidity. TGA measurement suggests that the water content in the film increases with humidity. At the humidity of 11.30%, the water content in the film is 0.9%, whereas it rises to 23.3% at the high humidity of 93.58%(Figure S11 and Table S2). This means that the electrostatic interactions between PLL chains and the 2D OL bilayers would be significantly weakened, since the dielectric constant of water is 80 times smaller than in the vacuum. FT-IR spectra manifests that the wavenumber of the N-H vibrational band at 3400 cm^{-1} have increased with humidity(Fig. 3f and Table S2), indicating the hydrogen bonds that drives the well-defined folding of the PLL chains have been weakened. This means that the PLL chains on its own can hardly fold regularly; the electrostatic interactions between the PLL chains and the OL bilayers are crucial for the forced intramolecular hydrogen bonding.

CTE-based FRET leading to color tunable CPL

The excitation independent CTE of PLL in the PLL-OL film is very alike conventional emission generated with conjugated molecules. We then move a further step to check whether this CTE is able to undergo Förster resonance energy transfer (FRET) as its conjugated counterparts do. Since the emission of PLL in the film

overlaps well with the absorption of fluorescein sodium (FS)(Fig. S12a), FS was doped as the energy acceptor into the film via coprecipitation. With increasing the doping amount of FS, the blue CTE of PLL decreased gradually, and the yellow emission of FS centered at 555 nm rose up(Figs. 4a and 4b). The maximum FS emission was observed at the FS doping rate of 0.87 wt%. Further increase of FS resulted in decrease of the emission intensity, due to the notorious ACQ^{66,67}. This means that CTE, just like conventional fluorescence, is able to undergo FRET in the presence of energy donor. Table S3 shows the changes of fluorescence lifetime, energy transfer efficiency and absolute quantum yield of the PLL-OL $\supset$ FS film with different FS doping rate. Before FS doping, the fluorescence lifetime τ_D of PLL in the film is approximately 5.68 ns(Fig. S12b and Table S3). In case of 0.87 wt% FS doping, the CTE lifetime of PLL in the film decreased to 2.39 ns. Based on these fluorescent lifetime variations, the efficiency of energy transfer from the folded PLL to FS is estimated to be 57.9%. It is noticed that in this FRET process, the absolute quantum yield of the system has been amplified from 5.56% to 21.9%. Most strikingly, the supramolecular chirality of PLL was also transferred to FS, leading to a broad negative CD signal in the range of 300-500 nm, with a sharp peak occurred at 521 nm(Fig. S13). On the meanwhile, a bright yellow right-handed CPL was observed at 575 nm(Fig. 4c), and the g_{lum} of the maximum emission is enlarged from -0.016 to -0.018(Fig. S14). This means that FS has complexed efficiently with the folded PLL chains. Based on the above experimental results, a possible energy transfer mechanism is proposed in Fig. 4d. The amplified QY and g_{lum} in the process of FRET

makes it possible to obtain color tunable CPL simply by varying the doping ratio of the acceptors. This greatly broadens the application versatility of CTE, endowing it all the functions of traditional emissions.

Figure 4. Color tunable CPL through FRET. **a** Emission spectra (Ex=365 nm) and **b** photos of natural light and 365 nm UV light of PLL-OL/FS films with different FS doped heavy. **c** CPL spectra (Ex=342 nm, FS:0.87%) of PLL-OL and PLL-OL/FS film. **d** Energy level diagram for ET in PLL-OL/FS film.

Discussion

The chain folding state of PLL is very critical for the generation of CTE-based CPL. Here, the desired chain folding of PLL can be induced by the regularly arranged negative charges on the 2D surface of OL bilayers. Because the electrostatic interactions, the quaternized amide groups in the PLL chains are forced to align according to the negative charge density on the 2D surface. On the meanwhile, these

quarternized amide groups would form hydrogen bonds with other O and N atoms, which are in the form of through-space-conjugation(TSC). In this way, the clusteroluminogens are aligned on the surface of the 2D OL bilayers. With increasing the environmental humidity, the physically adsorbed water would bond preferably with the ionic groups of PLL and OL⁴⁴, with weakens the electrostatic interaction between them. As a result, the PLL chains would swell, and the hydrogen bonding between the clusteroluminogens was destroyed. Consequently, the N and O atoms forming TSC could not be aligned any more, resulting in the vanishing of the supramolecular chirality. Because the electrostatic interaction in the presence of water would always be weakened, it is hard to obtain CPL in aqueous media via electrostatic interactions. That's why the PLL/OL vesicles do not display CPL. In this sense, SPMSA would be very efficient in generating CTE-based CPL, and the CPL can be manipulated with environmental humidity. Since the acquiring and loss of water via humidity change is reversible, the CTE-based CPL is therefore can be reversibly switched on and off by controlling the environmental humidity, rendering it an efficient approach to create smart CPL materials.

In summary, we made the first CTE-based CPL with the strategy of solid phase molecular self-assembly (SPMAS). The CTE material PLL was forced to well-aligned on the surface of the self-assembled oleate bilayers, so that the CTE molecule PLL not only clustering but formed supramolecular structure and generate 2D supramolecular exciton chirality. By controlling the folding state of PLL with environmental humidity, the supramolecular chirality status of PLL can be manipulated on and off. The

emission maximum of CTE in the SPMAS is excitation independent, making it in analogy to conventional luminescence. In this way, the CTE-based CPL can be further transferred and magnified via a FRET process. We believe that the SPMAS can be an efficient strategy to transform CTE molecules from random clusters into regular arranged superstructures. This opens a new avenue in generating CPL from economic and sustainable CTE.

Methods

Solid Phase Molecular Self-Assembly of PLL-OL

Poly-L-lysine (PLL), with a purity of 95%, was purchased from BYD Pharmaceuticals. Sodium oleate (NaOA), chemically pure, was purchased from Sinopharm Group. The experimental water was ultra-pure water (Milli-Q water) with a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$ obtained by a Millipore ultra-pure water machine. An aqueous solution of PLL and an aqueous solution of NaOA was added, reaching final concentrations of 50 mM for the ammonium positive charges of PLL and 50 mM for the carboxylate negative charges of NaOA. White precipitates were immediately formed after the mixing, and they were separated from the suspensions by centrifugation with a speed of 12,000 rpm for 15 min. The collected precipitates were then treated in two parallel ways: subjected to a pressure imposed by finger pressing and noodle machine manufacturing under ambient environment.

Humidity control experiment

The newly prepared films were suspended in an atmosphere equilibrated with different saturated salt solutions and equilibrated for a week. The relative humidity of

the saturated salt solution is as follows: LiCl-11.30%, MgCl₂-32.78%,
Mg(NO₃)₂-52.89%, NaCl-75.29%, KNO₃-93.58.

Dyes doping

After leaving the newly prepared PLL-NaOA film for 12 hours, weigh and cut each film to 0.056 g, and then gradually add 1.3×10⁻⁵ to 1.3×10⁻¹ mol/L FS aqueous solution 1- 10 µml, press again to get PLL-NaOA⊃FS film with different FS mass fraction.

Estimation of the orientation order

The orientation order parameter (f) was estimated using the azimuthal angle plots obtained from the 2D SAXS images⁶⁸. The f values range between 0 and 1, where the former corresponds to an isotropic structure, and the latter corresponds to perfect orientation along the director. A Maier-Saupe distribution function was used to fit the azimuthal angle plots:

$$I = I_0 + A \exp[\omega \cos^2(\varphi - \varphi_0)]$$

where I_0 denotes the free baseline intensity, φ_0 is the azimuth at the position of the maximal intensity, φ is the azimuth and ω is the parameter that determines the width of the distribution. After the curve fitting of this function to the azimuthal angle plot, parameters I_0 , A and ω were obtained. The orientation order parameter f was determined using the following equation:

$$f = \frac{\int_{-1}^1 P_2(\cos\varphi) \exp(\omega \cos^2\varphi) d\cos\varphi}{\int_{-1}^1 \exp(\omega \cos^2\varphi) d\cos\varphi}$$

where the function $P_2(\cos\varphi)$ is the second-order Legendre polynomial of $\cos\varphi$, often referred to as the Hermans orientation function:

$$P_2(\cos\varphi) = \frac{1}{2}(3\cos^2\varphi - 1)$$

Estimation of the efficiency of the transfer

The rate of energy transfer is inversely proportional to the sixth power of the distance, r , between the donor and acceptor. The efficiency of energy transfer E_{FRET} is defined with respect to r and R_0 , the characteristic Förster distance⁶⁹ for the donor and acceptor pair by

$$E_{FRET} = \frac{1}{1 + \left(\frac{r}{R_0}\right)^6}$$

where R_0 is a characteristic distance for the donor-acceptor combination at which EFRET takes the value 0.5. Experimentally, FRET can be detected in several ways⁷⁰⁻⁷⁴. Energy transfer causes quenching of donor fluorescence and sensitized fluorescence of the acceptor. It also reduces the donor lifetime and decreases the rate of irreversible photobleaching of the donor. In this work, experimental FRET efficiencies (E) were obtained from steady-state measurements using

$$E = 1 - \frac{\tau_{DA}}{\tau_D}$$

where τ_{DA} and τ_D are the measured donor fluorescence lifetimes in absence and in presence of acceptor, respectively.

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Figures

Figure 1

Solid Phase Molecular Self-Assembly (SPMSA) of PLL-OL. a The schematic illustration of the Solid Phase Molecular Self-Assembly (SPMSA) of PLL-OL. b Turbidity of PLL-OL aqueous suspension at different Lys:OL ratio ([Lys]=10 mM). c TEM image for the structures formed in the PLL-OL suspension (Lys:OL=1:1,

[OL]=[Lys]=10 mM). d Emission spectra of PLL-OL aqueous suspension at different excitation wavelengths (Lys:OL=1:1, [OL]=[Lys]=50 mM). e The film obtained by pressing the precipitate. f The photo of the film under daylight (upper) and 365 nm UV light (lower), respectively. g Emission spectra of PLL-OL film at different excitation wavelengths.

Figure 2

The multilayer ordered structure of the PLL-OL film. a small-angle XRD patterns, b 2D SAXS image, c azimuthal angle (φ) plot, and d TEM image of the PLL-OL films. e Schematic illustrations of PLL-OL self-assembled multilayer ordered structure. f Exemplified through space electronic communications among N and O units in PLL-OL film. g Exemplified intermolecular interaction between PLL chains.

Figure 3

Humidity responsiveness of the CTE-based CPL. a CD and UV-Vis spectra and b CPL spectra ($\lambda_{ex} = 330$ nm) of PLL-OL film (RH: 11.30%). c g_{lum} value, d CPL spectra ($\lambda_{ex} = 330$ nm), e XRD patterns, and f FT-IR spectra of the PLL-OL film at different relative humidity.

Figure 4

Color tunable CPL through FRET. a Emission spectra(Ex=365 nm) and b photos of natural light and 365 nm UV light of PLL-OL FS films with different FS doped heavy. c CPL spectra (Ex=342 nm, FS:0.87%) of PLL-OL and PLL-OL FS film. d Energy level diagram for ET in PLL-OL FS film.

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