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Self-assembly of discotic liquid crystal porphyrin into more controllable ordered nanostructure mediated by fluorophobic effect

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The novel nanoscale discotic liquid crystal porphyrin with partial chain perfluorination, which has the same basic structure as the best photoreceptor in nature (chlorophyll), shows an exceptionally enhanced tendency to self-assemble into ordered nanostructure. Defect-free homeotropically aligned fluorinated porphyrin thin films were, for the first time, fabricated and characterised. The ability to self-assemble large π-conjugated discotic molecules into highly ordered nanostructure via partial chain perfluorination provides new insight for the bottom-up nanofabrication of molecular devices. The controllable ordered porphyrin nanostructure with directed molecular arrangement holds great promise for use in high-performance electronic devices.

Keywords: partially perfluoroalkylated liquid crystal porphyrin; self-assembly; ordered nanostructure; uniform alignment; defect-free homeotropically aligned porphyrin thin films

1. Introduction

The ability to control molecular self-assembly by non-covalent interactions is a major driving force in the bottom-up nanofabrication of molecular devices. Large π-conjugated discotic liquid crystals (LCs) capable of being uniformly aligned represent a striking example of self-assembly mainly driven by π-π interactions together with the intrinsic nature of LCs. Such discotic LCs, viewed as a new generation of organic semiconductors due to their ability to carry charges more efficiently than conventional conjugated polymers (*1*, *2*), provide tremendous opportunities as well as challenges in fundamental science that could open the door for applications such as photovoltaics (*3–5*), light-emitting diodes (*6*) and field effect transistors (*7*). The alignment control of large π-conjugated discotic LCs is crucial for their practical applications. Homeotropic alignment, in which columns formed by intermolecular π-π stacking are perpendicular to the substrate, is required for photovoltaics and light-emitting diodes, whereas homogeneous alignment, in which columns are parallel to the substrate, is required for field-effect transistors (Figure 1). However, compared with the well-established alignment technology of rod-shaped LCs in the display industry (*8*), these discotic LCs are difficult to align uniformly due to high viscosity resulting from the large π-conjugated system necessary for electronic devices. Some attempts, e.g. coating PTFE (polytetrafluoroethylene) on substrate, controlling cooling rate from isotropic phase and using zone-casting technique were used to achieve large area uniform orientation of large π-conjugated discotic molecules with limited success (*9–12*). Undoubtedly, a major challenge for device performance is to obtain sufficient controllability of defect-free large area thin films with directed molecular arrangement.

Here, we report the synthesis of a novel nanoscale discotic LC porphyrin **1** with partial chain perfluorination (Figure 2). The fluorinated material exhibits an exceptionally enhanced uniform alignment and self-assembly, resulting in a controllable ordered nanostructure and solving the problems in their practical applications mentioned above. To the best of our knowledge, this is the first fluorinated LC porphyrin capable of being homeotropically and/or homogenously aligned, as well as the first partially perfluoroalkylated LC porphyrin to be synthesised.

The interest behind the design of a new discotic LC with partially perfluorinated chains mainly results from perfluoroalkyl group having more rigid, lower van der Waals forces and larger steric bulk than the corresponding perhydrogenated one, which can greatly reduce intercolumnar interactions and enhance the stability of columnar phase. Previously, it has been shown that chain perfluorination of a small discotic system, i.e. triphenylenes, supports columnar packing (*13*). There appears no report on any success that introducing perfluoroalkyl chains into large π-conjugated discotic molecule leads to a strong tendency for a homeotropic alignment, which is important for their applications, although large conjugated perfluoroalkylated discotic LC such as hexabenzocoronenes were synthesised (*14*, *15*). Meanwhile, the use of porphyrin as the building block for discotic materials is because it has the basic structure of the best photoreceptor in

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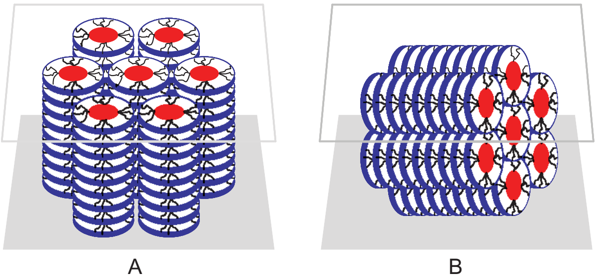


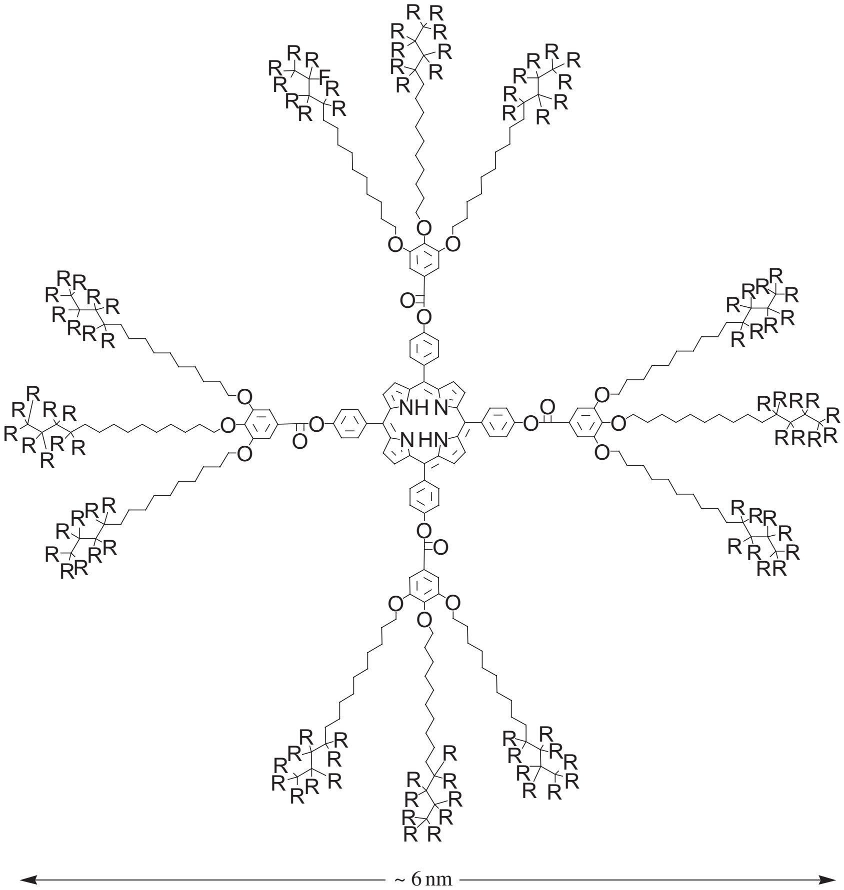
Figure 1. Schematic representations of homeotropic alignment (A) and homogeneous alignment (B).

nature – chlorophyll – and has many desirable features such as a highly conjugated disc plane, high stability, efficient absorption of sunlight and a small gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. From a molecular point of view, porphyrin systems are superior to other systems such as triphenylenes. Unfortunately, it is not easy to achieve the advantageous homeotropic alignment of discotic LC porphyrins (*16*), although LC porphyrins as promising organic electronic materials have been reported (*17–19*).

2. Experimental section

2.1 Materials and methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$. Chemical shifts are in δ units (ppm) with the residual solvent peak as the internal standard. The coupling constant (*J*) is reported in hertz (Hz). NMR splitting patterns are designed as follows: s, singlet; d, doublet; t, triplet; and m, multiplet. Column chromatography was carried out on silica gel (60–200 mesh). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh F254 glass plates. Spots were rendered visible by exposing the plate to UV light. Elemental analysis was performed by Robertson Microlet Inc. Mass spectrum was taken



1 R = F; **2** R = H

Figure 2. Molecular structures of partially perfluoroalkylated discotic LC porphyrin **1** and its corresponding non-fluorinated counterpart **2**.

by Mass Spectrometry & Proteomics Facility of Ohio State University. Textures and transition temperatures were observed by optical microscopy using a Leitz polarising microscope in conjunction with a Linkam TMS temperature controller. Calorimetric measurements were performed in a Perkin Elmer DSC using indium as a standard calibration. For the synchrotron X-ray diffraction (XRD) on the homeotropically aligned thin films, the samples were sandwiched between 50 μm thick bare glass plates with an 8.0 μm gap. The glass cells were slowly cooled from isotropic to mesophase in order to obtain the homeotropically aligned textures. The sample cell was mounted inside a Hot Stage that controlled the sample temperature a precision of ±0.02°C. The samples were exposed to 50 μm × 50 μm size synchrotron X-ray beam at the Advanced Photon Source (APS) at Argonne National Laboratory (Midwestern University Collaborative Access Team's facilities on Sector 6). An X-ray wavelength of 0.7653 Å was used. The diffraction patterns were recorded at different temperatures during heating to an isotropic phase using a high resolution Mar3450 area detector placed at a distance of 506.2 mm from the cell. The recorded XRD patterns were analysed using 'FIT2D' software developed by A. P. Hammersley of the European Synchrotron Radiation Facility. For the synchrotron XRD on unaligned powder sample, samples were sandwiched between two 8 μm thick Kapton films. The samples were exposed to the 200 μm × 200 μm size synchrotron beam with 0.7653 Å wavelength. The other samples were processed in the same way as those on homeotropically aligned thin films.

2.2 *Synthesis*

Partially perfluoroalkylated porphyrin **1** was synthesised starting from 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane by radical addition, reduction, bromination, Williamson ether formation, hydrolysis and esterification in seven steps (Figure 3). Its chemical structure was well identified by ^{1}H NMR, ^{13}C NMR, MS and elemental analysis. ^{1}H (400 MHz, $CDCl_3$): –2.78 (s), 1.36 (m, 120H), 1.58 (m, 48H), 1.80 (m, 8H), 1.92 (m, 16H), 2.06 (m, 24H), 4.15 (m, 24H), 7.60 (s, 8H), 7.63 (d, 8H, J = 8.4 Hz), 8.28 (d, 8H, J = 8.4 Hz), 8.94 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): 20.10, 26.15, 29.14, 29.28, 29.34, 29.39, 29.46, 29.56, 29.67, 30.41, 30.57, 30.79, 31.02, 69.33, 73.63, 108.74–124.03(m), 108.74, 119.33, 120.17, 124.03, 131.47(b), 135.44, 139.67, 143.19, 151.06, 153.13, 165.25; Anal. Calcd for $C_{240}H_{274}F_{108}N_4O_{20}$: C, 51.60; H, 4.94; N, 1.00. Found: C, 51.40, H, 4.82, N, 0.92; Mass calcd for $C_{240}H_{275}F_{108}N_4O_{20}$ (M + H): 5585; Found: m/e 5585.

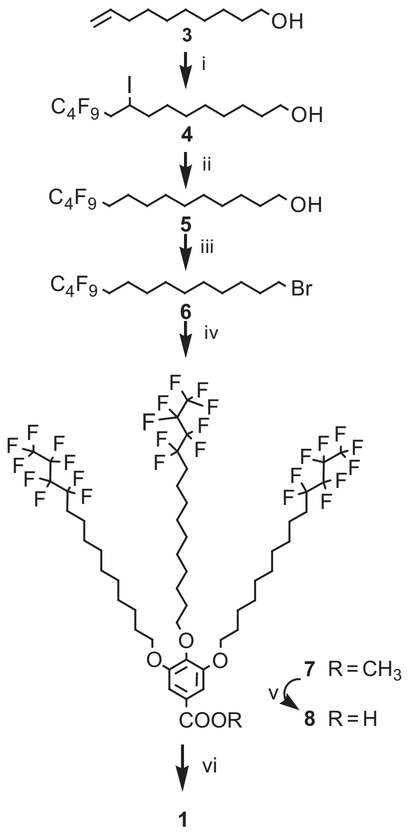


Figure 3. Synthesis of partially perfluorinated discotic LC porphyrin **1**. i: C_4F_9I, $(Ph_3P)_4Pd(0)$; ii: $LiAlH_4$; iii: 48% HBr; iv: Methyl 3,4,5-trihydroxy benzoate, K_2CO_3; v: KOH; vi: 5,10,15,20-tetra(4′-hydroxyphenyl) porphyrin.

3. Results and discussion

The fluorinated porphyrin **1** is thermally stable even at 300°C. As expected, optical measurements of its thin films show a strong absorption in the solar spectrum. Its phase behaviour was investigated by crossed polarising optical microscope (POM) equipped with a temperature controller, differential scanning calorimetry (DSC) and synchrotron XRD. The result shows this material **1** has similar hexagonal LC phases but much wider thermal range compared with its corresponding non-fluorinated porphyrin **2** (*6b*) (Table 1).

On cooling from isotropic phase, it first goes into a shearable LC phase at 240.4°C with the growth of distinct dendritic domains. The pattern is characteristic of the hexagonal columnar phase. This phase then proceeds to another phase with high viscosity at 120.2°C which persists through room temperature. In the phase below 120.2°C the texture of the hexagonal columnar phase remains unchanged. The results of X-ray investigations for unaligned powder **1** are shown in Figure 4. The diffraction patterns in Figure 4A and 4B consist of two diffused rings one large (Figure 4A) and another small (Figure 4B) angles corresponding to

Table 1. Phase transition temperature (°C) and enthalpies (J/g)[a].

1	I	240.4 (2.7)	Colh	120.2 (4.1)	Colho<0
2	I	135.4 (2.5)	Colh	115.7 (3.8)	Colho −13.7 (10.0)

[a] I = isotropic liquid; $\mathrm{Col_h}$ = hexagonal phase; $\mathrm{Col_{ho}}$ = more ordered hexagonal phase.

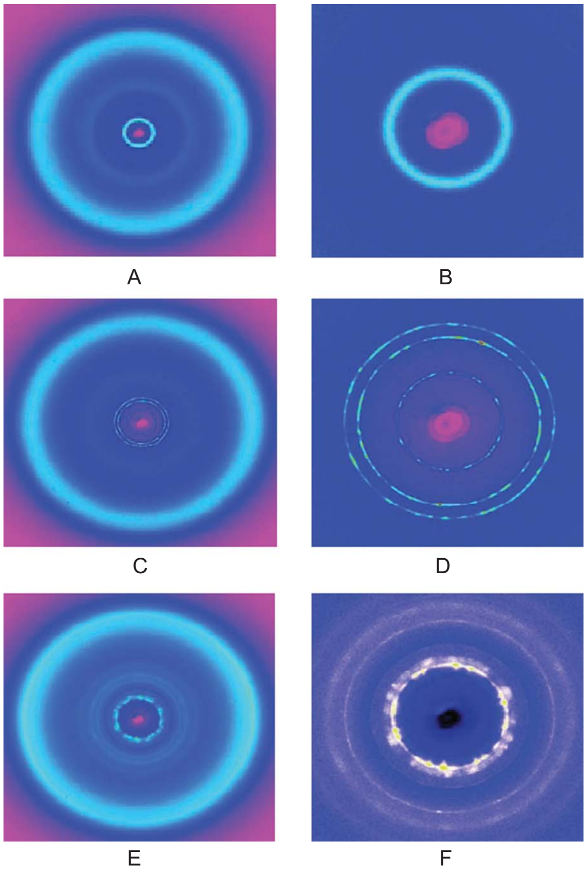


Figure 4. Synchrotron X-ray diffraction patterns of unaligned powder **1** at 243°C (isotropic phase: A and B), 123°C (hexagonal phase: C and D) and 83°C (more ordered hexagonal phase: E and F); wide angle scattering: A, C and E; Small angle scattering: B, D and F.

5.5 Å and 39.0 Å, respectively, indicating the presence of the isotropic phase. The weak scattering near medium angle originates from the experimental setup. There are three inner rings at 123°C corresponding to the three d-spacings 41.0 Å, 23.8 Å and 20.6 Å in a ratio of $1:1/\sqrt{3}:1/2$ while the outer ring retains the diffuse liquid-like character, indicating the hexagonal phase. The X-ray diffraction patterns in Figure 4E and 4F at 102.9°C correspond to the more ordered hexagonal LC phase as observed from the non-fluorinated homologus compounds in our previous study (*20*).

Porphyrin **1** is fluid in the isotropic phase and can be capillary-filled into thin cells. In films thinner than 10 μm it shows an exceptionally strong tendency towards homeotropic alignment compared with its corresponding non-fluorinated counterpart **2** on cooling at 2°C/min, i.e. it is much easier to obtain a large area defect-free homeotropically aligned thin film than its non-fluorinated counterpart (Figures 5 and 6). Moreover, the homeotropic alignment remains stable through room temperature once the transition from the isotropic phase to the hexagonal columnar phase is complete. The completely dark texture (Figure 5A) and the symmetric cross in the conoscopic image (Figure 5C) confirm the homeotropically aligned architecture in which their molecules stack into columns perpendicular to the substrate (Figure 1A). Synchrotron XRD obtained from an optically dark homeotropic monodomain in **1**'s thin film at 126.0°C also confirms the homeotropically aligned architecture (Figure 7). The d-spacings are 41.5Å, 24.0Å and 20.8Å in a ratio of $1:1/\sqrt{3}:1/2$. Azimuthal intensity distribution of the peak confirms the hexagonal columnar phase with a homeotropic orientation.

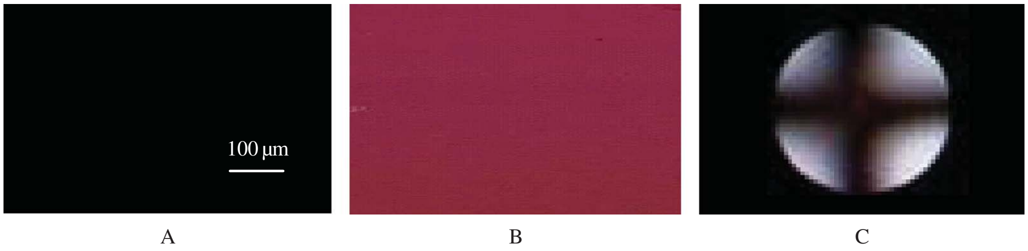


Figure 5. Optical textures of homeotropically aligned **1** at room temperature with crossed polarisers (A), without crossed polarisers (B) and the conoscopic image in a 5 μm cell (C).

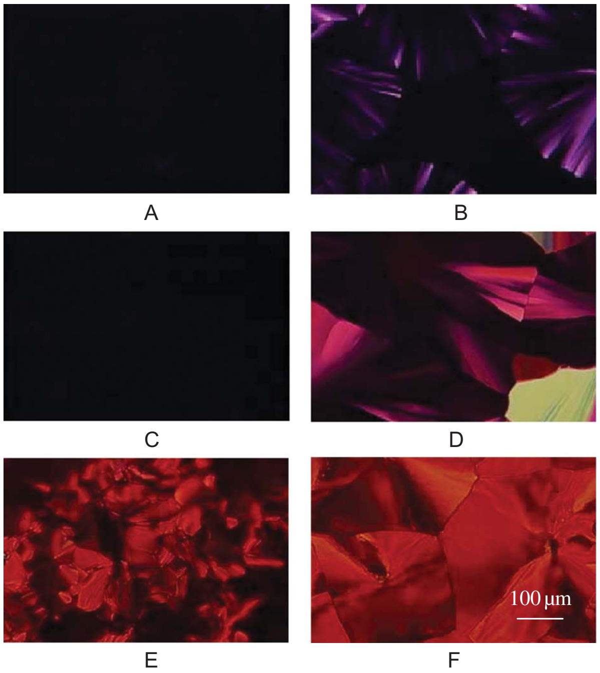


Figure 6. Crossed polarised optical textures of **1** (A: 5 μm thick; C: 9 μm thick; E: 20 μm thick) and its corresponding non-fluorinated counterpart **2** (B: 5 μm thick; D: 9 μm thick; F: 20 μm thick) at room temperature. The dark areas represent homeotropic alignment, and the bright domains appear where the porphyrin planes are oblique to the substrates.

The experimental results show that a modified substrate surface such as ITO-coated glass and polyimide-coated glass with and without mechanical rubbing seems to have no bearing on obtaining defect-free homeotropic alignment of **1**. The dominant factors in obtaining large area defect-free homeotropic alignment appear to be film thickness and thermal treatment. The thinner the film is, the more uniform homeotropic alignment can be achieved. In addition to, homeotropic alignment, material **1** can also easily yield a uniform homogeneous alignment by mechanical shearing a homeotropically aligned cell at 220°C (Figure 8). The homogeneous superstructure is maintained through room temperature as soon as it is achieved.

4. Conclusions

In conclusion, one novel nanoscale discotic LC porphyrin **1** was synthesised. Introducing fluorine into the chains of self-assembling discotic LC porphyrin provides a structural change that supports and enhances the tendency towards uniform alignment and self-assembly. The defect-free homeotropically aligned fluorinated porphyrin thin films, for the first

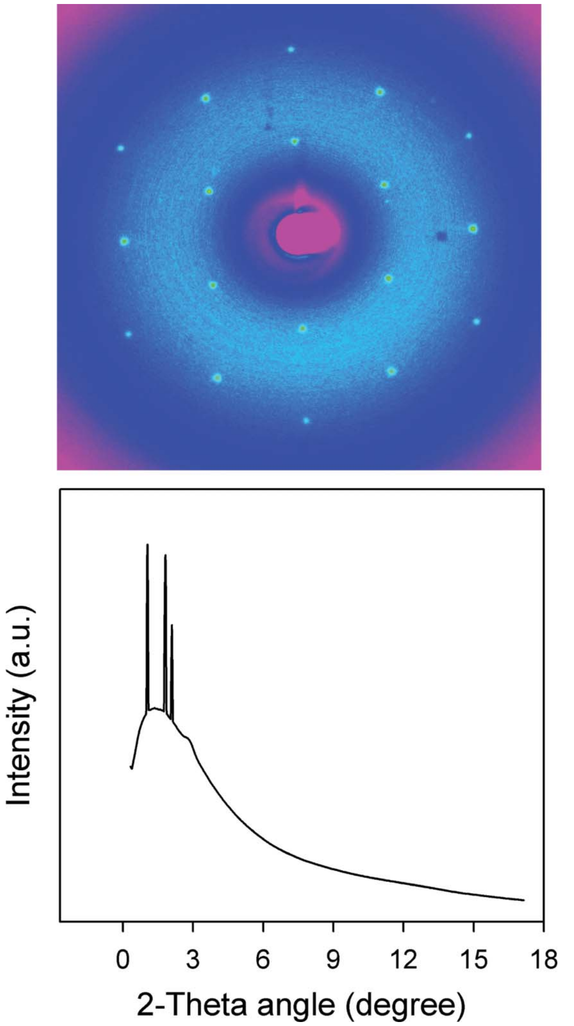


Figure 7. Synchrotron X-ray diffraction pattern (top) and X-ray intensity vs diffraction angle plot (bottom) obtained from homeotropic monodomain of sandwiched sample **1** with an 8 μm gap at 126°C.

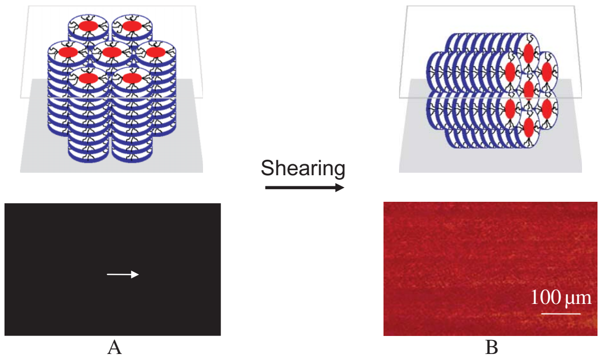


Figure 8. Schematic representations and crossed polarised optical textures of the fluorinated porphyrin **1** in a cell at 220°C (A: homeotropic alignment before shearing; B: homogeneous alignment after shearing). Arrow indicates shearing direction.

time, were fabricated and characterised. The ability to self-assemble large π-conjugated discotic molecules into highly ordered nanostructure via partial chain perfluorination provides new insight for the bottom-up nanofabrication of molecular devices, and the controllable ordered porphyrin nanostructure with directed molecular arrangement holds great promise for high-performance electronic devices.

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