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Photopatterning of Poly(arylene dienylene) by the Photoacid-Catalyzed Deprotection−Elimination Reaction of a Precursor Polymer

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ABSTRACT: Precursor polymers prepared from 1,4-dialkoxy-1,4-diarylcyclohexane monomers are converted to the conjugated poly(arylene dienylene)s during the course of an acid-catalyzed deprotection−elimination reaction. These materials are employed as combined active materials and photoresists in the surface patterning of luminescent conjugated polymers.

Introduction

Conjugated organic materials are appealing candidates for a wide variety of applications, including organic light-emitting devices (OLED),[1] organic electronics,[2] solar cells,[3] and sensors.[4] In these applications, devices are typically constructed by deposition of the conjugated organic materials on a substrate by either vapor phase processes or solution coating, the latter being preferred for the coverage of extended areas and for conjugated polymers. Many applications require the surface patterning of the active material, such as in the tracing of circuit elements or of pixels for displays. Approaches for addressing this requirement have included inkjet printing, contact printing including soft lithography, and pattern photobleaching or laser ablation.[5] By contrast, photolithographic techniques remain by far the most common methods for the surface patterning of inorganic substances, but the numerous and sometimes harsh processing steps (solvent or acid/base washes, etc.) are often ill-suited for organic substrates which solubility profiles are, by comparison to inorganic materials, much closer to those of typical resists.[6] Herein, we report the application of a different approach for the photopatterning of conjugated polymers, in which a nonconjugated precursor polymer is converted to the target poly(arylene dienylene) on a substrate surface by the means of a photoacid-catalyzed deprotection−elimination reaction (Figure 1).

Inspired by the precedents of Gin and Grubbs,[7] and by results derived from our synthesis of strained cyclic oligophenylenes,[8] we surmised that a partially nonconjugated precursor polymer **P1** could be reacted in a sequence of acid-catalyzed deprotection and dehydration (or direct alcohol elimination) steps to give the poly(arylene dienylene) **P2** (Figure 1).[9] Combining **P1** with a catalytic amount of a photoacid generator (PAG) would consequently enable the direct surface patterning of **P2** in an expeditious fashion using conventional photolithographic techniques. Instead of requiring separate chemically amplified resists and active materials, and the development of compatible chemistries for the selective coating and removal of each layer, the components are combined in a single material.[10]

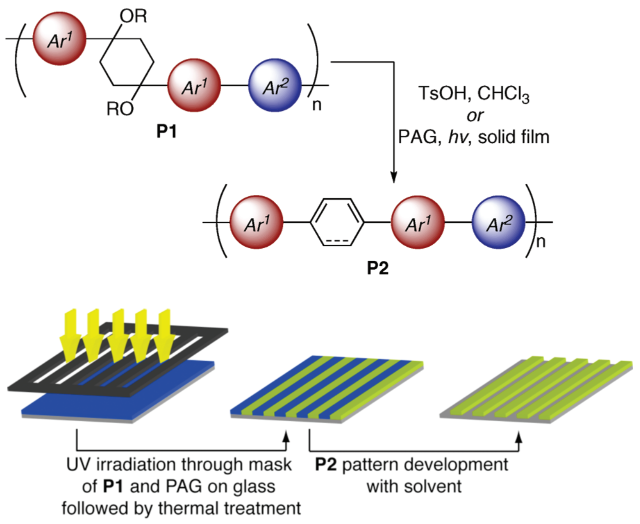

Figure 1. Precursor approach to conjugated polymers through an acid-catalyzed deprotection−elimination reaction (top) and its application to photopatterning (bottom).

Results and Discussion

To demonstrate the feasibility of this concept, precursor polymer **P1a**, representative of light-emitting polymers of the polyfluorene family, was prepared in high yield ($>99\%$) and good molecular weight ($DP_n = 48$) by Suzuki−Miyaura cross-coupling polymerization with 5 mol % $Pd(PPh_3)_4$ and Et_4NOH in toluene−water.[11] The key monomer **2** is conveniently obtained on a gram scale by the addition of 4-iodophenyllithium to 1,4-cyclohexanedione, followed by MOM protection of the resulting tertiary alcohol with chloromethyl methyl ether and *N*,*N*-diisopropylethylamine in dichloromethane (Scheme 1; see the Supporting Information for details).[12]

The commercially available tolylcumyliodonium tetrakis(pentafluorophenyl)borate was identified as a suitable PAG that can be spun-cast with polymer **P1a** from chloroform solutions to result in uniform mixed films without phase separation, as evidenced by comparable film thickness and morphology (Supporting Information). Photopatterning conditions were

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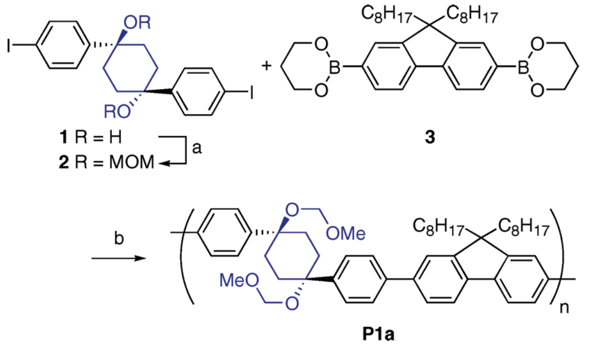
optimized to minimize photobleaching of the conjugated polymer, which can be significant upon extended irradiation.[13] Under these conditions, ca. 120 nm thick films obtained from **P1a** (1 wt % in $CHCl_3$) with PAG (10% vs **P1a**) on glass or quartz substrates were irradiated through a mask with a high-pressure Hg arc lamp (70 mW/cm^2) for 1 s, followed by heat treatment at 100 °C for 30 min. The patterns were then developed by immersion in toluene (10 min.), which selectively dissolves the unexposed parts of the film (Figure 2). The higher solubility of **P1a** compared to that of **P2a** is likely attributable to the higher density of flexible solubilizing side chains (e.g., MOM groups) in **P1a** and to greater intermolecular interactions (e.g., $\pi-\pi$ stacking) in **P2a** given its more planar structure. Partial cross-linking of the resulting diene groups in the solid state could also contribute to the lower solubility of **P2a** and may not be entirely ruled out, but its extent is limited since the patterned films obtained after irradiation are fully soluble in better solvents such as chloroform. Under these conditions, line and space (LS) patterns with a resolution down to 50 μm are easily obtained using simple laboratory equipment. However, narrower line widths would require a more careful optimization of the patterning conditions, as the fidelity of pattern transfer is impeded by acid migration during the heat treatment.[14] The observed thickness (height) of the developed lines of **P2a** (50−80 μm, with some apparent wrinkles) is smaller than that of the initial film. This is likely attributable to changes in the molecular structure of the polymer backbone (kinked vs planar), to the annealing of the solid-state packing that is concomitant with the heat treatment and solvent development of the patterned lines, and finally to a certain extent to partial dissolution occurring during the development step.

Scheme 1. Synthesis of Precursor Polymer P1a[a]

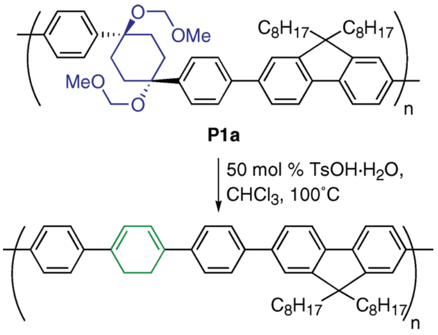


[a] Reagents and conditions: (a) MOMCl, iPr_2NEt, CH_2Cl_2, 0 °C → 25 °C (68%); (b) 5 mol % $Pd(PPh_3)_4$, aqueous Et_4NOH-PhMe, 90 °C (>99%).

The spectroscopic properties of polymer **P2a** are consistent with a poly(arylene dienylene) structure. Polymer **P1a** is colorless in chloroform solutions, with an absorption maximum consistent with a 2,7-diphenylfluorene chromophore (λ_{max} = 336 nm), and exhibits a deep-blue emission upon UV irradiation (λ_{em} = 368 nm, Φ = 0.79).[15] Thin solid films of polymer **P1a** are characterized by small bathochromic shifts compared to the solution values and a marked decrease in fluorescence quantum yield (λ_{max} = 338 nm, λ_{em} = 370 nm, Φ = 0.07). By contrast, thin films of polymer **P2a** obtained after photoirradiation of **P1a** in the presence of a PAG present dramatically red-shifted absorption and emission bands (λ_{max} = 402 nm, λ_{em} = 484 nm, Φ = 0.05), which is characteristic of an extended conjugated structure. While the solid-state photoluminescence quantum yield of **P2a** is objectively low, it is nevertheless comparable to that of annealed films of MEH−PPV (Φ = 0.07),[16] one of the prototypical photoluminescent and electroluminescent conjugated polymers. The optical band gap of **P2a** is smaller than that of poly(dioctylfluorene) (λ_{max} = 364 nm) or poly(dioctylfluorene biphenylene) (λ_{max} = 365 nm), but slightly larger than that of poly(dioctylfluorene vinylene) (λ_{max} = 419 nm), as expected for a poly(arylene dienylene) structure.[17]

To ascertain that the green-emissive, less soluble material generated during the photopatterning reaction indeed arises from an acid-catalyzed deprotection−elimination reaction resulting in the formation of conjugated 1,3-cyclohexadiene units along the polymer backbone, polymer **P3a** was prepared by treating polymer **P1a** with a catalytic amount of *p*-toluenesulfonic acid in chloroform at 100 °C (sealed tube), as shown in Scheme 2. In addition, model compound **4** was prepared by the Suzuki−Miyaura cross-coupling of **2** with boronic acid **6** in the presence of 5 mol % $Pd(PPh_3)_4$ and Et_4NOH as catalyst and base, respectively. Following acid-catalyzed deprotection−elimination as for **P3a**, the colorless model

Scheme 2. Preparation of Model Polymer P3a



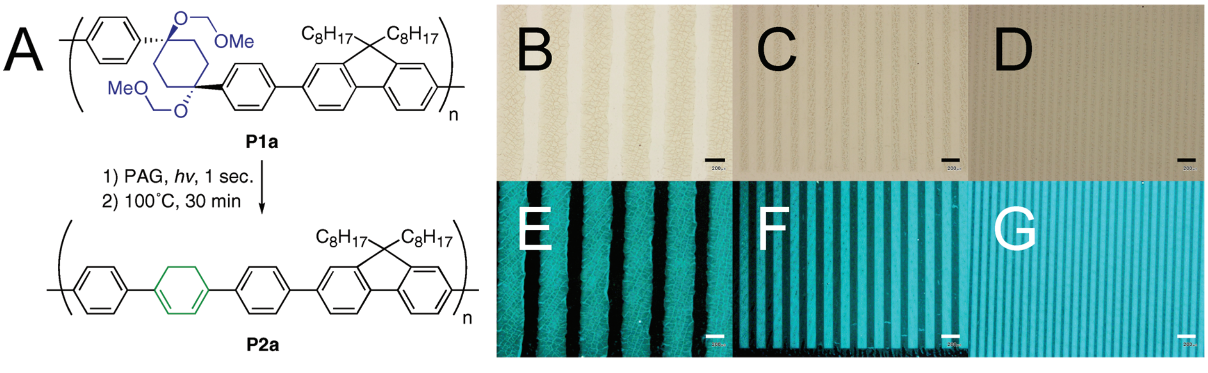
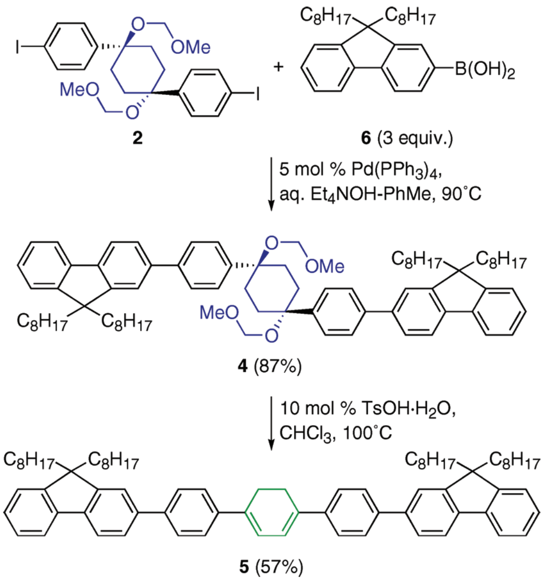


Figure 2. (A) Conversion of **P1a** into **P2a** by photoirradiation in the presence of a PAG followed by thermal treatment. (B−D) Optical micrographs of the resulting line and space patterns of **P2a** on a glass substrate with line widths of 200, 100, and 50 μm, observed under ambient light, black bar = 200 μm. (E−G) Patterns as above, observed under UV irradiation with a hand-held Hg lamp (λ = 365 nm), white bar = 200 μm.

Scheme 3. Synthesis of Model Compounds 4 and 5



compound **4** is converted to the greenish-yellow and strongly fluorescent 1,4-diarylcyclohexa-1,3-diene **5**, isolated in 57% yield after recrystallization (Scheme 3). ^{1}H NMR analysis of polymer **P3a** indicates the MOM groups have been completely cleaved (e.g., $\leq$5% residual) and shows new peaks associated with cyclohexadiene units at the same chemical shifts as observed in model compound **5** (Supporting Information). The exact extent of cyclohexadiene formation cannot be precisely determined ^{1}H NMR due to the low tumbling rate of the polymer chains in the viscous $CDCl_3$ solutions at the concentrations required to obtain a satisfactory signal-to-noise ratio; nevertheless, by comparisons to the other polymer and model compounds prepared, **P3a** constitutes a suitable model for a highly conjugated fluorene cyclohexadienylene structure.[18] The absorption spectra of **P3a** in chloroform solution differs from that of **P1a** by the presence of a new red-shifted absorption band centered at ca. 410 nm that is assigned to the more highly conjugated segments of the poly(arylene dienylene) structure (Figure 3, center). As expected, this band parallels the corresponding band seen in the absorption spectra of **P2a** thin films. Interestingly, the prominence of the new red-shifted absorption band of **P3a** in films is reduced compared to that of the solution spectrum. This rare apparent hypsochromic shift going from solution to the solid state might reflect a disordered packing arrangement of the polymer chains in the solid state that disrupt the extent of effective conjugation. Nevertheless, the onset of absorption at ca. 470 nm parallels that of **P2a**. **P3a** is highly fluorescent in solution (λ_{em} = 467 nm, Φ = 0.83) and in thin films (λ_{em} = 476 nm, Φ = 0.18), and the latter spectra closely match that of **P2a** thin films. The same behavior is illustrated by the growth of new red-shifted absorption (λ_{max} = 388 nm vs 318 nm) and emission (λ_{em} = 458 nm vs 340 nm) bands that accompany the conversion to model compound **5** from its precursor **4** (Figure 3, bottom). The extent of effective conjugation is more constrained in model compound **5** than in polymer P3a, as illustrated by small blue shifts in its absorption (Δ = 12 nm) and emission (Δ = 9 nm) maxima with respect to **P3a**.

The photophysical properties of conjugated polymers are to a large extent affected by the presence of structural defects.[19] The solid-state photoacid-catalyzed conversion of polymer **P1a** into **P2a** may result in a percentage of defect sites in the form of ethers groups that have not been eliminated to yield the corresponding diene. A partially conjugated polymer model was prepared to assess the effect of an incomplete deprotection–elimination reaction on its photophysical properties. The partially conjugated polymer **P4a** was prepared by treating polymer **P1a** with a catalytic amount of *p*-toluenesulfonic acid in chloroform in the presence of methanol (Scheme 4). ^{1}H NMR analysis of polymer **P4a** indicates that the all the MOM groups have been cleaved and that backbone is comprised of a ca. 1:3 mixture of conjugated cyclohexadiene units and of units that have been subject to methanolysis (mixture of diastereoisomers). Importantly, the polymer chain length remains unaffected during the course of this transformation. The extended conjugation of **P4a** (yellow) with respect to **P1a** (colorless) is reflected the growth of a new red-shifted absorption band (λ_{max} = 392 nm) that parallels that of

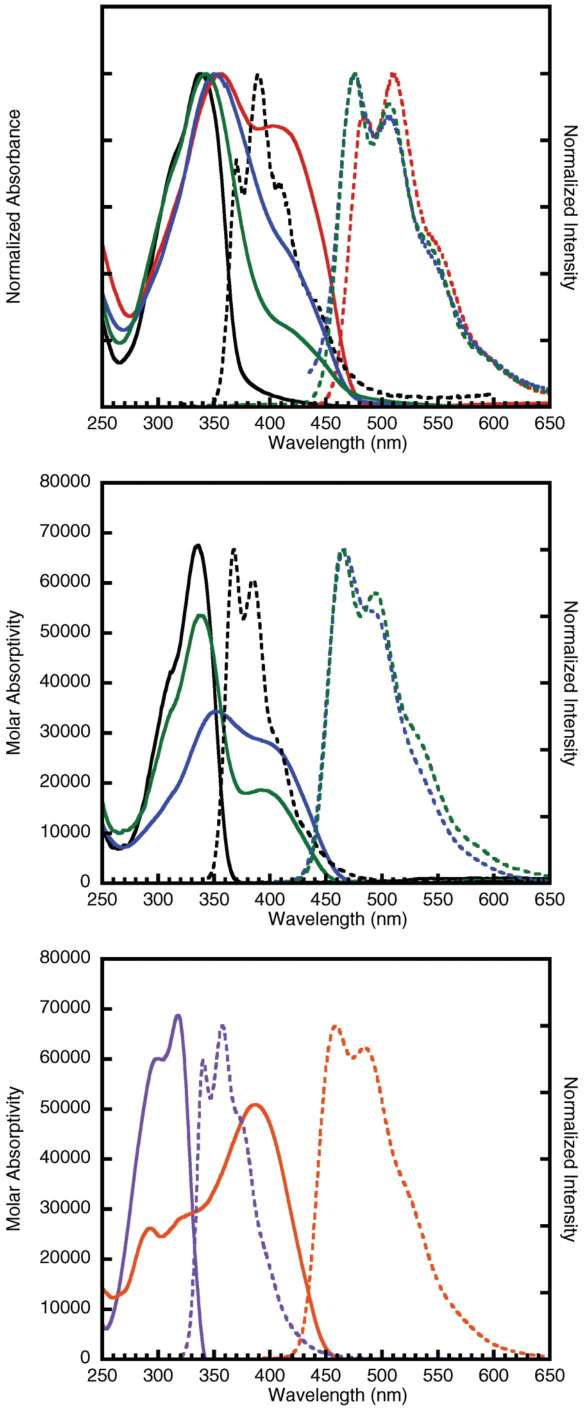


Figure 3. Absorption (plain lines) and fluorescence emission (dashed) spectra of thin films (top) and chloroform solutions (center and bottom) of **P1a** (black), **P2a** (red), **P3a** (blue), **P4a** (green), **4** (purple), and **5** (orange).

Scheme 4. Synthesis of the Partially Conjugated Model Polymer P4a

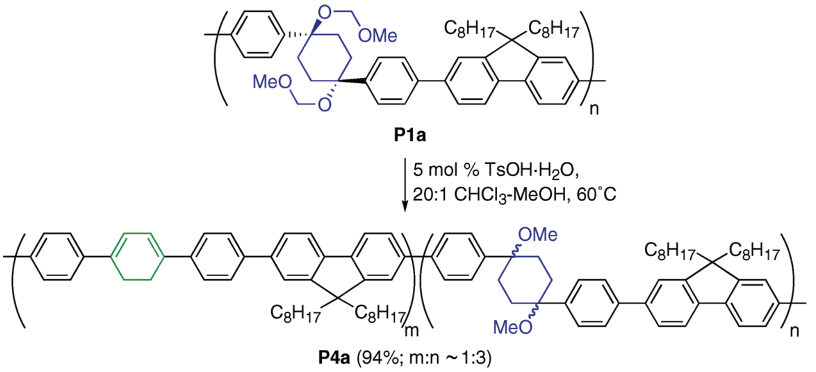


Table 1. Summary of Photophysical Properties

		λ_{max} (nm)		λ_{em} (nm)		Φ	
	$M_n/M_w/DP_n$[a] (10^3 g mol^{-1})	solution (CHCl$_3$) (ε/L mol^{-1} cm^{-1})[b]	thin film	solution (CHCl$_3$)	thin film	solution (CHCl$_3$)	thin film
P1a	35.8/80.2/48	336 (67 500)	338	368	370, 389	0.79	0.07
P2a			402, 356		484, 510		0.05
P3a	≥12.5/12.7/20[c]	~400 (28 000), 351 (34 400)	~410, 350	467	476	0.83	0.18
P4a	21.4/43.1/32[d]	392 (18 700), 337 (53 600)	~410, 342	464, 496	476, 506	0.59	0.25
4		318 (70 500)		340, 357			
5		388 (51 000)		458			

[a] Determined by GPC in THF against PS standards. [b] Molar absorptivity based on the molecular weight of a repeating unit. [c] **P3a** is only partially soluble in THF, but fully so in CHCl$_3$; GPC data are given for the THF-soluble fraction of the sample. [d] **P4a** was prepared from a second sample of **P1a** with $DP_n \sim 35$ (see Supporting Information for details).

P2a and **P3a**. The fluorescence emission spectrum of **P4a** is also characterized by the complete disappearance of the emission band of **P1a** centered near 370 nm and the appearance of a new bathochromically shifted bands (λ_{em} = 464, 496 nm (first and second vibronic), Φ = 0.59). The new emission band similarly parallels that of **P2a** and **P3a**. These photophysical properties are indicative of very efficient energy migration pathways leading to emission from the more extended conjugation regions of the polymer backbone (fluorene dienylene) both in solution and in thin films.[20] Consequently and gratifyingly, the presence of defects in the form of nonconjugated cyclohexane units that may remain after the photopatterning of **P2a** will likely have only a minor influence on its emission spectra. Polymer **P4a**, unlike its precursor polymer **P1a**, remains highly emissive in the solid state (λ_{em} = 476, 506 nm, Φ = 0.25). In solution, the precursor polymer **P1a** and the conjugated polymer model **P3a** exhibit higher florescence quantum yields than the partially conjugated polymer model **P4a**. In the solid state, however, polymer packing likely overcomes that trend, with the partially (**P4a**) and conjugated (**P3a**) polymer models showing higher quantum yields than either the precursor (**P1a**) or the thermally annealed patterned (**P2a**) polymers.

Conclusions

In summary, we have demonstrated that the acid-catalyzed deprotection–elimination reaction of conjugated polymers precursors prepared from monomers such as **1** can be used for their surface patterning using simple photolithographic techniques. The modular character of the synthetic route with respect to the arylmetal reagent (e.g., *para* linkages with 4-iodophenyllithium for **1**) and organoboron comonomers makes this approach amenable to a wide array of conjugated polymers with electronic and photophysical properties tailored to specific applications. The combinations of the resist and active material functions in single polymer streamline the fabrication process, reducing the need for selective washing or etching steps. Finally, the presence of highly efficient energy migration pathways in the solid state confers this technique an additional tolerance for defects that may arise during the photolithographic process.

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Supporting Information Available: Complete experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) It may not be ruled out that a portion the cyclohexadienylene units in **P3a** (and/or **P2a**) are further oxidized (dehydrogenated) to the corresponding *p*-phenylene units, as recently observed in a related reaction employed in the preparation of [12]cycloparaphenylene (ref 8a). The spectroscopic and emissive features (e.g., $\lambda_{\max}$, λ_{em}) of both polymers are, however, dominated by the arylene cyclohexadienylene segments. The acid-catalyzed deprotection−elimination of **4** does not give rise to significant amounts of the fully aromatized product under the indicated conditions (Scheme 4).

(19) Selected recent examples; see also ref 11 and references therein. (a) Satrijo, A.; Kooi, S. E.; Swager, T. M. *Macromolecules* **2007**, *40*, 8833–8841. (b) Chan, K. L.; McKiernan, M. J.; Towns, C. R.; Holmes, A. B. *J. Am. Chem. Soc.* **2005**, *127*, 7662–7663. (c) Becker, K.; Lupton, J. M.; Feldmann, J.; Nehls, B. S.; Galbrecht, F.; Gao, D.; Scherf, U. *Adv. Funct. Mater.* **2006**, *16*, 364–370.

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