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Liquid Crystals

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To cite this Article Yao, Lihua, Li, Hengfeng and Wen, Jianxun(2005) 'Synthesis and mesomorphic properties of fluorinated phenyl 4-[(4-*n*-alkoxy-2,3-difluorophenyl)ethynyl]benzoates', *Liquid Crystals*, 32: 4, 527 – 531

To link to this Article: DOI: 10.1080/01443610400023130

URL: <http://dx.doi.org/10.1080/01443610400023130>

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Synthesis and mesomorphic properties of fluorinated phenyl 4-[(4-*n*-alkoxy-2,3-difluorophenyl)ethynyl]benzoates

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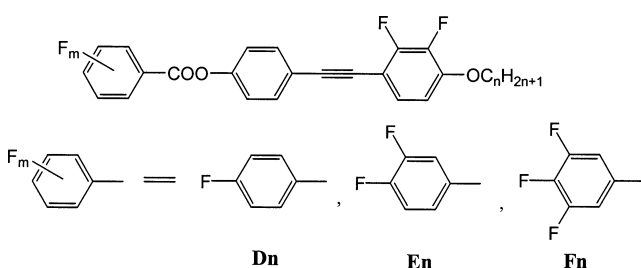
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(Received 20 June 2004; accepted 29 September 2004)

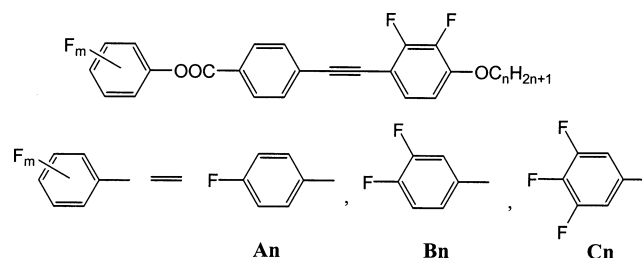
Three series of fluorinated phenyl 4-[(4-*n*-alkoxy-2,3-difluorophenyl)ethynyl]benzoate liquid crystals have been synthesized. Their phase transition temperatures were measured by texture observation in a polarizing microscope and confirmed by DSC. Their mesomorphic properties and fluoro-substituent effects were studied in detail.

1. Introduction

2,3-Difluorophenyl groups in liquid crystalline compounds have long been observed to depress the range of high ordered smectic phases but increase the stability of tilted smectic phases [1–4]. 2,3-Difluorophenyl groups are also the main unit of negative liquid crystals [5–7], so they are important in smectic liquid crystal design. However, reports on their effect on the nematic phase are very few. We have reported synthesis and mesomorphic properties of fluoro-substituted benzoate liquid crystals (scheme 1) in previous work [8], the results showing that the introduction of the 2,3-difluorotolan unit broadens the nematic phase range, and decreases the clearing point of liquid crystals. In order to obtain a more comprehensive understanding of the relationship between the structure and mesomorphic properties, and to discover novel liquid crystal materials, three series of novel liquid crystals with the structures shown in scheme 2 were prepared, from fluorinated phenol and their mesomorphic properties determined.



Scheme 1.



Scheme 2.

2. Experimental

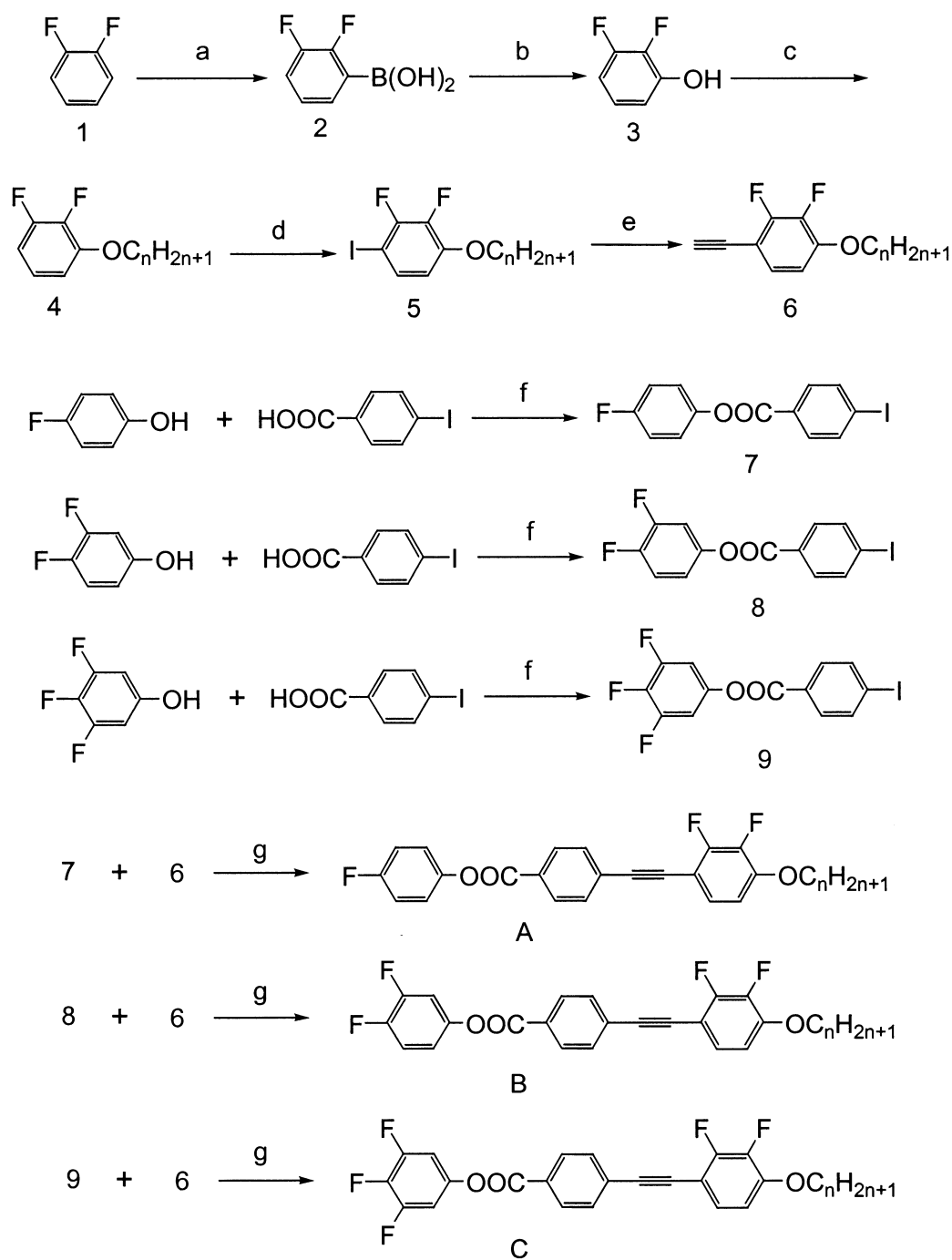
2.1. Synthesis

The synthesis of the target compounds is outlined in scheme 3. The preparation of 4-alkoxy-2,3-difluorophenylacetylene (**6**) was reported previously [9–11]. First, fluorinated phenyl 4-iodobenzoates (**7**, **8**, **9**) were prepared via a mild esterification procedure between 4-iodobenzoic acids and fluorinated phenols in the presence of dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) as catalyst. The target compounds (**An**, **Bn**, **Cn**) were then produced by a Sonogashira coupling reaction between the aromatic iodide (**7**, **8**, **9**) with **6** with catalysis by bis(triphenylphosphine)palladium dichloride and copper (I) iodide.

2.2. Analysis

The structures of the target products and intermediates were elucidated by a variety of spectral methods. IR spectra were recorded on a PE-983G spectrophotometer, using KBr pellets of solids or films of liquids. ¹H NMR spectra with tetramethylsilane (TMS)

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Reagents and conditions □ a) i. ${}^n\text{BuLi}$, $-78\text{ }^\circ\text{C}$; ii. B(OMe)_3 , HCl . b) H_2O_2 , Et_2O . c) $\text{C}_n\text{H}_{2n+1}\text{Br}$, K_2CO_3 , acetone. d) i. ${}^n\text{BuLi}$, $-78\text{ }^\circ\text{C}$; ii. I_2 , THF . e) i. $\text{Me}_3\text{SiC}\equiv\text{CH}$, CuI , $\text{Pd(PPh}_3)_2\text{Cl}_2$, Et_3N . ii. NaOH , acetone, CH_3OH . f) 4-iodobenzoic acid, DCC , DMAP , CH_2Cl_2 . g) $\text{Pd(PPh}_3)_2\text{Cl}_2$, CuI , Et_3N .

Scheme 3. Synthetic route.

as internal standard, and ^{19}F NMR spectra with trifluoroacetic acid (TFA) as external standard, were recorded on a Bruker 300 spectrometer (300 MHz), a Varian EM360L spectrometer (60 MHz) or a FX-90Q spectrometer (90 MHz). For ^{19}F NMR spectra the high field was positive. MS spectra were measured with a Finnigan-4021 spectroscopy using electrical ionization. The phase transition temperatures of the target compounds were measured visually by polarizing optical microscopy (Olympus PM-6) using a heating stage (Mettler FP-80) and a control unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter) with a data system and heating/cooling rate 5°C min^{-1} . The transition temperatures reported in this paper were the peak values of the transition on DSC traces. Phase identification was made by comparing the observed textures with literature reports [12, 13]. Typical synthesis steps are described below.

2.3. 4-Fluorophenyl 4-iodobenzoate (7)

4-Fluorophenol (2.0 g, 17.9 mmol), 4-iodobenzoic acid (5.0 g, 20.1 mmol), DCC (5.0 g, 24.8 mmol), DMAP (10 mg) and dry dichloromethane (30 ml) were mixed in a dry flask, then stirred at room temperature for 48 h under nitrogen. After the reaction was complete, the precipitate formed was filtered off and washed with water, then dried over anhydrous magnesium sulphate. The solvent was removed *in vacuo* and the residue

purified by column chromatography on silica gel using petroleum ether (b.p. $60\text{--}90^\circ\text{C}$)/ethyl acetate (20/1) as the eluant, to give 4.53 g of white crystals of **7**, yield 79%. ^1H NMR (CDCl_3 , 300 MHz): δ_{H} 7.88 (m, 4H), 7.19–7.08 (m, 4H) ppm. ^{19}F NMR (CDCl_3 , 56.4 MHz): δ_{F} 41.2 (s, 1F) ppm. MS (m/z): 342 (M^+ , 3.65), 231 (100.00).

2.4. 4-Fluorophenyl 4-[(4-*n*-propoxy-2,3-difluorophenyl)ethynyl]benzoate (A3)

Compound **7** (200 mg, 0.585 mmol), 4-propoxy-2,3-difluorophenyl acetylene (**6**, 138 mg, 0.702 mmol), bis(triphenylphosphine) palladium dichloride (10 mg), copper(I) iodide (15 mg), triphenylphosphine (25 mg) and anhydrous triethylamine (10 ml) were mixed and stirred at 60°C for 48 h under nitrogen. After the reaction was complete, the precipitate formed was filtered off and washed with water, then dried over anhydrous magnesium sulphate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. $60\text{--}90^\circ\text{C}$)/dichloromethane (3/1) as the eluant to give pale yellow crystals, which were recrystallized from petroleum ether to yield 200 mg of white flaky crystals of **A3**, yield 83%, m.p. 130.8°C . ^1H NMR (CDCl_3 , 300 MHz): δ_{H} 1.07 (t, 3H, $J=7.38$ Hz, CH_3), 1.82–1.96 (m, 2H), 4.04 (t, 2H, $J=6.55$ Hz, OCH_2), 6.70–6.76 (m, 1H), 7.09–7.26 (m, 5H), 7.61–7.68 (m, 2H), 8.16–8.19 (m, 2H) ppm. ^{19}F NMR (CDCl_3 ,

Table. Phase transition temperatures of target compounds, Cr=crystal; SmA=smectic A phase; N=nematic phase; I=isotropic; Rec=recrystallization.

| Compounds | <i>n</i> | Transition temperature/ $^\circ\text{C}$ |
|-----------|----------|--|
| A | 3 | Cr 130.8 N 205.7 I 204.6 N 103.6 Rec |
| A | 4 | Cr 128.5 N 199.5 I 198.2 N 97.5 Rec |
| A | 5 | Cr 107.3 SmA 137.8 N 189.5 I 188.5 N 136.7 SmA 85.4 Rec |
| A | 6 | Cr 83.9 SmA 143.4 N 185.0 I 184.0 N 142.2 SmA 68.4 Rec |
| D | 6 | Cr 84.1 N 192.3 I 191.1 N 48.3 Rec |
| A | 7 | Cr 92.9 SmA 149.0 N 178.1 I 177.1 N 147.9 SmA 70.3 Rec |
| A | 8 | Cr 84.1 SmA 151.9 N 174.5 I 173.5 N 150.7 SmA 67.2 Rec |
| B | 3 | Cr 115.7 SmA 135.0 N 179.1 I 177.3 N 133.1 SmA 87.5 Rec |
| B | 4 | Cr 112.2 SmA 145.9 N 176.5 I 175.3 N 144.4 SmA 82.0 Rec |
| B | 5 | Cr 96.5 SmA 150.2 N 168.6 I 167.4 N 149.3 SmA 57.8 Rec |
| B | 6 | Cr 82.5 SmA 153.0 N 166.6 I 165.4 N 151.7 SmA 58.2 Rec |
| E | 6 | Cr 73.0 N 172.1 I 171.0 N 36.4 Rec |
| B | 7 | Cr 79.6 SmA 155.4 N 162.0 I 160.9 N 154.1 SmA 60.5 Rec |
| B | 8 | Cr 76.4 SmA 156.5 N 160.4 I 158.9 N 155.3 SmA 57.6 Rec |
| C | 3 | Cr 126.7 SmA 133.5 N 152.3 I 151.3 N 132.1 SmA 110.3 Rec |
| C | 4 | Cr 126.8 SmA 141.8 N 152.6 I 151.7 N 140.5 SmA 100.8 Rec |
| C | 5 | Cr 112.9 SmA 140.4 N 145.0 I 144.3 N 139.0 SmA 63.3 Rec |
| C | 6 | Cr 116.5 SmA 140.1 I 139.7 N 136.3 SmA 48.7 Rec |
| F | 6 | Cr 79.1 SmA 125.7 N 150.5 I 149.4 N 124.7 SmA 50.4 Rec |
| C | 7 | Cr 103.7 SmA 147.7 I 145.9 SmA 54.7 Rec |
| C | 8 | Cr 99.8 SmA 142.3 I 140.8 SmA 60.3 Rec |

56.4 MHz): δ_F 41.6 (s, 1F), 58.6 (m, 1F), 83.1 (m, 1F) ppm. IR: ν_{\max} 2982, 2882, 2219, 1727, 1635, 1519, 1300, 1269, 1191, 1086, 878 cm^{-1} . MS (m/z): 409 (M^+-1 , 4.84), 299 (100.0). Elemental analysis for $\text{C}_{24}\text{H}_{17}\text{F}_3\text{O}_3$: calcd, C 70.24, H 4.18, F 13.89; found, C 70.11, H 4.09, F 13.78 %.

All of the other target compounds and intermediates have satisfactory elemental analyses and appropriate ^1H and ^{19}F NMR, IR and MS spectral data.

3. Results and discussion

The phase transition temperatures of all the compounds were determined by DSC with heating and cooling rates of 5°C min^{-1} . Mesomorphic textures were observed by POM for determining the types of mesophases. The transition temperatures summarized in table 1 are the maxima of transition peaks on each DSC trace. The dependence of transition temperatures of series **An**, **Bn**, **Cn** on the number of carbon atoms in terminal alkoxy chains are shown in figures 1–3, respectively.

In series **An**, only the nematic phase is observed when n is less than 5. But the smectic A phase appears and becomes more stable with increasing length of the terminal alkoxy chain. At the same time, the nematic phase becomes unstable and the melting points of the compounds decrease. In series **Bn**, all compounds exhibit nematic and smectic A phases; with increasing length of alkoxy chain the nematic phase becomes unstable but the smectic A phase increases in stability. In series **Cn**, the nematic phase appears only for short

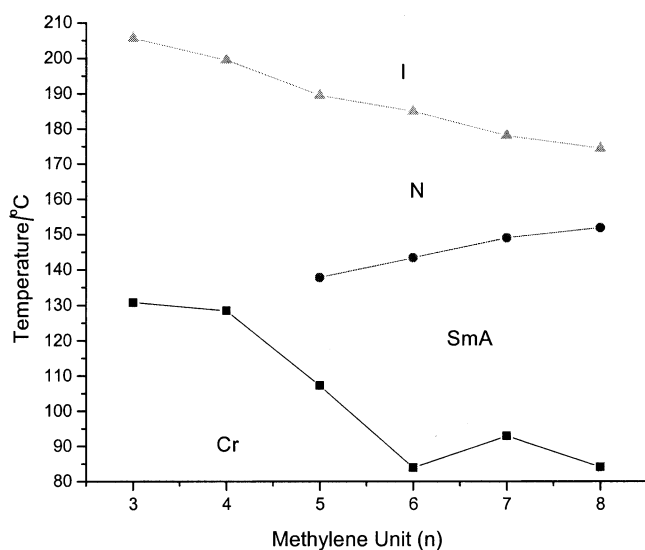


Figure 1. The transition behaviour of compounds **An**: dependence of transition temperatures on the number (n) of the alkoxy chain.

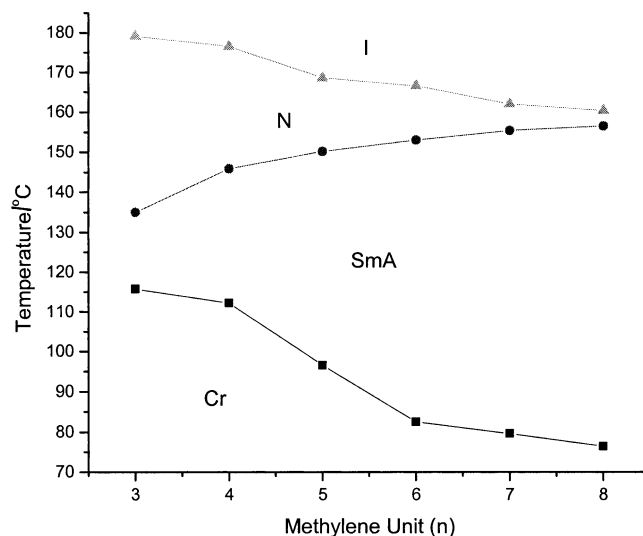


Figure 2. The transition behaviour of compounds **Bn**: dependence of transition temperatures on the number (n) of the alkoxy chain.

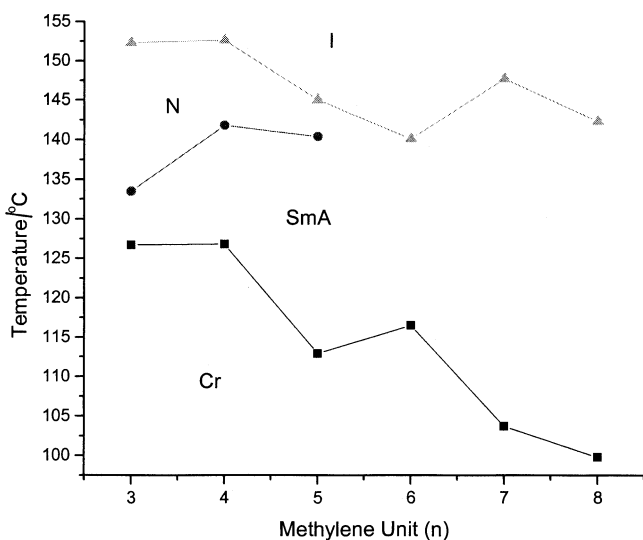
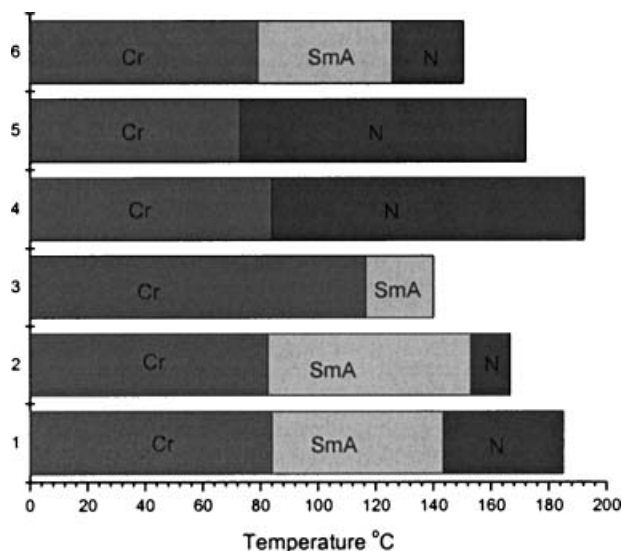


Figure 3. The transition behaviour of compounds **Cn**: dependence of transition temperatures on the number (n) of the alkoxy chain.

alkoxy chains ($n=3, 4, 5$); the smectic A phase is observed in all members of the series.

The number and positions of fluoro-substituents in the terminal phenyl ring in series **An**, **Bn** and **Cn** are different. In general, a greater number of fluoro-substituents causes larger polarity in the axis direction of the mesogens; but the introduction of three and five fluoro-substituents increases the width of the mesogens, so steric and polar factors have differing effects on the



1: A6; 2: B6; 3: C6; 4: D6; 5: E6; 6: F6

Figure 4. Comparison of mesomorphic properties of selected compounds.

liquid crystalline properties of these compounds. When both steric and polar factors both exist and have a positive effect, the former is the more advantageous factor. So the mesomorphic properties of series **Bn** and **Cn** are less favourable than those of series **An**. This result shows that lateral fluoro-substitutions have a considerable effect on mesomorphic properties, resulting in the reduction of nematic thermostabilities due to broadening the molecule and reduction in intermolecular forces.

The mesomorphic properties of compounds **Dn**, **En** and **Fn**, which have a differing direction of the ester bond from compounds **An**, **Bn** and **Cn**, were reported previously [8]. Six compounds with the same alkoxy chain ($n=6$) were chosen and their mesomorphic properties compared in figure 4. We find that changing the direction of the ester bond decreases the clearing points and melting points, and increases the stability of

the nematic and smectic A phases in 4-fluoro-substituents (**A6**, **D6**) and 3,4-difluoro-substituents (**B6**, **E6**). But in 3,4,5-trifluoro-substituents (**C6**, **F6**), melting points increase, the nematic phase disappears and the mesomorphic phase range becomes narrow. All of the fluorinated phenyl esters (**An**, **Bn** and **Cn**) have a greater tendency to form smectic A phases and a lesser tendency to form nematic phases than the similarly fluorinated benzoate esters (**Dn**, **En** and **Fn**). For different levels of fluoro-substitution, the stability order of the nematic phase $4-F > 3,4-F > 3,4,5-F$ is seen in both **An**, **Bn**, **Cn** and **Dn**, **En**, **Fn** sequences.

Acknowledgements

The authors acknowledge gratefully the National Natural Science Foundation of China for financial support.

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