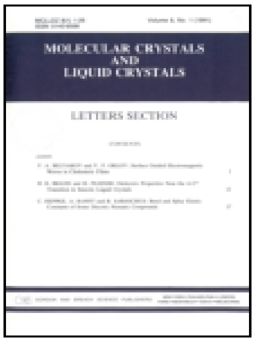
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Liquid Crystalline Properties of 6-(4-Cyanobiphenyl-4'-yloxy)hexyl 4'-[*ω*-(*p*-Nitrophenyloxy)alkoxy]-4-biphenylcarboxylates

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A new series of liquid crystalline compounds, which contained two biphenyl and one p-nitrophenyl groups linked by two flexible spacers, were prepared. The flexible spacer between two biphenyl groups is fixed and consists of nine (odd number) atoms. The compounds showed nematic phase, although some of them exhibited nematic and smectic phases upon cooling. The isotropic-nematic transitional properties depended on the length and parity of the flexible spacers between the biphenyl and p-nitrophenyl groups. Such odd–even effect was in consistency with the feature of liquid crystal trimers. The liquid crystalline properties were compared with those of the related compounds.

Keywords Liquid crystal trimer; nematic liquid crystal; odd-even effect; *p*-nitrophenyl group

Introduction

Increasing interest is being shown in the liquid crystalline properties of liquid crystal dimers, trimers, and tetramers, which are the molecules containing two, three, and four mesogenic groups linked by flexible spacers, respectively, because the properties exhibit a remarkable dependence on the length and parity of the flexible spacers [1–15]. That is to say, the liquid crystalline properties of the compounds with odd-membered flexible spacers may be conspicuously different from those with even-membered flexible spacers. The effect of the flexible spacers on the liquid crystalline properties is attributed to the dependence of the molecular shape on the parity of the spacer considered in the all-*trans* conformation. We have also studied the unique liquid crystalline properties of liquid crystal dimers [16], trimers [17], and tetramers [18].

In the previous paper [19], we reported the liquid crystsalline properties of the compounds (1), which contained two biphenyl and one *p*-nitrophenyl groups linked by two flexible spacers. Although liquid crystalline properties of simple alkyl- or alkoxybenzenes are hardly known, the *p*-nitrophenyl group played a role of mesogen. Similar liquid crystalline behaviors of the nematogens connected with a terminal phenyl group via flexible spacers had been reported by some groups of workers [20–22]. The flexible spacer

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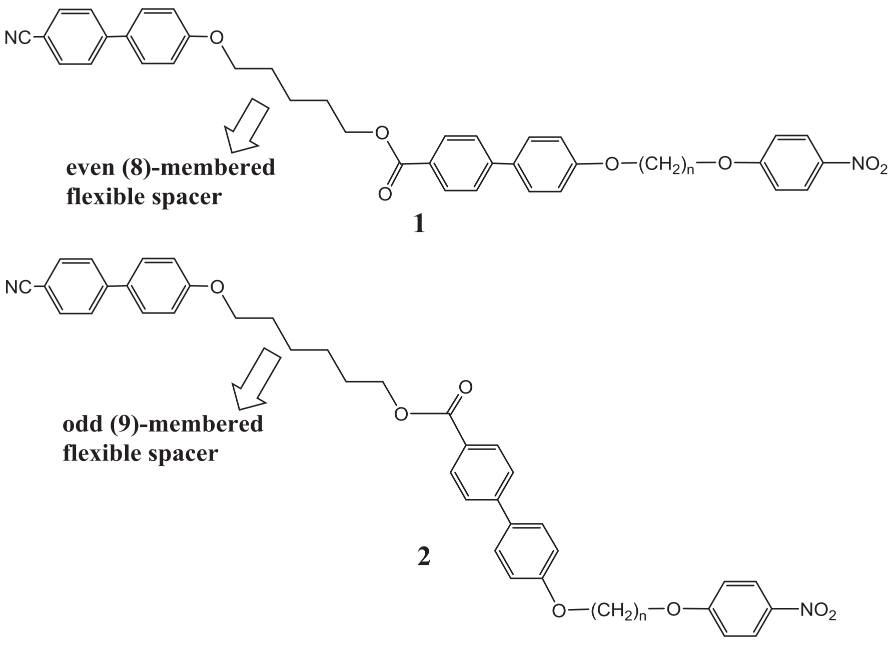

a: n = 4, **b**: n = 5, **c**: n = 6, **d**: n = 7, **e**: n = 8,
f: n = 9, **g**: n = 10, **h**: n = 11, **i**: n = 12

Figure 1. The structures of series **1** and **2**.

Table 1. Yields and elemental analyses of **2**

	n	Yield	Calcd.	Found
2a	4	48	$C_{42}H_{40}N_2O_7$: C, 73.67; H, 5.89; N, 4.09	C, 73.54; H, 5.90; N, 4.11
2b	5	50	$C_{43}H_{42}N_2O_7$: C, 73.91; H, 6.06; N, 4.01	C, 73.89; H, 6.05; N, 4.04
2c	6	52	$C_{44}H_{44}N_2O_7$: C, 74.14; H, 6.22; N, 3.93	C, 73.97; H, 6.13; N, 3.97
2d	7	48	$C_{45}H_{46}N_2O_7$: C, 74.36; H, 6.38; N, 3.85	C, 74.39; H, 6.38; N, 3.89
2e	8	47	$C_{46}H_{48}N_2O_7$: C, 74.57; H, 6.53; N, 3.78	C, 74.54; H, 6.56; N, 3.81
2f	9	46	$C_{47}H_{50}N_2O_7$: C, 74.78; H, 6.68; N, 3.71	C, 74.83; H, 6.64; N, 3.77
2g	10	48	$C_{48}H_{52}N_2O_7$: C, 74.98; H, 6.82; N, 3.64	C, 75.00; H, 6.83; N, 3.69
2h	11	45	$C_{49}H_{54}N_2O_7$: C, 75.17; H, 6.95; N, 3.58	C, 75.00; H, 6.99; N, 3.59
2i	12	46	$C_{50}H_{56}N_2O_7$: C, 75.35; H, 7.08; N, 3.51	C, 75.30; H, 7.02; N, 3.54

Table 2. IR spectral data of **2**

	cm^{-1} ($CDCl_3$)
2a	2943, 2873, 2227 (CN), 1711 (OCO), 1606, 1516 (NO_2), 1496, 1471, 1342 (NO_2), 1265, 1248, 1182, 1113
2b	2945, 2872, 2227 (CN), 1711 (OCO), 1606, 1516 (NO_2), 1496, 1471, 1342 (NO_2), 1265, 1248, 1182, 1113
2c	2945, 2862, 2227 (CN), 1711 (OCO), 1606, 1516 (NO_2), 1496, 1471, 1342 (NO_2), 1266, 1250, 1182, 1113
2d	2943, 2862, 2227 (CN), 1711 (OCO), 1606, 1514 (NO_2), 1496, 1471, 1342 (NO_2), 1267, 1250, 1182, 1113
2e	2941, 2860, 2227 (CN), 1711 (OCO), 1606, 1514 (NO_2), 1496, 1471, 1342 (NO_2), 1267, 1250, 1182, 1113
2f	2939, 2858, 2227 (CN), 1711 (OCO), 1606, 1514 (NO_2), 1496, 1471, 1342 (NO_2), 1267, 1250, 1182, 1113
2g	2935, 2858, 2227 (CN), 1711 (OCO), 1606, 1514 (NO_2), 1496, 1471, 1342 (NO_2), 1267, 1250, 1182, 1113
2h	2933, 2856, 2227 (CN), 1711 (OCO), 1606, 1514 (NO_2), 1496, 1471, 1342 (NO_2), 1267, 1250, 1182, 1113
2i	2933, 2856, 2227 (CN), 1711 (OCO), 1606, 1514 (NO_2), 1496, 1471, 1342 (NO_2), 1267, 1250, 1182, 1113

between two biphenyl groups in series 1 is fixed and consists of eight (even number) atoms. However, when the number of the atoms of the flexible spacer is odd number, the liquid crystalline properties may be conspicuously different from those of series 1. From such a viewpoint, we prepared a new series of compounds (2). The structure of series 2 is similar to that of series 1, but the flexible spacer between two biphenyl groups of series 2 consists of 9 (odd number) atoms (Fig. 1). In the present paper, the comparison of liquid crysrtalline properties between series 1 and 2 will be reported.

Experimental

Elemental analyses were performed at the Analytical Center of Kyushu University. ^{1}H-NMR spectra (400 MHz) were obtained with a JEOL GSX 400 spectrometer. The chemical shifts (δ-values) were measured in parts per million (ppm) down-field from tetramethylsilane as an internal reference. IR spectra were recorded with a JASCO FT/IR-420 spectrometer. Measurements in $CDCl_3$ were made with a 0.1 mm KBr cell. Differential scanning calorimetry (DSC) measurements were carried out with a Shimadzu DSC-60. Polarizing microscopy observations were performed under a Nikon Eclipse E600 POL equipped with a hot stage (Linkam LK-600PH).

6-(4-cyanobiphenyl-4'-yloxy)hexyl 4'-[ω-(p-nitrophenyloxy)alkoxy]-4-biphenylcarboxylate (2)

A mixture of 6-(4-cyanobiphenyl-4'-yloxy)hexyl 4'-hydroxy-4-biphenylcarboxylate (1 mmol) [17] and *p*-(ω-bromoalkoxy)nitrophenol ($n = 4$–12) (2 mmol) [19] in *N*,*N*-dimethylformamide (100 mL) in the presence of K_2CO_3 (1 mmol) was stirred at room temperature for 8 hr. The reaction mixture was evaporated to give a residue, which was

Table 3. ^{1}H NMR spectral data of **2**

	δ ($CDCl_3$)
2a	8.20 (d, 2H, $J = 8.8$ Hz), 8.08 (d, 2H, $J = 8.0$Hz), 7.69–7.51 (m, 10H), 7.00–6.97 (m, 6H), 4.36 (t, 2H, $J = 6.4$ Hz), 4.16 (t, 2H, $J = 6.4$ Hz), 4.10 (t, 2H, $J = 6.4$ Hz), 4.03 (t, 2H, $J = 6.4$ Hz), 2.05 (m, 4H), 1.85 (m, 4H), 1.59 (m, 4H).
2b	8.20 (d, 2H, $J = 8.8$ Hz), 8.08 (d, 2H, $J = 8.0$ Hz), 7.69–7.51 (m, 10H), 7.00–6.97 (m, 6H), 4.36 (t, 2H, $J = 6.4$ Hz), 4.10 (t, 2H, $J = 6.4$ Hz), 4.05 (t, 2H, $J = 6.4$ Hz), 4.03 (t, 2H, $J = 6.4$ Hz), 2.0–1.5 (m, 14H).
2c	8.20 (d, 2H, $J = 8.8$ Hz), 8.08 (d, 2H, $J = 8.0$ Hz), 7.69–7.51 (m, 10H), 7.00–6.97 (m, 6H), 4.36 (t, 2H, $J = 6.4$ Hz), 4.08 (t, 2H, $J = 6.4$ Hz), 4.03 (t, 4H, $J = 6.4$ Hz), 1.87 (m, 8H), 1.58 (m, 8H).
2d	8.20 (d, 2H, $J = 8.8$ Hz), 8.08 (d, 2H, $J = 8.0$ Hz), 7.69–7.51 (m, 10H), 7.00–6.97 (m, 6H), 4.36 (t, 2H, $J = 6.4$ Hz), 4.06 (t, 2H, $J = 6.4$ Hz), 4.03 (t, 2H, $J = 6.4$ Hz), 4.01 (t, 2H, $J = 6.4$ Hz), 1.94 (m, 8H), 1.54 (m, 10H).
2e	8.20 (d, 2H, $J = 8.8$ Hz), 8.08 (d, 2H, $J = 8.0$ Hz), 7.69–7.51 (m, 10H), 7.00–6.97 (m, 6H), 4.36 (t, 2H, $J = 6.4$ Hz), 4.05 (t, 2H, $J = 6.4$ Hz), 4.03 (t, 2H, $J = 6.4$ Hz), 4.01 (t, 2H, $J = 6.4$ Hz), 1.83 (m, 8H), 1.6–1.4 (m, 12H).
2f	8.20 (d, 2H, $J = 8.8$ Hz), 8.08 (d, 2H, $J = 8.0$ Hz), 7.69–7.51 (m, 10H), 7.00–6.97 (m, 6H), 4.36 (t, 2H, $J = 6.4$ Hz), 4.05 (t, 2H, $J = 6.4$ Hz), 4.03 (t, 2H, $J = 6.4$ Hz), 4.00 (t, 2H, $J = 6.4$ Hz), 1.84 (m, 8H), 1.6–1.3 (m, 14H).
2g	8.20 (d, 2H, $J = 8.8$ Hz), 8.08 (d, 2H, $J = 8.0$ Hz), 7.69–7.51 (m, 10H), 7.00–6.97 (m, 6H), 4.36 (t, 2H, $J = 6.4$ Hz), 4.04 (t, 2H, $J = 6.4$ Hz), 4.03 (t, 2H, $J = 6.4$ Hz), 4.00 (t, 2H, $J = 6.4$ Hz), 1.84 (m, 8H), 1.6–1.3 (m, 16H).
2h	8.20 (d, 2H, $J = 8.8$ Hz), 8.08 (d, 2H, $J = 8.0$ Hz), 7.69–7.51 (m, 10H), 7.00–6.97 (m, 6H), 4.36 (t, 2H, $J = 6.4$ Hz), 4.04 (t, 2H, $J = 6.4$ Hz), 4.03 (t, 2H, $J = 6.4$ Hz), 4.00 (t, 2H, $J = 6.4$ Hz), 1.84 (m, 8H), 1.6–1.3 (m, 18H).
2i	8.20 (d, 2H, $J = 8.8$ Hz), 8.08 (d, 2H, $J = 8.0$ Hz), 7.69–7.51 (m, 10H), 7.00–6.97 (m, 6H), 4.36 (t, 2H, $J = 6.4$ Hz), 4.04 (t, 2H, $J = 6.4$ Hz), 4.03 (t, 2H, $J = 6.4$ Hz), 4.00 (t, 2H, $J = 6.4$ Hz), 1.82 (m, 8H), 1.6–1.25 (m, 20H).

chromatographed over silica gel. Elution with chloroform gave 2**a-i**. The yields and the elemental analyses are shown in Table 1. The IR and ^{1}H NMR spectral data are summarized in Tables 2 and 3, respectively.

Results and Discussion

A series of compounds **(2a-i)** ($n = 4$–12) were prepared according to a procedure similar to the synthesis of series **1** [19]. The structures of the new compounds were characterized by elemental analyses, ^{1}H-NMR and IR spectral data. The IR spectral data showed the presence of a cyano group at 2227 cm^{-1}, an ester group at 1711 cm^{-1} and a nitro group at 1514 and 1342 cm^{-1}. The ^{1}H-NMR data were similar to those of series **1**, except for the absorptions of the methylene groups.

The thermal mesomorphic phases of series **2** were investigated by differential scanning calorimetry (DSC) and polarizing microscopy (POM). All the compounds exhibited nematic phase upon heating and/or cooling. Figure 2 shows the DSC thermogram of series **2** upon heating. The compounds **(2a)**, **(2c–e)** and **(2h,i)** displayed nematic phase upon heating.

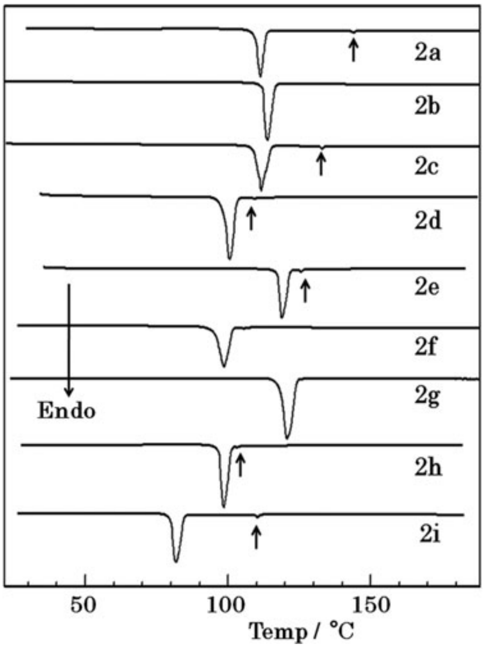

Figure 2. DSC thermogram of series **2** upon heating. Rate: 5°C/min.

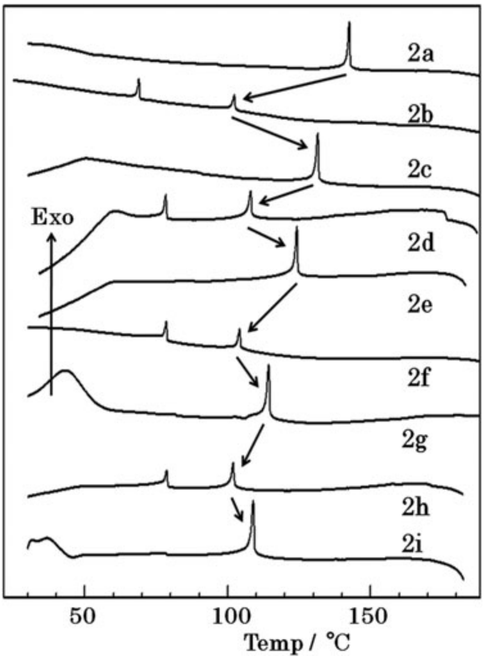

Figure 3. DSC thermogram of series **2** upon cooling. Rate: 5°C/min.

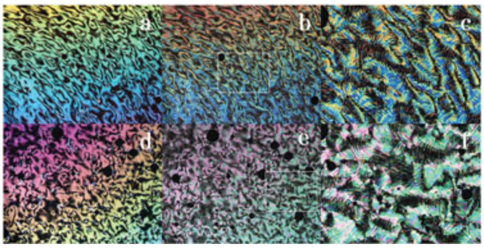

Figure 4. Representative polarizing microscopic images of series **2**. (a): **2d**, nematic phase at 100°C upon cooling. (b) **2d**, smectic phase at 70°C upon cooling. (c) Expanded figure of **b**. (d) **2f**, nematic phase at 90°C upon cooling. (e) **2f**, smectic phase at 70°C upon cooling. (f) Expanded figure of **e**.

The peaks of the nematic–isotropic transition were very small, compared with the melting transition, and the peaks are shown by the arrows in Fig. 2. However, **2b**, **2f**, and **2g** exhibited the nematic phase upon cooling but did not show liquid crystalline properties upon heating.

The compounds **(2b)**, **(2d)**, **(2f)**, and **(2h)** showed nematic and smectic phases upon cooling. Figure 3 shows the DSC thermogram of series **2** upon cooling. The nematic–smectic transition peaks of **2b**, **2d**, **2f**, and **2h** are clearly found in Fig. 3. The textures of the nematic and smectic phases of **2d** and **2f** are shown in Fig. 4. In view of the expanded figures of the smectic phase, we surmised that the state was smectic C, although the state was not able to be determined correctly. Series **1** showed only nematic phase, while series **2** exhibited nematic and smectic phases upon cooling. Furthermore, it can be seen from Fig. 3 that the isotropic–nematic transition temperature shows an odd–even effect as the length of the spacers is varied.

The transitional properties of series 2 are summarized in Table 4. The isotropic–nematic transition temperature upon cooling is a little lower than the nematic–isotropic transition temperature upon heating for 2a, 2c-e, 2h and 2i, but the entropy changes associated with the two transitions are similar to each other very much. Therefore, we compared the isotropic–nematic transitional properties of series 2 with the nematic–isotropic transitional properties of series 1. The transition temperature of both series showed an odd–even effect

Table 4. The transitional properties of **2**

	T_{CN} (°C)	T_{NI}	T_{IN}	T_{NS}	$\Delta S_{CN}/R$	$\Delta S_{NI}/R$	$\Delta S_{IN}/R$	$\Delta S_{NS}/R$
2a	111	144	143	–	13.9	0.34	0.33	–
2b	114	–	102	69	16.3	–	0.09	0.09
2c	112	133	132	–	17.6	0.39	0.40	–
2d	101	109	108	78	15.9	0.14	0.15	0.12
2e	119	126	124	–	16.4	0.39	0.41	–
2f	99	106	104	79	17.3	0.14	0.13	0.16
2g	121	–	114	–	20.0	–	0.38	–
2h	99	103	102	79	20.7	0.20	0.20	0.13
2i	82	110	109	–	17.6	0.47	0.49	–

Notes. CN: crystal–nematic transition. NI: nematic–isotropic transition. IN: isotropic–nematic transition upon cooling. NS: nematic–smectic transition upon cooling. R: gas constant.

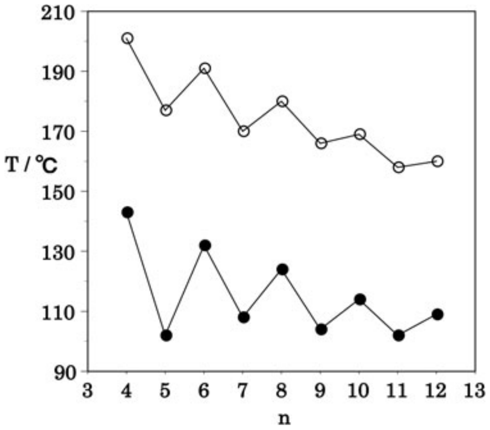

Figure 5. The dependence of the transition temperature on the number (*n*) of carbon atoms in the alkyl chains for series **1** and **2**. Symbol "○" shows nematic–isotropic transition temperature of series **1**. Symbol "•" shows isotropic–nematic transition temperature of series **2**.

as the length of the spacers was varied, in which the even members exhibited higher values (Fig. 5). The transition temperature of series 2 was notably lower than that of series 1. The result may be explained in terms of molecular shapes. Although the differences in the transition temperature between the odd members and the even members are attenuated on increasing the number (*n*) of the carbon atoms of the alkyl chains, it is interesting that the difference of series 2 is somewhat larger than that of series 1.

The entropy changes associated with the transition of series 2 also depended on the length and the parity of the flexible spacers between the biphenyl and *p*-nitrophenyl groups (Fig. 6). The results suggest that the *p*-nitrophenyloxy group in series 2 plays a role of mesogen, although the values of entropy changes of series 2 are considerably smaller than the related values of series 1. Furthermore, the differences of the entropy changes between

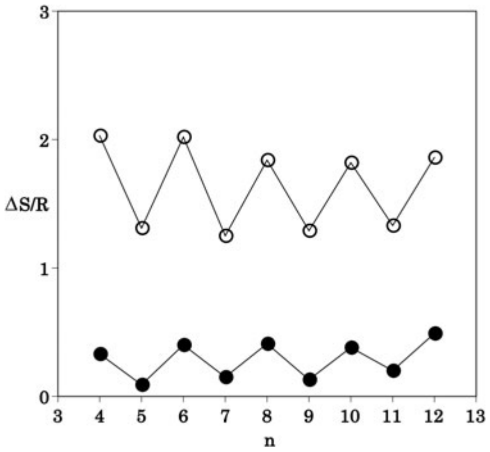

Figure 6. The dependence of the entropy changes on the number (*n*) of carbon atoms in the alkyl chains for series **1** and **2**. Symbol "○" shows nematic–isotropic transition of series **1**. Symbol "•" shows isotropic–nematic transition of series **2**. *R*: gas constant.

the odd members and the even members of series 2 were ca. half of the difference of series 1. The differences may result from the strength of the interactions between the p-nitrophenyl and the biphenyl groups in the direction of director of nematic liquid crystals.

Conclusions

The transitional properties of series **1** and **2**, which are the compounds containing two biphenyl and one *p*-nitrophenyl groups linked by two flexible spacers, were compared by means of DSC and POM. The difference among both is the carbon number (n) of the alkyl chains between two biphenyl groups. That is, the number (n) of series **1** is 5, therefore, the flexible spacer consists of eight (even number) atoms. On the other hand, the number (n) of series **2** is 6, therefore, the flexible spacer consists of 9 (odd number) atoms. Series **1** showed only nematic phase. On the other hand, some members of series **2** exhibited nematic and smectic phases upon cooling. The clearing temperature and the associated entropy change of series **2** were notably lower than those of series **1**. However, the transitional properties of series **2** showed an odd–even effect as the length of the spacers was varied, in which the even members exhibited higher values. On the basis of these data, we conclude that the parity of the flexible spacer between two biphenyl groups has a remarkable effect on the liquid crystalline properties, but not only series **1** but also series **2** show liquid crystal trimer-like behavior.

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