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A novel photochromic liquid crystal system based on biindenylidenedione derivatives†

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A novel class of photochromic biindenylidenedione derivatives containing two mesogenic biphenyl units connected with flexible alkyl chains were designed and synthesized. All of them exhibited photochromism in solid states on UV-Vis irradiation accompanied by the simultaneous generation of stable organic radicals, two of them displayed monotropic liquid crystals properties. These were the first examples which had three different kinds of functional properties (photochromism, light-induced radical behavior and liquid crystal properties) in a pure compound. The correlation between the molecular structure, electronic factors and properties has been discussed.

Introduction

The combination of photochromic and liquid crystalline properties in the same molecule has led to bifunctional material useful for many practical applications such as data storage and display devices and has received much attention in recent years.[1–3] However, the synthesis of this kind of new material exhibiting both photochromic and liquid crystalline properties is challenging as the combination usually results in the loss of one of these properties. Up to now, most of the reported photochromic liquid crystal materials are polymers modified with the photochromic units and mesogenic moieties.[4–7] The low-molar-mass photochromic liquid crystalline systems are relatively scarce,[8–10] although the many organic photochromic molecular systems such as azobenzenes,[11] spiroxazines,[12] naphthopyrans,[13] furylfulgides,[14] diarylethenes[15] and biindenylidenediones[16] have been explored. Among the different families of photochromic compounds, [2,2′-bi-1*H*-indene]-3,3′-dialkyl/diaryl-3,3′-dihydroxy-1,1′-diones, which were first studied systematically by our research group, are unusual materials in that they simultaneously undergo photochromism in the crystalline state as well as the generation of radicals.[16–19] From the structure analysis, we know that the biindenylidenedione compound contains many unsaturated groups resulting in a large conjugation system in the molecule, which makes it possible to get a novel kind of photochromic liquid crystalline material with light-induced radical behavior by rational molecular design. Herein, we report the synthesis and multi-properties of this new series of biindenylidenedione derivatives containing a mesogenic core with long alkyl groups.

Experimental

Materials and methods

2,2′-Biindanylidene-1,1′,3,3′-tetraone[20] and 4-*n*-alkyl-4′-bromobiphenyl[21] were prepared according to the literature procedures. The other starting materials were commercially available and used as received. The solvents used were of analytical grade and pre-dried by refluxing under nitrogen with appropriate drying agents.[22]

IR spectra were recorded on a Shimadzu 435 infrared spectrometer. ^{1}H NMR spectra were recorded on Bruker NMR spectrometer working at 300 MHz. $CDCl_3$ was used as solvent. Ultraviolet photoirradiation was performed by using a Moritex high-pressure mercury lamp (200 W) filtered through a band pass glass filter (transition maximum, around 365 nm). Ultraviolet spectra were recorded on a TU-1901 UV-Vis spectrometer. Elemental analysis was performed on a YANACO CHNCORDER MT-3 apparatus. ESR spectra were reported on a Bruker EMX-6/1 EPR spectrometer. The optical observations were made with an Olympus BX51 polarizing optical microscopy with a hot stage. Thermal properties of the bulk materials were studied with a Perkin-Elmer DSC-7a differential scanning calorimeter with a heating and cooling rate of 5 °C min^{-1} and pre-calibrated with an indium standard (156.6 °C, 3.3 kJ mol^{-1}). All measurements were carried out under a flow of nitrogen gas to prevent decomposition of the sample. The X-ray data were collected on a Bruker SMART 1000 diffractometer with Mo Kα radiation.

General procedure for the syntheses of compounds 1a–1f. Under N_2 atmosphere, to a four-necked 100 ml round-bottomed flask containing a stir bar and a reflux condenser with a drier, fitted with a pressure-equalizing dropping funnel, was added Mg (0.37 g, 0.015 mol), anhydrous THF (5 ml), and one or two drops of 1,2-dibromoethane. Then a solution of 4-*n*-hexyl-4′-bromobiphenyl (0.014 mol) in 25 ml anhydrous THF was added at rate of a slight reflux from the pressure-

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equalizing dropping funnel, the resulting mixture was stirred for about an hour after the Mg had completely disappeared. To the mixture solution, 2,2′-biindanylidene-1,1′,3,3′-tetraone (0.50 g, 1.736 mmol) suspended in 30 ml dry benzene was added portionwise over a period of 15 min at rt, the dark green reaction mixture soon turned to be yellow-brown. The solution was stirred continually for 15 h under a nitrogen atmosphere, and then it was exposed to the air for another 5 h. Finally, the reaction mixture was quenched with saturated aqueous NH_4Cl (2.4 g) solution and filtered to give the crude compounds **1a–1f**, which were purified by column chromatography on a silica gel.

trans-*anti*-3,3′-(4′-*n*-pentyl-4-biphenyl)-3,3′-dihydroxyl-[2,2′-bi-1*H*-indene]-1,1′-dione **1a**. Yellow powder; Yield: 87.2%; mp 282.5 °C; ^{1}H MNR (300 MHz, $CDCl_3$) δ: 7.74–7.18 (m, 24H), 7.031 (s, 2H), 2.63–2.58 (t, J = 7.5 Hz, 4H), 1.67–1.60 (m, 4H), 1.35–1.30 (m, 8H), 0.91–0.86 (t, J = 6.6 Hz, 6H). IR (KBr) ν: 3341, 1679 cm^{-1}. Ms (ESI): m/z 735.59 (M − 1). Anal. Calcd for $C_{52}H_{48}O_4$: C 84.75; H 6.57. Found: C 84.67; H 6.61%.

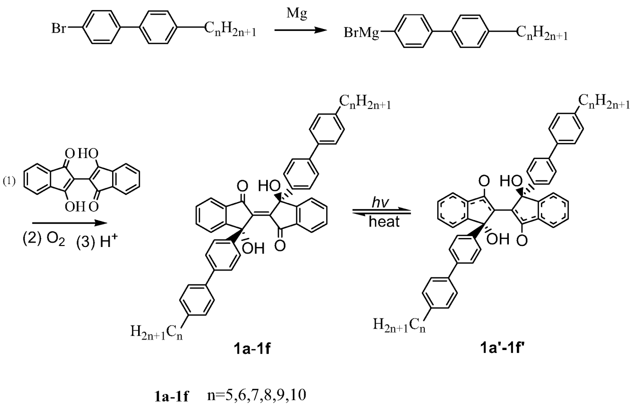
trans-*anti*-3,3′-(4′-*n*-hexyl-4-biphenyl)-3,3′-dihydroxyl-[2,2′-bi-1*H*-indene]-1,1′-dione (**1b**). Yellow powder; Yield: 70.1%; mp 277.7 °C. ^{1}H MNR (300 MHz, $CDCl_3$) δ: 7.72–7.18 (m, 24H), 7.03 (s, 2H), 2.64–2.58 (t, J = 7.5 Hz, 4H), 1.64–1.56 (m, 4H), 1.33–1.27 (m, 12H), 0.90–0.85(t, J = 6.6 Hz, 6H). IR (KBr) ν: 3329, 1678 cm^{-1}. Ms (ESI): m/z 763.27 (M − 1). Anal. Calcd for $C_{54}H_{52}O_4$: C 84.78; H 6.85. Found: C 84.63; H 6.64%.

trans-*anti*-3,3′-(4′-*n*-heptyl-4-biphenyl)-3,3′-dihydroxyl-[2,2′-bi-1*H*-indene]-1,1′-dione (**1c**). Yellow powder; Yield, 85.8%; mp 257.6 °C; ^{1}H MNR (300 MHz, $CDCl_3$) δ: 7.75–7.19 (m, 24H), 7.04 (s, 2H), 2.63–2.58(t, J = 7.5 Hz, 4H), 1.66–1.58 (m, 4H), 1.32–1.27 (m, 6H), 0.89–0.85(t, J = 6.6 Hz, 6H). IR (KBr) ν: 3348, 1677 cm^{-1}. Ms (ESI): m/z 791.67 (M − 1). Anal. Calcd for $C_{56}H_{56}O_4$: C 84.81; H 7.12. Found: C 84.56; H 7.15%.

trans-*anti*-3,3′-(4′-*n*-octyl-4-biphenyl)-3,3′-dihydroxyl-[2,2′-bi-1*H*-indene]-1,1′-dione (**1d**). Yellow powder; Yield: 63.9%; mp 237.9 °C; ^{1}H MNR (300 MHz, $CDCl_3$) δ: 7.75–7.19 (m, 24H), 7.04 (s, 2H), 2.63–2.58 (t, J = 7.5 Hz, 4H), 1.66–1.59 (m, 4H), 1.30–1.26 (m, 20H), 0.89–0.85 (t, J = 6.6 Hz, 6H). IR (KBr) ν: 3345, 1677 cm^{-1}. Ms (ESI): m/z 819.15 (M − 1). Anal. Calcd for $C_{58}H_{60}O_4$: C 84.84; H 7.37. Found: C 84.63; H 7.30%.

trans-*anti*-3,3′-(4′-*n*-nonyl-4-biphenyl)-3,3′-dihydroxyl-[2,2′-bi-1*H*-indene]-1,1′-dione (**1e**). Yellow powder, Yield, 62.8%; mp 229.7 °C; ^{1}H MNR (300 MHz, $CDCl_3$) δ: 7.75–7.19 (m, 24H), 7.04 (s, 2H), 2.63–2.58 (t, J = 7.5 Hz, 4H), 1.63–1.59 (m, 4H), 1.30–1.26 (m, 24H), 0.87–0.85 (t, J = 6.6 Hz, 6H). IR (KBr) ν: 3351, 1678 cm^{-1}. Ms (ESI): m/z 847.20 (M − 1). Anal. Calcd for $C_{60}H_{64}O_4$: C 84.87, H 7.60. Found: C 84.88, H 7.69%.

trans-*anti*-3,3′-(4′-*n*-decyl-4-biphenyl)-3,3′-dihydroxyl-[2,2′-bi-1*H*-indene]-1,1′-dione (**1f**). Yellow powder, Yield, 56.9%; mp 214.5 °C; ^{1}H MNR (300 MHz, $CDCl_3$) δ: 7.75–7.18 (m, 24H), 7.03 (s, 2H), 2.63–2.58 (t, J = 7.5 Hz, 4H), 1.69–1.59 (m, 4H), 1.34–1.25 (m, 28H), 0.89–0.85 (t, J = 7.5 Hz, 6H). IR (KBr) ν: 3338, 1679 cm^{-1}. Ms (ESI): m/z 875.23 (M − 1). Anal. Calcd for $C_{62}H_{68}O_4$: C 84.89; H 7.81. Found: C 84.71; H 7.80%.



Scheme 1 Synthesis of the compounds **1a–1f**.

Results and discussion

Syntheses

The compounds **1a–1f** in this work were prepared according to the similar procedures reported by our research group[17] and the synthetic route is shown in Scheme 1. The key step was to perform an unusual oxidation procedure before the general Grignard reaction was quenched by adding saturated NH_4Cl aqueous solution. The crude products **1a–1f** were obtained by filtrating the mixture solution, which were first purified by column chromatography on silica gel and then crystallized from dichloromethane at room temperature. All compounds were characterized by ^{1}H NMR, mass spectrometry, infrared spectroscopy and elemental analyses. The data are collected in the experimental section.

Photochromic properties and light-induced radical behavior in the solid state

The photocolor reaction was monitored by UV-Vis spectra in the solid state. All the prepared compounds **1a–1f** showed photochromism. The compounds **1b**, **1d**, **1e** and **1f** were seleted to investigate the photochromic properties, and the results are given in Fig. 1. Fig. 1 shows the absorption spectra in the visible region of the selected samples measured before and after irradiation with ultraviolet light for 30 min at room temperature. From Fig. 1, we can clearly see that all the compounds **1b**, **1d**, **1e** and **1f** have an apparent increase of UV absorption in the wavelength range of 500–800 nm and the color of samples turned from yellow to orange by irradiation with ultraviolet light. In this study, although the color change for compound **1** is visually slight, it can be observed by the naked eye, which is in agreement with our previous observations of this type of compounds.[18] Furthermore, it is worthwhile to note that the photochromic state produced by means of irradiation of ultraviolet light is very stable in the air and does not revert to the original color at room temperature even after several months. However, the photochromic state can be turned back to the original state upon heating up to 110 °C in the air. This process is thermochromism.

The light-induced radical behavior was studied by ESR measurements which were carried out in air at room temperature. The compounds **1b** and **1f** were also selected to

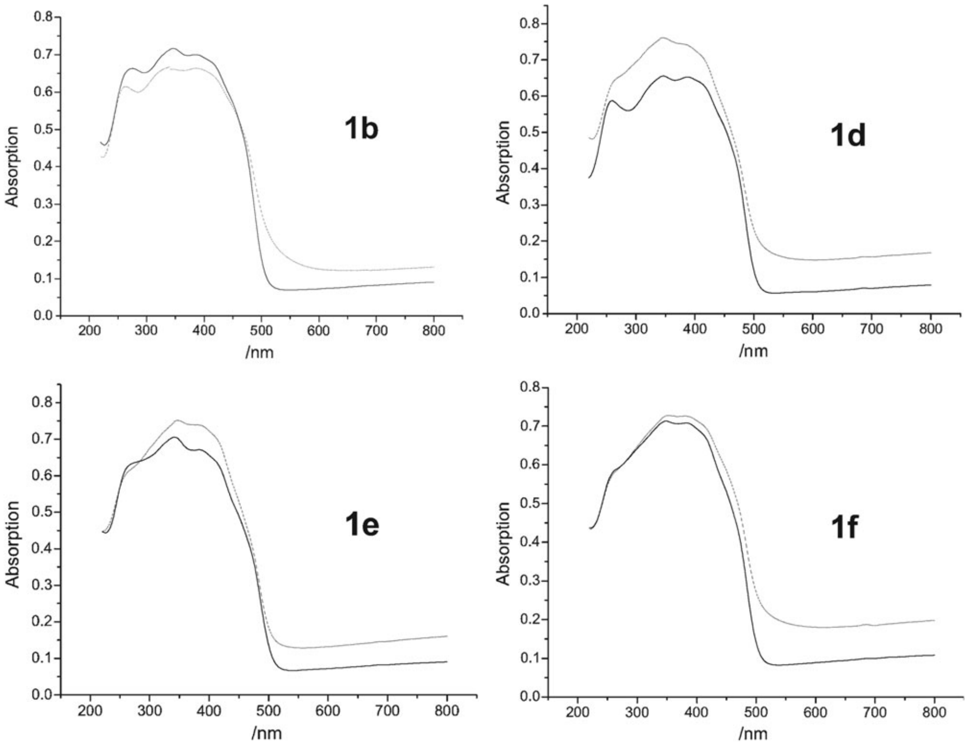


Fig. 1 Absorption spectra of **1b**, **1d**, **1e**, and **1f** in the solid, (—): before irradiation, (—): irradiation for 30 min with a 200 W high-pressure mercury lamp.

investigate the light-induced radical behavior. Neither of the unirradiated yellow compounds **1b** and **1f** showed any ESR signals. In contrast, the corresponding samples after irradiation with a 200 W high-pressure mercury lamp exhibited very distinctive ESR signals, which are shown in Fig. 2 and Fig. 3, respectively. The photochromism and light-induced radical behavior happen simultaneously in the biindenylidenedione compounds in this work. The ESR signal and UV absorption change are consistently associated with the photochromism of this type of compound after irradiation, which also provide solid evidence for the photochromism. From Fig. 2 and Fig. 3, we can also clearly see that the ESR signal shapes of **1b′** and **1f′** are very similar, and the *g* values of **1b′** and **1f′** are 2.003 and 2.002, respectively. Both characteristics mean that the light-induced radical behavior of this kind of compound is mainly controlled by the biindenylidenedione structure; the side alkyl chains have little effect on the light-induced radical behavior.

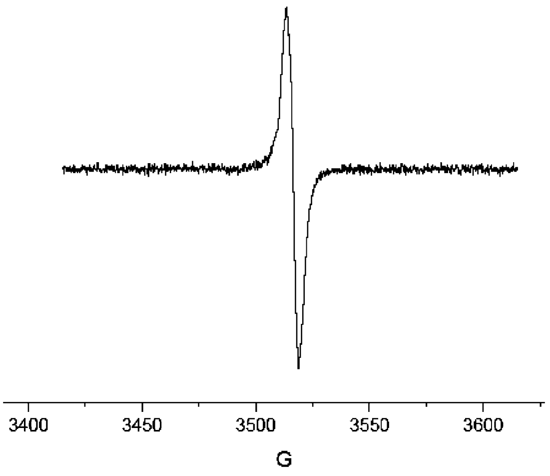


Fig. 2 ESR spectrum of **1b′**, Measurement conditions: center field, 3515.000 G; sweep width, 200.000 G; modulation, 100.00 kHz; modulation amplitude, 0.6 G. $g = 2.003$.

The photochromic properties and the light-induced stable radical behavior could be explained by the delocalized π-spin system shown in Scheme 1. The irradiation resulted in the reorganization of electron distribution and generated two unpaired singlet radicals with antiparallel orientation. The singlet biradicals were stabilized by conjugation to the whole molecular system while the oxygen atoms of carbonyls contributed to the spin density distribution due to their electronegativity, which is consistent with the results reported previously by our research group.[19]

Liquid crystalline properties

The liquid-crystalline properties of the compounds **1a–1f** were investigated by using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The phase transition temperatures and associated enthalpy changes of compounds **1a–1f** are listed in Table 1. As shown in Table 1, the first three homologues **1a–1c** do not show a liquid crystalline phase, which may be due to the short alkyl chain and the length-to-width ratios of the corresponding compounds being

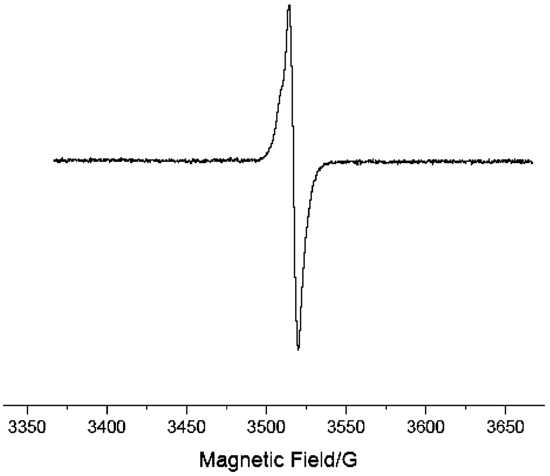


Fig. 3 ESR spectrum of **1f′**, Measurement conditions: center field, 3517.140 G; sweep width, 300.000 G; modulation frequency, 100.00 KHz; modulation amplitude, 1.00 G. $g = 2.002$.

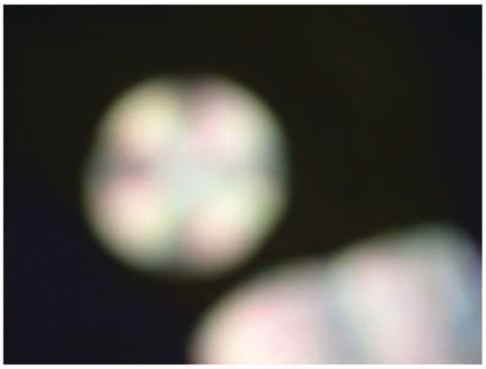


Fig. 4 Texture of **1d** under crossed polarizers, cooling, 171 °C, SmA phase, magnification 200×.

not large enough to form the mesophase. In contrast, compound **1d** exhibits a monotropic smectic phase even though the mesomorphic temperature range is very narrow. Under polarizing microscopic observation, this smectic phase exhibits a fan-shaped texture (see Fig. 4) when formed on cooling the isotropic liquid, a similar texture could also be seen in the reported literature.[23] In addition, the fan texture is easily changed to a pseudo-isotropic texture (homeotropic alignment) by cover-slip displacement. Upon further cooling the sample of the mesomorphic state, the fan-shaped texture changed into a very fine spherulitic texture with a Maltese cross extinction pattern (see Fig. 5), which is the typical texture of solid state. These characteristic textures show that this mesomorphic phase could be identified as smectic A.[24] As the terminal alkyl chain is increased, the mesomorphic temperature range of **1f** is much wider than that of **1d**, which can be easily understood by taking account of the structure difference. According to the texture (see Fig. 6) observed under the polarizing microscopy and the molecular structure of **1f**, the mesophase of **1f** may be a smectic phase, but further work is needed to confirm this. All the results observed under the POM are consistent with the DSC data, which also support the conclusion that compounds **1d** and **1f** are mesogens. In contrast, the compound **1e** does not exhibit any liquid crystalline properties, a finding that could likely be explained by the well-known odd-effect of the alkyl terminal chains in calamitic liquid crystals.[25]

Table 1 Transition temperature (°C) as determined by DSC

Compound	n	Phase transition[a]	T/°C[b]	ΔH/ kJ mol^{-1}
1a	5	Cr → Iso	282.5	67.3
1b	6	Cr → Iso	277.7	66.6
1c	7	Cr → Iso	257.6	64.5
		I → Recr	159.7	−28.7
1d	8	Cr → Iso	237.9	66.6
		I → S_A	175.7	—[c]
		S_A → Recr	173.4	−49.0
1e	9	Cr_1 → Cr_2	116.0	28.3
		Cr_2 → Iso	229.7	71.7
		I → Recr	153.1	−50.2
1f	10	Cr_1 → Cr_2	93.2	28.6
		Cr_2 → Iso	214.5	65.8
		Iso → SmX	151.1	−9.4
		SmX → Recr	135.3	−20.5

[a] Cr = crystalline, SmA = smectic A, SmX = smectic X, Iso = isotropic. [b] T the peak temperature. [c] The peaks overlapped and could not be integrated accurately.

Crystal structure determination

The single crystal of **1b** suitable for X-ray crystallographic analysis† was obtained by slow evaporation from dichloromethane and acetone (1 : 1) at room temperature. The crystal data and structure refinement for **1b** are summarized in Table 2. The molecular structure and the packing mode of compound **1b** are depicted in Fig. 7 and Fig. 8, respectively. The X-ray investigation on the single crystal of **1b** reveals the bond joining the two loops of indandione is definitely a double bond C8–C8A (1.347(4) Å), the two symmetrical indandione moieties linked by the double bond made an angle of 0°, so the two loops of indandione are almost perfectly parallel and the double bond has little distortion. The two aryl substituted biphenyl groups locate at different sides of the double bond

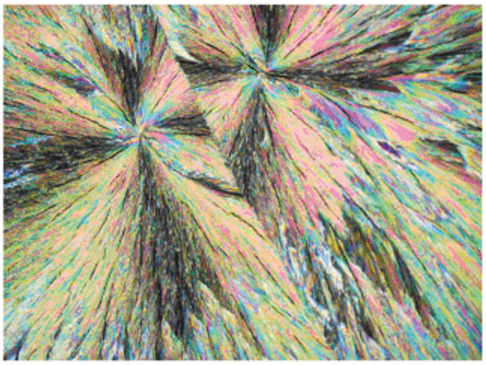


Fig. 5 Spherulitic texture of **1d** under crossed polarizers, cooling, 148 °C, solid state, magnification 200×.

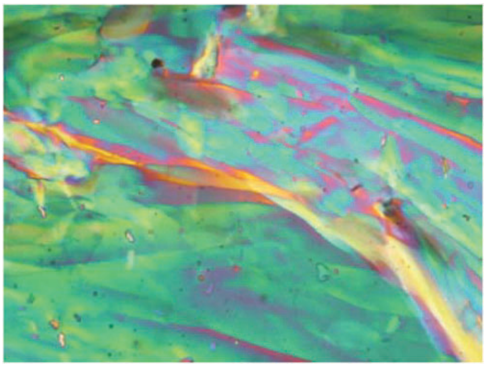


Fig. 6 Texture of **1f** under crossed polarizers, cooling, 150 °C, SmX phase, magnification 200×.

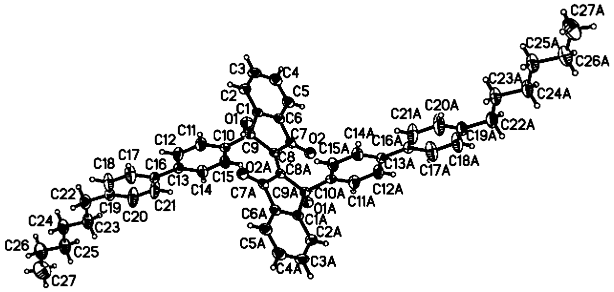


Fig. 7 The molecular structure of compound **1b**.

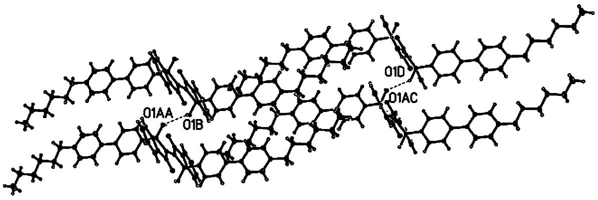


Fig. 8 The stacking structure of compound **1b**.

with *trans*-configuration referring to the indandione planes. This kind of conformation is beneficial to form the extended conjugation, which is crucial to the formation of the photochromic and photoinduced properties. The π-conjugation extends throughout the whole molecule and the UV-Vis absorption spectra display considerable changes after irradiation. The irradiation of the compounds may result in the reorganization of electron distribution and generate the singlet biradical at the same time. The singlet biradical exhibiting ESR signals was stabilized by the extended π-conjugation connected with the double bond to the whole molecular system. There are intramolecular (O1–H1···O2A in Fig. 7) and intermolecular (O1B–H1B···O1AA in Fig. 8) hydrogen bonds in the structure of **1b**. The hydrogen bond lengths (Å) and angles (°) of **1b** are listed in Table 3. These hydrogen bonding interactions make the molecules form a rodlike shape along the *a*-axis, and the molecules are arranged in a layered structure (see Fig. 7 and Fig. 8). Both of these factors are beneficial to the formation of the smectic mesophase.

Table 2 Some selected crystal data and refinement for compound **1b**

Empirical formula	$C_{54}H_{52}O_4$
Formula weight	764.96
T/K	293(2)
Wavelength/Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 6.2667(9), α = 83.907(2)° b = 8.5979(12) Å, β = 89.471(2)° c = 19.959(3)Å, γ = 77.551(2)°
Volume	1044.1(3) $Å^3$
Z	2
Calculated density	1.217 g cm^{-3}
Absorption coefficient	0.075 mm^{-1}
F(000)	408
Crystal size	0.22 × 0.12 × 0.04 mm
θ range for data collection	2.05–25.03°
Limiting indices	$-7 \le h \le 7, -8 \le k \le 10, -23 \le l \le 23$
Reflections collected/ Unique	5743/3659 [R_{int} = 0.0265]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/ parameters	3659/0/264
Final R indices [$I > 2$ sigma(I)]	R_1 = 0.0529, wR_2 = 0.1342
R indices (all data)	R_1 = 0.1149, wR_2 = 0.1626
Largest diff. peak and hole	0.188 and −0.223 e A^{-3}

Table 3 Hydrogen-bonding geometry for **1b**

D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/°
O1–H1···O2′	0.820	1.967	2.697	147.93
O1B–H1B···O1AA	0.820	2.440	2.830	110.23

Conclusions

In summary, six new homologous biindenyldenedione derivatives **1a–1f** containing two biphenyl substituents have been synthesized and fully characterized. All of them exhibit photochromic properties and light-induced radical behavior simultaneously upon irradiation with 365 nm UV light, and the photochromic state may be returned to the original form thermally. The compounds **1d** and **1f** display a monotropic smectic mesophase, which was confirmed by DSC and POM. These are first examples of photochromic, light-induced radical behavior and liquid crystalline properties occurring in a pure compound. The relationship between the single crystal structure and properties has been discussed in the paper.

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