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Rewritable color recording media consisting of leuco dye and biphenyl developer with a long alkyl chain

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Media formulated using two compounds (a leuco dye and 4-alkoxyl-4′-hydroxybiphenyl) were colored in the amorphous state and colorless in the crystalline state. As the alkyl chain length of the biphenyl compound increased, the contrast ratio and thermal stability of the amorphous states increased. Additionally, the crystallization velocity increased for the media with a long alkyl chain. Leuco dyes with a high glass transition temperature also produced thermally stable amorphous states. The origin of the long alkyl chain effects is discussed.

Rewritable color media can be considered to have a function located between those of hard copies and reflective color displays.[1–3] An example of this is a rewritable card with a simple display function. These new media are expected to be environmentally beneficial because they would save cards, paper, and OHP sheets. Their superior functionality could lead to the creation of a new market. Amorphous–crystal transitions can be used to develop rewritable media which require only heat treatment. In previous papers,[4,5] the author and co-workers have established a theoretical relationship between the thermodynamic parameters of phase transitions and amorphous thermal properties such as the glass transition temperature (T_g), the maximum crystallization velocity (MCV) and the crystallization temperature (T_c). In addition, the author and co-workers have developed a molecular design rule that enables control of these amorphous properties. Using this design rule, we have developed rewritable color recording media consisting of three components: a color former (leuco dye), a developer (phenol compound) and a reversible matrix (steroid).[6–8] The media were colored in the crystalline state, and colorless in the amorphous state. The contrast was high and the media were found to be suitable for negative-type recording using a thermal printer head (TPH).

In the present study we describe a new kind of medium, which is a ‘positive-type’ two-component medium including a biphenyl developer with a long alkyl chain. A few two-component media including a developer with a long alkyl chain have already been reported.[1–3] The present biphenyl developers have structures similar to those of liquid crystalline molecules. The relationship between the rewritable properties and thermodynamic properties of the specific structures has been discussed.

Results

Thermal properties of compounds

The molecular structures of the compounds used are shown. Tables 1 and 2 show the thermal properties of long alkyl biphenyl developers (C_nOBPOH) and leuco dyes, respectively.

There was little difference in the melting temperatures of C_nOBPOH for different alkyl chains. The melting points and the phase transition temperatures are essentially determined by the 4-hydroxybiphenyl skeleton. C_nOBPOH compounds are crystalline and did not produce amorphous states.

Leuco dyes in Table 2 produced a stable glass by quenching the fusion. The glass did not change to a crystalline state during the DSC measurement. Glass transition temperatures (T_g) increased as $\Delta S_m/N$ values decreased according to the amorphous theory the author and co-workers established.[4,5] N is the number of heavy atoms per molecule (excludes hydrogen atoms).

Rewritable properties

The media consisted of two components: a color former and a long alkyl biphenyl developer. Tables 3 and 4 show contrast ratios (CR) of colored and colorless states for various C_nOBPOH–PSD-150 ratio media after heating at 40 °C for 150 h and after heating at 55 °C for 150 h, respectively. CR values were averaged for 3–5 samples. The CR decreased initially within a day and became almost a constant value as shown in Fig. 1. The thermal stability of CR was high enough for the alkyl developers longer than C_{18}OBPOH. High CR values after heating were obtained for 1 : 2 (C_nOBPOH–PSD-150) weight ratio media. Fig. 2 shows the variation of optical density with numbers of amorphous–crystal transitions for the C_{20}OBPOH–PSD-150 (1 : 2 w/w) medium sandwiched between glass sheets. Good contrast was obtained after 100 cycles. Table 5 indicates the decolorization time of C_nOBPOH–PSD-150 (1 : 2 w/w) media sandwiched between glass sheets ($24 \times 32 \times 0.15$ mm^3) on a hot plate at 100 °C. The decolorization (crystallization) time was shorter for longer chain developer.

Table 6 shows CR and absorption wavelength values for C_{22}OBPOH–various leuco dyes (1 : 2 w/w) media. For black dyes (PSD-150, ODB-1, ODB-2 and TH-107), CR values decreased as T_g values of the leuco dyes decreased. For color dyes (blue CVL, magenta IR and cyan GN-2), higher CR values after heating were observed, nevertheless T_g values were not so high.

Thermal and optical analysis of rewritable media

Fig. 3 shows a DSC curve and a visible light transmittance curve of the C_{20}OBPOH–PSD-150 (1 : 2 w/w) medium which was quenched and then kept at 40 °C for 2.5 h. At room temperature, no structure was observed in the black medium with a polarized optical microscope. This indicates that the quenched medium is amorphous. A clear glass transition temperature was observed at 54 °C. A quenched medium without annealing did not show a clear glass transition temperature. After the glass transition temperature, the transmittance increased gradually because the black color became paler. Small crystalline grains were observed near 100 °C and

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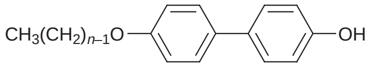
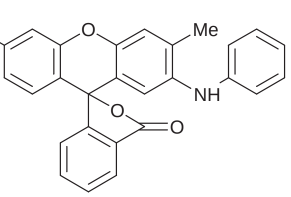
Table 1 Thermal properties of C*n*OBPOH

n	6	8	10	12	14	18	20	22
T_m/K	420	427	410	408	418	410	412	411
T_{tr1}/K	350	386	391	390	414	368	382	385
T_{tr2}/K	390	—	398	—	—	390	390	391
ΔH_{tr1}/kJ mol^{-1}	24.6	38.5	14.4	27.9	49.2	47.4	71.9	67.7
ΔH_{tr1}/kJ mol^{-1}	3.8	7.8	23.5	28.0	13.3	2.5	2.8	2.5
ΔH_{tr2}/kJ mol^{-1}	3.8	—	10.4	—	—	27.6	3.7	8.0
$\Sigma\ \Delta H_{tr,m}$/kJ mol^{-1}	32.2	46.0	48.3	56.0	62.4	77.6	78.4	78.2
$\Sigma\ \Delta S_m$/J K^{-1} mol^{-1}	79.2	110.2	122.4	140.1	150.4	201.9	190.7	191.16

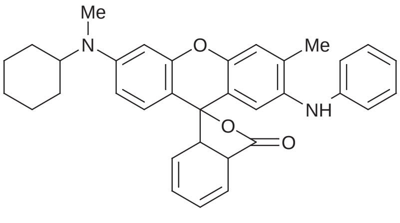
Table 2 Thermal properties of leuco dyes

compound	PSD-150	ODB-1	ODB-2	TH-107	CVL	IR	GN-2
T_m/K	478	468	456	458	453	505	446
T_g/K	372	364	336	329	337	336	325
N	39	36	40	40	31	34	—
$(\Delta S_m/N)$/J K^{-1} mol^{-1}	2.2	2.1	2.7	2.9	2.5	2.9	—

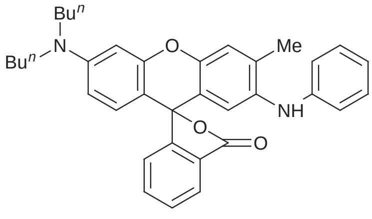

C*n*OBPOH



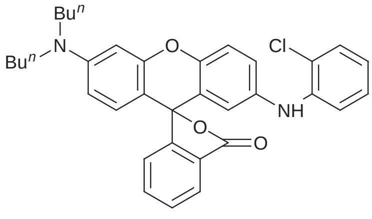
ODB-1



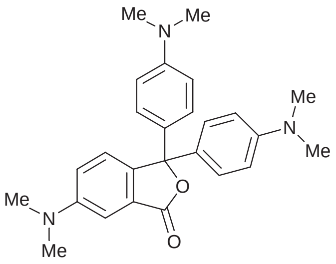
PSD-150



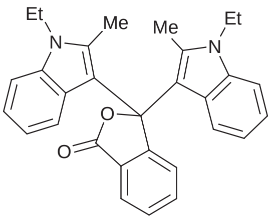
ODB-2



TH-107



CVL



IR

the transmittance decreased due to light scattering. The grains melted near 120 °C. The melted material was then cooled from 180 °C. A crystallization peak was observed near 100 °C.

Discussion

Rewritable mechanism

The color change is considered to be attributable to the following mechanism. In the amorphous state, the color former and the developer are mixed. In this state, the developer interacts with the color former to develop color. When crystallization occurs, the amorphous color former is separated from the developer crystals. A schematic explanation of the rewritable mechanism is shown in Fig. 4.

Polycrystalline PSD-150 melted at 205 °C and produced a stable glass by quenching the fusion. The PSD-150 glass showed a glass transition temperature at 99 °C and did not change to a crystalline state during the DSC measurement. C_nOBPOH compounds are crystalline and did not produce amorphous states. Therefore, appropriate mixtures of PSD-150 and C_nOBPOH showed amorphous–crystal transition, that is, rewritable properties. Tables 3 and 4 indicate that the weight ratio of 0.5 is an appropriate value for C_nOBPOH ($n > 18$)–PSD-150 media.

The long alkyl chain decreased the decoloring (crystallization) time for the media as shown in Table 5. High crystalline properties of the long alkyl compounds probably cause the phase-separation to accelerate. A similar effect of the long alkyl chain has been observed for fatty alcohols in the four-component rewritable media reported by the author and co-workers.[9,10] A long alkyl developer does not dissolve the color former molecules much near its melting point. However, it does dissolve them at much higher temperatures. In the amorphous state, the long alkyl developer super-dissolves the color former molecules. Above a glass transition temperature and near its melting point of about 100 °C, the molecules can move. The long alkyl developer excludes other molecules very rapidly because the viscosity of the long alkyl developer fusion is low. The biphenyl skeleton can be considered to increase the crystalline properties. When the mixture is cooled to room temperature, crystalline states of the long alkyl developer are obtained.

Stability of colored amorphous states

Stability for the colored amorphous states was not determined by the melting temperatures of C_nOBPOH. Fig. 5 shows the dependence of sums of the fusion and transition entropy and enthalpy changes of C_nOBPOH on the alkyl chain length. Between $n = 6$ and 18, the entropy and enthalpy values

Table 3 Contrast ratios (CR) for C_nOBPOH–PSD-150 media before and after heating at 40 °C for 150 h

weight ratio of C_nOBPOH–PSD-150	CR after heating $n=6$	8	12	14	18	20	22
3	1.4±0.2						
2	1.5±0.1	1.6±0.2				1.8±0.4	
1	1.1±0.2	1.6±0.2	2.1±0.4	1.4±0.3	2.1±0.4	4.0±0.1	3.7±0.7
0.5		1.5±0.1	2.0±0.2	2.2±0.2	1.7±0.6	4.6±0.4	6.7±0.3
0.33					3.1±0.1	3.9±0.4	4.4±0.1
0.25					2.6±0.7	2.6±0.2	3.4±0.5
0.2					1.9±0.1		
	CR before heating						
3	1.6±0.2						
2	1.8±0.2	3.7±0.5				2.9±0.8	
1	2.2±0.9	4.6±0.5	5.2±2.1	4.9±1.0	3.1±1.0	7.2±0.4	4.9±1.1
0.5		3.2±0.6	4.0±1.9	6.2±2.2	2.9±1.3	7.2±0.9	10.1±1.1
0.33					5.6±0.7	7.6±0.8	7.3±0.8
0.25					3.7±1.1	6.0±1.1	6.2±0.9
0.2					2.0±0.1		

Table 4 Contrast ratios for C_nOBPOH–PSD-150 media before and after heating at 55 °C for 150 h

weight ratio of C_nOBPOH–PSD-150	CR after heating $n=18$	20	22
2		1.3±0.2	
1		3.7±0.1	3.0±0.7
0.5		3.9±0.9	5.4±1.0
0.33	2.3±0.1	3.5±0.6	4.7±0.6
0.2	2.7±0.4	3.7±0.9	3.5±0.5
	CR before heating		
2		1.5±0.8	
1		7.4±0.6	4.6±1.3
0.5		7.0±1.2	10.2±1.0
0.33	4.1±0.6	6.5±2.3	8.3±0.3
0.2	1.8±0.1	6.0±0.2	5.8±0.5

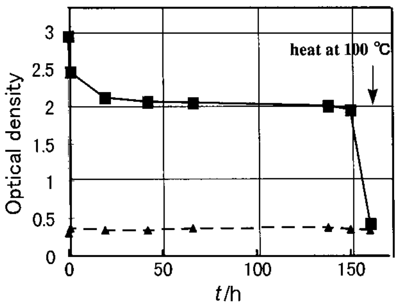


Fig. 1 Annealing-time dependence at 55 °C of optical density for $C_{22}OBPOH$–PSD-150 (1/2 w/w) medium sandwiched between glass sheets: ■: colored state, ▲: colorless state

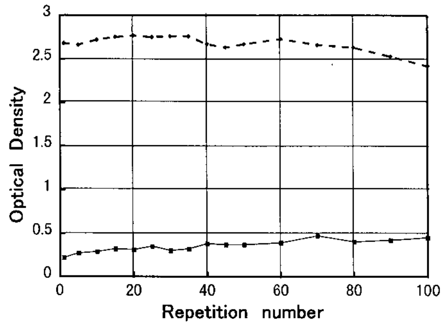


Fig. 2 Variation of optical density with number of amorphous–crystal transitions for $C_{20}OBPOH$–PSD-150 (1/2 w/w) medium sandwiched between glass sheets

Table 5 Decolorization time of C_nOBPOH–PSD-150 (1 : 2 w/w) media[a]

n	6	8	12	14	18	20	22
t/s	3.7±0.3	3.8±0.2	1.7±0.3	1.9±0.3	1.7±0.3	1.6±0.3	1.4±0.2

[a] The media were sandwiched between glass sheets ($24 \times 32 \times 0.15$ mm^3) on a hot plate at 100 °C.

increased linearly with n. However, the values for $n=20$ and 22 deviated from linearity. This shows an interaction between the developer molecules, probably intertwining of long alkyl chains, remains in the fusion. The intertwining gives thermal stability to the amorphous media. A similar effect was observed for flexible polymers which have glass transition temperatures higher than the expected values.[5]

Leuco dyes with a high glass transition temperature produced a thermally stable colored state. For black dyes with similar structures, amorphous colored stabilities corresponded to the T_g values. For colored dyes (CVL, IR, and GN-2), however, amorphous stabilities were high despite their relatively low T_g values. Calculated LUMO levels of colored molecular structures for PSD-150, CVL and IR (their lactone rings were opened) were −5.3, −4.7 and −4.7 eV, respectively. This indicates that the colored CVL and IR are more stable for reduction by a phenolate anion into a colorless state than the colored PSD-150.

We constructed rewritable cards by dispersing the two-component media in a binder polymer. The binder polymer was required to make the rewritable layer uniform, and was chosen so as to retain the rewritable characteristics. The details will be shown elsewhere.

Conclusion

Media composed of a leuco dye and 4-alkoxy-4′-hydroxybiphenyl were colored in the amorphous states and colorless in the crystalline states. As the alkyl chain length of the biphenyl compound increased, the contrast ratio and thermal stability of the amorphous states increased. Additionally, the crystallization velocity increased for the media with a long alkyl chain. Leuco dyes with a high glass transition temperature also produced thermally stable amorphous states. The long alkyl chain effects were probably based on the intertwining and crystallization properties.

Table 6 Contrast ratios and absorption wavelength for $C_{22}OBPOH$–various leuco dyes media (1 : 2 w/w) before and after heating at 55 °C for 75 h

	PSD-150	ODB-1	ODB-2	TH-107	CVL	IR	GN-2
CR after heating	8.3 ± 1.0	7.0 ± 0.8	3.3 ± 0.2	3.1 ± 0.1	4.4 ± 0.3	10.5 ± 0.7	8.7 ± 2.5
CR before heating	10.3 ± 0.9	10.6 ± 1.1	8.8 ± 0.4	6.0 ± 0.6	5.9 ± 0.1	14.9 ± 2.0	11.5 ± 2.0
CR_a/CR_b	0.8	0.7	0.4	0.5	0.8	0.7	0.8
λ_{max}/nm	570,460				620	540	635

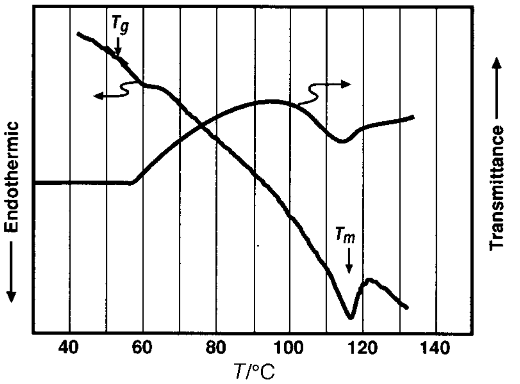


Fig. 3 DSC curve and visible light transmittance curve of $C_{20}OBPOH$–PSD-150 (1 : 2 w/w) medium. The medium was quenched and then kept at 40 °C for 2.5 h.

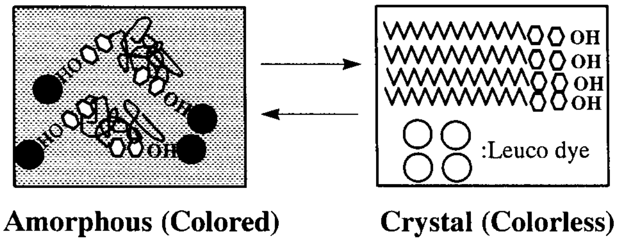


Fig. 4 Schematic explanation of rewritable mechanism

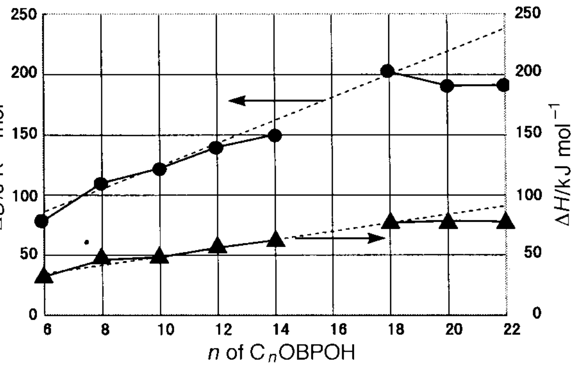


Fig. 5 Dependence of sums of the fusion and transition entropy and enthalpy changes of C_nOBPOH on the alkyl chain length: ●: sum of the entropies, ▲: sum of the enthalpies

Experimental

Materials

PSD-150 was supplied by Nippon Soda Co., Ltd. (Japan). ODB-1, ODB-2, IR and GN-2 were supplied by Yamamoto Chemical Inc. (Japan). TH-107 was supplied by Hodogaya Chemical Co., Ltd. (Japan). CVL was purchased from Tokyo Kasei Kogyo Co. Ltd. (Japan). The molecular structure of GN-2 is not known. $C_{20}OBPOH$ and $C_{10}OBPOH$ were purchased from Sogo Pharmaceutical Co., Ltd. (Japan). C_8OBOPH and $C_{14}OBPOH$ were supplied by Honshu Chemical Co., Ltd. (Japan). These compounds were used without further purification. The author checked purity for PSD-150 (mainly used in this paper) and CVL by GC-MS, ^1H NMR and ^{13}C NMR methods. No impurity was observed.

$C_{22}OBPOH$, $C_{18}OBPOH$, $C_{12}OBPOH$ and C_6OBPOH were synthesized from 4,4′-dihydroxybiphenyl (Tokyo Kasei) and alkyl bromide (Tokyo Kasei) by the author. The main by-products were 4,4′-bis(alkyloxy)biphenyl. For long alkyl compounds ($n > 12$), the by-products were almost completely removed.

GC-MS spectra were taken with an EI method on a JEOL GC mate spectrometer: column; DB1-ht (nonpolar, film thickness 0.1 μm), 0.25 mm x 30 m. The column oven was held at 40 °C for 2 min and then heated at 20 °C min^{-1}, and was held at 320 °C for 30 min. He flow rate; 1 ml min^{-1} injected sample; 1 μl of 0.5 wt.% solution ($CHCl_3$–DMSO = 9 : 1). ^1H NMR (399.7846 MHz) and ^{13}C NMR spectra were taken on a JEOL JNM-LA400WB spectrometer. Elemental analysis was carried out in Shonan Analytical Center Co. Ltd. (Japan).

4-Docosyloxy-4′-hydroxybiphenyl ($C_{22}OBPOH$)

18.54 g (0.0996 mol) of 4,4′-dihydroxybiphenyl, 17.50 g (0.045 mol) of 1-bromodocosane and 1.81 g (0.045 mol) of sodium hydroxide were refluxed at 80 °C in 400 ml of ethanol for 8 h. The reaction mixture was allowed to stand overnight. The mixture was filtered. The filtrate was evaporated and dried in a vacuum. The residue was washed with methanol, and with hot toluene. 16.66 g of white plate-like crystals were obtained (yield: 75%). GC (retention time/min): 21.35; *m*/*z*: 494 (M^+, 53%), 186 (100), 157 (4). Anal. calc. for $C_{34}H_{54}O_2$: C, 82.53; H, 11.00. Found: C, 82.56, H, 11.20%. δ_H($CDCl_3$–[$^2H_6$]DMSO): 8.87 (OH, 0.93H), 7.35, 7.33, 7.28, 7.26 (2,2′-H of biphenyl, 4.0H), 6.84, 6.82, 6.79, 6.77 (3,3′-H of biphenyl, 4.0H), 3.90, 3.87, 3.87 (CH_2O, 2.0H), 1.73, 1.71, 1.70, 1.68, 1.66 (2-CH_2 of docosyl chain, 2.0H), 1.41, 1.39, 1.38, 1.36, 1.34 (3-CH_2, 2.0H), 1.17 (CH_2, 37H), 0.81, 0.79, 0.77 (CH_3, 3.0H). δ_C($CDCl_3$–[$^2H_6$]DMSO): 157.13 (4-C of biphenyl), 155.69 (4′-C of biphenyl), 132.56 (1-C of biphenyl), 130.95 (1′-C of biphenyl), 126.64 (2′-C of biphenyl), 126.49 (2-C of biphenyl), 114.98 (3′-C of biphenyl), 113.89 (3-C of biphenyl), 67.16 (1-C of alkyl chain), 30.98 (20-C), 28.98, 28.65, 28.47, 28.40 (2, 4-19-C), 25.14 (3-C), 21.75 (21-C), 13.31 (22-C). The GC-MS data showed that a trace amount (0.1%) of $C_{20}OBPOH$ was present.

4-Eicosyloxy-4′-hydroxybiphenyl ($C_{20}OBPOH$)

GC (retention time/min): 19.36; *m*/*z*: 467 (18%), 466 (M^+, 46), 186 (100), 157 (4). Anal. Calc. for $C_{32}H_{50}O_2$: C, 82.35; H, 10.79. Found: C, 82.41; H, 10.88%. δ_H($CDCl_3$–[$^2H_6$]DMSO): 8.96 (OH, 0.97H), 7.35, 7.33, 7.28, 7.26 (2,2′-H of biphenyl, 4.0H), 6.84, 6.82, 6.78, 6.76 (3,3′-H of biphenyl, 4.0H), 3.91, 3.88, 3.87 (CH_2O, 2.0H), 1.73, 1.71, 1.70, 1.68, 1.66 (2-CH_2 of eicosyl chain, 2.0H), 1.40, 1.38, 1.36, 1.34 (3-CH_2, 2.0H), 1.17 (CH_2, 33.3H), 0.81, 0.79, 0.78 (CH_3, 3.1H). δ_C($CDCl_3$–[$^2H_6$]DMSO): 157.52 (4-C of biphenyl), 155.17 (4′-C of biphenyl), 132.88 (1-C of biphenyl), 131.21 (1′-C of biphenyl), 127.00 (2′-C of biphenyl), 126.85 (2-C of biphenyl), 115.40 (3′-C of biphenyl), 114.33 (3-C of biphenyl), 67.51 (1-C of alkyl chain), 31.36 (18-C), 29.11, 29.03, 28.85, 28.78 (2, 4-17-C), 25.54 (3-C), 22.13 (21-C), 13.74 (20-C). The GC-MS and NMR measurements showed no impurity.

4-Octadecyloxy-4′-hydroxybiphenyl (C_{18}OBPOH)

15.59 g (0.0837 mol) of 4,4′-dihydroxybiphenyl, 27.91 g (0.0837 mol) of 1-bromooctadecane and 3.35 g (0.0837 mol) of sodium hydroxide were heated at 80 °C in 150 ml of ethanol for 1 h. The reaction mixture was filtered, and washed with diluted hydrochloric acid then with water. The precipitate was washed with 300 ml of hot ethanol, and was recrystallized from 400 ml of a toluene solution. 16.3 g of white plate-like crystals were obtained (yield: 44%). GC (retention time/min): 18.10; *m/z*: 439 (13%), 438 (M^+, 438, 40), 186 (100), 157 (4). Anal. Calc. for $C_{30}H_{46}O_2$: C, 82.14; H, 10.57. Found: C, 82.14; H, 10.95%. δ_H($CDCl_3$–[$^2H_6$]DMSO): 8.71 (OH, 0.86H), 7.36, 7.34, 7.29, 7.27 (2,2′-H of biphenyl, 4.0H), 6.85, 6.82, 6.81, 6.79 (3,3′-H of biphenyl, 4.0H), 3.91, 3.89, 3.87 (CH_2O, 2.0H), 1.74, 1.72, 1.70, 1.68, 1.67 (2-CH_2 of octadecyl chain, 2.0H), 1.41, 1.40, 1.38, 1.36, 1.34 (3-CH_2, 2.0H), 1.17 (CH_2, 28.7H), 0.81, 0.79, 0.77 (CH_3, 3.1H). δ_C($CDCl_3$–[$^2H_6$]DMSO): 157.57 (4-C of biphenyl), 156.01 (4′-C of biphenyl), 133.10 (1-C of biphenyl), 131.58 (1′-C of biphenyl), 127.14 (2′-C of biphenyl), 126.99 (2-C of biphenyl), 115.37 (3′-C of biphenyl), 114.28 (3-C of biphenyl), 67.63 (1-C of alkyl chain), 31.43 (16-C), 29.20, 29.17, 29.11, 28.93, 28.86, 28.85 (2, 4-15-C), 25.59 (3-C), 22.20 (17-C), 13.69 (18-C). No impurity was detected by GC-MS and NMR measurements.

4-Tetradecyloxy-4′-hydroxybiphenyl (C_{14}OBPOH)

GC (retention time/min): 16.25; *m/z*: 383 (25%), 382 (M^+, 84), 186 (100), 157 (10). Anal. Calc. for $C_{26}H_{38}O_2$: C, 81.63; H, 10.01. Found: C, 81.29; H, 9.92%. δ_H($CDCl_3$–[$^2H_6$]DMSO): 8.58 (OH, 0.86H), 7.36, 7.34, 7.30, 7.28 (2,2′-H of biphenyl, 4.41H), 6.85, 6.83, 6.82, 6.80 (3,3′-H of biphenyl, 4.0H), 3.91, 3.89, 3.87 (CH_2O, 2.0H), 1.74, 1.72, 1.70, 1.69, 1.67 (2-CH_2 of tetradecyl chain, 2.0H), 1.41, 1.40, 1.38, 1.36, 1.34 (3-CH_2, 2.0H), 1.18 (CH_2, 20.3H), 0.81, 0.79, 0.78 (CH_3, 2.9H). δ_C($CDCl_3$–[$^2H_6$]DMSO): 157.74 (4-C of biphenyl), 156.10 (4′-C of biphenyl), 133.30 (1-C of biphenyl), 131.85 (1′-C of biphenyl), 127.33 (2′-C of biphenyl), 127.19 (2-C of biphenyl), 115.53 (3′-C of biphenyl), 114.43 (3-C of biphenyl), 67.79 (1-C of alkyl chain), 31.61 (12-C), 29.34, 29.27, 29.10, 29.04, 29.02 (2, 4-11-C), 25.76 (3-C), 22.38 (13-C), 13.85 (14-C). GC-MS and NMR measurements showed no impurity.

4-Dodecyloxy-4′-hydroxybiphenyl (C_{12}OBPOH)

19.70 g (0.106 mol) of 4,4′-dihydroxybiphenyl, 26.4 g (0.106 mol) of 1-bromododecane and 4.27 g (0.106 mol) of sodium hydroxide were heated at 80 °C in 150 ml of ethanol for 8 h. The reaction mixture was allowed to stand overnight. The precipitate was filtered and washed with diluted hydrochloric acid and then with water. The precipitate was washed with 300 ml of hot ethanol, with 200 ml of hot toluene and then with 100 ml of dichloromethane. 24.35 g of white plate-like crystals were obtained (yield: 65%). GC (retention time/min): 15.43, 22.09; *m/z* of the 15.43 min peak: 355 (7%), 354 (M^+, 34), 186 (100), 157 (5); *m/z* of the 22.09 min peak: 522 [M^+, 86%, 4,4′-bis(dodecyloxy)biphenyl], 354 (15), 186 (100). Anal. calc. for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 81.38; H, 10.19%. δ_H($CDCl_3$–[$^2H_6$]DMSO): 8.89 (OH, 0.86H), 7.37 [2,2′-H of bis(dodecyloxy)biphenyl, 0.05H], 7.35, 7.33, 7.28, 7.26 (2,2′-H of biphenyl, 4.0H), 6.85, 6.84, 6.79, 6.77 (3,3′-H of biphenyl, 4.0H), 3.91, 3.89, 3.87 (CH_2O, 2.1H), 1.73, 1.71, 1.70, 1.68, 1.66 (2-CH_2 of dodecyl chain, 2.1H), 1.40, 1.38, 1.36, 1.34 (3-CH_2, 2.0H), 1.18 (CH_2, 17.2H), 0.81, 0.79, 0.77 (CH_3, 3.2H). δ_C($CDCl_3$–[$^2H_6$]DMSO): 157.65 (4-C of biphenyl), 156.23 (4′-C of biphenyl), 133.07 (1-C of biphenyl), 131.46 (1′-C of biphenyl), 127.16 (2′-C of biphenyl), 127.01 (2-C of biphenyl), 115.50 (3′-C of biphenyl), 114.42 (3-C of biphenyl), 67.67 (1-C of alkyl chain), 31.50 (10-C), 29.24, 29.21, 29.18, 29.90, 28.92 (2, 4-9-C), 25.67 (3-C), 22.28 (11-C), 13.84 (12-C). According to the ^{1}H NMR spectrum, the amount of 4,4′-bis(dodecyloxy)biphenyl was about 3%.

4-Decyloxy-4′-hydroxybiphenyl (C_{10}OBPOH)

GC (retention time/min): 15.01, 18.33; *m/z* of the 15.01 min peak: 327 (14%), 326 (M^+, 56), 186 (100), 157 (10); *m/z* of the 18.33 min peak: 467 (24%), 466, [M^+, 76, 4,4′-bis(dodecyloxy-biphenyl)], 326 (15), 186 (100), 157 (6). Anal. calc. for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26. Found: C, 79.84; H, 9.81%. δ_H($CDCl_3$–[$^2H_6$]DMSO): 8.86 (OH, 0.73H), 7.38 [2,2′-H of bis(decyloxy)biphenyl, 0.2H], 7.35, 7.33, 7.29, 7.27 (2,2′-H of biphenyl, 3.8H), 6.86 [3,3′-H of bis(decyloxy)biphenyl, 0.2H], 6.84, 6.83, 6.80, 6.78 (3,3′-H of biphenyl, 3.8H), 3.91, 3.89, 3.87 (CH_2O, 2.4H), 1.73, 1.72, 1.70, 1.68, 1.66 (2-CH_2 of decyl chain, 2.4H), 1.40, 1.38, 1.36 (3-CH_2, 2.0H), 1.18 (CH_2, 14.9H), 0.81, 0.79, 0.77 (CH_3, 3.6H). δ_C($CDCl_3$–[$^2H_6$]DMSO): 157.41 [4,4′-C of bis(decyloxy)biphenyl], 157.21 (4-C of biphenyl), 155.75 (4′-C of biphenyl), 132.65 (1-C of biphenyl), 132.27 [1,1′-C of bis(decyloxy)biphenyl], 131.06 (1′-C of biphenyl), 126.73 (2′-C of biphenyl), 126.59 (2-C of biphenyl), 115.05 (3′-C of biphenyl), 114.01 (3-C of biphenyl), 67.23 (1-C of alkyl chain), 31.04 (8-C), 28.74, 28.71, 28.56, 28.47 (2, 4–7-C), 25.23 (3-C), 21.54 (9-C), 13.39 (10-C). According to the ^{1}H NMR spectrum, the amount of bis(decyloxy)biphenyl was about 10%.

4-Octyloxy-4′-hydroxybiphenyl (C_8OBPOH)

GC(retention time/min): 114.15; *m/z*: 299 (7%), 298 (M^+, 30), 186 (100), 157 (55). Anal. calc. for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 79.30; H, 8.84%. δ_H($CDCl_3$–[$^2H_6$]DMSO): 8.80 (OH, 0.89H), 7.36, 7.34, 7.30, 7.28 (2,2′-H of biphenyl, 4.0H), 6.85, 6.83, 6.82, 6.80 (3,3′-H of biphenyl, 4.0H), 3.91, 3.89, 3.87 (CH_2O, 2.0H), 1.74, 1.72, 1.70, 1.69, 1.67 (2-CH_2 of octyl chain, 2.0H), 1.40, 1.39, 1.36 (3-CH_2, 2.0H), 1.24, 1.21 (CH_2, 8.2H), 0.83, 0.81, 0.79 (CH_3, 3.0H). δ_C($CDCl_3$–[$^2H_6$]DMSO): 157.43 (4-C of biphenyl), 155.89 (4′-C of biphenyl), 132.90 (1-C of biphenyl), 131.38 (1′-C of biphenyl), 127.00 (2′-C of biphenyl), 126.84 (2-C of biphenyl), 115.25 (3′-C of biphenyl), 114.15 (3-C of biphenyl), 67.47 (1-C of alkyl chain), 31.21 (6-C), 28.76, 28.72, 28.64 (2,4,5-C), 25.47 (3-C), 22.06 (7-C), 13.59 (8-C). GC-MS and NMR measurements showed no impurity.

4-Hexyloxy-4′-hydroxybiphenyl (C_6OBPOH)

28.97 g (0.156 mol) of 4,4′-dihydroxybiphenyl, 25.69 g (0.156 mol) of 1-bromohexane and 6.22 g (0.156 mol) of sodium hydroxide were heated at 80 °C in 150 ml of ethanol for 5 h. The reaction mixture was allowed to stand overnight. The precipitate was filtered and washed with methanol. The precipitate was recrystallized from 300 ml of an ethanol–toluene mixed solution to yield 8.78 g of white powder (yield: 21%). GC(retention time/min): 13.25, 15.09; *m/z* of the 13.25 min peak: 271 (5%), 270 (M^+, 25), 186 (100), 157 (7); *m/z* of the 15.09 min peak: 355 (14%), 354 [M^+, 50, 4,4′-bis(hexyloxy)biphenyl], 270 (17), 186 (100), 157 (8). Anal. calc. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 78.99; H, 8.46%. δ_H($CDCl_3$–[$^2H_6$]DMSO): 8.89 (OH, 0.79H), 7.38 [2,2′-H of bis(hexyloxy)biphenyl, 0.2H], 7.36, 7.34, 7.30, 7.27 (2,2′-H of biphenyl, 3.8H), 6.86 [3,3′-H of bis(decyloxy)biphenyl, 0.2H], 6.85, 6.84, 6.81, 6.78 (3,3′-H of biphenyl, 3.8H), 3.91, 3.89, 3.87 (CH_2O, 2.2H), 1.72, 1.70, 1.68 (2-CH_2 of hexyl chain, 2.2H), 1.41, 1.39, 1.37 (3-CH_2, 2.2H), 1.28, 1.27, 1.26 (CH_2, 4.5H), 0.85, 0.83, 0.81 (CH_3, 3.3H). δ_C($CDCl_3$–[$^2H_6$]DMSO): 157.42 [4,4′-C of bis(hexyloxy)biphenyl], 157.21 (4-C of biphenyl), 155.75 (4′-C of biphenyl), 132.66 (1-C of biphenyl), 132.28 [1,1′-C of bis(hexyloxy)biphenyl], 131.09 (1′-C of biphenyl), 126.77 (2′-C of biphenyl), 126.61 (2-C of biphenyl), 115.07 (3′-C of biphenyl), 114.01 (3-C of biphenyl), 67.23 (1-C of alkyl chain), 30.79 (4-C), 28.47 (2-C), 24.94 (3-C), 21.81 (5-C), 13.36

(6-C). According to the ^{1}H NMR spectrum, the amount of dihexyloxybiphenyl was about 10%.

Quantum chemical calculation

A Pariser–Parr–Pople (PPP) MO program was purchased from Maruzen,[11] and was used on a personal computer. The detailed procedure has been described in a previous paper.[12] Program parameters were modified so that the calculated absorption wavelengths (λ_{cal}) agreed with the observed absorption wavelengths (λ_{obs}): PSD-150, λ_{cal} 574 nm, λ_{obs} 570 nm; CVL, λ_{cal} 614 nm, λ_{obs} 620 nm; IR, λ_{cal} 549 nm, λ_{obs} 540 nm. We increased the ionization potential parameter [I_p (N^+)] from 24 (default value) to 27 eV for polarization energy. For steric hindrance, we modified bond order parameters A_0(NH–Ph of PSD-150) from -2.24 to -1.0 eV, and A_0(C–PhCOOH) from -2.04 to -1.0 eV.

Measurement of rewritable properties

The compounds were mixed and fused in a glass tube, and a small amount of the cooled mixture was spread between two sheets of cover glass on a hot plate. The colored amorphous states were obtained by melting the media on a hot plate at 200 °C followed by injecting them into water. The colorless crystalline states were obtained by putting the amorphous states on a hot plate at 100 °C. Reflective optical density (OD) was measured with a Macbeth RD918 photometer. Contrast ratio (CR) was OD for a colored state divided by OD for a colorless state. The OD values for colorless states were measured by heating the colored state samples, whose OD had been measured. Thermodynamic parameters were measured by differential scanning calorimetry (DSC) using a Mettler FP-85 TA Cell. Polycrystalline samples of 2–5 mg were put in aluminium pans and heated at a scan rate of 10 K min^{-1}. The phase transition temperatures (T_{tr}) and the corresponding enthalpy changes were measured. Indium metal was used as the standard. After melting, the samples were cooled at the same rate to observe the crystallization temperature (T_{c2}). The compounds which underwent crystallization were quenched to form glasses by inserting them in their fused states into liquid nitrogen or by putting them on a cooled aluminium block. The resulting glasses were heated again under the same conditions to measure the glass transition temperature (T_g) and crystallization temperature (T_{c1}).

DSC measurement and optical microscopy were simultaneously carried out with a Mettler FP84HT Microscope Cell with a glass pan. Visible light transmittance was also measured with a photodiode attached to the microscope.

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