Supporting information

Photochromic and fluorescent LC gels based on bent-shaped azobenzene-containing gelator

Alexey Bobrovsky\textsuperscript{a*}, Valery Shibaev\textsuperscript{a}, Věra Hamplová\textsuperscript{b}, Vladimíra Novotna\textsuperscript{b}, Miroslav Kašpar\textsuperscript{b}

\textsuperscript{a} Faculty of Chemistry, Moscow State University, Leninskie gory, Moscow, 119992 Russia, e-mail: bbrvsky@yahoo.com
\textsuperscript{b} Institute of Physics, Academy of Sciences of the Czech Republic, 182 21 Prague 8, Czech Republic

1. Synthesis of 10BVIABr.

LC-gelator 10BVIABr synthesis is presented in Scheme S1. The preparation of mesogenic phenol \textbf{I} and acid chloride \textbf{II} has been described in details in previous papers.\textsuperscript{51,52}

\begin{center}
\begin{equation}
\begin{array}{c}
\text{CH}_3\text{O} & \text{OCOO} & \text{H} - \text{C}_{10}\text{H}_21 \\
\text{CH}_3 & & \text{C} & \text{OCl} \\
\end{array}
\end{equation}
\end{center}

1. pyridine
2. NH\textsubscript{4}OH

\begin{center}
\begin{equation}
\begin{array}{c}
\text{HO} & \text{C} & \text{O} & \text{H}_21 \\
\text{H} & \text{O} & \text{C} & \text{OCl} \\
\end{array}
\end{equation}
\end{center}

\begin{center}
\begin{equation}
\begin{array}{c}
\text{C}_{10}\text{H}_21 & \text{O} & \text{C} & \text{O}
\end{array}
\end{equation}
\end{center}

\begin{center}
\begin{equation}
\begin{array}{c}
\text{O} & \text{O} & \text{O} & \text{O} \\
\text{O} & \text{C} & \text{O} & \text{H}_21 \\
\end{array}
\end{equation}
\end{center}

1. NaNO\textsubscript{2}
2. phenol

\begin{center}
\begin{equation}
\begin{array}{c}
\text{Br(CH}_2\text{}_2)\text{Br} & \text{N}=\text{N} & \text{O} & \text{H}_21 \\
\end{array}
\end{equation}
\end{center}

\begin{center}
\begin{equation}
\begin{array}{c}
\text{Br(CH}_2\text{}_2)\text{O} & \text{N}=\text{N} & \text{O}
\end{array}
\end{equation}
\end{center}

1. KOH
2. H\textsubscript{2}SO\textsubscript{4}

\begin{center}
\begin{equation}
\begin{array}{c}
\text{Br(CH}_2\text{}_2)\text{O} & \text{N}=\text{N} & \text{O}
\end{array}
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\text{Br(CH}_2\text{}_2)\text{O} & \text{N}=\text{N} & \text{O}
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\text{Br(CH}_2\text{}_2)\text{O} & \text{N}=\text{N} & \text{O}
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\begin{equation}
\begin{array}{c}
\text{Br(CH}_2\text{}_2)\text{O} & \text{N}=\text{N} & \text{O}
\end{array}
\end{equation}
\end{center}

10BVIABr

Scheme S1 Schematic synthetic route for 10BVIABr preparation.
1.1. Synthesis of mesogenic phenol III

p-Acetamidophenol (0.1M) was alkylated with 0.2M of 1,6- dibromohexane in dioxane/water (1:1) mixture with 0.1M of KOH. The reaction mixture was refluxed under stirring for 3 days, cooled, diluted by water and filtered. The solid was hydrolysed using 20 % solution of sulphuric acid by boiling for 2 hrs and after addition of water the suspension was left to stand overnight. The crystals of sulphate were separated by suction and washed with n-hexane to remove the excess of dibromohexane. The sulphate was dissolved in 100 ml of glacial acetic acid and diazotation was carried out. The arising diazonium salt was copulated with phenol. The product was separated, acidified with HCl and crystallized from ethanol (the insoluble residue was a four ring dimer). The orange crystals III were dried in vacuo at 50 °C. Total yield was 45%.

$^1$H-NMR of III (CDCl$_3$, 300 MHz):
7.82 dd (4H, ortho to N=N); 6.99 d (2H, ortho to -OR); 6.92 d (2H, ortho to -OH);
4.02 t (2H, CH$_2$OAr); 3.43 t (2H,CH$_2$Br); 1.20–1.85 m (8H, CH$_2$).

1.2. Synthesis of final product 10BVIABr

Final product was prepared by esterification of the acylchloride II and mesogenic phenol III in pyridine/dichloromethane mixture under stirring and boiling for 3 days. The reaction mixture was washed with dilute HCl and after evaporation of solvents the crude product was crystallized from toluen/acetone mixture and purified by column chromatography on silicagel using mixture of dichloromethane and acetone (99.8 : 0.2) as an eluent. Then recrystallization was made twice from ethanol.

The molecular structure of the compound and its purity was checked using standard analytical methods. $^1$H-NMR spectra were acquired on a spectrometer Varian 300 MHz, deuterochloroform serving as solvent and the signals of the solvent were used as internal standards. The chemical purity of the materials were checked by high pressure liquid chromatography (HPLC), which was carried out using a silica gel column (Bioshere Si 100-5µm, 4x250, Watrex) with a mixture of 99.8 % of toluene and 0.2 % of methanol as an eluent, and detection of the eluting products by a UV-VIS detector ($\lambda = 290$ nm). The chemical purity of the synthesized compound was found within 99.6 - 99.9%.
1H-NMR of 10BVIABr (CDCl₃, 300 MHz): 9.08 s (1H, isophtal. ortho to –COO); 8.50 d (2H, isophtal. ortho to -COO); 7.90 – 8.00 m (6H, ortho to N=N and ortho and para to -OCH₃); 7.73 t (1H, isophtal. meta to -COO); 7.50 – 7.60 dd (4H, ortho to –Ar); 7.40 m (5H, ortho to –OCO); 7.00 m (4H, ortho to –OCH₂); 4.05 m (4H, CH₂OAr); 3.97 s (3H, OCH₃); 3.41 t (2H, CH₂Br); 1.20 - 1.90 m (24H, CH₂); 0.92 t (3H, CH₃).

13C-NMR of 10BVIABr (CDCl₃, 300 MHz, for numbering see Fig. S1): 164.56 (C-16), 163.97 (C-23), 163.24 (C-9), 161.68 (C-31), 158.79 (C-1), 152.07 (C-24), 151.33 (C-12), 150.58 (C-27), 149.71 (C-8), 146.76 (C-28), 144.12 (C-21), 138.85 (C-13), 135.30 (C-18), 135.16 (C-20), 132.60 (C-4), 132.02 (C-22), 130.10 (C-21), 129.71 (C-17), 129.20 (C-19), 128.49 (C-10), 128.09 (C-3), 127.76 (C-6), 124.82 (C-26), 123.82 (C-29), 123.39 (C-14), 123.05 (C-15), 122.20 (C-25), 121.85 (C-7), 114.78 (C-2), 114.68 (C-30), 113.96 (C-11), 68.08 (CH₂O), 68.05 (CH₂O), 56.21 (CH₃O), 33.80 (CH₂Br), 32.63 (CH₂CH₂Br), 31.81 (CH₂CH₂CH₃), 28.94 - 29.41 (CH₂), 27.89 (CH₂(CH₂)₂Br), 26.05 (CH₂(CH₂)₂O), 25.26 (CH₂(CH₂)₂O), 22.66 (CH₂CH₃), 14.11 (CH₂CH₃).

Fig. S1. Numbering of C atoms in the studied molecule of 10BVIABr.

2. Mesomorphic behavior of 10BVIABr

Table S1. The melting point, m.p., and the phase transition temperature, T_tr, were indicated on the second heating and cooling run, resp. Corresponding enthalpies, ΔH, are in square brackets in kJ/mol and the thermographs were taken at a rate 5K/min. Molecular weight is 983 g/mol.

<table>
<thead>
<tr>
<th></th>
<th>M. p. [ΔH]</th>
<th>T_Cr [ΔH]</th>
<th>T_tr [ΔH]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10BVIABr</td>
<td>181 [+73.2]</td>
<td>160 [-28.9]</td>
<td>SmCP 172 [-16.3]</td>
</tr>
</tbody>
</table>
Fig. S2. Microphotograph of the planar texture for 10BVIABr taken at a temperature T= 168°C in the SmCP phase. Compound is observed in a glass cell of 5µm.

Fig. S3. DSC plot of 10BVIABr taken at the second heating and cooling run at a rate 5K/min.
Fig. S4. X-ray intensity in dependence on diffracted angle, 2θ, for 10BVIABr at temperature T=170°C. In the inset 2D x-ray pattern is presented for aligned sample evidencing a layered structure with the layer long spacing d=49 Å and distance between molecules about 4.5 Å. Arrow indicates alignment direction.

Fig. S5. Absorbance spectra of 10BVIABr solution in dichloroethane (0.08 mg/mL) before and after UV-irradiation (380 nm, 20 mW/cm²).
3. Optical properties of studied gels

Fig. S6. Photos of cholesteric LC mixture containing 1.6 wt% of gelator 10BVIABr before (a) and after (b) UV-irradiation (380 nm, ~8 mW/cm², 10 min).

Fig. S7. Absorbance spectra of the cholesteric mixture (MLC6816 48.8% + CholPel 25.9% + CholVal 23.6% + 10BVIABr 1.5% + DCM2 0.2%) in cell with planar alignment before and after UV-irradiation (380 nm, 20 min).
Fig. S8. Circularly-polarized components of emission of cholesteric mixture before and after UV-irradiation (380 nm, 20 min). Excitation wavelength is 532 nm. Thickness of the cell is 30 μm.

References