Supplementary Information

Photoresponsive liquid crystal based on (1-cyclehexenyl)phenyldiazene as a close analogue of azobenenze

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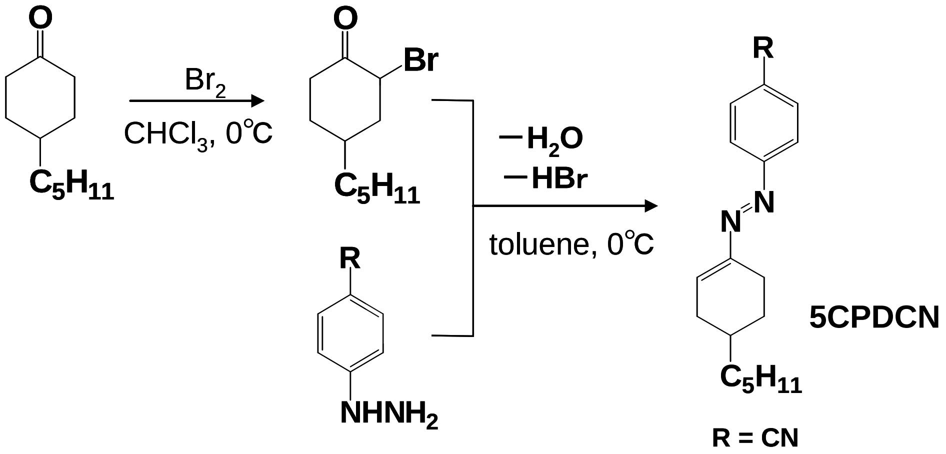
Synthesis of materials.

4-Pentylcyclohexanone and 4-cyanophenylhydrazine hydrochloride were purchased from Wako Pure Chemical Ind. Pentylaniline was obtained from Kanto Chemical Co.



5CPDCN

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This compound was synthesized by modified procedures of Caglioti et al. [1].

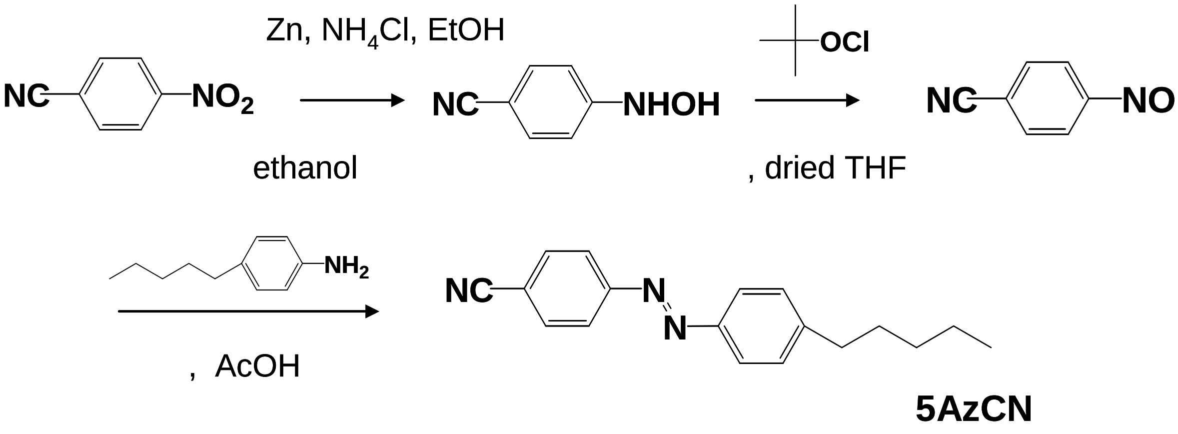
2-Bromo-4-pentylcyclohexanone. Bromine (3.52 g, 22 mmol) was added to 4-pentylcyclohexanone (3.37 g, 20 mmol) was dissolved in chloroform (100 mL) at 0°C. After stirring the dilute yellow solution for 30 min, the solution was washed with water and $NaHCO_3$ aqueous solution until it showed neutral pH. The organic phase was dried over $MgSO_4$ overnight, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate.

The resulting colorless oil was collected: yield 3.19 g (65%); ^{1}H-NMR ($CDCl_3$) δ 4.29 (1H, t , -CHBr-),δ 3.14 (1H, m, -CH-C(-Br)-), δ 2.33 (1H, m, -CH_2-(C=O)-), δ 2.13 (2H, m, -CH-), δ 1.85 (1H, m, -CH-), δ 1.33 (9H, m, -C_4H_8-, -CH-), δ 0.88 (3H, t, -CH_3)

[4-Pentyl-(1-cyclohexenyl)]-(4-cyanophenyl)diazene.

2-Bromo-4-pentylcyclohexanone (4.94 g, 20 mmol) was dissolved in toluene (30 mL), In a separate flask, 4-cyanophenylhydrazine converted from 4-cyanophanylhydrazine hydrochloride (3.39 g, 20mmol) with $NaHCO_3$ aqueous solution was added dropwise into the 2-bromo-4-pentylcyclohexanone solution. After stirred for 30 min, the organic phase was washed with water three times and dried over $MgSO_4$. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate. The resulting orange color solid was collected: yield 3.63 g (65%); mp 64 - 66 °C; ^{1}H-NMR ($CDCl_3$) δ 7.79 (2H, d, Ar-H), δ 7.74 (2H, d, Ar-H), δ 7.07 (1H, t, -CH=C-), δ 2.62 (2H, m, -CH_2-C(-Az)-), δ 2.26 (1H, m, -CH-C=C-), δ 2.13 (1H, m, -CH-), δ 1.95 (1H, m, -CH-C=C-), δ 1.67 (1H, m, -CH-), δ 1.33 (9H, m, -C_4H_8-, -CH-), δ 0.90 (3H, t, -CH_3); UV (THF) λ_{max}, nm (ε) 315 (27000); EI MS *m/z* 281 (M^+).

＜5AzCN>



4-Cyanophenyl hydroxylamine.[2] 4-Nitrobenzonitrile (4.89 g, 33mmol) was mixed with zinc powder 9.29 g (142 mmol) in ethanol (50 mL), and vigorously stirred by mechanical stirrer. In a separate flask, NH_4Cl 2.14 g (40 mmol) was dissolve in small volume of solution (H_2O/ethanol = 1/1) and slowly dropped into the 4-nitrobenzonitrile solution with taking notice of boil. After 30 min, the solution was purified with hot filtration and removed under reduced pressure. The collected red solid was used for synthesis of 4-nitrosobenzonitrile without purification.

4-Nitrosobenzonitrile[3] The crude 4-cyanophenylhydroxylamine (0.2 g) was dissolved in dried THF (50mL) under argon, and *tert*-butyl hypochlorite was dropped in the solution. After stirred at -78 ^{o}C for 5 minutes, the solution removed under reduced pressure at 0 °C. The collected crude 4-nitrosobenzonitrile was used for synthesis of 4-cyano-4’-pentylazobenzene without purification.

4-Cyano-4’-pentylazobenzene. 4-Pentylaniline 0.3g (1.8 mmol) and 4-nitrosobenzonitrile 0.12g (0.9 mmol) were dissolved acetic acid, and stirred for 9 hours. The solution removed under reduced pressure, residue was purified by column chromatography on silica gel and recrystallized from hexane/ethyl acetate. The resulting orange solid was collected: yield 0.17g (67%); mp 84-85 □; ^{1}H-NMR ($CDCl_3$) δ 7.97 (d, 2H, Ar-H) , δ 7.87 (d, 2H, Ar-H), δ 7.77 (d, 2H, Ar-H), δ 7.36 (d, 2H, Ar-H), δ 2.69 (t, 2H, Ar-CH_2-), δ 1.64 (m, 2H, -CH_2-), δ 1.33 (m, 4H, -C_2H_4-) , δ 0.87 (t, 3H, -CH_3); UV (THF) λ_{max}, nm (ε) 340 (26000).

Measurements.

^{1}H-NMR spectra of the hybrids were recorded on a 270GXS spectrometer (JEOL Co. Ltd.). Differential scanning calorimetry (DSC) profiles were taken on a DSC120U (Seiko Instruments, Inc.) with a scanning rate of 2 °C min^{-1} on both heating and cooling processes. Polarized optical microscope (POM) observations were performed with BH-2 and DP70 (Olympus Co. Ltd.) equipped with a Mettler FP82HT hot stage. UV-visible absorption spectra were taken on an Agilent Technology 8453 spectrometer. X-ray diffraction (XRD) measurements were made with an FR-E instrument (Rigaku Co. Ltd.).

Methods.

UV photoirradiation for solution samples was performed with a Supercure-203S (San-ei Electric, Co.) passing through an appropriate optical filter.

Observation of photoinduced phase transition was performed on an Olympus BU-2 fluorescence microscope equipped with a CCD camera (Olympus DP-12). The actinic UV beam (313 nm) for the photoisomerization was irradiated with a U-MWIB2 (Olympus). An LC cell was placed on a temperature-controlled stage (FP90, Mettler-Toledo). The LC texture was observed through a set of crossed polarizer and analyzer.

The 5CB LC cell containing 5CPDCN was fabricated using a pair of quartz plate (2 x 3 cm). On one of the plate, spherical silica particles of 4 μm were scattered as the spacer between the plates. The LC material was introduced into the cell via capillary action at an isotropic temperature (typically at 50 ^{o}C).

References

1. L. Caglioti, G. Rosini, F. Rossi, *J. Am. Chem. Soc.*, 1966. **88**, 3865.
2. O. Kamm, *Org. Synth.* I, 1941, 445.
3. M. H. Davy, V. Y. Lee, R. D. Miller and T. J. Marks, *J. Org. Chem.*, 1999, **64**, 4976.