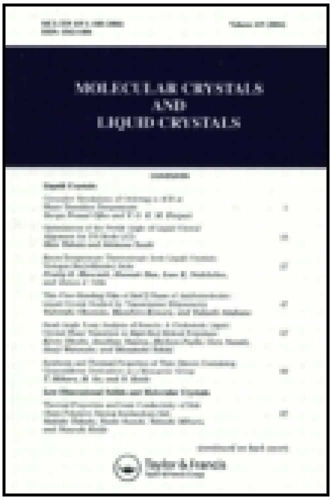

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A New High Twisting Power Material for Use as a Single Asymmetric Dopant in Cholesteric Displays with a Temperature Independence of the Helical Twisting Power

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A NEW HIGH TWISTING POWER MATERIAL FOR USE AS A SINGLE ASYMMETRIC DOPANT IN CHOLESTERIC DISPLAYS WITH A TEMPERATURE INDEPENDENCE OF THE HELICAL TWISTING POWER

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The synthesis of a novel chiral non-racemic TADDOL derivative is presented and discussed. When the material is placed in a suitable nematic host it forms a chiral nematic phase which has an independence of the helical twisting power (HTP) with temperature. The observed HTP is approximately twice as large as HTPs found in conventional chiral additives, and the independence of the HTP is seen over a 90°C temperature range. The HTP as a function of temperature may be modified by the addition of both liquid crystalline and non liquid crystalline achiral additives. The material is unique in that it is also soluble in commercial nematic host materials and has proven to be extremely robust in both thermal and photochemical testing.

Keywords: asymmetric; chiral nematic; cholesteric displays; HTP; synthesis; TADDOL

INTRODUCTION

Bistable cholesteric display devices are excellent candidates for low power consumption devices that offer high brightness and broad viewing angles [1].

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The chiral nematic media used in such devices are often generated by the inclusion of one or more chiral non-racemic dopants [2] into a suitable nematic host material, causing the nematic mixture to adopt a helical structure that reflects light according to Bragg's law. The addition of such asymmetric dopants will clearly affect the transition temperatures, viscosity, dielectric properties etc. of the host material, and usually in an adverse way. In order to minimize such problems it is desirable to add a very small concentration of the chiral dopant which must therefore possess a very large HTP in order to obtain a pitch in the visible region.

The wavelength (λ) of selective reflection is equal to the product np (n is the average refractive index of the chiral nematic host and p is the pitch of the chiral nematic helix). Since the reciprocal of the pitch length is related to the concentration x of the chiral dopant by $p^{-1} = \beta x$ (β is the HTP) it is clear that a tighter helical twist is generated as the concentration x is increased. Current asymmetric dopants have relatively low values of HTP and as a consequence are typically used at concentrations of 20% or higher in a nematic host material. Apart from the detrimental changes *vide supra*, the chiral non-racemic dopant is usually the most expensive chemical component adding an additional concern.

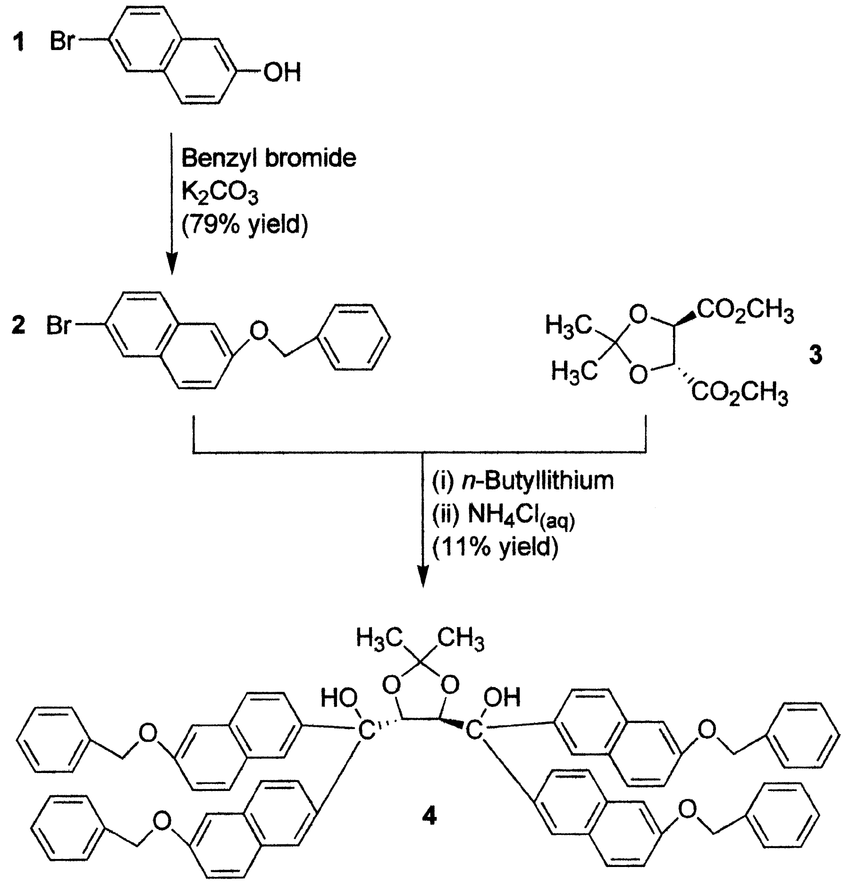
In order for the display to be of practical use it is essential that the display color remains constant over a wide temperature operating range. To obtain an independence of the HTP with temperature it is usually necessary to mix several chiral dopants which adds further cost and complexity to the system and it is clear that this is far from an optimum situation [3,4].

Recently we have synthesized and evaluated the first example of an asymmetric dopant that appears to fulfill all of the desired criteria for an ideal chiral additive. The single enantiomer material is derived from commercially available and inexpensive tartaric acid and has a HTP of $31\,\mu\text{m}^{-1}$. In addition, the material exhibits a near independence of the HTP with temperature over a 90℃ range. Rigorous testing has shown that mixtures containing this dopant are both thermally and photochemically stable.

SYNTHESIS

The preparation of **2** (Scheme 1) used the method of Freedman [5] with crystallization from acetonitrile providing a pure sample in excellent yield (78%).

The preparation of **4** was initially attempted using five equivalents of the Grignard derived from **2** according to the method of Beck *et al.* [6].



SCHEME 1 Synthesis of (4R,5R)-2,2-dimethyl-$\alpha,\alpha,\alpha',\alpha'$-tetrakis[6-(benzyloxy)-2-naphthyl]-1,3-dioxolan-4,5-dimethanol.

However, the Grignard proved extremely difficult to form even when using sonication and 1,2-dibromoethane as activators. Instead we chose to use an excess of the organolithium derived from **2** which proved to be a convenient replacement for the Grignard. Since this work we have successfully synthesized numerous TADDOL derivatives [7,8] using such organolithium methodology. Due to the steric crowding of TADDOL **4** it was found that formation of the desired product was difficult and low yields were accompanied by the formation of byproducts that were present due to incomplete reaction. However, this problem can always be resolved by careful chromatographic purification.

2-Benzyloxy-6-bromonaphthalene (2)

6-Bromo-2-naphthol (**1**) (39.18 g, 0.1756 mol), benzyl bromide (27.31 g, 0.1597 mol), anhydrous potassium carbonate (44.14 g, 0.3194 mol), and butan-2-one (500 mL) were heated under reflux for 3.6 days (for convenience). The potassium salts were filtered off and washed with diethyl ether (200 mL). The filtrate was washed with potassium hydroxide (5%, 500 mL) and the layers were separated. The aqueous layer was extracted with diethyl ether (2 × 250 mL) and the combined ether extracts were washed with water (500 mL) and dried ($MgSO_4$). The drying agent was filtered off and the solvent was removed *in vacuo* to yield a tan solid. The solid was mixed with acetonitrile and filtered. The off-white solid obtained was crystallized from acetonitrile and dried *in vacuo* (P_2O_5, paraffin wax, 72 h). Yield = 39.34 g (79%), mp = 114.3–114.5℃, purity (GC) = 100%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91(d, $J = 2.0$ Hz, 1H), 7.66(d, $J = 9.0$ Hz, 1H), 7.59(d, $J = 9.0$ Hz, 1H), 7.52–7.49(m, 1H), 7.49–7.33(m, 5H), 7.24(dd, $J = 8.0$, 3.0 Hz, 1H), 7.18(d, $J = 3.0$ Hz, 1H), 5.16(s, 2H). IR (neat) ν_{max} 2942, 1623, 1585, 1495 cm^{-1}.

(4*R*, 5*R*)-2,2-dimethyl-α,α,α′,α′-tetrakis[6-(benzyloxy)-2-naphthyl]-1,3-dioxolan-4,5-dimethanol (4)

n-Butyllithium (22.3 mL, 56 mmol, 2.5 M in hexane) was added dropwise to a stirred solution of **2** (19.95 g, 63.70 mmol) and anhydrous THF (555 mL) at −75℃ to −77℃ under dry argon (the solution gradually turned yellow during the addition). After the addition was complete the reaction mixture was stirred at −77℃ for an additional 45 min. A solution of **3** (2.90 g, 13.3 mmol) in anhydrous THF (27 mL) was added dropwise to the reaction mixture at −75 to −77℃ and the bright red solution obtained was stirred at −77℃ for 2 h and then allowed to warm gradually to room temperature. After 36 h at room temperature, the reaction was cooled to −5℃ and a saturated solution of ammonium chloride (470 mL) was added dropwise at 0 to −5℃. The mixture was stirred for 5 h at room temperature and the layers were separated and the aqueous layer extracted with dichloromethane (2 × 225 mL). The combined organic extracts were washed with sodium bicarbonate (50 mL saturated solution plus 750 mL water) and dried ($MgSO_4$). The drying agent was filtered off and the solvent was removed *in vacuo* to yield an orange-brown semi-solid. The crude material was purified twice by column chromatography using the following eluent systems: (i) [petroleum ether (40–60℃) : dichloromethane, 1:1, followed by a gradual increase in polarity using additional dichloromethane], (ii) [ethyl acetate : petroleum ether (40–60℃), 1:4, then increasing to 30% ethyl acetate]. The product was crystallized from cyclohexane to give an off-white powder which was dried *in vacuo* (P_2O_5, paraffin wax, 72 h). Yield = 1.577 g (11%), mp = 118.3–124.7℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04(app. s, 2H), 7.77(app. s, 2H), 7.74(d, $J = 9.3$ Hz, 2H), 7.62(d, $J = 8.8$ Hz, 2H), 7.60–7.55(m, 4H), 7.50–7.45 (m, 4H), 7.43–7.27(m, 20H), 7.24–7.18(m, 4H), 7.14(2H, dd, $J = 10.0$ Hz, 3.3), 7.04(2H, d, $J = 3.3$ Hz), 5.17(s, 4H), 5.10(s, 4H), 4.89(s, 2H), 4.14(s, 2H), 1.12(s, 6H). ^{13}C NMR ($CDCl_3$) δ 157.29, 157.26, 140.94, 138.80, 137.16, 137.07, 133.93, 130.37, 128.89, 128.23, 128.03, 127.81, 127.76, 127.12, 127.06, 126.61, 126.23, 125.98, 119.29, 119.25, 110.0, 107.08, 81.69, 78.74, 70.32, 70.22, 27.70 ppm. IR (neat) ν_{max} 3316, 3032, 2986, 2925, 1632, 1603, 1502, 1262, 1218 cm^{-1}. HRMS calcd for $C_{75}H_{62}O_8Na^+$ 1113.433688 amu, found 1113.42915 amu, Anal. Calcd. for $C_{75}H_{62}O_8$: C, 82.54; H, 5.73. Found: C, 82.38; H, 6.00, Optical rotation: $[\alpha]^{\mathrm{D}}_{23.5℃} = -68.0^{\circ}$ ($CHCl_3$, c = 0.050 g/mL).

PHYSICAL STUDIES

With TADDOL **4** in hand we evaluated the twisting power of **4** and its temperature dependence compared to other TADDOL derivatives with the following general structure (Fig. 1)

Comparison with **5** (Aldrich) showed that although **4** had a lower HTP (31 μm^{-1}), this was offset by a near temperature independence of the HTP over a 90℃ range. In comparison, **5** had a steep negative dependence of helical twist with temperature (Fig. 2).

Different nematic hosts were evaluated and the temperature dependence and magnitude of the HTP of **4** were found to vary widely as would be expected for the differing solvent-solute interactions (Fig. 3). It is clear that the TADDOL dopants will require structural tailoring to provide a temperature independence of HTP for various nematic hosts. This tailoring is straightforward using methodology analogous to that described above and promising TADDOLs are now being systematically evaluated and will provide us with unique insight into chirality transfer in such systems [9].

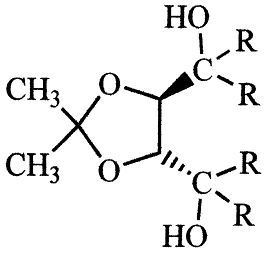


FIGURE 1 Generic TADDOL structure.

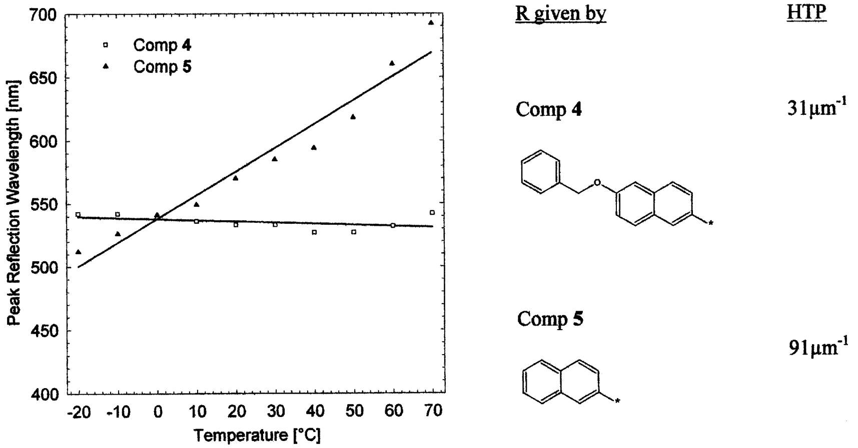
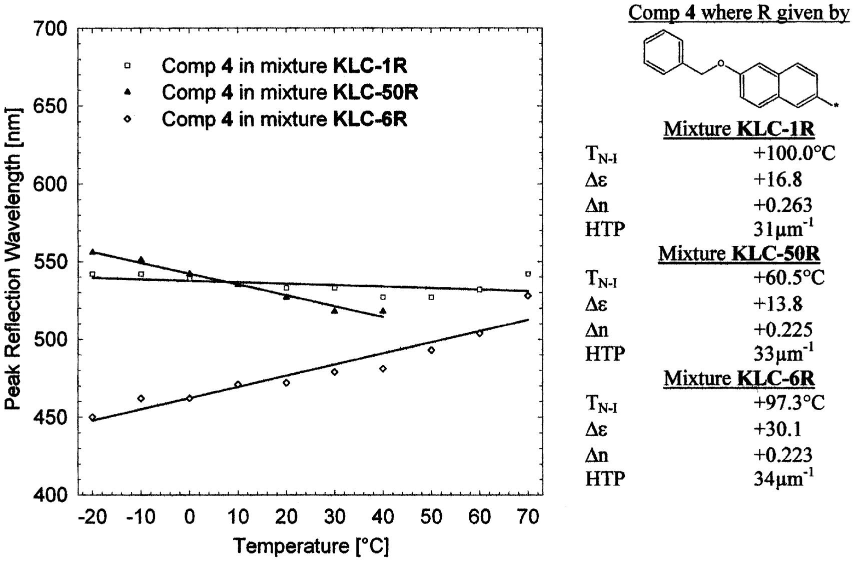
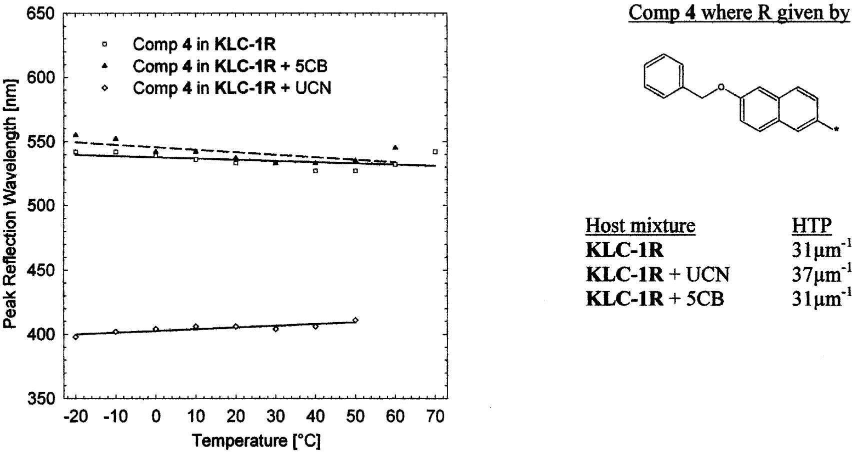


FIGURE 2 Peak reflection wavelength as a function of temperature for compounds **4** and **5** in KLC-1R. The (*) denotes the point of attachment to the dioxolane ring.



	Mixture KLC-1R
$T_{N\text{-}I}$	+100.0°C
Δε	+16.8
Δn	+0.263
HTP	31μm⁻¹
	Mixture KLC-50R
$T_{N\text{-}I}$	+60.5°C
Δε	+13.8
Δn	+0.225
HTP	33μm⁻¹
	Mixture KLC-6R
$T_{N\text{-}I}$	+97.3°C
Δε	+30.1
Δn	+0.223
HTP	34μm⁻¹

FIGURE 3 Peak reflection wavelength as a function of temperature for **4** in KLC-1R, KLC-50R, and KLC-6R. Physical properties of the three nematic mixtures are also shown. The clearing points of the mixtures of **4** in the above nematic host materials are 79°C, 47°C, and 88°C respectively. The (*) denotes point of attachment to the dioxolane ring.



Host mixture	HTP
KLC-1R	31μm^{-1}
KLC-1R + UCN	37μm^{-1}
KLC-1R + 5CB	31μm^{-1}

FIGURE 4 Peak reflection wavelength as a function of temperature for **4** in nematic mixture KLC-1R, and in KLC-1R plus the denoted achiral additives. Additives are present in the mixture at a concentration of 4% by weight. The (*) denotes point of attachment to the dioxolane ring.

A temperature independence of the HTP may also be attained by the addition of other chiral non-racemic or achiral additives. As part of our exploratory program we have evaluated the use of inexpensive achiral additives (Fig. 4) such as undecylcyanide (UCN) and 4-cyano-4′-pentylbiphenyl (5CB).

Achiral additives again provide a pathway for altering the solvent-solute interactions although low concentrations of these additives must be used to avoid detrimental physical property changes *vide supra*.

CONCLUSION

We have synthesized the first commercially useful soluble and stable single-enantiomer dopant that forms a chiral nematic phase (when placed in a suitable nematic host material) with a temperature independence of the HTP. A major program of work is underway to uncover further TADDOL dopants that display such characteristics and to use this work to study the phenomenon of chirality transfer in liquid crystalline systems.

REFERENCES

[1] Crawford, G. P. (2000). *IEEE Spectr.*, *37*, 40.
[2] Kuball, H.-G., Weiβ, B., Beck, A. K., & Seebach, D. (1997). *Helv. Chim. Acta.*, *80*, 2507.

[3] Moia, F. (1989). In *Freiburger arbeitstagung flüssigkristalle*, Freiburg: Germany, Vol. 18.
[4] Gerber, P. R. (1980). *Phys. Lett. A*, *78*, 285.
[5] Freedman, H. H. & Dubois, R. A. (1975). *Tetrahedron Lett.*, *38*, 3251.
[6] Beck, A. K., Gysi, P., Vecchia, L. L., & Seebach, D. (1999). *Org. Synth.*, *76*, 12.
[7] Seed, A. J., Walsh, M. E., Doane, J. W., & Khan, A., Unpublished Results.
[8] Khan, A., Doane, J. W., Seed, A., & Falana, O. (2002). In *2002 NSF design, service and manufacturing grantees and research conference*, Engineering communications and marketing, college of engineering, Iowa State University: San Juan, Puerto Rico.
[9] Solladié, G. & Zimmermann, R. G. (1984). *Angew. Chem. Int. Ed. Engl.*, *23*, 348.