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ChemComm

Cite this: *Chem. Commun.*, 2012, **48**, 7064–7066

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Thermochromic discotic 6-oxoverdazyls†

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Received 27th April 2012, Accepted 29th May 2012
DOI: 10.1039/c2cc33051b

Downloaded by University of Massachusetts - Amherst on 12 October 2012
Published on 29 May 2012 on http://pubs.rsc.org | doi:10.1039/C2CC33051B

6-Oxoverdazyls 1b[*n*], substituted with three 3,4,5-trialkoxyphenyl groups (*n* = 8 and 10), exhibit a columnar hexagonal phase ($\mathrm{Col_h}$) below 130 °C. They display reversible color change from red to green at the transition to the isotropic phase. XRD and magnetization data do not support dimerization of the radicals in the mesophase.

Liquid crystalline radicals in which spin is delocalized in the π system are still very rare and sought after for fundamental studies and applications in photovoltaics. Recently we reported that 1,3,5-tris(3,4,5-trialkylsulfanylphenyl)-6-oxoverdazyls (**1a[*n*]**, *n* = 6, 8, and 10, Chart 1) form a monotropic columnar rectangular phase ($\mathrm{Col_r}$) below 60 °C.[1] The compounds are dark blue due to a broad absorption band in the visible region ($\lambda_{\max}$ = 540 nm and 610 nm in hexane). Their redox potentials are $E^{0/+1}{}_{1/2}$ = +0.99 V and $E^{0/-1}{}_{1/2}$ = −0.45 V *vs.* SCE, and photovoltaic studies of **1a[8]** revealed a hole mobility of $\mu_h \approx 1.5 \times 10^{-3}\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$ in the mesophase with an activation energy $E_a = 0.06 \pm 0.01$ eV. While, electrochemical and photophysical properties of **1a[*n*]** are favorable, the metastable nature of the discotic phase is problematic for potential applications.

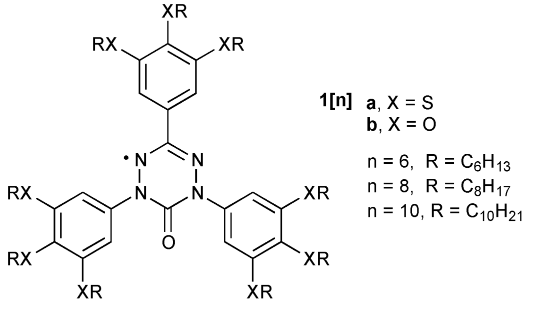
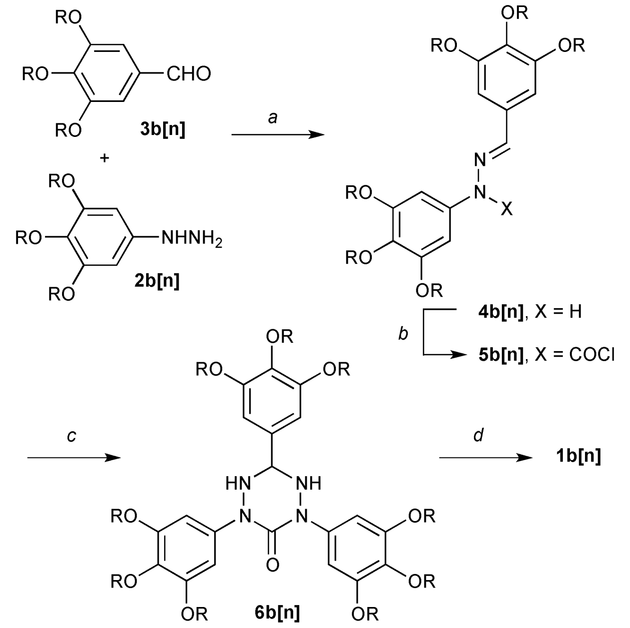


Chart 1

We have now prepared the oxy analogue of **1a[*n*]**, the achiral 3,4,5-trialkoxyphenyl derivatives **1b[*n*]** (Chart 1), which exhibit a broad range enantiotropic columnar hexagonal phase ($\mathrm{Col_h}$) and unusual thermochromism that is unrelated to that observed in some chiral phases (such as N*). Here we describe the detailed investigation of the first two members of this series, **1b[8]** and **1b[10]**.

Radicals **1b[*n*]** were synthesized similarly to **1a[*n*]**[1] from hydrazines **2b[*n*]**[2] and benzaldehydes[3,4] **3b[*n*]** according to the Milcent method[5] (Scheme 1). Thus, crude hydrazines[2] were converted to hydrazones **4b[*n*]**, which were reacted with triphosgene to give carbonyl chlorides **5b[*n*]**. After isolation and purification, the chlorides were reacted with hydrazines **2b[*n*]**. The resulting tetrazanes **6b[*n*]** were partially purified and oxidized either with $\mathrm{PbO_2}$ or $\mathrm{K_3Fe(CN)_6}$ to give radicals **1b[*n*]** in about 10% overall yield.

Hexane solutions of radical **1b[8]** exhibit low intensity absorption bands in the visible range (maxima at 486 nm and 614 nm, Fig. 1). According to TD-DFT results for the **1b[1]** model, the observed bands originate from several π → π*



Scheme 1 Synthesis of **1b[*n*]**. Reagents and conditions: (a) EtOH, cat. AcOH, reflux; (b) $\mathrm{CO(OCCl_3)_2}$, pyridine, $\mathrm{CH_2Cl_2}$, rt; (c) **2b[*n*]**, $\mathrm{Et_3N}$, benzene, 50 °C; (d) $\mathrm{PbO_2}$, $\mathrm{Na_2CO_3}$, toluene/MeCN or $\mathrm{K_3Fe(CN)_6}$, 0.5 M $\mathrm{Na_2CO_3}$, $\mathrm{[Bu_4N]^+Br^-}$ (cat.), $\mathrm{CH_2Cl_2}$.

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† Electronic supplementary information (ESI) available: Synthetic, measurements, and theoretical details. See DOI: 10.1039/c2cc33051b

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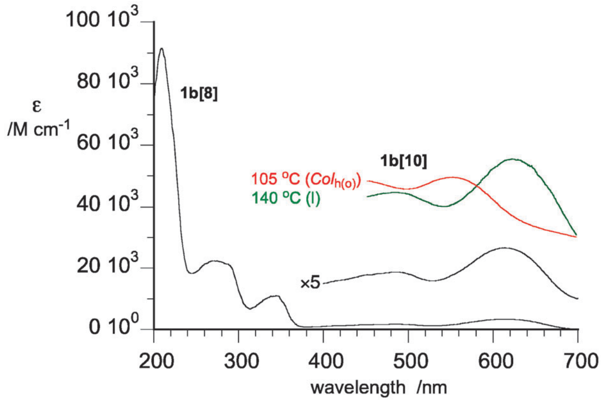

Fig. 1 Electronic absorption spectrum of **1b[8]** in hexane. The inset shows enlarged low-energy portion of the spectrum and solid-state spectra of **1b[10]** in isotropic (green) and columnar (red) phases.

Table 1 Transition temperatures (°C) and enthalpies (kJ mol^{-1}, in italics) for **1b[*n*]**[a]

n	Phase transition data
8	Cr < 25 Col$_{h(o)}$ 127 (*55.5*) I
10	Cr < Col$_{h(o)}$' 20 (*23.3*) Col$_{h(o)}$ 121 (*57.3*) I

[a] Determined by DSC (5 K min^{-1}) in the heating mode: Cr = crystal; Col$_{h(o)}$ = ordered columnar hexagonal; I = isotropic.

electronic transitions involving mainly the 5 highest occupied MOs, localized mostly on the benzene rings, to the LUMO, localized solely on the verdazyl unit.[6] The two lowest energy excitations at 614 nm and 514 nm have a small contribution from the SOMO to LUMO transition, associated with the verdazyl unit. However, the excitation due mostly to this transition is calculated at 427 nm (f = 0.004).

Compounds **1b[8]** and **1b[10]** come out from AcOEt as a dark red waxy substance. DSC analysis revealed only one transition on heating at 127 °C for the former and two transitions at 20 °C and 118 °C with moderate endotherms for **1b[10]** (Table 1 and Fig. 2). However, on cooling DSC analysis for both compounds revealed two exothermic transitions above 100 °C, which for **1b[10]** appeared as a broad peak with a maximum at 115 °C and a sharp peak at 111 °C with a total exotherm of 54.3 kJ mol^{-1}. The ratio of the two peaks is cooling rate dependent. At low cooling rate (1 K min^{-1}) only the high temperature peak is observed, while at higher rates (8 K min^{-1}) the sharp low temperature peak is more pronounced. These results indicate the formation of another, high-temperature metastable phase.

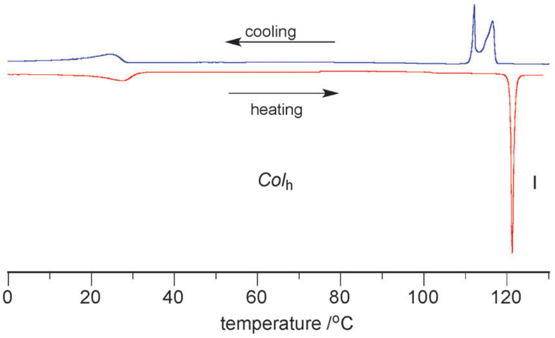

Fig. 2 DSC trace of **1b[10]**. The heating and cooling rates are 5 K min^{-1}.

The radicals have limited thermal stability. Repeated cycling between 100 °C and 135 °C at a rate of 5 K min^{-1} demonstrated progressively lower transition temperature and peak broadening. For instance, in the third cycle the Col → I transition was 1.4 K lower with a 40% smaller enthalpy.

The observed clearing temperature of **1b[10]** is higher by 70 K than that observed[1] for the sulfur analogue **1a[10]** and 24 K lower than that reported for the analogous triazine derivative.[7] The oxygen and sulfur analogues **1b[8]** and **1a[8]** are immiscible and their 4 : 1 mixture phase separates below 125 °C.

Optical analysis of a thin film of **1b[*n*]** revealed that the texture of the phase obtained on cooling is typical of a columnar discotic phase Col$_h$ (Fig. 3b). Surprisingly, at the transition to the isotropic phase, the sample undergoes a reversible color change from red to green (Fig. 1 and Fig. 3a), as revealed by temperature-dependent absorption spectroscopy studies. Detailed analysis demonstrated that the change in color corresponds to a 78 nm shift of the low energy absorption band from 552 nm in Col$_h$ to 630 nm in the isotropic phase. The latter absorption wavelength is similar to that observed for **1b[*n*]** in hexane solutions (λ_{max} = 614 nm). Thus, self-assembly of the molecules in columns results in a significant alteration of the electronic structure of the radicals and suggests close π–π interactions in the columnar phase.

Verdazyls typically do not form π-dimers or close π associates,[8] however a rare example of an intramolecular dimer was described recently.[9] 1,1′-Bis(6-oxoverdazyl)ferrocene (**7**) crystallizes with the two radicals forming a co-facial dimer in the solid-state, which is accompanied by a 70 nm blue-shift of the low energy absorption band. This suggests that the formation of columns by **1b[*n*]** has a similar effect as enforcing co-facial orientation of the verdazyls by geometry of ferrocene in **7**.

Powder XRD analysis for **1b[8]** and **1b[10]** confirmed the existence of a columnar hexagonal phase (Col$_h$) either in samples obtained from solutions or from the melt. Diffractograms of the mesophase obtained above 30 °C showed a series of sharp reflections that can be indexed assuming a 2D hexagonal lattice (Fig. 4 and Table 2). The wide angle region of the diffractograms shows two broad halos at around 4.5 Å and 3.9 Å and a distinct reflection at about 4.3 Å. The diffused signals correlate with the mean distance between the molten alkyl chains (former) and the mean separation between benzene rings (latter). The sharper signal at about 4.3 Å indicates a long-range positional correlation along the column length (correlation length 210 Å at 110 °C and 370 Å at 30 °C for **1b[10]**), and is possibly related to verdazyl–verdazyl distance. No evidence for dimer formation was found.

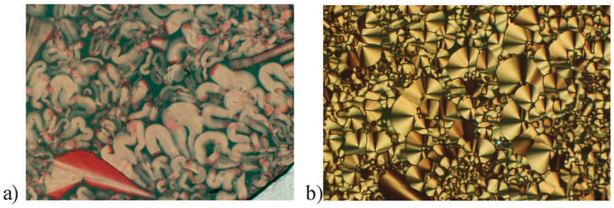
a) b)

Fig. 3 Optical textures of **1b[10]**: (a) growth of a red Col$_h$ phase out of the green isotropic phase (no polarizers) and (b) fully grown Col$_h$ phase.

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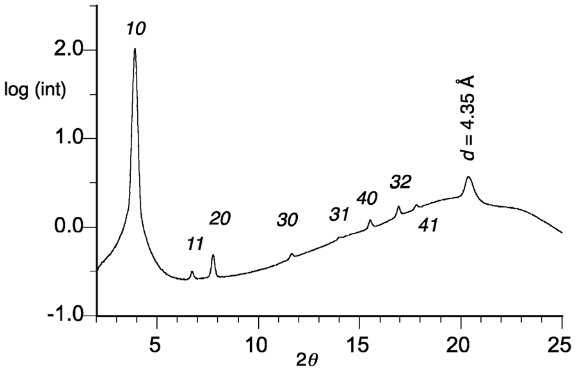

Fig. 4 2D XRD pattern for **1b[8]** at 115 °C.

Table 2 Selected X-ray diffraction data for Col_h phase of **1b[*n*]**

n	Temp/°C	Miller indices *hk*	*d* spacing/Å	Lattice parameter/Å
8	115	10	22.81 4.35	a = 26.35
10	30	10	24.56 4.26	a = 28.35
	110	10	25.07 4.33	a = 28.95

Analysis of the low temperature phase observed by DSC for **1b[10]** revealed another signal in the small angle region indicating the formation of a superlattice with doubling the basic lattice periodicity, occasionally observed in some Col_h phases.[10] This is consistent with a low hysteresis of the transition, suggesting minimal molecular reorganization.

The cell constant a = 26.35 Å for **1b[8]** (Table 2) is smaller than the calculated molecular size of **1b[8]** (32 Å). For **1b[10]**, the cell constant a increases with temperature at a rate of 5.49×10^{-3} Å K^{-1}.

Magnetic studies at 500 Oe revealed paramagnetic behavior of **1b[8]** in the liquid crystalline phase and do not support formation of dimers in the columnar phase. The effective magnetic moment (μ_{eff}) in the mesophase was found to be 1.591(4) in a temperature range of 200–360 K, which is close to the value of 1.732 for an ideal paramagnet and corresponds to 92 ± 1% of spins. The number of spins increases to 96% near the isotropic transition. Cooling of the sample from the nearly isotropic phase to 2 K at 500 Oe showed that molar susceptibility χ_m is well described by the Curie law down to 200 K where antiferromagnetic interactions gradually increase. The results are similar to those found for **1a[8]** and indicate that spins remain largely isolated at $>$200 K.

Time-of-Flight (ToF) measurements determined that the hole mobility (μ_h) in an unaligned sample of **1b[8]** was $3.3 \pm 0.2 \times 10^{-3}$ $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ in the temperature range of 40–110 °C and showed weak temperature dependence. However, the charge photogeneration was inefficient and the resulting photocurrent was only 6.0×10^{-13} S cm^{-1} at 90 °C, comparable with dark current (4.0×10^{-13} S cm^{-1} at 90 °C). No photoconductivity was detected in the isotropic phase of **1b[8]**.

Electrochemical analysis of **1b[8]** in CH_2Cl_2 (10^{-3} M) revealed two quasi-reversible redox pairs. The measured potentials, $E^{0/+1}{}_{1/2} = +0.83$ V and $E^{0/-1}{}_{1/2} = -0.60$ V *vs.* SCE, are shifted cathodically by about 0.16 V relative to those reported for **1a[6]**.[1] The observed cell potential $E_{\text{cell}} = 1.43$ V is consistent with a relatively low disproportionation energy calculated for **1b[1]** (rigid, 107.5 kcal mol^{-1}; relaxed, 92.3 kcal mol^{-1}).

In conclusion, achiral liquid crystalline 6-oxoverdazyl radicals **1b[*n*]** exhibit unprecedented reversible thermochromism at the transition from the hexagonal columnar (Col_h) to the isotropic phase. XRD and magnetization results do not support dimerization of the radicals in the Col_h phase, although the discs exhibit significant correlation length along the column. In contrast to the sulfur analog **1a[8]**, charge photogeneration in **1b[8]** was inefficient; however, charge mobility in both compounds is comparable. Further studies to understand the origin of the observed thermochromism and low efficiency of charge photogeneration are currently in progress.

This work was supported by Vanderbilt University Discovery Grant and NSF grant (DMR-0907542). We thank Prof. Andrzej Twardowski for funding SQUID measurements and Ms Ola Kruczkowska for her technical assistance.

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