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Synthesis and properties of a novel family of liquid crystalline building blocks based on 5,5′-substituted-2,2′-bipyridine

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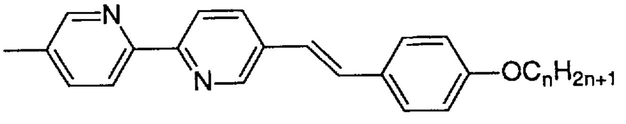
Novel liquid crystalline compounds based on 5-methyl-5′-(4-*n*-alkoxyphenylvinyl)-2,2′-bipyridine were synthesized and their mesomorphic properties investigated. All members of this series exhibit nematic, smectic A and smectic B phases. For the octyloxy compound an hexatic phase is also observed.

Transition metal complexes forming liquid crystals have been extensively studied [1]. The range of ferroelectric and non-linear optical properties exhibited by these mesomorphic materials has been dramatically increased. Although paramagnetic liquid crystalline compounds have been described, their interaction with a magnetic field has been scarcely studied [2]. These molecules have attracted particular attention as it is possible to control their alignment and orientation in mesophases using a magnetic field [3]. Surprisingly, non-polymeric materials possessing liquid crystallinity associated with optical properties such as luminescence have been little studied from a fundamental point of view [4]. Based on an understanding of liquid crystals, one can try to generate ordered fluorescent materials and study their luminescent properties as a function of the mesophase nature.

Oligopyridines (for example, bipyridines, phenanthrolines, terpyridines) exhibit an almost *universal* complexation site for a wide variety of paramagnetic metals [5,6], and also allow the synthesis of luminescent transition metal complexes with long-lived metal-to-ligand charge transfer excited states [7]. Moreover, functionalization of 2,2′-bipyridine with 'stilbene type' chromophores gives rise to luminescent ligands [8]. This has prompted us to design, synthesize and characterize a new family of mesogenic compounds (see structure below, where $n = 8, 10, 12, 14, 16$), based on a 2,2′-bipyridine core (potential complexation site) with an appended stilbene linker in one 5-position (luminescent sensor). Thermotropic liquid crystalline polymers based on homopolyesters of 5,5′-substituted-2,2′-bipyridine [9] and alkanoyl derivatives of 6,6′-diamino-2,2′-bipyridine and their metal complexes [Cu(II), Ni(II), Co(II), and Pd(II)] [10] have previously been studied.



We report here our preliminary results on the preparation and liquid crystal properties of a novel family of ligands derived from 5-methyl-5′-(4-*n*-alkoxyphenylvinyl)-2,2′-bipyridine (n = 8, 10, 12, 14, 16).

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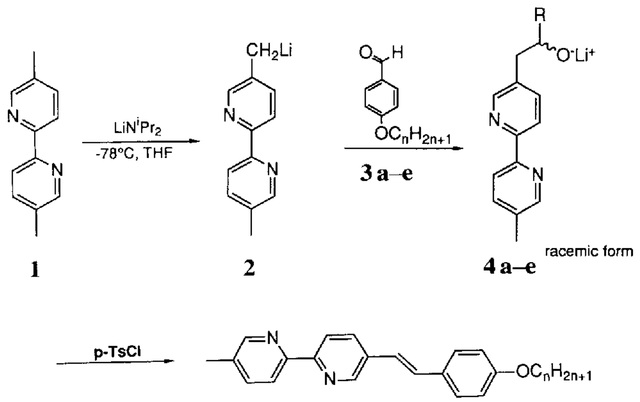


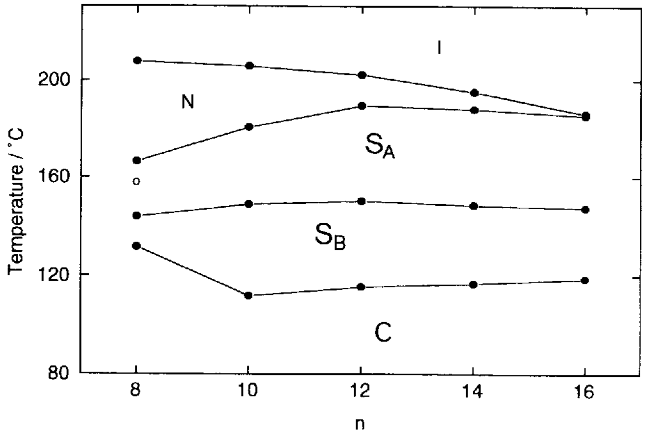
5a $n = 8$, **5b** $n = 10$, **5c** $n = 12$,
5d $n = 14$, **5e** $n = 16$.

Synthesis of the 5,5′-substituted-2,2′bipyridine liquid crystalline ligands.

The new chelates were readily prepared by adapting a literature procedure [11] (see the scheme). Monolithiation of 5,5′-dimethyl-2,2′-bipyridine **1** [12], using one equivalent of lithium diisopropylamine in tetrahydrofuran at − 78°C, gave compound **2**, which on reaction with the appropriate aldehyde **3a–e** [13] produced the racemic form of the alcoholate **4a–e**. Addition of *p*-toluenesulphonyl chloride to alcoholates **4a–e**, at room temperature, afforded the vinyl compounds **5a–e** (average isolated yield over three steps: 20 per cent). The *trans* stereoisomeric form of the double bond has unambiguously been assigned by the determination of a characteristic AB system with a coupling constant $J_{AB} = 16{\cdot}4$ Hz in the proton NMR spectrum [14]. All compounds were purified by column chromatography using Al_2O_3 and CH_2Cl_2/hexane 3/7 as eluant ($R_f = 0{\cdot}62$ for **5a**, 0·63 for **5b**, 0·66 for **5c**, 0·66 for **5d**, 0·66 for **5e** in dichloromethane) and characterized by ^{1}H, ^{13}C{^{1}H} NMR, UV, IR, luminescence and elemental analysis. A strong luminescence was observed (λ_{em} 426 nm) for all compounds when irradiated within their π–π^* absorption bands (λ_{max} 338 nm) in CH_2Cl_2 solution.

The mesomorphic properties of compounds **5a–e** were investigated by differential scanning calorimetry (Perkin–Elmer DSC7, heating and cooling rates of 5°C min^{-1}), polarizing optical microscopy (Leitz Orthoplan, Mettler FP 82 hot stage) and X-ray diffraction studies. The DSC thermograms registered upon heating and subsequent cooling between 0 and 230°C show the presence of sharp peaks indicative of four first order transitions (see the figure). The one occurring at the lowest temperature involves an important enthalpy change which increases with the length of the molecules ($15 < \Delta H < 45$ kJ mol^{-1}) corresponding to the disordering of the paraffin chains and melting of the crystal into a mesomorphic phase. Of relatively small enthalpy ($\Delta H \leq 3$ kJ mol^{-1}), the other transitions correspond to the change from one mesophase to another and ultimately to full melting into an isotropic liquid. The optical textures observed upon slow cooling from the isotropic melt show the existence of three distinct mesophases, namely, a nematic (Schlieren texture), a smectic A (focal conics and homeotropic texture), and an ordered smectic (mosaic texture) mesophase (see the figure). In the particular case of the octyloxy derivative, the DSC thermograms contain an additional, hardly visible ($\Delta H = 0{\cdot}01$ kJ mol^{-1}) peak, located at about 159°C (open circle in the figure), suggesting a fifth, very weakly first order phase transition. Optical observations (advent of a finely threaded texture on cooling) fully confirm this transition and allow us to identify a further mesomorphic phase occurring between the smectic A and the ordered smectic phase.

The structures of the liquid crystalline phases were elucidated by X-ray diffraction (pin-hole camera) on magnetically oriented samples. The nematic phase was unambiguously established by the presence in the diffraction patterns of two equatorial diffuse spots at about 4·5 Å, related to the lateral correlations of the elongated molecules, and of two meridional diffuse spots at about $1/L$ (L being the molecular length), related to the longitudinal correlations of the molecules within cybotactic groups. The smectic A phase was clearly confirmed by the sudden replacement of the diffuse meridional spots by a series of equidistant sharp Bragg reflections, related to a smectic period of $d = L$. The smectic B phase was definitely proven by the replacement of the two diffuse equatorial spots (subsisting in the S_A phase) by two sharp reflections at 4·37 Å, related to the hexagonal lateral packing of the molecules within the smectic layers (corresponding to a molecular area of $22{\cdot}0_5$ Å^2). Finally,



Phase diagram of compounds **5a–e** (I: isotropic liquid; N: nematic phase; S_A: smectic A phase; S_B: smectic B phase; C: crystalline phase).

the additional mesophase observed with the octyloxy derivative between the S_A and S_B phases, seems to be hexatic in nature [15]. Indeed, the X-ray patterns registered using the suspended film technique (X-ray primary beam normal to the smectic layers) contain six thick, short arcs at about 4·4 Å, related to the in-plane long-range orientational order of the molecules.

In conclusion, we have reported a novel family of luminescent bipyridine-containing thermotropic liquid crystals. Photophysical studies: quantum yield, excited state lifetimes, co-operative effects (for example, excimers, exciplexes) in the different alignments and the influence of the chain packing are currently being examined. Paramagnetic metallomesogens are also being synthesized. Complete details about these studies will be given in a subsequent full paper.

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