CHEMCOMM
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Liquid crystalline non-covalent supermolecules of a styrylstilbazole ligand

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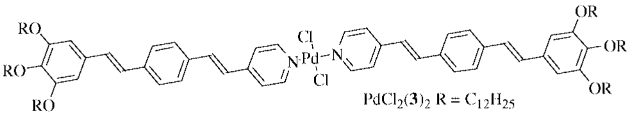
*Received (in Cambridge, UK) 26th February 2001, Accepted 1st June 2001
First published as an Advance Article on the web 21st June 2001*

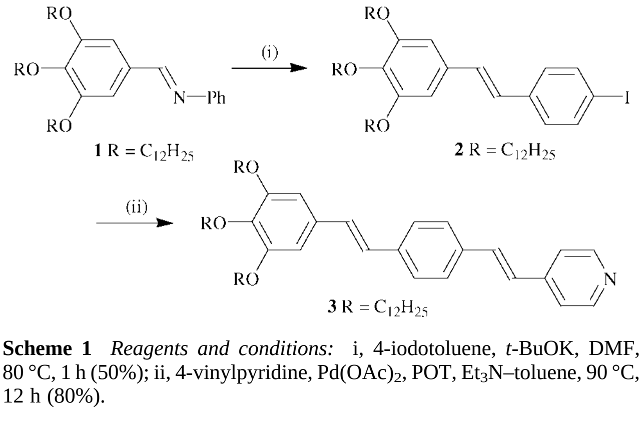
Dimerization of a new styrylstilbazole ligand through non-covalent interactions leads to polycatenar calamitic supramolecular structures with liquid crystalline properties.

The organization of a molecular assembly into a liquid crystalline phase requires a microphase separation resulting from the amphipathic character of two chemically incompatible parts in the molecules, in general a rigid core and paraffinic chains. The self-assembly of building blocks through non-covalent bonds is also able to generate such a structural segregation, thus allowing molecular units without intrinsic mesomorphic properties to form supramolecules presenting liquid crystalline properties.[1–7] The most widely used interactions to obtain self-assembled structures with mesomorphic properties are coordination to a metal center[2–4] (metallomesogens) or hydrogen bonds.[5–7] The use of weaker interactions such as van der Waals or hydrophobic forces have been probed to a much lesser degree.[8] Here we report on the synthesis of a calamitic polycatenar non-mesogenic pyridine containing ligand, and the preparation of supramolecular mesogens by using coordination to a metal and ionic bonds, but also van der Waals forces.



$PdCl_2(\mathbf{3})_2$ R = $C_{12}H_{25}$

The synthesis of **3** is depicted in Scheme 1. Treatment of benzaldimine **1**[7] with 4-iodotoluene under Siegrist conditions gave iodostilbene *E*-**2**. Subsequent Heck coupling of *E*-**2** with 4-vinylpyridine with $Pd(OAc)_2$ as catalyst in Et_3N–toluene in presence of tri-*o*-tolylphosphine (POT) gave **3** in 80% yield. All of the spectroscopic studies and elemental analyses were consistent with the proposed molecular structures.† In particular, coupling constants of *ca.* 16.5 Hz for the two AB systems corresponding to the two sets of vinylic protons in the ^{1}H-NMR spectrum confirmed the *E* stereochemistry of both double bonds in **3**. The electronic absorption and emission of styrylstilbazole **3** are reported in Fig. 1. Compound **3** exhibits a strong absorption (λ_{max} = 367 nm). Interestingly, addition of increasing amounts of TFA to a solution of **3** causes dramatic changes in the absorption spectrum, the peak being completely shifted at *ca.* 10 equivalents of acid added. Isosbestic points are maintained at 313 and 388 nm indicating that a single chemical process occurs, *i.e.* protonation of the pyridine ring. The initially pale yellow solution becomes orange–yellow at the end of titration. The addition of acid also leads to changes in the emission properties (λ_{exc} = 313 nm, isosbestic point). The strong blue luminescence of the ligand (λ_{max} = 501 nm) progressively disappears and a very weak red-shifted emission (λ_{max} = 615 nm) corresponding to the luminescence of protonated **3** is detected at the end of the titration (Fig. 1). Addition of a base (DBU) restores the initial absorption and luminescence properties. Therefore ligand **3** also presents characteristic features that make it an interesting building block for the preparation of new molecular switches.[9]



Scheme 1 *Reagents and conditions:* i, 4-iodotoluene, *t*-BuOK, DMF, 80 °C, 1 h (50%); ii, 4-vinylpyridine, $Pd(OAc)_2$, POT, Et_3N–toluene, 90 °C, 12 h (80%).

The observation of **3** under optical microscopy does not reveal any liquid crystalline properties and only shows a melting point at 83 °C. It is well known that metal complexes of polycatenar stilbazole derivatives show mesomorphic properties.[3,4] Ligand **3** is also a suitable building block for the preparation of related metallomesogens. The *trans*-Pd(II) complex of **3** has been prepared according to the procedure developed by Bruce and co-workers.[3] Treatment of **3** with $PdCl_2(CH_3CN)_2$ in a mixture of CH_2Cl_2–CH_3CN 1 : 1 afforded $PdCl_2(\mathbf{3})_2$ in 95% yield.‡

Observation of this Pd(II) complex under a polarizing microscope reveals typical textures of a columnar mesophase from 165 to 234 °C. Differential scanning calorimetry (DSC) analyses and X-ray diffraction patterns recorded for $PdCl_2(\mathbf{3})_2$ at different temperatures were in full agreement with these observations. Indeed, the X-ray pattern is characterized in the small angle region by two sharp reflections in the ratio $1 : \sqrt{3}$, corresponding to a two-dimensional hexagonal lattice. The

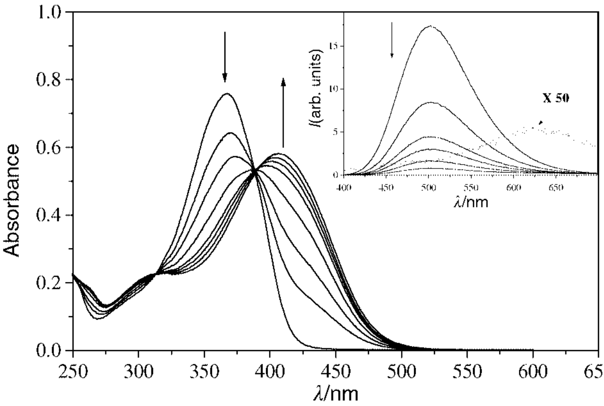


Fig. 1 Absorption and (inset) fluorescence (λ_{exc} = 313 nm, isosb. point) spectra of CH_2Cl_2 solutions of ligand **3** containing 0, 0.5, 1, 2, 4, 6, 10, 100 equiv. of TFA (the emission spectrum recorded after addition of 100 eq. of TFA is multiplied by a factor of 50).

DOI: 10.1039/b103563k

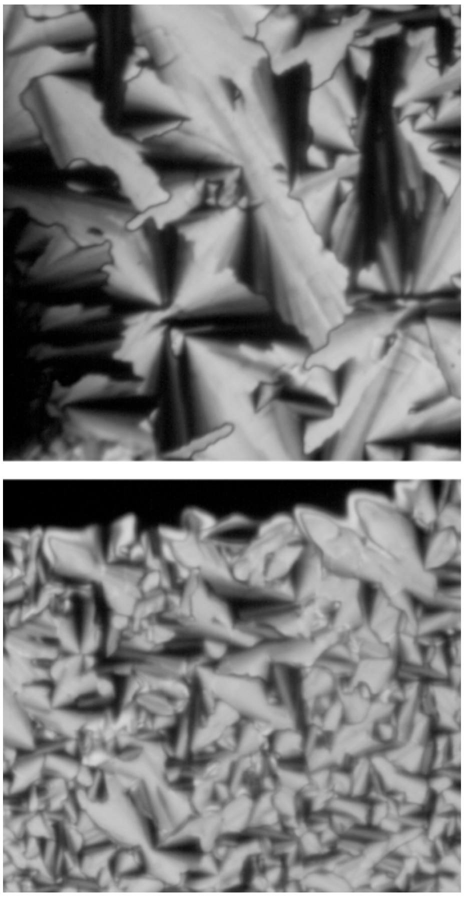


Fig. 2 Top: optical texture observed with a polarizing microscope at 150 °C for the complex prepared from **3** and perfluorosuberic acid. Bottom: optical texture observed with a polarizing microscope at 120 °C for the complex prepared from **3** and TFA.

dimerization of **3** *via* coordination to a metal center is therefore able to produce a polycatenar calamitic supramolecule with liquid crystalline properties.

It has been shown that H-bonding can be used to assemble pyridine derivatives with carboxylic acids to produce linear structures that exhibit liquid crystalline behavior.[5] The treatment of styrylstilbazole **3** with various dicarboxylic acids (oxalic acid, α,ω aliphatic dicarboxylic acids of different lengths and terephthalic acid) was therefore attempted in order to obtain supramolecular derivatives with an appropriate shape to produce columnar mesophases. Unfortunately, homogeneous samples could not be obtained and macrophase separation was observed in all the cases. The interactions (if any) of **3** with these dicarboxylic acid derivatives seem to be too weak to allow the preparation of the desired supramolecular assemblies. This observation prompted us to use a more acidic derivative able to protonate styrylstilbazole **3** in order to produce a stable adduct thanks to the resulting ionic interactions. Slow evaporation of a CH_2Cl_2 solution of **3** and perfluorosuberic acid [HO_2C-$(CF_2)_6CO_2H$; 0.5 equiv.] afforded an orange crystalline solid. The orange color and the presence of a strong band at 1623 cm^{-1} in the IR spectrum (neat) are in good agreement with the formation of a carboxylate salt.

Observation of the resulting complex under a polarizing microscope reveals an optical texture characteristic of a columnar mesophase from 124 to 170 °C (Fig. 2). The dicarboxylic acid and **3** seem therefore able to form a supramolecular dimer stabilized by electrostatic forces with the appropriate polycatenar calamitic shape to produce a columnar liquid crystalline phase.

The treatment of **3** with TFA (1 equiv.) under similar conditions also leads to an orange crystalline solid and the development of typical columnar texture was observed from 70 to 143 °C for the resulting compound (Fig. 2). In addition to the electrostatic interactions among **3** and TFA, it seems that fluorophilic interactions allow the dimerization of the resulting **3** TFA species and, thus are able to direct their self-organization into a columnar liquid crystalline phase. It is worth noting that salts prepared from **3** and inorganic acids such as HCl do not exhibit any mesomorphic properties. The latter observation shows that protonation of **3** alone is not sufficient to produce liquid crystalline derivatives. Thus the fluorophilic interactions must play an important role.

The mesomorphic properties of the complexes obtained from **3** and perfluorosuberic acid or TFA have been studied by DSC and X-ray diffraction. The hexagonal lattice parameters deduced from the X-ray patterns (50 Å at 140 °C for the adduct with perfluorosuberic acid and 48 Å at 140 °C for the adduct with TFA) are similar to that found for the complex $PdCl_2(\mathbf{3})_2$ (45 Å at 160 °C). This observation strongly suggests an effective dimerization of **3** through non-covalent interactions as discussed above.

Treatment of **3** with a palladium salt, perfluorosuberic acid or TFA afforded discrete assemblies with new properties. Effectively, **3** itself does not show any mesomorphic properties, but its dimerization through self-assembling by coordination, ionic or fluorophilic interactions leads to discrete supramolecular structures with liquid crystalline properties.

We thank B. Heinrich for his help with the X-ray measurements and L. Oswald for technical assistance.

Notes and references

† *Selected spectroscopic data* for **3**: Yellow crystals (mp 83 °C). UV-Vis (CH_2Cl_2): 367 (40000). δ_H (200 MHz, $CDCl_3$): 8.58 (d, *J* 6, 2 H), 7.53 (s, 4 H), 7.37 (d, *J* 6, 2 H), 7.12 (AB, *J* 16.5, 2 H), 7.02 (AB, *J* 16.5, 2 H), 6.73 (s, 2 H), 4.03 (t, *J* 6.5, 4 H), 4.00 (t, *J* 6.5, 2 H), 1.80–1.70 (m, 6 H), 1.50–1.20 (m, 54 H), 0.90 (t, *J* 6.5, 9 H). Anal. calc. for $C_{57}H_{89}NO_3$: C 81.86, H 10.73, N 1.67; found: C 81.58, H: 10.75, H 1.66%.

‡ *Selected spectroscopic data* for $PdCl_2(\mathbf{3})_2$: Yellow crystals. UV-Vis (CH_2Cl_2): 392 (118000). δ_H (200 MHz, $CDCl_3$): 8.70 (d, *J* 7, 4 H), 7.56 (s, 8 H), 7.42 (d, *J* 7, 4 H), 7.41 (d, *J* 16.5 Hz, 2 H), 7.08 (d, *J* 16.5, 2 H), 7.06 (AB, *J* 16, 4 H), 6.74 (s, 4 H), 4.01 (t, *J* 6.5 Hz, 8 H), 3.98 (t, *J* 6.5, 4 H), 1.80–1.70 (m, 12 H), 1.50–1.20 (m, 108 H), 0.90 (t, *J* 6.5, 18 H). Anal. calc. for $C_{114}H_{178}N_2O_6PdCl_2$: C 74.01, H 9.70, N 1.51; found: C 73.61, H: 9.52, H 1.55%.

1 J.-M. Lehn, *Supramolecular chemistry-concepts and perspectives*, VCH, Weinheim, 1995.

2 C. Tschierske, *Angew. Chem., Int. Ed.*, 2000, **39**, 2454 and references cited therein.

3 B. Donnio and D. W. Bruce, *J. Chem. Soc., Dalton Trans.*, 1997, 2745; D. J. Price, K. Willis, T. Richardson, G. Ungar and D. W. Bruce, *J. Mater. Chem.*, 1997, **7**, 883.

4 D. W. Bruce, *Acc. Chem. Res.*, 2000, **33**, 831.

5 T. Kato, *Handbook of Liquid Crystals*, D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, eds, Wiley: VCH, Weinheim, 1998, Vol. 2B, pp. 969–979.

6 M. Suarez, J.-M. Lehn, S. C. Zimmerman, A. Skoulios and B. Heinrich, *J. Am. Chem. Soc.*, 1998, **120**, 9526; A. El-ghayoury, E. Peeters, A. P. H. J. Schenning and E. W. Meijer, *Chem. Commun.*, 2000, 1969; A. P. H. J. Schenning, P. Jonkheijm, E. Peeters and E. W. Meijer, *J. Am. Chem. Soc.*, 2001, **123**, 409.

7 J.-F. Eckert, J.-F. Nicoud, D. Guillon and J.-F. Nierengarten, *Tetrahedron Lett.*, 2000, **41**, 6411.

8 D. Felder, B. Heinrich, D. Guillon, J.-F. Nicoud and J.-F. Nierengarten, *Chem. Eur. J.*, 2000, **6**, 3501; J. L. M. van Nunen, B. F. B. Folmer and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1997, **119**, 283.

9 N. Armaroli, J.-F. Eckert and J.-F. Nierengarten, *Chem. Commun.*, 2000, 2105.