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A high contrast mechanochromic luminescent diacetylene-linked bis-benzothiadiazole derivative

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Two new rod-shaped molecules based on a directly-linked or a diacetylene-linked bis-benzothiadiazole core, flanked by two p-nonylphenyl groups have been synthesized and their potential stimuli-responsive behaviour investigated. The high molecular anisotropy and the presence of flexible chains induces these molecules to organize into lamellar self-assemblies, which can be influenced by the action of external stimuli. The two compounds present a polymorphic transformation upon heating which can be reversed upon shearing, but only in the diacetylene linked derivative this transformation is accompanied by a change of its emission colour. In fact, in this material the phase interconversion involves a high contrast luminescent alteration which can be rationalized considering the high conformational flexibility of the bridging unit which offers a great opportunity to change the surrounding of the molecules in the solid upon minor stimuli. Conversely in the directly connected bis-benzothiadiazole, molecules are closely tightened in the layers, through cooperative chalcogen and aromatic interactions, probably preventing the displacement of the molecules within the layers and therefore changes in the environment of their aromatic parts responsible of the colour and emissive properties of the solids. The results of this study point to the flexible diacetylene moiety as an attractive design element in the construction of stimuli responsible light emitting materials. We hope that this observation will facilitate the design of new mechanochromic materials in the near future.

Introduction

Mechanochromic materials, that is, solids possessing optical properties that vary upon mechanical stimulation, arouse much interest for rewritable paper,1 recording2 or stress sensing.3 Many organic4,5 and organometallic compounds6 have been recently reported whose color or luminescent properties are altered upon grinding, pressing or stretching. The origin of this interesting phenomenon can be usually found in the high dependence of the optical properties of molecular materials on their surrounding.7,8 This high dependence offers many opportunities to synthesize materials which can respond to external stimuli by varying their supramolecular arrangement, however only in a few examples a precise understanding about the origin of the colour change has been achieved. Single crystals diffraction analysis is probably the most powerful tool to attain such understanding, as it provides accurate information on the relative arrangements of neighbouring molecule and the interactions involved among them.9,10 However, although there are remarkable examples in the literature of molecular materials that retain their crystal integrity after a mechanical operation,11–14 the emission switching between polymorphs is rather exceptional as it involves the transformation of the molecular structure in the constrained environment of the crystal. Notwithstanding, some design hints have been already proposed to induce a mechanochromic behaviour15,16 among them the presence of weak interaction planes which allow the relative slippage of the molecules affecting the interactions with their next neighbours, and consequently their optical properties.17–19 However, despite the impressive progress of this field in recent years, to date the discovery of new mechanochromic compounds is still largely based on serendipity.

In the quest for new organic stimuli responsive materials, the 2,1,3-benzothiadiazole moiety (BTD) have emerged as a promising building block, as the absorption and emission properties of its derivatives are strongly influenced by their external environment.20,21 In the last few years several BTD-based chromogenic and fluorogenic materials have been reported, but although there are some recent exceptions,19,22,23 in most examples crystalline-to-amorphous transitions are in the origin of this behaviour.20,24–28 This fact prevents an in-depth understanding of the mechanism behind
the different optical properties observed. We have recently reported on a BTD-derivative which crystallize in two distinctive luminescent crystal phases (blue and green emitting) which can be reversibly switched by the action of pressure and solvent vapours. In this molecule, the BTD moiety is flanked by two phenyl groups substituted with flexible nonyl chains, which induces the assembly of these molecules into layers and provide weak interaction planes which are presumably responsible of the switchable properties by facilitating mechanically induced sliding processes and provoking the displacement of the molecules with respect to the layer normal.\textsuperscript{19}

In this work, we have explored the possibility of extending this design principle to obtain BTD-based mechanochromic materials with larger contrast switchable emission colours. To this end we have synthesized two different rod-shaped BTD-dimeric molecules (with the two BTD subunits either directly linked or separated by a diacetylene bridge) flanked by two 4-nonylphenyl groups. By dimerizing the BTD molecule, we could significantly red-shift the absorption and emission properties linked or separated by a diacetylene bridge) flanked by two 4-nonylphenyl groups. By dimerizing the BTD molecule, we could significantly red-shift the absorption and emission properties of these materials in the solid state while the presence of flexible chains induces their self-assembly into layers thus providing weak interaction planes. Interestingly although in the two cases a polymorphic transformation can be observed upon shearing, only in the case of the diacetylene-linked derivative a change of colour can be observed.

Results and discussion

Synthesis and characterization.

The synthesis of the dimeric compounds 4 and 5 was performed starting from 4-bromo-7-(4-nonylphenyl)benzo[c][1,2,5]thiadiazole 2 which can be readily obtained starting from commercial 4,7-dibromo-benzo[c][1,2,5]thiadiazole 2 through Suzuki coupling with one equivalent of 4-nonylphenylboronic acid as has been previously reported.\textsuperscript{22}

Self-reaction coupling of 2 catalysed by Pd(OAc)\textsubscript{2} in polyethylene glycol (PEG4000),\textsuperscript{29,30} rendered straightforwardly compound 4 in good yield (Scheme 1). Compound 5 was obtained by Cu-catalysed oxidative Eglinton coupling of the corresponding ethynyl derivative 3, which is readily accessed in two steps by Sonogashira coupling of 2 with ethynyl trimethylsilane, followed by deprotection with KF (Scheme 1).

All new compounds were purified by silica gel column chromatography, using a mixture of hexane/CH\textsubscript{2}Cl\textsubscript{2} (3:1) as eluent and characterized by $^1$H NMR, $^{13}$C NMR, and mass spectrometry (see the ESIF for experimental details).

The photophysical properties of the new molecules were studied by UV-vis and fluorescence spectroscopy. The UV-vis absorption spectra of 4 and 5 in CH\textsubscript{2}Cl\textsubscript{2} exhibit one absorption band, localized around 280 nm (associated to $\pi$-$\pi$ transition) and a lower energy band around 400 nm (see Figure 1a) which can be ascribed to charge transfer transitions. Both bands are slightly red-shifted when going from 4 to 5 in agreement with a better electron delocalization facilitated by the diacetylene linker. The fluorescence spectra of both compounds in CH\textsubscript{2}Cl\textsubscript{2} are characterized by an emission band peaking at 511 and 499 nm for 4 and 5 respectively (Figure 1a).

All compounds can be easily reduced to stable radical anions reflecting the strong acceptor character of the BTD core. In both derivatives, it is possible to observe two reversible one electron reduction waves, indicating that the first reduction yields a monoanion stabilized by delocalization over both electron accepting units, and confirming the good electronic communication between the two BTD moieties. The two-reduction waves of 5 are slightly shifted anodically when compared to 4 suggesting that the diacetylene bridge renders the system more electron deficient. Interestingly compound 4 presents an amphoteric redox character as it can be also easily oxidized in the accessible solvent window (Figure 1b).
Scheme 1: Synthesis of compounds 1-5.

Figure 1. a) Normalized UV–vis (lines) and fluorescence (dots) spectra of compounds 4-5 in CH2Cl2, c = 5 × 10^{-6} M solutions. b) Cyclic voltammograms of compounds 4-5 at [C]=1 × 10^{-3} M recorded at a scan rate 100 mV s^{-1} in CH2Cl2/0.1 M TBAPF6 measured versus Ag/AgCl.

Crystal Growth and Structure determination of 4

In order to shed light on the influence of the bridging mode on the supramolecular arrangement of these molecules we have attempted to grow single crystals of both compounds. Yellow single crystals suitable for X-ray structure determination of 4 were obtained by slow evaporation of a CH2Cl2 solution. Compound 4 crystallize in the triclinic space group P-1, with five crystallographic independent molecules in the asymmetric unit cell (see SI Figure S7), which differ slightly in the torsion between the two BTD moieties (situated anti to each other with dihedral angles of 36.9-37.8°) and between the external phenyl rings and the neighbouring BTD (with torsion angles that vary from 34.0 and 40.2). The crystal packing presents a lamellar organization with no interdigitation of alkyl chain, confirming in this case the presence of weak interactions planes (Figure2a).

Within the layers, each independent molecule interacts with its symmetry-related molecules forming sheets that grow along the a direction. In the sheets each molecule is connected with its two next neighbours through chalcogen bonding 2S-2N squares. As a result all the thiadiazole rings are involved in this type of interactions. Please note that the highly directional 2S-2N square motif, has emerged as a powerful synthon in supramolecular chemistry and crystal engineering. These sheets are further connected along the c direction through the cooperative action of a number of S-N, CH-π and S-π (Figure3).

Conversely all attempts to obtain crystals of 5 of sufficient quality for structure determination by slow evaporation of a...
variety of pure solvents and different solvents mixtures were unfruitful. However, these experiments confirmed the existence of two polymorphs with a similar yellowish colour under visible light but which can be easily differentiated upon irradiation with a 365 nm lamp. Thus evaporation from toluene led to yellow emitting plate-like crystals while slow evaporation of a CH$_2$Cl$_2$:propanol mixture gave rise to orange-emitting ribbon-like crystals, with a highly anisotropic shape that bent and twist as they grow, giving rise in some cases to curious helicoidal morphologies (Figure 4c and 4d). This behaviour has been commonly observed in crystals with a lamellar packing. Unfortunately these crystals in spite of having the appearance of single crystals diffract poorly and their crystal structure could not be solved.

X-ray powder diffractograms of both polymorphs, show a similar packing arrangement characterized by a major primary diffraction peak at 3.17° and 2.83° for the yellow and the orange polymorphs respectively (see SI, Figure S8 and S9), which agrees with lamellar structures with interlayer distances of 27.8 Å and 31.2 Å. Figure 5 show the absorption and emission spectra of compound 4 and polymorphs 5α and 5β. As can be observed in Figure 5 the absorption spectra of the three compounds are very similar, however, while the emission spectra 4 and polymorphs 5α ($\lambda_{\text{max}} = 525$ nm) also coincide, the emission spectrum of polymorphs 5β is redshifted by 80nm ($\lambda_{\text{max}}$=605nm).

Polymorphic Transformation and mechanochromic/thermochromic behaviour

The lamellar organization observed in both compounds (and therefore the presence of weak interaction planes in the crystals) together with the evidence of the existence of at least two polymorphs of 5 induced us to evaluate in more detail the possible polymorphic transformation by exposing them to different physical stimuli.

Thus, thermal treatment of 4 produced a polymorphic transformation at 70°C as could be monitored by powder X-ray diffraction (Figure 6). This transformation is not reverted upon cooling but shearing the cooled sample with a spatula gives rise again to the initial phase. X-ray powder diffractograms of both polymorphs, are dominated by a primary diffraction peak at 2.84° (as obtained) and 2.94° (after a heating-cooling cycle), which suggest that the lamellar packing is maintained after the thermal treatment although differ slightly in the interlayer distance. Heating a single crystal of the as-obtained polymorph under a polarizing microscope (POM) equipped with a hot-stage allowed us to visualize the progressive changes in the birefringence that accompanies this phase transformation. In this case, although the outer shape of the single crystal is maintained, its integrity is lost as evidence by the emergence of numerous cracks in its surface.

Curiously in this case the polymorphic transformation is not accompanied by a colour or luminescence alteration. This behaviour suggests that although the presence of weak interaction planes allow some layer sliding, upon external stimulation the compact network of intermolecular interactions that connect the molecules within the layers maintain the relative position of the aromatic moieties unaltered (see Figure 6a).

Both polymorphs of compound 5 were subjected to similar thermal and shearing treatments, which allowed us to confirm that both polymorphs can be interconverted. Thus, heating the orange emitting polymorph 5α at 120°C gives rise to polymorph 5β as could be confirmed by powder X-ray diffraction. As previously observed on compound 4, this transformation is not reverted upon cooling. On the other hand, shearing the yellow emitting polymorph 5β (obtained after the thermal treatment) at room temperature gives rise again to the orange polymorph (Figure 7). These easy transformations can be understood considering the high flexibility and low rotational barrier imposed by the diacetylene linker which allows for the easy modulation of the local geometry of the molecules and intermolecular interactions in the crystal, with evident influence in their optical properties. The reversible switching is maintained at least for 10 cycles, which together with the high degree of contrast in the emitting colour between the two polymorphs,
confers this material much interest as rewritable paper or anticounterfeiting solutions.\textsuperscript{35}

**Figure 6.** a) POM images of the polymorphic transformation occurring on a single crystal at 70ºC. b) Thermal and subsequent mechanochromic polymorphic transformations followed by powder X-ray diffraction pattern changes.

Interestingly the thermal phase transformation could be visualized on isolated crystals under a microscope as evidenced by the progressive change in the emission colour upon heating above 110ºC under illumination with a 365 nm lamp. In this case no cracking was observed, confirming the higher elasticity of the assembly in this case, again in close relation with the flexibility provided by the diacetylene linker.

**Figure 7.** (a) Photograph of the interconversion between polymorphs 5α and 5β illuminated with 365 nm lamp. (b) Thermal and subsequent mechanochromic polymorphic transformations followed by powder X-ray diffraction pattern changes.

**Figure 8.** Photomicrograph of the transformation of 5α into 5β under upon thermal heating illuminated with 365 nm lamp.

**Conclusions**

Two new rod-shaped molecules based on a directly-linked or a diacetylene-linked bis-benzothiadiazole core, flanked by two \( p \)-nonylphenyl groups have been synthesized and their potential mechanochromic behaviour investigated. The high molecular anisotropy and the presence of flexible chains induces the self-assembly of these molecules into layers thus providing weak interaction planes, which has been previously found to be an attractive design principle to obtain stimuli responsive materials. Indeed, in both materials a reversible polymorphic transformation could be observed, which confirms the validity of this approach although only in one of them, the transformation is accompanied by a variation in their optical properties. The different behaviour can be ascribed to the different linkage between the BTD moieties which influences on the flexibility of the molecules and also on how molecules interact with each other in the solids after mechanically or thermally induced sliding processes. Thus, in the directly connected bis-BTD derivative, molecules are involved in a cooperative network of intermolecular interactions which probably hinders the displacement of the molecules within the layers while in the diacetylene-bridged derivative, the flexibility of the linker provides multiple easily accessible conformations which will influence on how molecules interact with each other in the solid. In fact, in this material the phase interconversion involves a high contrast luminescent alteration (with a variation of its maximum emission wavelength of 80 nm). Such behaviour confers this material much interest, towards its potential applications and point to the flexible
diacetylene moiety as an attractive design element in the construction of stimuli responsible light emitting materials. The result of this study indicates that the presence of weak interaction planes is not sufficient to obtain BTD-based mechanochromic materials but also loosely bound molecules within the layers will be required.

Conflicts of interest

There are no conflicts to declare.

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