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A Conjugated Polymer from 2-Benzylidene-4,5-dicyano-1,3-dithiole

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1,2-Dicyanoarenes and -alkenes typically react with alkali metal alkoxides in alcohols to give molecular cyclotetramers, the best known example of these being the phthalocyanines.[1] In marked contrast to the prior literature,[1] we now report that 2-benzylidene-4,5-dicyano-1,3-dithiole (**1**) reacts with lithium *n*-butoxide in *n*-butanol at reflux to give a new polymer with a conjugated backbone structure.

Previously available as a minor reaction byproduct,[2] **1** was synthesized in the present work from the known diester[3] by conversion to a bis-amide, mp 248−249 °C (dec), using aqueous NH_3. The amide was reacted with $POCl_3$ in pyridine to give **1**, a red-orange solid, mp 146−147 °C, completely characterized by infrared, ^{1}H, and ^{13}C NMR spectra, mass spectrum, and elemental analysis. In tetrahydrofuran (THF) solution **1** exhibits the following electronic spectrum: λ_{max}, 460 nm (log ϵ = 3.24). The fluorescence spectrum of **1** in the same solvent exhibits a maximum at 530 nm when excited with 460 nm light.

In refluxing *n*-butanol, **1** and *n*-BuOLi react over 2−3 h to give a dark blue solution from which a blue-black amorphous (by X-ray powder diffraction) solid **2** is isolated, after hydrolytic workup in chloroform and 10% HCl, in 53% yield; mp (capillary) 170 °C (dec). In the absence of butoxide, **1** is recovered unchanged from refluxing *n*-butanol. From the broad resonances of ^{1}H NMR and molecular weight estimation (weight-average MW 14 000−60 000 (GPC, versus polystyrene standards), $M_w/M_n = 2.01$), **2** is found to be polymeric, and its color and electronic spectrum in THF solution (λ_{max} 530−550 nm, tailing past 1000 nm) indicate a conjugated backbone. The absorption spectrum of **2** in THF is shown in Figure 1. Absorption spectra of **2** in dimethylformamide or dimethyl sulfoxide give broad maxima at 575−580 nm, with shoulders at 630 and 850 nm, with tailing past 1000 nm. It is not likely that the long absorption tail is due to scattering from insoluble polymer. Solutions were filtered before spectra were recorded, and in the solutions used for spectra, no precipitates formed on standing for times in excess of a month. Similar polymers were isolated from reaction of **1** with sodium pentoxide in refluxing *n*-pentanol and in refluxing (dimethylamino)-2-propanol.

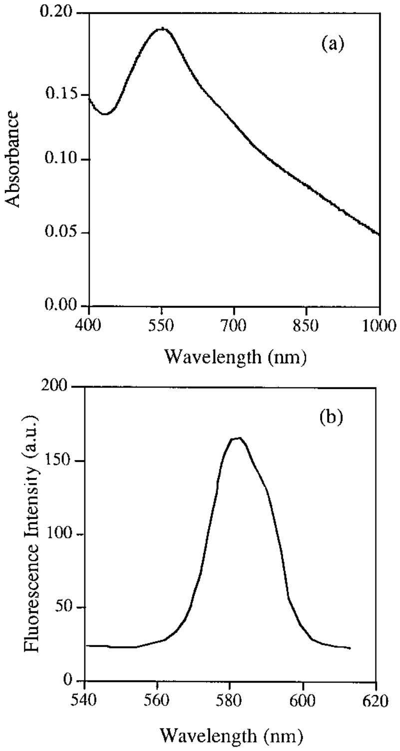

Figure 1. (a) Electronic absorption spectrum of **2** in THF solution (concentration 24 mg/L). (b) Fluorescence spectrum of **2** in THF solution.

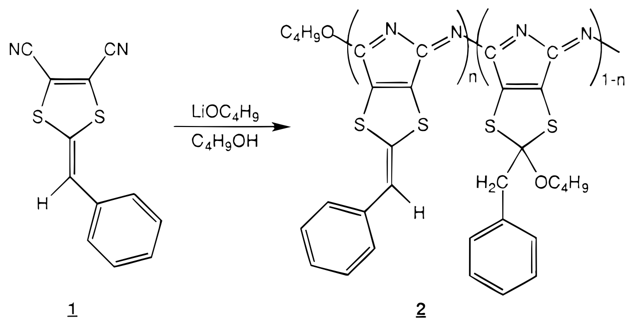

Figure 2. Polymerization of 2-benzylidene-4,5-dicyano-1,3-dithiole (**1**); *n* ~ 0.5.

An approximate structure for **2**, depicted in Figure 2, is proposed on the basis of elemental analysis, IR, and ^{1}H and ^{13}C NMR spectra. The atomic ratio of S:N is unity and indicates the preservation of the 1,3-dithiole ring during the polymerization. The absence of a −CN stretch in the IR spectrum and lack of a −CN resonance near 115 ppm in the ^{13}C NMR spectrum, along with the intense visible and near-infrared electronic spectrum, suggest a conjugated backbone structure formed by cyclopolymerization across the dicyanoalkene moiety. Support for this proposal follows from the observation of ^{13}C resonances between 165 and 175 ppm assigned to the backbone carbons for the structure in Figure 2. These resonances are not readily observed, and typically 20 000−50 000 scans were required for their detection. Resonances for similar carbons are found in this range in phthalocyanines and diiminoisoindolines,[4] the carbons in polyazines[5] are found at 155−161 ppm, and the quinonediimine carbons in insulating polyaniline are observed[6] at approximately 160 ppm. The position of the nonterminal *n*-butoxy group in **2** is suggested by elemental analysis and the decrease of the vinylic proton resonance near δ 6.7 ppm.

Polymers with backbone structures similar to that indicated for **2** have been previously suggested[7] for materials obtained from diphenylmaleonitrile, succinonitrile, and phthalonitrile. Phthalonitrile was reported in a patent[8] to react with sodium methoxide in methanol to lead to polyisoindoline, but only phthalocyanine was

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obtained by us in such experiments. An analogous structure was also suggested for polymers obtained from reaction of bis(3″,4″-dicyanophenoxy)-4,4′-biphenyl with diamines.[9] To the best of our knowledge, the present work is the first to support such a structure with ^{13}C NMR evidence.

A spin-coated film of **2** from DMF has a broad absorption maximum at 578 nm, also tailing past 1000 nm. The film maximum is red-shifted compared to the THF solution spectrum of the same sample, suggesting interchain interactions. The absorption maxima of **2** in both solution and the solid state are at wavelengths shorter than those reported for a variety of cyclotetramers. These are typically found at 660−700 nm.[1] This situation implies that the number of repeat units in near-planar conjugation is less than 4. We note that cyclotrimers of phthalonitrile with boron in the center of the ring, known as subphthalocyanines, have absorption maxima near 570 nm.[10] The absorption edge for partially crystalline or amorphous conjugated polymers is typically associated with a valence band-to-conduction band transition.[11] The suggestion here that less than four repeat units contribute to the absorption maximum at 550−580 nm implies a far more localized situation for **2** and the possibility of a coiled or helical chain conformation.

Thermogravimetric analysis data indicate that the material experiences a 15% weight loss at 160 °C and a further 20% weight loss at 275 °C. The fluorescence spectrum of **2** in THF solution, shown in Figure 1b, exhibits an intense, relatively narrow emission maximum at 588 nm when excited with 460 nm light. The fluorescence spectra of thin films spin-coated from DMF exhibit similar emissions. Films cast from DMF show dc conductivities in the range 5.5×10^{-6}−7.5×10^{-7} (ohm·cm)$^{-1}$. This range is comparable to that found in undoped metal phthalocyanine polymers.[12] When the film with the larger conductivity is exposed to iodine vapor, the conductivity increases to 1.1×10^{-4} (ohm·cm)$^{-1}$.

In summary, we have observed an unexpected polymerization of **1** from reaction with alkoxides in alcohols. At this time, we defer a mechanistic discussion of possible reasons that **1** undergoes polymerization and not cyclotetramerization. The structure proposed for the polymer **2** involves a conjugated backbone structure and is deduced from spectral and elemental analysis data. Further studies of chemical, optical, and electronic processes in **2** and the synthesis of related polymers are in progress.

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