[2.2]Paracyclophanes incorporated within poly(3-butylthiophene): synthesis and photoelectrical properties

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The synthesis and photoelectrical properties of [2.2]paracyclophanes, containing conjugated acetylenic triple bonds in the linear side-chain, are described. These compounds were incorporated as an electroactive component within a conductive polymer, *i.e.* poly(3-butylthiophene). The blend showed a photoelectrical response higher than that of the neat polymer. Surprisingly, it was found that the application of an electric bias during the preparation of the blend led to an increase in the photocurrent.

Introduction

Organic oligomers and polymers hold great promise for the widely applicable design and fabrication of optoelectronic devices.[1] In particular, thiophene oligomers and polymers have received great attention, mainly because of their photo-induced charge-transport properties.[2–4]

However, the favourable transport characteristics that are demonstrated in molecular systems are not adaptable to the polycrystalline films of many organic semiconductors; in fact, they are expected to satisfy specific criteria relating to both the structure of the material and the orientation of the molecules, since the most efficient charge transport occurs along the direction of intermolecular π–π stacking. In this regard, it was previously reported[5] that vacuum deposition at 60–80 °C affords highly textured alkyl-substituted and unsubstituted oligothiophenes films. These considerations suggest the combination of conductive polythiophenes with molecular systems characterized by extended π-conjugation.

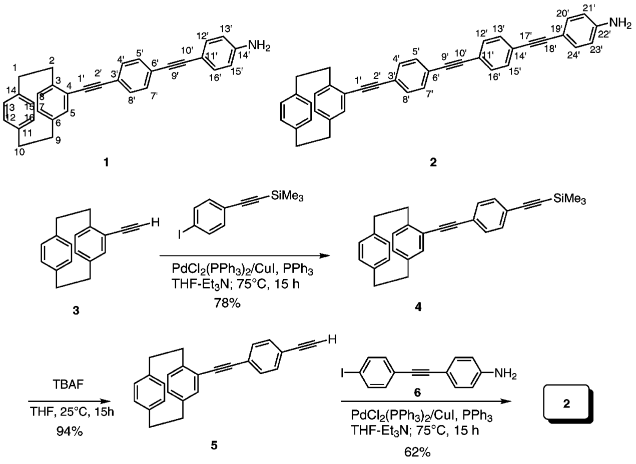
In this paper we report the synthesis and photoelectrical properties of two [2.2]paracyclophane-derivatives, **1** and **2** (Scheme 1), bearing conjugated alkyne units in the linear side-chain. Cyclophanes display an excellent π-conjugation[6] and, in combination with photoexcited electron donors such as polythiophenes, are expected to be beneficial for the testing of new paradigms in charge transfer management. It must be pointed out that [2.2]paracyclophanes have already been used as a framework to construct π-systems of interest because of their photophysical properties.[7]

In view of the aforementioned issues, it is of interest the study of the photoelectrical properties of blends of conducting poly(3-butylthiophene) (P3BT) with [2.2]paracyclophane derivatives **1** and **2**.

Results and discussion

[2.2]Paracyclophane derivative **1** (Scheme 1) has been prepared according to a previously reported procedure.[8] An outline of the synthetic steps used to prepare the [2.2]paracyclophane derivative **2** is given in Scheme 1; the synthesis being based on an iterative Pd/Cu-catalyzed Sonogashira reaction.[9] Coupling between 4-ethynyl[2.2]paracyclophane (**3**)[8,10] and 4-(iodophenylethynyl)trimethylsilane, followed by removal of the trimethylsilyl group using tetrabutylammonium fluoride (TBAF), led to aryldiethynylcyclophane **5**. Subsequent coupling of **5** with **6**[11] gave **2** in 46% overall yield. The structure of this compound and those of the related intermediates were assigned by extensive ^{1}H and ^{13}C NMR investigations, especially $^{1}H\{^{1}H\}$ NOE experiments and long-range hetero-correlations.

The typical photoelectrical response of **1** and **2** thin films to on/off light illumination cycles in air is shown in Fig. 1. The main feature of interest in the photoelectrical temporal behavior is the fast growth/decay of the photocurrent in response to the on/off illumination step, together with an enhanced increase of conductivity for **2** under illumination (Fig. 1a).



Scheme 1 Synthesis of the cyclophane derivative **2**.

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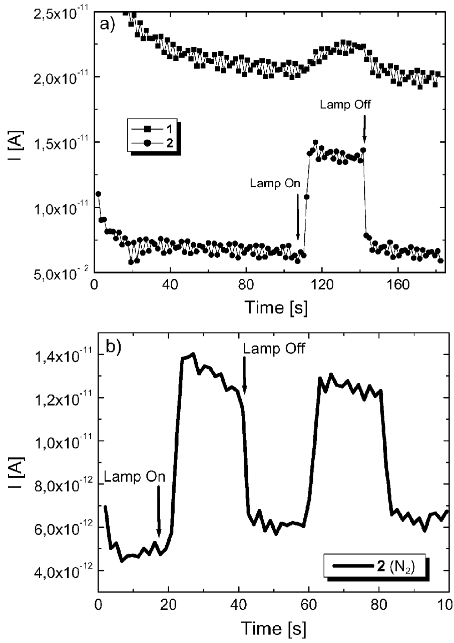


Fig. 1 (a) Evolution of the **1** and **2** film current during light-on and light-off steps (the arrows indicate light-on and light-off events) in air. (b) Evolution of the **2** film current during light-on and light-off steps (the arrows indicate light-on and light-off events) in a nitrogen atmosphere.

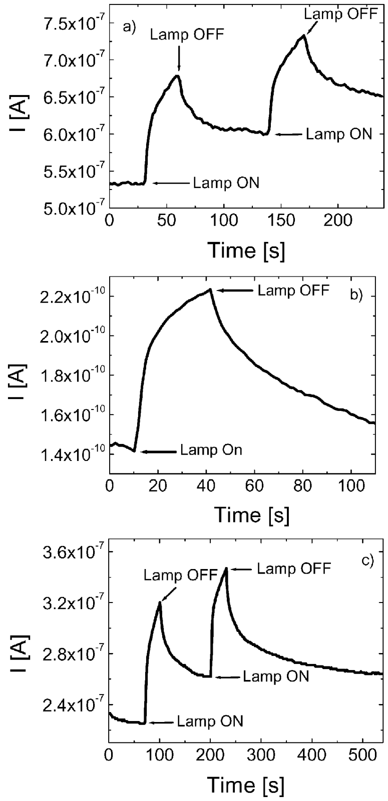


Fig. 2 Evolution of the (a) P3BT, (b) P3BT/**1** and (c) P3BT/**2** film current during light-on and light-off steps in a nitrogen atmosphere.

Moreover, it is evident that the photoelectrical response measured in a nitrogen atmosphere for sample **2** (Fig. 1b) is similar to that observed in air, with an evident photocurrent stability when exposed to several on/off cycles.

The current of P3BT, and those of P3BT/**1** and P3BT/**2** blends, were monitored as a function of the time as the light was switched on and off. Analysing the diagrams shown in Fig. 2 indicates that changes of the conductance under illumination of the neat polymer (Fig. 2a) was lower than that of the blends (Fig. 2b and 2c). Moreover, the diagrams show that whereas the on and off currents of the P3BT/**1** blend are markedly lower than that with neat polymer, those of P3BT/**2** are slightly lower.

In this regard, we found that the overall conductivity and three-dimensional architecture are guided by the application of a potential during the evaporation process. This phenomenon may be attributed to the prominent push–pull polarizable structure of compounds **1** and **2**, which are highly π-conjugated systems consisting of phenylene rings, acetylenic triple bonds and a [2.2]paracyclophane framework. Under the conditions of an external electric field, these compounds could undergo changes to their final molecular architectures and the conductivity of their blends. The current–voltage (*I*/*V*) characteristics of **2**, P3BT and P3BT/**2** films (Fig. 3a) have been exploited. A comparative analysis of the electrical response and behavior obtained under stringently identical conditions revealed interesting similarities and differences between the neat polymer and the blend. The first observation is that all of the systems obtained by electric field-assisted evaporation exhibit a higher conductivity. The differences in the conductivity and photoresponse of the P3BT/**2** blend (Fig. 3b), compared to other systems, are that the on and off currents of the blend increased and exhibited total recovery when the light was switched off. The inset of Fig. 3b shows that, even if the dark current of **2** is much higher than that in the case of **2** prepared by simple drop casting without electric bias, the photoelectrical response of **2** prepared is less than 5%.

Next, a critical question arises as to the origin of the "switch" in charge carrier mobility, ongoing from the P3BT/**2** blend deposited without electric bias to the P3BT/**2** with electric bias.

A possible mechanism could be related to a less favorable molecular alignment than the corresponding blend when deposited under an electric field. As the voltage is applied, the net molecular orientation and crystallite size become more favorable for charge transport, and consequently the mobility increases. Indeed, higher magnification scanning electron micrographs (SEMs) of a P3BT/**2** film deposited without electric bias exhibits the presence of isolated features (Fig. 4a). With such discontinuities, this film morphology is much less favorable for efficient charge transport than is the morphology seen for a P3BT/**2** film grown with a voltage of 20 V (Fig. 4b), where the onset of grain coalescence is evident.

Experimental

General remarks

Melting points were determined on a Büchi melting point apparatus and are uncorrected. Adsorption chromatography

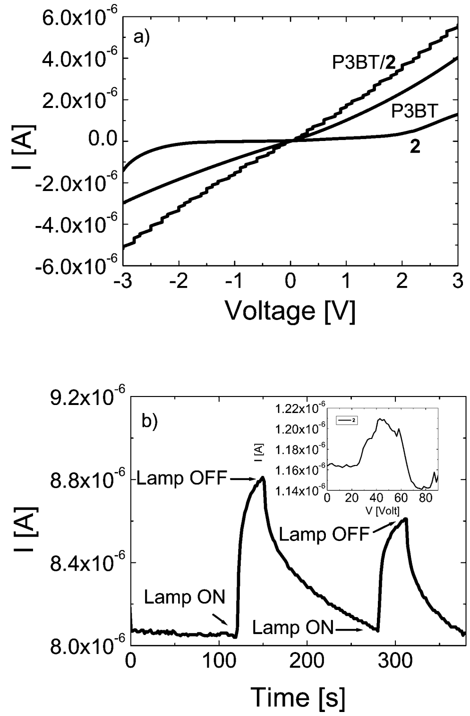


Fig. 3 (a) I/V characteristics of **2**, P3BT and P3BT/**2** films obtained under evaporation with a voltage of +20 V. (b) Evolution of the current under light-on and light-off steps in a nitrogen atmosphere for the P3BT/**2** film deposited at +20 V. The inset shows the evolution of the current during light-on and light-off steps in a nitrogen atmosphere for a film of **2** deposited at +20 V.

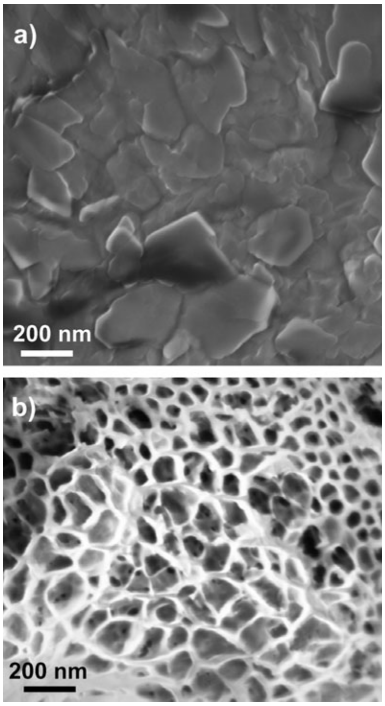


Fig. 4 SEMs of P3BT/**2** films deposited at (a) 0 V and (b) +20 V (scale bar 200 nm).

was carried out on Riedel de Haën silica gel (32–63 μm; 230–400 mesh ASTM). UV-vis spectra were recorded on a Kontron Uvikon 923 spectrophotometer. NMR spectra were recorded on a Varian Associates VXR-400 multi-nuclear instrument (internal Me_4Si). Petroleum ether as a 40–60° boiling fraction was used. Poly(3-butylthiophene) was purchased from Sigma-Aldrich.

4-({*para*-[(trimethylsilyl)ethynyl]phenyl}ethynyl)[2.2]paracyclophane (4)

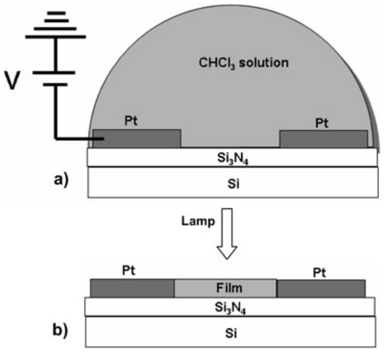
Dry THF (13 ml), 4-(iodophenylethynyl)trimethylsilane (0.41 g, 1.38 mmol), triphenylphosphine (0.037 g, 0.14 mmol), CuI (0.013 g, 0.07 mmol), $PdCl_2(PPh_3)_2$ (0.049 g, 0.07 mmol) and triethylamine (6 ml) were placed in a flask and de-gassed with Ar at 0 °C. 4-Ethynyl[2.2]paracyclophane (**3**) (0.25 g, 1.06 mmol) was then added and the mixture kept at 75 °C for 15 h. The solvent was then removed under reduced pressure and the residue chromatographed on silica gel (petroleum ether : chloroform = 4 : 1) to give compound **4** (78%) as white crystals. mp 98–99 °C (MeOH). ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 9 H, $SiMe_3$), 2.89 (ddd, 1 H, J = 13.1, 10.5, 5.5 Hz, H-2), 2.95–3.16 (m, 5 H, H-1, Hs-9, Hs-10), 3.24 (m, 1 H, H-1), 3.64 (ddd, 1 H, J = 13.1, 10.2, 2.7 Hz, H-2), 6.47–6.55 (m, 5 H, H-7, H-8, H-12, H-13, H-16), 6.58 (d, 1 H, J = 1.8 Hz, H-5), 6.98 (dd, 1 H, J = 7.7, 1.8 Hz, H-15) and 7.45–7.52 (m, 4 H, H-4′, H-5′, H-7′, H-8′). ^{13}C NMR ($CDCl_3$) δ 0.1 ($SiMe_3$), 34.6, 34.7, 35.4, 35.7 (C-1, C-2, C-9, C-10), 91.9 (C-1′), 92.7 (C-2′), 96.4 (C-10′), 105.0 (C-9′), 123.0, 124.2 (C-3′, C-6), 124.8 (C-4), 130.3 (C-15), 131.4 (C-4′, C-8′), 132.2 (C-5′, C-7′), 132.7, 132.9, 133.2 (C-12, C-13, C-16), 133.5 (C-7), 134.1 (C-8), 137.2 (C-5), 139.5 (C-11), 139.6(C-6), 140.0 (C-14) and 142.7 (C-3). UV-vis ($CHCl_3$) [λ_{max}/nm (log ε)]: 322 (4.47). Anal. calc. for $C_{29}H_{28}Si$: C, 86.08; H, 6.97. Found: C, 86.19; H, 6.95%.

4-[(*para*-ethynylphenyl)ethynyl][2.2]paracyclophane (5)

To a solution of compound **4** (0.35 g, 0.88 mmol) in dry THF (5 ml) was added tetrabutylammonium fluoride (0.88 ml). The mixture was kept under N_2 and magnetically stirred at 25 °C for 15 h. The solvent was then removed *in vacuo*. The residue was chromatographed on silica gel (petroleum ether : chloroform = 8 : 1) to obtain compound **5** (94%) as white crystals. mp 99–100 °C (MeOH). ^{1}H NMR ($CDCl_3$) δ 2.91 (ddd, 1 H, J = 13.2, 10.4, 5.3 Hz, H-2), 2.96–3.17 (m, 5 H, H-1, Hs-9, Hs-10), 3.18 (s, 1 H, H-10′), 3.24 (m, 1 H, H-1), 3.65 (ddd, 1 H, J = 13.2, 10.2, 2.7 Hz, H-2), 6.47–6.55 (m, 5 H, H-7, H-8, H-12, H-13, H-16), 6.58 (d, 1 H, J = 1.9 Hz, H-5), 6.98 (dd, 1 H, J = 7.8, 1.7 Hz, H-15) and 7.49–7.55 (m, 4 H, H-4′, H-5′, H-7′, H-8′). ^{13}C NMR ($CDCl_3$) δ 34.6, 34.7, 35.3, 35.7 (C-1, C-2, C-9, C-10), 79.1 (C-10′), 83.5 (C-9′), 92.0 (C-1′), 92.5 (C-2′), 121.9 (C-6′), 124.6 (C-3′), 124.7 (C-4), 130.4 (C-15), 131.5 (C-4′, C-8′), 132.3 (C-5′, C-7′), 132.7, 132.9, 133.5 (C-12, C-13, C-16), 133.3 (C-7), 134.2 (C-8), 139.6 (C-11), 139.7 (C-6), 137.2 (C-5), 140.0 (C-14) and 142.8 (C-3). UV-vis ($CHCl_3$) [λ_{max}/nm (log ε)]: 319 (4.32). Anal. calc. for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.80; H, 6.07%.

para-{[*para*-({*para*-[[2.2]paracyclophan-4-ylethynyl]phenyl}ethynyl) phenyl]ethynyl}aniline (2)

Dry THF (6 ml), iodide compound **6** (0.13 g, 0.42 mmol), triphenylphosphine (0.021 g, 0.08 mmol), CuI (0.008 g, 0.04



Scheme 2 Schematic illustration of the voltage-assisted dewetting procedure used for depositing thin films of compounds **1**, **2** and P3BT/PCP blends: (a) A drop of a dilute solution was placed onto biased Pt electrodes set on a Si_3N_4/Si substrate. (b) After solvent evaporation, the photoconductivity of the films was measured between the electrodes.

mmol), $PdCl_2(PPh_3)_2$ (0.028 g, 0.04 mmol), triethylamine (2.5 ml) and compound **5** (0.2 g, 0.6 mmol) were placed in a flask and de-gassed with Ar. The mixture was kept at 75 °C for 15 h. The solvent was then removed under reduced pressure and the residue chromatographed on silica gel (petroleum ether : chloroform = 2 : 1) to give compound **2** (62%) as yellow crystals. mp 213–214 °C (MeOH). ^1H NMR ($CDCl_3$) δ 2.91 (ddd, 1 H, $J = 13.1, 10.3, 5.3$ Hz, H-2), 2.97–3.16 (m, 5 H, H-1, Hs-9, Hs-10), 3.26 (m, 1 H, H-1), 3.66 (ddd, 1 H, $J = 13.1, 10.4, 2.7$ Hz, H-2), 6.48–6.56 (m, 5 H, H-7, H-8, H-12, H-13, H-16), 6.59 (d, 1 H, $J = 8.1$ Hz, H-5), 6.64 (m, 1 H, H-20′ or H-24′), 7.0 (dd, 1 H, $J = 7.8, 1.8$ Hz, H-15), 7.34 (m, 1 H, H-20′ or H-24′) and 7.46–7.52 (m, 4 H, H-12′, H-13′, H-15′, H-16′). ^{13}C NMR ($CDCl_3$) δ 34.6, 34.8, 35.4, 35.7 (C-1, C-2, C-9, C-10), 87.4 (C-17′), 91.0, 91.3 (C-9′, C-10′), 92.0 (C-11), 92.6 (C-18′), 92.8 (C-2′), 112.6 (C-19′), 115.0 (C-21′, C-23′), 122.4, 123.0, 124.0, 124.3 (C-3′, C-6′, C-11′, C-14′), 124.9 (C-4), 130.4 (C-15), 131.5, 131.8 (C-12′, C-13′, C-15′, C-16′), 131.6, 131.7 (C-4′, C-5′, C-7′, C-8′), 132.7, 132.9, 133.3 (C-12, C-13, C-16), 133.3 (C-20′, C-24′), 133.5 (C-7), 134.1 (C-8), 137.2 (C-5), 139.6 (C-11), 139.7 (C-6), 140.0 (C-14), 142.8 (C-3) and 147.1 (C-22′). UV-vis ($CHCl_3$) [λ_{max}/nm (log ε)]: 355 (4.83). Anal. calc. for $C_{40}H_{29}N$: C, 91.74; H, 5.58; N, 2.67. Found: C, 91.50; H, 5.59; N, 2.69%.

Films of **1** and **2** were prepared by sonication of a *N*,*N*-dimethylformamide (DMF) solution (10 mg ml^{-1}), which was then allowed to dry *in vacuo* (10^{-3} Torr). For the preparation of the blends, P3BT (1 mg) was dissolved in 1 ml of $CHCl_3$. Compound **1** or **2** was then added to the P3BT solution (10 : 1 w/w). The PCP/P3BT blends were then sonicated for 2 h.

Samples for the photoelectrical study were prepared by depositing a drop (0.4 μl) of the solutions of compounds **1**, **2** and the PCP/P3BT blends, and leaving the solutions to evaporate in a nitrogen stream while applying a fixed bias voltage (0 V and +20 V) (Scheme 2) to platinum patterned electrodes (electrode distance 3 μm), set on a Si_3N_4/Si substrate. Photoelectrical measurements were obtained for the films over several on/off light illumination cycles. The conductivity of the films was monitored as a function of exposure time through a solar simulator under air mass (AM) 0 conditions (Xenon lamp) with an input power of 300 mW cm^{-2}.

For the dark conductivity measurements, a Keithly 4200 source measuring unit was used for taking the *I*/*V* characteristics.

The morphologies of the obtained structures were then characterized by field emission scanning electron microscopy.

Conclusions

The synthesis of a new [2.2]paracyclophane **2** has been described. These studies show how linearly-functionalized [2.2]paracyclophanes **1** and **2**, interacting with poly(3-butylthiophene), are largely responsible for the generation of charge carriers in this semiconducting conjugated polymer under illumination. We have also found the possibility of modifying the morphology and conductivity of the blends by applying an electric bias during the evaporation of the solvent. Such a simple deposition method provides the means for an evident trend towards the facile preparation of photoactive materials of high current interest. This result may suggest that this methodology provides an orientation of the molecules along the direction of intermolecular π–π stacking. Verifying this evidence will remain a challenging task in our future work.

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