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Antibatic photovoltaic response in zinc-porphyrin-linked oligothiophenes

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Abstract

We present the synthesis of oligohexylthiophenes starting from 3, 4′-dihexyl-[2, 2′]bithiophene (**1**) 3, 4′, 4″, 4‴-tetrahexyl-[2, 2′; 5′, 2″; 5″, 2‴]quarterthiophene (**2**), 3, 4′, 4″, 4‴, 4⁗, 4′′′′′, 4′′′′′′, 4′′′′′′′-octahexyl-[2, 2′; 5′, 2″; 5″, 2‴; 5‴, 2⁗; 5⁗, 2′′′′′; 5′′′′′, 2′′′′′′; 5′′′′′′, 2′′′′′′′]octithiophene (**3**) and 3, 4′, 4″, 4‴, 4⁗, 4′′′′′, 4′′′′′′, 4′′′′′′′, 4′′′′′′′′, 4′′′′′′′′, 4′′′′′′′′′, 4′′′′′′′′′, 4′′′′′′′′′′, 4′′′′′′′′′′, 4′′′′′′′′′′′, 4′′′′′′′′′′′-hexadecahexyl-[2, 2′; 5′, 2″; 5″, 2‴; 5‴, 2⁗; 5⁗, 2′′′′′; 5′′′′′, 2′′′′′′; 5′′′′′′, 2′′′′′′′; 5′′′′′′′, 2′′′′′′′′; 5′′′′′′′′, 2′′′′′′′′′; 5′′′′′′′′′, 2′′′′′′′′′′; 5′′′′′′′′′′, 2′′′′′′′′′′′; 5′′′′′′′′′′′, 2′′′′′′′′′′′′]hexadecathiophene (**4**) by regioselective bromination using *N*-bromosuccinimide and regioselective lithiation using lithiumdiisopropylamide in ethylbenzene/THF/heptane followed by reaction with trimethylstannylchloride and subsequent palladium catalysed Stille coupling. We further synthesised 5,15-bis(3, 4′, 4″, 4‴, 4⁗, 4′′′′′, 4′′′′′′, 4′′′′′′′-octahexyl-[2, 2′; 5′, 2″; 5″, 2‴; 5‴, 2⁗; 5⁗, 2′′′′′; 5′′′′′, 2′′′′′′; 5′′′′′′, 2′′′′′′′]octithiophene-5-yl)-10, 20-bis(3, 5-ditertbutylphenyl)zinc(II)porphyrin (**5**) from trimethyl(3, 4′, 4″, 4‴, 4⁗, 4′′′′′, 4′′′′′′, 4′′′′′′′-Octahexyl-[2, 2′; 5′, 2″; 5″, 2‴; 5‴, 2⁗; 5⁗, 2′′′′′; 5′′′′′, 2′′′′′′; 5′′′′′′, 2′′′′′′′]octithiophene-5-yl)stannane (**3-SnMe$_3$**) and 5, 15-dibromo-10, 20-bis(3, 5-ditertbutylphenyl)zinc(II)porphyrin (**6**) by Stille coupling. All the products were characterised by size exclusion chromatography (SEC), NMR, MALDI-TOF and elemental analysis and purified by preparative SEC before subjecting them to photophysical studies. UV–vis and emission spectroscopy were used to determine quantum yields and energy transfer. The photon balance was established and used to rationalise the photovoltaic behaviour of **4** and **5**. While **4** gave rise to photovoltaic devices giving a moderate photovoltaic response that was symbatic with the absorption spectrum, **5** showed a photovoltaic response

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that was antibatic with a part of the absorption spectrum of the zinc-porphyrin constituent. We ascribe this behaviour to efficient internal conversion of the energy absorbed by (and the energy transferred to) the zinc-porphyrin constituent.

Keywords: Organic photovoltaics; Antibatic response; Oligothiophenes; Porphyrins; Dye-linked homopolymers

1. Introduction

Organic photovoltaics [1] based on polymer materials have been an active field of research for the past 10 years. Early reports were based on simple homopolymers sandwiched between two electrodes having different workfunctions. The efficiencies obtained with such devices were of the order of 0.001% giving short circuit current densities in the order of $10\,\mu A\,cm^{-2}$. [2] A major advancement was made with the introduction of fullerenes and their derivatives as efficient electron conductors. A layer of C_{60} sublimed onto the conjugated polymer film before evaporation of the final electrode giving a heterojunction improved the efficiency by 1–2 orders of magnitude. [3] The final state of the art was provided by mixing a soluble derivative of C_{60} with the conjugated polymer material giving a bulk heterojunction yielding current densities of a few $mA\,cm^{-2}$ and corresponding efficiencies of 2–5%. [4] The reason for the success of applying fullerenes is ascribed to their high electron affinity and the provision of efficient electronic conduction paths. Most conjugated polymer materials are efficient hole conductors but poor electron conductors. The introduction of fullerenes and their derivatives thus efficiently solves this problem. There have been few reports on high-efficiency polymer-based photovoltaics that do not include fullerenes. [5] The crucial point in the process of photovoltaic energy conversion is the efficient separation of charge carriers and while the fullerene solution does this elegantly there is a large interest in developing alternative systems that by deliberate design allow for efficient light harvesting, energy transfer and charge carrier separation either by appropriate injection at electrodes or by separation in the bulk via a molecular cascade. We believe that the appropriate connection of molecular domains with individual function will enable the design and organisation of an efficient macromolecular photovoltaic. We recently demonstrated the design of a two-domain molecule with efficient internal energy transfer properties and the ability to organise at surfaces giving rise to a 100-fold increase in the photovoltaic response as compared to the homopolymer domain on its own.

In this paper we present the synthesis, photophysical and photovoltaic properties of a three-domain structure based on well-defined oligothiophenes and a zinc-porphyrin.

2. Experimental

Compounds **1**, **2** and **3** were prepared as described below and had analytical data in agreement with Ref. [6] unless otherwise stated. Compound **6** was prepared as