



Charge recombination losses in thiophene-substituted porphyrin dye-sensitized solar cells



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ABSTRACT

Two new porphyrins that incorporate thiophene substituents as spacers between the conjugated porphyrin core and the anchoring cyanoacrylate group have been synthesised. The two dyes differ in the number of thiophene bridges; porphyrin **1a** has only one thiophene group and porphyrin **1b** has two thiophene rings connected by a double bond. The measured light-to-energy conversion efficiencies in **1a** and **1b** were assessed using two different electrolytes, LP1 and LP2, which differ in the presence of *tert*-butyl pyridine in LP1. An efficiency of 6% under standard measurement conditions has been achieved for **1a** + LP1. However, for porphyrin **1b** the use of electrolyte LP1 led to lower efficiencies and a value of approximately 4% was obtained. The differences between the two types of solar cells and the electrolytes have been studied in-depth using photo-induced time-resolved techniques such as CE (Charge Extraction) and TPV (Transient PhotoVoltage).

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1. Introduction

Mesoporous TiO₂ dye-sensitized photo-electrochemical solar cells, also known as Grätzel solar cells, have achieved efficiencies as high as 12% under sun-simulated conditions [1]. Recently, the first application of Building Integrated Photo-Voltaic technology (BIPV) was demonstrated and this showed the potential of a colourful and transparent solar cell technology [2]. In this type of solar cell the properties of the dye, such as colour, molecular extinction coefficient and robustness under illumination, are of utmost importance. Among the examples of dyes published in the literature [3] for Grätzel solar cells, porphyrins [4] have pleasant colours [5], excellent molecular extinction coefficients [6,7] and good robustness [8,9]. Moreover, based on the work of Yella and co-workers [1], efficiencies that surpass the values obtained with ruthenium sensitizers have been achieved. However, these remarkable

asymmetric porphyrins, which are based on D- π -A molecular structures (Donor- π -Acceptor), are difficult to synthesise and scale up to kilogram quantities and this represents a major drawback for their use in solar modules for BIPV.

Several groups, including our own, have proposed other types of porphyrins [10–14] that are easier to synthesise and purify and show efficiencies of around 5–7% under sun-simulated light irradiation conditions [15–20].

In the work described here we synthesised two novel Zn-porphyrin-based structures (Fig. 1) that contain thiophene moieties as spacers between the Zn-porphyrin and the anchoring cyanoacrylic acid. The electronic properties of the compounds were studied and they were also evaluated as components in solar cells. The novel A₃B Zn-porphyrins are tri-substituted with triphenylamine groups (TPA) as secondary electron donors (D); the volume of the TPA groups also helps to diminish the natural tendency of porphyrins to aggregate, which in turn diminishes the antenna effect of the porphyrins.

The efficiencies of the solar cells in two different electrolytes are discussed and compared in terms of charge density, as measured by the charge extraction technique, and device recombination kinetics under working conditions, as measured using the photo-induced transient photovoltage. The aim of the study was to demonstrate

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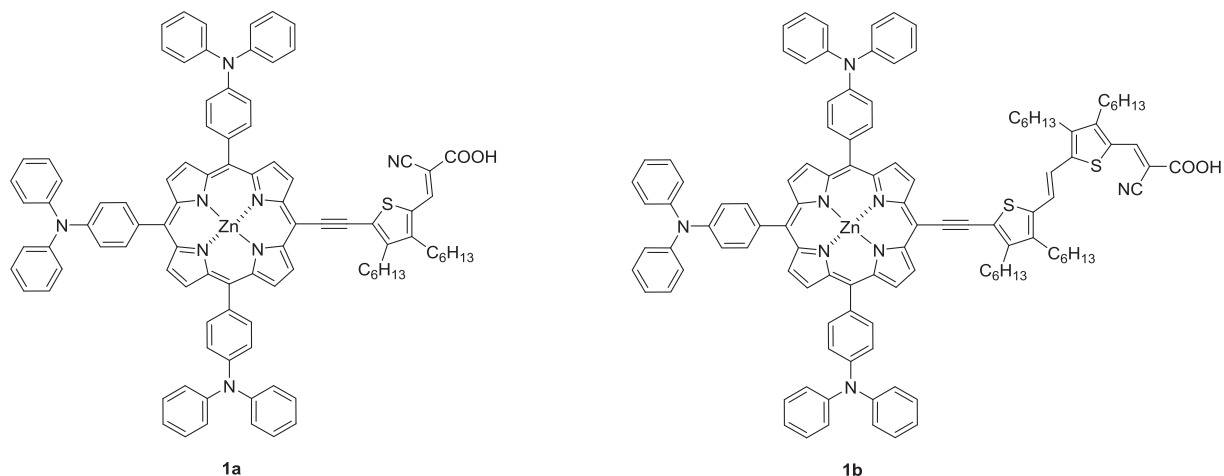


Fig. 1. Structures of dyes **1a** and **1b**.

that the electrolyte interaction with the dye plays a critical role and this could have a different effect on two porphyrins that differ only in the length of the conjugated thiophene-based system used in the π -conjugated molecular bridge.

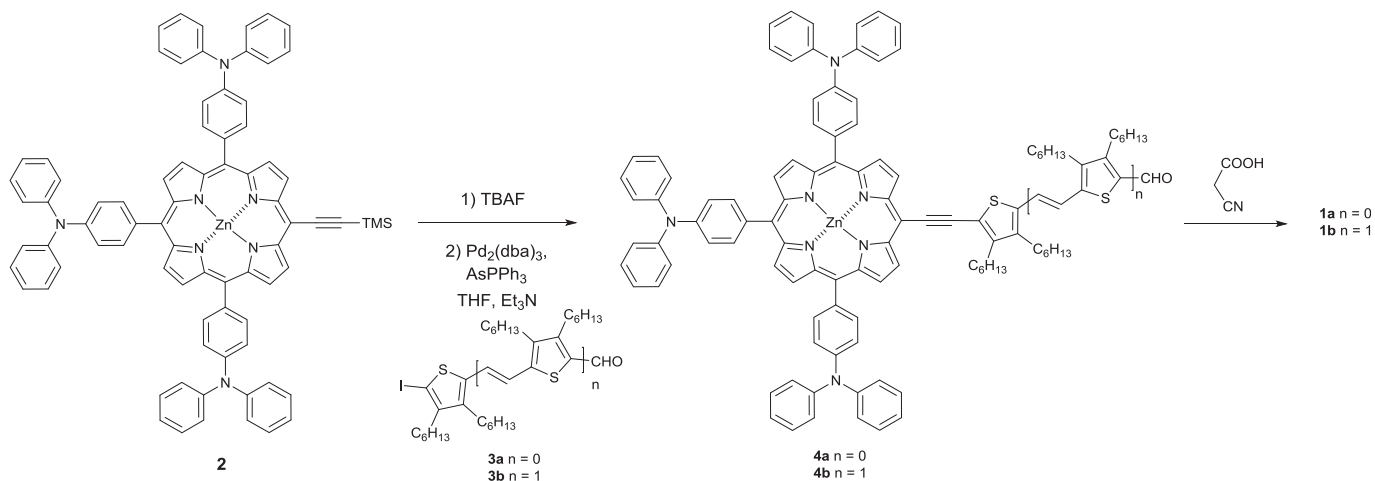
2. Results and discussion

The synthesis of dyes **1a,b** was performed starting from trimethylsilylporphyrin **2** (Scheme 1) [10,21]. Firstly, the trimethylsilyl group was quantitatively removed by reaction with TBAF and this was followed by copper-free Pd-catalysed Sonogashira coupling [22] with 2-iodothiophene derivatives **3a–b** [23,24]. Under these conditions, the reaction proceeded smoothly to afford aldehydes **4a,b** in 83% and 80% yield, respectively. Subsequent Knoevenagel condensation of **4a,b** with cyanoacetic acid, using piperidine as base, yielded **1a,b** in 89% and 82% yields, respectively, after purification by column chromatography (silica gel, chloroform: methanol 10:1). All new compounds were fully characterised by FT-IR, ^1H and ^{13}C NMR spectroscopies and by MALDI-TOF mass spectrometry (see experimental section and ESI). It should be noted that in **4b** and **1b** the *trans* character of the double bond was confirmed by the coupling constant of around 15 Hz between the two vinyl protons in the ^1H NMR spectra. Compounds **1a,b** were reasonably soluble in several common organic solvents, such as CH_2Cl_2 , CHCl_3 and THF,

and this allowed the preparation of DSSCs. The thermal stabilities of compounds **1a,b** were evaluated by thermogravimetric analysis (TGA) under nitrogen, with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. The decomposition temperatures (T_d) were estimated from the TGA plots as the temperature of the intercept of the leading edge of the weight loss curve. Under these conditions, compounds **1a** and **1b** display excellent thermal stability up to $200\text{ }^\circ\text{C}$ (Figs S17 and S18, ESI) and this makes them suitable for application in photovoltaic devices.

2.1. Optical properties

The optical properties of **1a,b** were studied by UV-Visible spectrophotometry in solution and both compounds exhibited a panchromatic absorption in the visible region. A solution of **1a** in THF exhibited the characteristic absorption pattern of a Zn-chelated porphyrin, with an intense Soret band (B band) at 471 nm ($\log \epsilon = 4.99$) and an intense intermolecular charge transfer (ICT) band at 662 nm ($\log \epsilon = 4.53$); between these bands, one of the Q bands was observed at 583 nm ($\log \epsilon = 3.93$). Extension of the conjugation on the bridge by the introduction of a new thienylenevinylene unit had a significant effect on the absorption spectrum of **1b**, leading to a panchromatic absorption as the Soret band was red-shifted to 460 nm ($\log \epsilon = 5.21$) and a new absorption band



Scheme 1. Synthetic route to dyes **1a** and **1b**.

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