Dyes and Pigments 112 (2015) 298–304

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis, photophysical and electrochemical properties of perylene dyes

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ARTICLE INFO

Article history:
Received 15 April 2014
Received in revised form
1 July 2014
Accepted 18 July 2014
Available online 29 July 2014

Keywords:
Perylene dyes
Alkyne bridge
Cyanoacetic group
Solar cells
ss-DSCs
Light harvesting materials

ABSTRACT

Perylene dyes comprising: (i) 4-alkoxyphenylamino moiety in the 9-position as a strong donating group, (ii) cyanoacrylic acid as electron acceptor and anchoring group and (iii) a triple bond as short and rigid linker between perylene core and the acceptor group have been successfully synthesized. Their photophysical (i.e. absorption and emission spectra, molar extinction coefficients, fluorescence quantum yields and lifetime measurements) and electrochemical properties were investigated. The dyes display intense absorption in the visible exhibit high molar absorption coefficients making them good light harvesting materials for ss-DSCs.

1. Introduction

Perylene derivatives have been widely applied in various optical devices due to their excellent photophysical properties (e.g. high absorption coefficient and high fluorescence quantum yield), charge transfer properties, as well as outstanding chemical, thermal and photochemical stability [1,2].

Perylene monoimides (PMI) or monoanhydrides (PMA) are being intensively investigated as sensitizers in dye-sensitized solar cells (DSCs) [3]. Keeping only one acceptor group, i.e. imide or anhydride, and introducing a donor group in the 9-position (such as diarylamine) proved to be important in order to obtain a favorable orbital partitioning strength and dipole moment of perylene compounds for DSCs. One way to control optical and electrochemical properties of perylenes dyes is achieved by functionalizing *peri* and *bay* positions of perylene core with different substituents. In a simplified view, the *peri* groups coarsely tune the spectroscopic and electrochemical properties whereas the *bay* functional groups provide an additional fine tuning [4–7]. To date, the PMA derivative with a bis (4-(2,4,4-trimethylamynopentan-2-yl)phenylamino in 9-position and phenylthio groups in 1 and 6 positions of perylene core has shown to be the highest efficient perylene sensitizer in DSCs with liquid electrolyte (iodide/tri-iodide redox couple), delivering an incident monochromatic photo-to-current conversion efficiency of 87% and yielding a power conversion efficiency of 6.8% (6 μm thick mesoporous TiO_2 film) under standard AM 1.5 solar conditions [8]. In comparison, the same sensitizer tested in solid-state DSC (ss-DSC) yield a power conversion efficiency of only 1.8% (1.8 μm thick mesoporous TiO_2 film), showing that sensitizer design needs to be adapted according to the cell type.

Based on the aforementioned, the key challenge is to obtain efficiencies that are comparable to that for the optimized I^-/I_3^-/volatile solvent cell by using a Hole Transport Material (HTM), which may be a solid-state material. However, the poor filling of the mesoporous semiconductor and short diffusion length of charge carriers in HTM have limited the mesoscopic titania layer to a thickness of 2–3 μm. To increase the amount of light harvesting by ss-DSCs, organic dyes with high molar extinction coefficients, broad absorption in visible spectrum and with suitable geometry for control of molecular orientation and arrangement on the TiO_2 surface are needed [9,10].

Here we report the design, synthesis and characterization of new perylene dyes (Scheme 1) comprising: (1) a 4-alkoxyphenylamino moiety in the 9-position as a strong donating group, (2) a cyanoacrylic acid as electron acceptor and anchoring group and (3) a triple bond as short and rigid linker between perylene core and the acceptor group. The photophysical and electrochemical properties of these dyes were investigated, and the

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http://dx.doi.org/10.1016/j.dyepig.2014.07.019
0143-7208/