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Synthesis, spectral and electrochemical properties of pyrimidine-containing dyes as photosensitizers for dye-sensitized solar cells

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ABSTRACT

Six novel donor–π–acceptor organic dyes bearing a pyrimidine as the anchoring group have been obtained in good yields by combination of the microwave-assisted Suzuki cross-coupling and nucleophilic aromatic substitution of hydrogen reactions. Their absorption, photoluminescence and electrochemical properties were fully investigated in detail. The infrared spectra of dyes adsorbed on TiO_2 indicate the formation of coordinate bonds between the pyrimidine ring of dyes and the Lewis acid sites (exposed Ti^{n+} cations) of the TiO_2 surface. This work demonstrates that the pyrimidine rings of dye sensitizers that form a coordinate bond with the Lewis acid site of a TiO_2 surface are promising candidates as the electron-withdrawing anchoring group. The data from quantum calculations show that all of the dyes are potentially good photosensitizers for dye-sensitized solar cells.

1. Introduction

During the last decade fluorescent organic molecules and polymers bearing π-conjugated triphenylamine or carbazole fragments have attracted the attention of chemists from both experimental and theoretical communities. Thanks to the presence of highly delocalized π-electronic systems these molecules have found wide applications in organic light-emitting diodes (OLEDs), nonlinear optics, dye-sensitized solar cells and field-effect transistors (FETs) [1–4].

Due to the global challenge for development of renewable energy sources, photovoltaic technologies cause a growing interest in the design of cells to convert the solar energy into electrical energy. Even though a multi-junction solar cell has been successfully obtained at the laboratory level with up to 40% conversion efficiency, a high production cost, toxicity and environmental problems are still barriers to use solar electricity in a large scale [5]. Considering the feasibility to develop a solar cell, organic molecules and polymers appear to be the most promising alternatives. Use of thin film technology resulted in development of dye-sensitized solar cells (DSSC) [3]. A typical DSSC construction involves a dye-adsorbed wide band gap oxide semiconductor (such as TiO_2), an electrolyte containing the I^-/I^{-3} redox couple, and a platinum counter electrode. In spite of considerable progress in the field of high-performance DSSCs with organic sensitizers, there is still a long way to go to achieve their large-scale production. In order to improve the efficiency of DSSCs, many chemists put their efforts to obtain highly efficient sensitizers. However, laboratory stage of development of dye-sensitizers used in DSSCs often invokes a trial-and-error approach which requires extensive synthetic studies and rather expensive materials processing, thus becoming a laborious and slow process. Fortunately, theoretical screening of potential organic dye-sensitizers by using quantum chemical calculations (such as TDDFT) appears to be a very promising approach to reduce

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the cost of research and development of effective dye-sensitizers [6]. Theoretical studies on the physical and chemical properties of dye-sensitizers are very important to understand the relationship between the structure and properties, thus enabling one to design new molecules for this purpose. To be useful for DSSC, a sensitizer is supposed to meet the following structural requirements: it has to contain an electron-donating part, a unit to adjust the absorption spectrum and an electron-acceptor part [3b,6].

Recently, the series of dipolar compounds containing a triarylene bridge were prepared by convenient methods and can be used as highly efficient dye sensors in organic solar cells. In their structures, either a triphenylamino (type **I**) or a carbazolo (type **II**) group was attached to a terminal of a mono- or diarylene bridge as an electron donor, while a cyanoacrylic acid moiety on the other end as an acceptor (Fig. 1) [7–11]. The a mono- or diarylene bridges consist of phenyl and/or thienyl groups linked together in a linear fashion. These compounds exhibited a high absorptivity in the UV/vis region of solar light. The DSSC devices fabricated by using these materials as dyes displayed remarkable solar-to-electric power conversion efficiency (η), typically in a range of 4–6%.

In addition, there are a number of fluorescent dyes (for examples see Fig. 2) with a pyridine ring as electron-withdrawing-injecting anchoring group [12–18]. These new sensitizers **IIIa**–**e** have been developed and their photovoltaic performances in DSSCs are investigated. The short-circuit photocurrent densities and solar energy-to-electricity conversion yields of DSSCs based on **IIIa,b** are greater than those for the conventional D–π–A dye sensitizers with a carboxyl group as the electron-withdrawing anchoring group. The IR spectra of **IIIa**–**e** adsorbed on TiO_2 indicate the formation of coordinate bonds between the pyridine ring of dyes **IIIa**–**e** and the Lewis acid sites (exposed Ti^{n+} cations) of the TiO_2 surface. These works demonstrate that the pyridine rings of D–π–A dye sensitizers that form a coordinate bond with the Lewis acid site of a TiO_2 surface are promising candidates as not only electron-withdrawing anchoring group but also electron-injecting group, rather than the carboxyl groups of the conventional D–π–A dye sensitizers that form an ester linkage with the Brønsted acid sites of the TiO_2 surface.

On the other hand, π-conjugated compounds bearing the pyrimidine fragment have been studied as promising candidates to obtain functional photoelectric materials owing to the intriguing structural and electronic properties of the pyrimidine ring [19].

Therefore, combinations of the pyrimidine fragment with triphenylamine or carbazole units are expected to give materials with excellent fluorescence properties. Indeed, elementary pyrimidine-triphenylamine **(IV)** and pyrimidine-carbazole **(V)** dyads have been obtained and used as luminescent materials, exhibiting good solvability, film forming, high stability, and quantum efficiency (Scheme 1) [20]. In addition, diphenyl-(4-pyrimidin-4-yl)-amine **(A)** was examined as a fluorescent ratiometric chemosensor for Hg^{2+} [21].

According to the above-mentioned points, we would like to present a facile and highly efficient method for the synthesis of a number of novel organic dyes of the following systematic molecular structure D–π–A [where A – acceptor, the pyrimidine unit as the anchoring group, D – a donating part, presented by triphenylamine or carbazole fragments, and π represents a thienyl and/or phenyl groups], which is based on combination of the Suzuki cross-coupling and nucleophilic aromatic substitution of hydrogen reactions (S_N^H) [22]. The electrochemical, UV–vis absorption and fluorescence properties of these compounds have also been elucidated. The time-dependent density functional theory (TDDFT) calculations were applied to shed a light on the nature of electron transitions between ground and exited states.

2. Experimental section

2.1. General information

All reagents and solvents were purchased from commercial sources and dried by using standard procedures before use. Tetrahydrofuran (THF) and H_2O for the microwave-assisted cross-coupling reaction were deoxygenated by bubbling argon for 1 h. The products **4a,c** have previously been characterized, and the data obtained corresponded satisfactorily with NMR and MS data, and comparison with authentic samples. Titanium (IV) oxide, anatase (nanopowder, <25 nm particle size) was purchased from Sigma–Aldrich.

Melting points were determined on Boetius combined heating stages and were not corrected. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. ^1H and ^{13}C NMR spectra were recorded on an AVANCE-500 instruments using Me_4Si as an internal standard. All signals in the ^1H and ^{13}C NMR spectra were

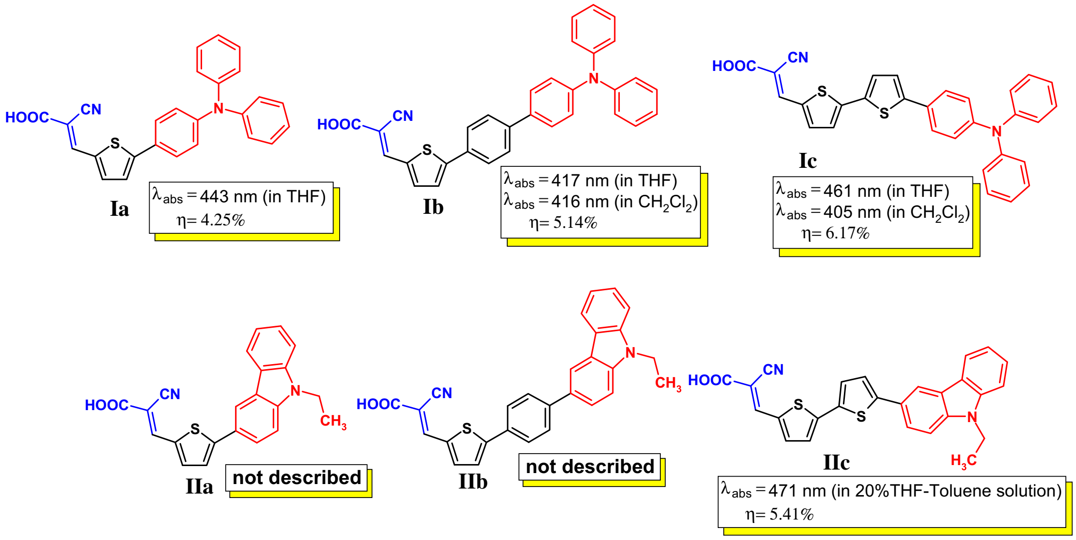

Fig. 1. Molecular structure of triphenylamine and carbazole dyes containing a cyanoacrylic acid as an electron-withdrawing anchoring group.