



Silicon-bridged triphenylamine-based organic dyes for efficient dye-sensitised solar cells



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ABSTRACT

Three dyes based on a triphenylamine (TPA) moiety using a silicon bridge have been synthesised, namely CL-1D, CL-OMe and CL-SiMe. Structural benefits of long alkyl chains and electron donor group on photo conversion efficiency (PCE) of dye sensitised solar cells is discussed. A previously synthesised dye, denoted CL-1, which contained long alkyl chains and exhibited an efficiency of 6.90%, was compared with CL-SiMe, which contained shorter alkyl chains and showed an efficiency of 3.41%. A large drop in J_{sc} and V_{oc} was found to be the reason for the appreciable decline in efficiency for CL-SiMe vis-à-vis CL-1. Electron donor group studies were performed using CL-1D and CL-OMe. CL-1D, which contained bulky aniline electron donor groups, showed an efficiency of 4.20%, whilst CL-OMe, featuring smaller methoxy donor groups had an efficiency of 5.50%. Theoretical UV–Vis absorption spectra were obtained for the CL-1D dye by time-dependent density functional theory (TD-DFT); the experimental and calculated values of the energy for maximum absorbance were in good agreement with experimental data.

1. Introduction

Dye-sensitised solar cells (DSSC), (O'Regan and Gratzel, 1991) are responsive to diffuse light irradiation as well as to light incident under acute irradiation angles. These have proven to be an attractive area of third-generation solar-cell research. Until recently, the highest efficiencies seen in solar cells have been achieved using ruthenium-based sensitisers which showed maximum power-conversion efficiencies of 11.9%. (Komiya et al. (2011)) However, ruthenium is expensive, has limited availability, and has an undesirable environmental impact when used in large amounts. Therefore, a new generation of organic dyes has been researched and developed in the hope of overcoming these shortcomings, especially metal-free dyes (Yella et al., 2011). Organic dyes have the distinct advantage of higher molar extinction coefficients, are less expensive, and have more flexibility in their synthesis. One very promising class of organic dyes is that of porphyrins. A recent report has described a porphyrin-based dye in combination with a Co-

complex-containing electrolyte, a redox mediator exhibiting higher reduction potentials than that of I_3^- , displaying a very impressive efficiency of 12.3% (Yella et al., 2011).

Organic dyes consist of three parts: an electron-donating group, π -bridge and an electron-withdrawing group. The focus of much research effort has been on altering systematically these features in order to achieve higher power conversion efficiencies. Particularly, organic sensitisers bearing dithienosilole as a π -linker have shown high efficiencies of 7.6–10.5%, due to its coplanarity (Lin et al., 2010; Wang et al., 2009, 2005; Yamaguchi, 1996; Zeng et al., 2010) and unique photophysical properties ($\sigma^*-\pi^*$ conjugation) (Jung et al., 2010; Park et al., 2012). The coplanarity facilitates subsequently electron transfer to semiconductor and enhances DSSC-device performance (Akhtaruzzaman et al., 2012; Biswas et al., 2015). The introduction of bulky substitution on silicon atom of dithienosilole ring may reduce dyes' π - π stacking interactions, and may be beneficial to high electron-injection yield and in boosting power-conversion efficiency (Lin et al., 2010; Wang et al., 2009, 2005).

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In recent years, extensive research has been carried out and reported in relation to short and long alkyl chains, ranging in length from one to ten carbon atoms. (Ko et al., 2012) Long alkyl chains help to prevent intermolecular charge transfer due to aggregation; electron delocalisation can be enhanced over the whole molecule, which in principle can contribute to spectral red-shifting due to weaker π - π stacking. Most importantly, having alkyl chains can further help to prevent losses within the cell by preventing intermolecular charge transfer due to molecular aggregation. (Pastore and De Angelis, 2010) Over the last few years, the concept of adding long alkyl chains has been applied to the linker part of dyes in order to increase lateral spacing of dye molecules adsorbed on TiO₂ surfaces.

Five-membered heterocycles containing silicon have attracted attention recently, in particular silole derivatives with a 2,2 bithiophene group connected by silicon. Dithienosilole derivatives have been used in many optoelectronic devices such as light-emitting diodes (Liao et al., 2007), whilst dithienosilole-based polymers have been used in polymer solar cells showing efficiencies ranging from 3% to 9% (Chu et al., 2012; Li et al., 2012). However, there have been only few reports on the use of these materials in DSSCs (Ko et al., 2010; Lin et al., 2010; Wang et al., 2005; Zeng et al., 2010). A dye dubbed CL-1 was synthesised by our group and contained a dihexyl-substituted dithienosilole linker group and a triphenylamine (TPA) electron donor group and showed a power conversion efficiency of 6.90%. (C. Lyons et al. (2017)) It was reported by Hagberg et al. (2009) that dimethylaniline electron donor groups attached to a thiophene bridge could lead to relatively high power-conversion efficiencies. A dye named D29 which contained dimethylaniline electron donor groups was synthesised by Hagberg et al. and showed an efficiency of 4.83% Hagberg et al. (2009). D29 is regarded as a dye with desirable spectral features, as the amine groups contain strong electron-donating properties and it was predicted through time-dependent density functional theory (TD-DFT) that there would be a systematic red shift when increasing the number of dimethyl amines in the functional groups (Hagberg et al., 2009).

In the present work, we have designed and synthesised a series of dithienosilole dyes named CL-OMe, CL-SiMe and CL-1D (cf. Scheme 1). CL-SiMe containing a dimethyl-substituted dithienosilole group was compared with our previously synthesised CL-1 to show the structural benefits of long alkyl chains. CL-1D and CL-OMe were compared to show the structural benefits of electron-donating groups. CL-1D and CL-OMe both contain dihexyl-dithienosilole groups but CL-1D contains a dimethylaniline electron donor group and CL-OMe contains a methoxy electron-donor group. Studies were carried out for CL-1D and CL-OMe to investigate the effects that different electron-donating groups have on solar-cell performance. This series of dyes can be used to study the impact of structural versus spectral benefits on overall solar-cell efficiency. The best-performing dye, CL-OMe showed a power-conversion efficiency of 5.50% under 1 Sun. The structures are shown below in Fig. 1. We also apply TD-DFT to gain a detailed understanding of the electronic transitions governing photo-excitation.

The aim of this paper is to investigate the effects, and contributions, of electron-donating groups (EDGs) and chain length on the performance of DSCs with higher-efficient dyes, to provide valuable insights into performance optimisation. In addition, many recently-reported synthesised dyes possess larger, bulkier structures which greater number of synthesis steps, which are often a deal more complex than those examined in the present study, as remarked and discussed with acuity recently by Kumavat (2017) and Prachumrak (2017). Naturally, it is of overriding import that the amount of time needed to synthesise any dye is reduced to render production more efficient. In the case of the reported synthesised dyes herein, the number of synthesis steps was minimised by using commercially and widely available starting groups, such as bithiophene and aniline groups, with little additional bulky groups added to these materials, therefore reducing the level of synthesis effort. Here, we demonstrate the desiderata of using large TPA and small methoxy EDGs (*vide infra*). Although many power-conversion

efficiencies have been recorded by other research groups using various different EDGs, little mechanistic insight has been afforded towards aniline-TPA and methoxy as electron-donating sources. By combining these EDGs with various bridges and electron-withdrawing groups (EWGs), it is believed that the power-conversion efficiencies of future novel organic dyes can be augmented further. The negative effects of methyl groups in the linker have been shown to give rise to a lower efficiency vis-à-vis CL-1 which contained hexyl chains. This was most probably due to dye aggregation on the TiO₂ surface. By using the knowledge and insight gleaned from the present work, future dyes have the potential to lead to an increase in power-conversion efficiency.

2. Methodologies

2.1. Materials

The following materials were used as received; 1-butyl-3-methyl imidazolium iodide (BMII, Merck 4.90187.0100), guanidinium thiocyanate (GuSCN, Merck 8.20613.0250), 1,10 phenanthroline (Acros organics: 157530050), hydrogen peroxide (30% ww, Sigma Aldrich: 21,676-3), dichlorodimethylsilane (Sigma Aldrich: 440272-100 ml), copper (ii) chloride (Sigma Aldrich: 61168-25-G-F), Aniline (Sigma Aldrich: 242284-100 ml), potassium iodide (Sigma Aldrich: 30315), tetrakis triphenylphosphine palladium (0) (Sigma Aldrich: 216666-1G), [1,1'-Bis (diphenylphosphino)ferrocene] palladium (II) Dichloride Dichloromethane Adduct (TCI Chemicals: B2064), palladium (II) acetate (Sigma Aldrich: 683124-500 mg), anisole Sigma Aldrich: 10520-250 ml), phosphorus (V) oxychloride (Sigma Aldrich: 20,117-0), sulfuric acid 95–97% (Merck: 1.01833.2500), acetic acid (Fluka: 45741), butyllithium solution (2.5 M) (Sigma Aldrich: 230707-100 ml), butyllithium solution (1.6 M) (Sigma Aldrich: 18,617-1), 2,2-bithiophene (Sigma Aldrich: 24,163-6), 4-(Diphenylamino)-benzaldehyde, 97%, (Sigma Aldrich: 647209-5G), lithium chloride (Sigma Aldrich: 62476-100 G-F), ammonium chloride (Sigma Aldrich: A9434-500 G), zinc powder (Sigma Aldrich: 14409), cyanoacetic acid (Sigma Aldrich: C8,850-5), N-Bromosuccinimide, 99%, (Alfa Aesar: A15922), thiophene-2-acetonitrile, thiophene-2-boronic acid, N,N-Dimethylacetamide anhydrous (DMAC) (Sigma Aldrich: 27,101-2), piperidine (Sigma Aldrich: 411027-100 ml), deuterated chloroform (Sigma Aldrich: 411027-100 ml), dimethylsulfoxide D6 (Sigma Aldrich: 156914), potassium carbonate (Sigma Aldrich: 20,961-9), potassium hydroxide (Sigma Aldrich: P1767-500 G), potassium tert butoxide (Sigma Aldrich: 156671), trimethyl borate (Sigma Aldrich: 92330-250 ml), tributyltin chloride, 98%, (Sigma Aldrich: STBB5068), dichlorodihexylsilane (TCI chemicals: D2712). Dichloromethane (CH₂Cl₂), toluene, tetrahydrofuran (THF), dimethylformamide (DMF), methanol, ethanol, hexane, petroleum ether and chloroform were all purchased from Sigma Aldrich. Toluene was distilled under sodium benzophenone and stored under argon. Dimethylformamide was dried using barium oxide. Tetrahydrofuran was collected from a Grubbs still. Titanium dioxide paste (Ti-Nanooxide D20), electrolyte (Iodolyte AN-50), Bynel film (Meltonix 1162-60) and fluorine doped tin oxide glass slides (TCO30-8 ~8 ohm/square) were purchased from Solaronix SA (Aubonne, Switzerland).

Three types of TiO₂ pastes were used to make cells, including the commercially purchased samples. The first was a 'transparent' type containing 20 nm particles of TiO₂ prepared from Evonik P25 powder using a standard fabrication procedure. (Ito et al., 2008) Ethyl cellulose (Fluka, #46080) and anhydrous terpineol (Fluka, #46070) were used as received to make a paste. A second paste of particles sized 150–250 nm purchased from DyeSol Ltd (WER 2-0) was used to form a light scattering layer. Both pastes were screen-printed with a 90 T mesh to yield electrodes of approximately 15 μ m in thickness (10 μ m transparent layer and a 5 μ m scattering layer). The standard liquid electrolyte used was labelled E1 (Ito et al., 2007) and comprised of 0.03 M iodine, 0.1 M guanidinium thiocyanate, 0.5 M 4-*tert*-butylpyridine and 0.6 M BMII in an acetonitrile:valeronitrile solvent mixture (85:15 by volume). The Solaronix paste was used without light-

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