



## Dissociation exists in s-triazine based donor-accepter organic systems by photo-induced electron transfer



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### ARTICLE INFO

#### Article history:

Received 17 October 2016

Received in revised form

1 December 2016

Accepted 7 December 2016

Available online 18 December 2016

#### Keywords:

Donor-acceptor system

Donor-acceptor1-acceptor2 architecture

Dissociation of chloride anion

Photo-induced electron transfer

Light-stability

S-triazine

### ABSTRACT

In the organic donor-acceptor system, the dissociation of the chloride anion in the s-triazine group as the acceptor was first investigated under irradiation. Introducing the electron-deficient chromophore as acceptor 2 to the donor-acceptor module allows the photo-induced electron transfer from the s-triazine module, making the dissociation less in the donor-acceptor1-acceptor2 architecture, which has been proven to be a good strategy to increase light-stability.

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### 1. Introduction

Organic solar cells (OSCs) have been developed rapidly as an inexpensive alternative to large-area Si-based solar modules, which have the potential for low-cost and high-throughput production. OSCs can be grouped into small organic molecule cells and polymer cells, which are distinguished by the type of molecular solids known as organic semiconductors, from which they are composed [1–6]. In some cases, the separation of the excitons in OSCs could also occur within the organic semiconductors that are used the donor-acceptor (D-A) architecture to achieve photo-induced

electron transfer. It is recognized that D-A materials do in fact improve the efficiencies of OSCs [7–12]. Moreover, some reports have focused on the light-stability of D-A materials, which has been proven to be the most important factor affecting the repeatability of device efficiency [13,14]. This means that the effective photo-induced electron transfer (PET) of the D-A architected material could improve the device efficiency of OSCs, but it may cause the material to photo-degrade, thereby affecting the light-stability of the device [15]. The light-stability of the OSC device determines its application value. Therefore, it is also important to study the light-stability of photovoltaic materials in the OSC devices and develop a better strategy, other than the traditional D-A architecture method, to promote PET and prevent photodegradation.

S-triazine as the electron-accepting module was the effective linker to improve the electron-injection and electron-transportation abilities of its conjugated derivatives [16,17]. In our previous work [12,18–20], we reported a series of D-A<sub>1</sub>-A<sub>2</sub> systems with the triphenylamine (MTPA) or indoline (YD) derivative as a donor, s-triazine derivative (TRC) as the first acceptor (A<sub>1</sub>), and anthraquinone derivative (AEAQ), or two perylene bisimide derivatives (PDI and PBI) as the second acceptors (A<sub>2</sub>), denoted as D-TRC-A<sub>2</sub>

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systems. Different charge separation efficiency and lifetime of CS states were achieved by changing the donor and second acceptor in D-TRC-A<sub>2</sub> systems. MTPA-TRC exhibits similarly low photoelectric conversion efficiency ( $\eta = 0.03\%$ ) in the single-layer OSCs with common organic semiconductors such as phthalocyanine, poly(phenylenevinylene) and triarylamine derivatives [9,21–23] of which the efficiency has been improved to greater than 6% and can even exceed 10% by the combined application of other semiconductors and the proper design of solar cell structures [9,24–27]. Importantly, the single-layer OSC constructed using MTPA-TRC-AEAQ ( $\eta = 0.89\%$ ) with long-lived CS states (650 ns) was found to be significantly more efficient than that using MTPA-TRC. It indicates that single-layer OSCs had been proven to be the highly effective cell structure reflecting the effect of CS states with different lifetimes of organic materials, and the far better photo-voltaic characteristics of D-TRC-A<sub>2</sub> than D-TRC suggests potential applications in OSCs, if better structural designing of OSCs.

In this paper, we investigate the effects of intramolecular electron transfer on the light-stability of D-TRC-A<sub>2</sub> systems, and report the results and analyse the effects of second acceptors on the degree of dissociation, which are relative to the electron transport process. D-A system MTPA-TRC and D-TRC-A<sub>2</sub> systems MTPA-TRC-AEAQ and MTPA-TRC-PBI will be taken as the examples (Chart 1), where experimental and computational results indicated that some dissociations of the chloride anions exist in MTPA-TRC due to the effective PET process from the excited MTPA to the TRC module. However, the dissociation has been found to be less frequent in MTPA-TRC-AEAQ and MTPA-TRC-PBI because of the sequential electron transfers from excited MTPA to the TRC followed by the AEAQ (or PBI) module, making MTPA-TRC-AEAQ and MTPA-TRC-PBI more stable under irradiation.

## 2. Experimental and computational methods

### 2.1. Materials

Structures of the key compounds being synthesized and studied in this work are provided in Chart 1. 4,4'-dimethyl-4''-styryl-triphenylamine (MTPA) [18], 4,4'-dimethyl 4''-(4-(4,6-dichloro-1,3,5-triazin-2-ylamino)styryl)triphenylamine (MTPA-TRC) [18], 1-(2-aminoethylamino)anthraquinone (AEAQ) [18], 1-((4,6-dichloro-1,3,5-triazin-2-ylamino)ethylamino)-9,10-anthraquinone (AEAQt) [18], 4,4'-dimethyl-4''-(4-(6-dichloro-1,3,5-triazin-2-ylamino-4-ethylamino)styryl)triphenylamine (MTPA-TRC-EA) [18], 4,4'-dimethyl-4''-(4-(6-dichloro-1,3,5-triazin-2-ylamino-4-phenylamino)styryl)triphenylamine (MTPA-TRC-BA) [20], D-A<sub>1</sub>-A<sub>2</sub> systems 4,4'-dimethyl-4''-(4-(4-chloro-6-(2-(9,10-dioxoanthracen-1-ylamino)ethylamino)-1,3,5-triazin-2-ylamino)styryl)triphenylamine (MTPA-TRC-AEAQ) [18], and 4,4'-dimethyl-4''-(4-(4-Chloro-6-(N-(1-hexylheptyl)-N'-(4-amino)phenyl)-1,7-di(4-tert-butylphenoxy)-perylene-3,4,9,10-tetracarboxylbisimide)-1,3,5-triazin-2-ylamino)styryl)triphenylamine (MTPA-TRC-PBI) [20] were prepared according to the literatures. cyanuric chloride (TRI) and melamine (Mela) were purchased. The synthetic pathways of 2,4-dichloro-6-anilino-1,3,5-triazine (TRC-Ph), 2-chloro-4,6-dianilino-1,3,5-triazine (TRC-diPh), 2,4,6-trianilino-1,3,5-triazine (TRC-triPh) and 4,4'-dimethyl-4''-(4-(6-dichloro-1,3,5-triazin-2-ylamino-4-cyano)styryl)triphenylamine (MTPA-TRC-CN) were illustrated in Scheme 1. All reagents and solvents were in reagent grade and further purified by the standard methods if necessary. All synthetic procedures were carried out under an atmosphere of dry nitrogen or dry argon unless otherwise indicated.

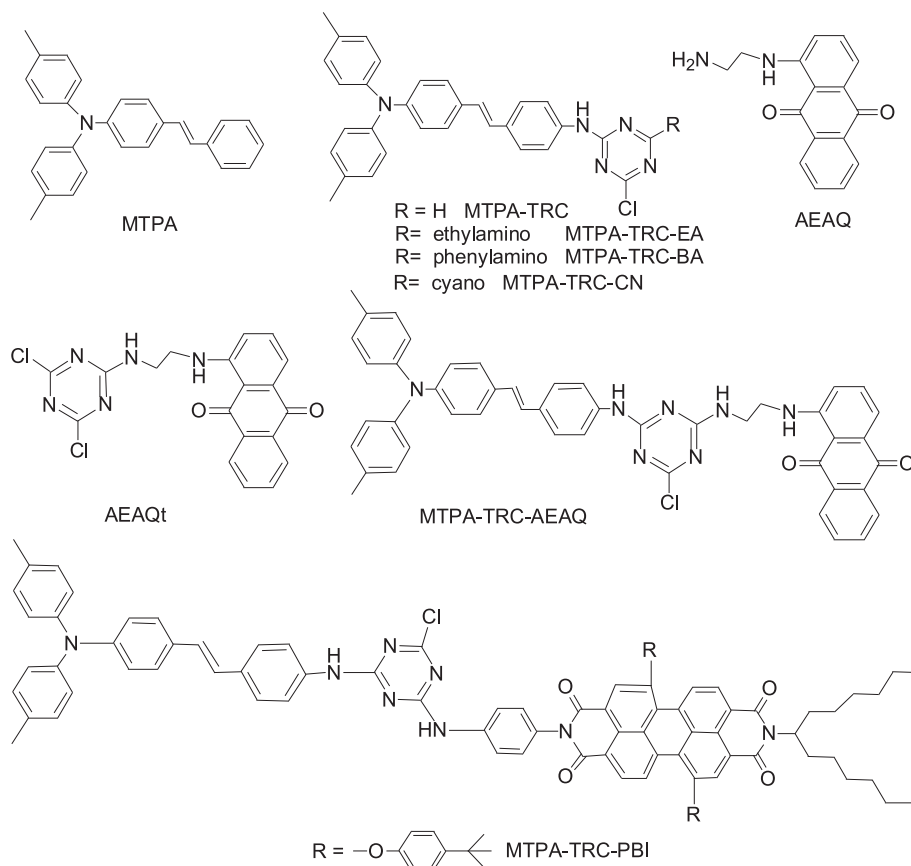


Chart 1. The structure of key compounds.

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