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Ultrafast multiexponential electron injection dynamics at a dye and ZnO QD interface: a combined spectroscopic and first principles study†

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The photophysical properties of a push–pull dye and the dynamics of electron transfer across a dye and ZnO quantum dot (QD) interface have been studied using a combination of steady-state, time-resolved fluorescence and femtosecond transient absorption (TA) spectroscopies. Spectroscopic measurements, along with quantum chemical calculations, provide evidence for the photoinduced intramolecular charge transfer (ICT) in a donor–π–acceptor dye. Wavelength dependent fluorescence decay of the dye infers the solvent relaxation of the ICT state. TA spectral measurements suggest electron transfer from dye to ZnO QD through the ICT state by monitoring the dye radical cation. Multiexponential electron injection with time constants of 775 fs and 25 ps at the dye@QD interface is demonstrated using the TA kinetics results. The thermodynamics of fast and slow electron injections is discussed. Furthermore, density functional theory (DFT) and time-dependent (TD)-DFT simulations were performed to identify the dye cation radical and to get a deep insight into the experimental observations.

1. Introduction

Quantum dots (QDs) have drawn much attention in recent years due to their dominating features of a tunable band gap, multiple exciton generation and facile synthesis.[1–7] The optical and electrical properties of QDs can be modulated *via* quantum confinement.[8,9] The application potential of QDs in medical and electronic fields, for example in bioimaging,[10–12] catalysis,[13,14] light harvesting[2,15] and photovoltaics[4,16–18] has been extensively studied in the past few years. Zinc oxide (ZnO) is a wide band gap semiconductor material like SnO_2, NiO, TiO_2, Nb_2O_5 *etc.* Bulk ZnO is widely utilized in photovoltaics as a light transparent conducting layer. For further technical advancements in dye sensitized solar cells (DSSCs) and QD sensitized solar cells (QDSSCs), the bulk material could be replaced by its quantum sized counterpart as it provides more interface area. Moreover, ZnO is a promising transparent conductive oxide (TCO) electrode for both organic and inorganic optoelectronic devices and also an active element for sensors and lasers.[19] It has also been exploited as a hole blocking and electron selective intermediate layer in organic light emitting diodes and solar cells with inverted device architectures.[20] In most of the applications, electron injection at the interface between the metal oxide and the organic active layer is the main process. In DSSCs, photoinduced electron transfer at the dye–semiconductor interface plays a key role in photon energy conversion.

The photosensitizer acts as the light harvesting antenna, which plays a vital role for efficient light harnessing and, thereby, generation of charges in solar cells. A good photosensitizer should possess a very broad absorption spectrum with a high molar extinction coefficient (ε) to enable efficient light harvesting. To fulfil the major requirements, various photosensitizers, including metal complexes, porphyrins, phthalocyanines and metal free organic dyes, have been designed and applied to DSSCs in the last two decades.[21–25] So far, the most efficient photosensitizers for DSSCs are ruthenium (Ru) complexes, particularly N719 $(Bu_4N)_2[Ru(dcbpyH)_2(NCS)_2]$ which possesses a superior photovoltaic performance in comparison to other metal complexes,[21] but their high cost and environmentally unfriendly nature still limits the large-scale applications of such dyes. Great efforts have been devoted to replacing these Ru complexes with metal-free organic dyes because of their easy synthesis, low cost and high molar absorption coefficient. One important strategy to develop efficient metal-free organic

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† Electronic supplementary information (ESI) available: Absorption spectra of ZnO QDs with TEM images, histogram for the particle size distribution of the ZnO QDs, MK-2 absorption spectra in methanol with and without acetic acid, MK-2 emission spectra in different solvents, TA spectra of MK-2 dye and MK-2@ZnO QD, simulated absorption spectra of pure and deprotonated dyes, and dye cation radicals in chloroform, molecular orbitals with NTO pictures of the dye and molecular structures of the dye attachment with ZnO nanoclusters. See DOI: 10.1039/c6cp04610j