

Role of TiO₂ nanoparticles on the photoinduced intramolecular electron-transfer reaction within a novel synthesized donor–acceptor system

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Abstract

Steady-state, FT-IR and time-resolved spectroscopic measurements were carried out on the two novel synthesized π -conjugated rigid naphthothiophene compounds, 7-methoxynaphtho[1,2-*b*]thiophene (7MNT) and 7-methoxynaphtho[1,2-*b*]thiophene-2-carboxylic acid (7MTCA) in chloroform (CHCl₃) medium as well as in presence of TiO₂ nanoparticles. 7MTCA multichromophoric system contains both electron donor (–OCH₃) and acceptor functionalities (–COOH) at the two different ends of the rigid naphthothiophene moiety whereas in 7MNT only the electron donor functional group, –OCH₃, is present. Thus 7MNT looks like the donor part of 7MTCA where –COOH group overlaps, due to its free rotation, with the electron rich site 7MNT part. The experimental findings observed from steady-state absorption, fluorescence and time-resolved spectroscopic (fluorescence lifetime and transient absorption) measurements demonstrate that the survival duration of charge-separated species formed within 7MTCA due to intramolecular photoinduced electron-transfer (PET) reactions between the donor –OCH₃ and acceptor –COOH functional groups, attached at the two different ends of this compound, could be enhanced by inhibiting the energy wasting charge recombination process through complexation of the carboxylate group (–COOH) with TiO₂ nanoparticles. Thus, in the present investigation TiO₂ appears not to act as an acceptor but its presence helps to survive or protect the charge-separated species formed within 7MTCA. The possibility of designing of low-cost artificial (model) solar energy conversion devices by linking the organic donor–acceptor (DA) systems like 7MTCA with TiO₂ core is hinted.

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1. Introduction

In contemporary materials research, organic–inorganic nanocomposites become a highly exciting area [1–6]. This type of research possesses immense importance not only from the basic research point of view but it has strong technological relevance, e.g., for constructing light emitting diodes, photovoltaic cells, future solar cells, etc. [7–15]. The key process involved in the solar cells is a photoinduced electron-transfer (PET) between the organic molecules and the nanocrystalline inorganic phase to generate the charge carriers [16,17]. Lately to develop

systems which act as both light-absorbing dye and a charge transport materials, attempts are made to combine nanocrystalline semiconductors like TiO₂, CdSe, ZnO, etc., with π -conjugated organic or polymer systems [18–20]. Some authors reported the PET process in heterosupramolecular assemblies of nanostructured TiO₂ or other similar nanocrystalline semiconductors (like ZnO, SnO₂, etc.) and various donor–acceptor contained organic molecules including the systems having the carboxylate group, –COOH [7,21–30].

Our primary objective is to investigate the interaction of TiO₂ nanoparticles in chloroform (CHCl₃) solvent with π -conjugated rigid naphthothiophene system, 7-methoxynaphtho[1,2-*b*]thiophene-2-carboxylic acid (7MTCA), containing both the donor (–OCH₃) and acceptor (–COOH) functionalities at the two different ends of the naphthothiophene moiety (Fig. 1).

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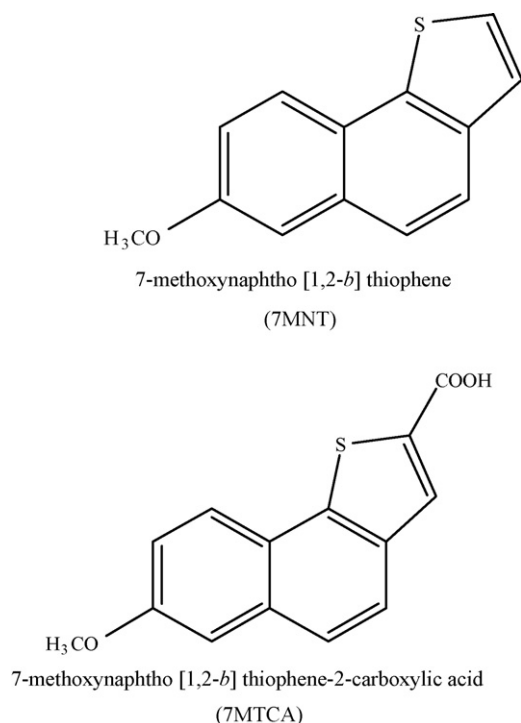


Fig. 1. Molecular structures of the compounds 7MNT and 7MTCA.

As $-\text{COOH}$ group is known to have a strong binding affinity, through hydrogen bonding or other mechanisms like formation of bidentate complex, with TiO_2 nanosurface, the present investigations were made to see whether such type of binding in the ground state has some effects on the charge-separated species formed due to photoinduced electron-transfer reactions between the donor and acceptor functional groups. Attempts are also made to examine whether survival duration of the charge-separated species could be enhanced by retarding the energy wasting charge recombination process through binding mechanisms of TiO_2 with the acceptor functionality $-\text{COOH}$ which is generally employed as an anchor to the semiconductor nanosurface [8]. To understand more clearly the photophysical properties of 7MTCA, the similar investigations were also made on 7-methoxynaphtho[1,2-*b*]thiophene (7MNT) where no $-\text{COOH}$ group is present but it contains only the donor functionality $-\text{OCH}_3$. Thus, 7MNT behaves as a donor part of the other multichromophoric system, 7MTCA. Our primary aim of the present investigation is to develop some nanocomposite systems of organic solutes being attached with TiO_2 nanoparticles. These simple nanocomposite systems have an advantage over various triads, tetrads, pentad systems to produce charge-separated states having prolonged lifetime. In donor-acceptor multichromophoric systems, considerable energies are lost during the multi-step electron-transfer processes in artificial long-range charge separation. Thus to design low cost hetero-supramolecular assemblies for solar-energy conversion devices, avoidances of such energy wasting and high-cost multi-step synthesis are absolutely necessary. The results obtained from the steady-state and time-resolved spectroscopic investigations on this simple rigid naphthothiophene system

7MTCA, containing both the donor and acceptor functionalities, in presence of TiO_2 nanoparticles are described in this paper.

2. Experimental

2.1. Materials

The synthesis and characterization of the compounds 7-methoxynaphtho[1,2-*b*]thiophene (7MNT) and 7-methoxynaphtho[1,2-*b*]thiophene-2-carboxylic acid (7MTCA) have been described elsewhere [31]. Chloroform (CHCl_3) (E. Merck, Germany) of spectroscopic grade was used as received.

2.2. Preparation of TiO_2 nanoparticles

Nanocrystals of TiO_2 were prepared by arrested hydrolysis of titanium isopropoxide (TIP) in anhydrous chloroform (CHCl_3) containing a little amount of 1-propanol and double distilled water in presence of the stabilizer stearic acid following the method described by Janssen and Beek [8a]. In a typical synthesis we take a reaction mixture containing 50 ml CHCl_3 , 1.5 ml 1-propanol, 0.05 ml TIP and 0.044 gm stearic acid. Another reaction mixture were prepared by mixing 1 ml 1-propanol and 8 μl double distilled water which were then added with the 1st reaction mixture drop wise with constant stirring. A clear solution of TiO_2 nanoparticles stabilized by stearic acid were obtained after 24 h. Then TiO_2 nanoparticles were precipitated by adding acetonitrile to the above solution separated by centrifugation and washed with ethanol several time and finally vacuum dried at 60 °C for 24 h. The UV-vis spectroscopy can be used to determine the diameter of semiconductor nanoparticle due to its quantum-confined phenomena. The UV-vis spectrum of nanoparticles in chloroform shows an absorption onset at about 340 nm. According to the earlier reports [32,33], an onset at 340 nm implies the average particle diameter of about 2 nm. Colloidal TiO_2 solution was prepared by dissolving the desired amount of TiO_2 particles into chloroform (CHCl_3). The size of the TiO_2 nanoparticles was also estimated from high resolution Transmission Electron Micrograph (TEM) as shown in Fig. 2. The particle diameter varies in the range of 2–4 nm. The average diameter of TiO_2 nanoparticle is found to be 4 nm.

2.3. Spectroscopic apparatus

At the ambient temperature (296 K), steady-state electronic absorption and fluorescence emission spectra of dilute solutions (10^{-4} to 10^{-6} mol dm^{-3}) of the samples were recorded using a 1 cm path length rectangular quartz cells by means of an absorption spectrophotometer (Shimadzu UV-vis 2101PC) and F-4500 fluorescence spectrophotometer (Hitachi), respectively. FT-IR spectra were recorded by using a FTIR 8400S Shimadzu spectrometer. Fluorescence lifetime measurements were carried out using the Time Master fluorimeter from Photon Technology International (PTI). The system measures fluorescence lifetimes using PTI's patented strobe technique and

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