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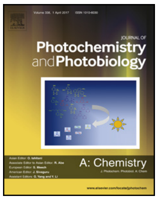

Efficient electronic communication-driven photoinduced charge-separation in 2-ureido-4[1*H*]-pyrimidinone quadruple hydrogen-bonded *N*,*N*-dimethylaniline-anthracene assemblies

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ABSTRACT

Four relatively rigid assemblies **I–IV** have been designed to understand the factor governing the photoinduced electron transfer (PET) process in 2-ureido-4[1*H*]-pyrimidinone quadruple hydrogen-bonded systems. Upon excitation, PET from the *N*,*N*-dimethylaniline group to the singlet anthracene takes place giving rise to a long-lived charge-separation state up to 56 μs for assembly **I** and 13 μs for assembly **II**. Moreover, the introduction of CH_2 group(s) to assemblies **I** and **II** can significantly influence, or even switch off the *intra-assembly* PET process. Spectroscopic and electrochemical studies demonstrate efficient electronic communication responsible for the PET process in 2-ureido-4[1*H*]-pyrimidinone quadruple hydrogen-bonded *N*,*N*-dimethylaniline-anthracene assemblies. The fast single-step electron-transfer and slow charge-recombination, as well as the high excitation energy conversion efficiency (78%), enable the assemblies to be advantageous for high light-energy conversion.

1. Introduction

Photosynthesis is a natural energy-conversion system that converts solar energy into chemical energy, the primary processes of which are a cascade of photoinduced excitation energy transfer and subsequent electron transfer (ET) between the electron donor and acceptor to attain a charge-separated (CS) state living on a time scale up to a second [1]. The success and importance of photosynthesis have inspired researchers to study ET and CS processes for developing artificial molecular systems for solar energy conversion [2]. Over the past decades, a set of donor-acceptor systems have been constructed, which upon photoexcitation, give rise to long-lived CS states with high quantum yields [3–9]. In this context, the investigation of photoinduced electron transfer (PET) process, wherein electronic donor and acceptor are assembled via hydrogen-bonding interaction has attracted much interest because the ET reactions in biological photosynthesis in nature are regulated through a network of hydrogen bonds [8]. These studies have been extended to the donor-acceptor assemblies linked either by two point hydrogen bonds [5], or by triple hydrogen bonds [6], or by multiple hydrogen bonds [7]. In some cases, the PET rates of the hydrogen-bonded assemblies are competitive with those of covalent-linked ones. However, the charge recombination (CR) rates of the assemblies in solution are generally faster with lifetimes on the order of pico- to nanosecond timescale [5–9].

2-Ureido-4[1*H*]-pyrimidinone module represents a fascinating self-complementary quadruple hydrogen-bonding module [10]. Owing to its great binding strength and directionality, this module has been employed to construct hydrogen-bonded donor-acceptor dyads [8] as well as extensive architectures in assembling and disassembling supramolecular systems, which have shown promising applications in light harvesting and photoelectronic devices [11–14]. Photoexcitation energy transfer process has been well established, but the PET process in these complementary quadruple hydrogen-bonded systems is rarely observed. We questioned whether the 2-ureido-4[1*H*]-pyrimidinone quadruple complementary hydrogen-bonds could be used as a conduit for the *intra-assembly* electron communication.

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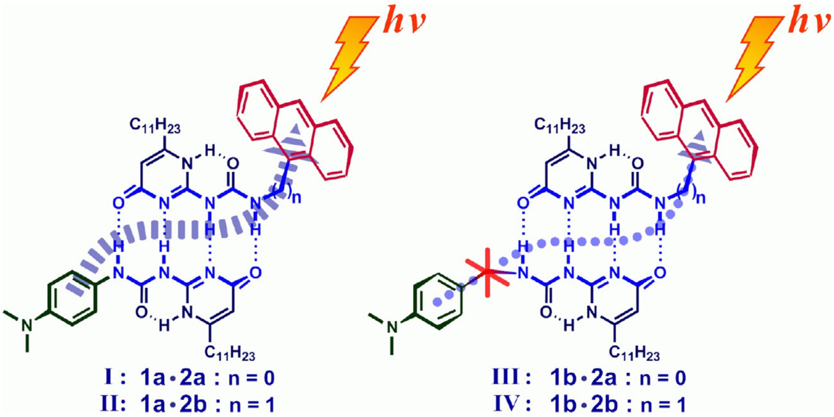

Scheme 1. 2-Ureido-4[1*H*]-pyrimidinone quadruple complementary hydrogen-bonds interfaced *N*,*N*-dimethylaniline-anthracene assemblies **I**–**IV**.

In this contribution, four relatively rigid *N*,*N*-dimethylaniline-anthracene assemblies **I**-**IV** (Scheme 1) are designed and synthesized to unravel the factor that influence the PET process in the 2-ureido-4[1*H*]-pyrimidinone quadruple hydrogen-bonded system; herein, the *N*,*N*-dimethylaniline and anthracene are served as the electronic donor and acceptor because they are a typically exothermic ET pair . It is anticipated that (1) the high binding strength of 2-ureido-4[1*H*]-pyrimidinone unit would enhance the *intra-assembly* electronic donor-acceptor interaction even at low concentration, and thus avoiding any intermolecular diffusion encounter between the donor and acceptor in the PET process; (2) the direct attachment to 2-ureido-4[1*H*]-pyrimidinone would suppress the collisions between the donor and acceptor via space interaction. As will be discussed later, the *intra-assembly* PET process takes place efficiently in the 2-ureido-4[1*H*]-pyrimidinone-bridged *N*,*N*-dimethylaniline-anthracene assemblies **I** and **II** with the formation of a long-lived CS state up to 56 μs and 13 μs, respectively. The introduction of CH_2 group(s) to assemblies **II**-**IV** significantly influences, or even switches off the PET process. Electrochemical and spectroscopic studies reveal that efficient electronic communication plays a crucial role in mediating the *intra-assembly* singlet PET process.

2. Experimental

2.1. Instruments

^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker Avance dpx 400 MHz instrument using TMS as an internal standard. UV/Vis spectra were obtained using a Shimadzu 1601PC spectrophotometer. Fluorescence spectra were recorded on a Hitachi 4500 fluorescence spectrophotometer. Mass spectra were obtained on Brucker APEX II spectrometers. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. Time-resolved fluorescence measurements were run on F-900 Edinburgh Analytical Instruments. The samples for the transient absorption spectroscopy experiments were purged with argon for 30 min. Nanosecond transient absorption spectra were performed on a LP-920 pump-probe spectroscopic setup (Edinburgh). The excited source was the unfocused third-harmonic (355 nm, 10 ns fwhm) output of a Nd:YAG laser (Continuum Surelite II); the probe light source was a pulse xenon lamp. Each kinetic trace was recorded as an average of several pulsed excitation. Electrochemical measurements were performed with a Princeton Applied Research Potentiostat Galvanostat model 283 either in dry THF with Pt wire auxiliary electrode, Ag/$AgNO_3$ non-aqueous reference electrode, and glassy carbon working electrode, or in CH_2Cl_2 with Pt wire auxiliary electrode, working electrode and SCE reference electrode. The inner solution of the Ag/$AgNO_3$ non-aqueous reference electrode was a mixture of 0.1 M $^nBu_4NPF_6$ and 10 mM $AgNO_3$ in CH_3CN. All solutions were purged with argon prior to measurements, and contained *ca.* 0.1 M $^nBu_4NPF_6$ as the supporting electrolyte.

2.2. Materials

NaH: 52% mineral oil dispersion. Anhydrous THF and toluene were obtained by distillation from sodium/benzophenone. Pyridine and Et_3N was heated under refluxing with CaH_2 for three hours, and then distilled. CH_2Cl_2 was washed with H_2SO_4, H_2O, dried with $CaCl_2$ and distilled from CaH_2. Other reagents were of analytical grade and were used as received.

2.3. Synthesis of 2-(4-N,N-dimethylaniline)uredio-6-(1-undecyl)-4[1H]-pyrimidinone (1a)

4-Dimethylaminobenzoic acid (295 mg, 1.78 mmol) and Et_3N (0.3 mL, 2.19 mmol) in dry toluene (10 mL) were stirred under an argon atmosphere till completely dissolved, then diphenylphosphoryl azide (DPPA) (0.49 mL, 2.29 mmol) was added into the mixture. The reaction solution was slightly heated at 40 °C for 1 h, and the temperature was raised to 80 °C for additional 4 h. Then **3** [15] (530 mg, 2.00 mmol) was added into the mixture and subsequently stirred at 80 °C for further 16 h. After evaporating the solvent, the resultant residue was thoroughly washed with cold methanol and then subjected to purification by chromatography on silica gel (CH_2Cl_2/MeOH, 100:1). Final recrystallization from $CH_3OH/CHCl_3$, afforded the product as white solids in 78% yield. ^{1}H NMR ($CDCl_3$ δ ppm): 13.06 (s, 1H), 12.14 (s, 1H), 11.86 (s, 1H), 7.41 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 5.80 (s, 1H), 2.85 (s, 6H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.55 (m, 2H), 1.19–1.23 (m, 16H), 0.80 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, *δ* ppm): 174.0, 155.7, 155.6, 153.4, 123.4, 114.2, 106.9, 42.0, 33.6, 32.7, 30.4, 30.3, 30.2, 30.0, 29.7, 27.8, 23.5, 15.0; MS (ESI) *m*/*z*: 428 $[M+H]^+$; Anal. Calcd. (%) for $C_{24}H_{37}N_5O_2$: C 67.42, H 8.72, N 16.38; found: C 67.31, H 8.76, N 16.57.

2.4. Synthesis of 2-(4-N,N-dimethylaniline)-methylene-uredio-6-(1-undecyl)-4[1H]-pyrimidinone (1b)

The synthetic procedure is similar to that of compound **1a**. ^{1}H NMR ($CDCl_3$, δ ppm): 13.08 (s, 1H), 11.94 (s, 1H), 10.07 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 2H), 5.81 (s, 1H), 4,35 (d, *J* = 5.6 Hz, 2H), 2.93 (s, 6H), 2.43 (t, *J* = 7.5 Hz, 2H), 1.62 (m, 2H), 1.26-1.31 (m, 16H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, δ ppm): 173.3, 156.8, 154.8, 152.5, 150.0, 128.8, 127.1, 112.9, 106.0, 58.6, 43.1, 40.9, 32.8, 32.0, 29.7, 29.6, 29.5, 29.3, 29.0, 27.1, 22.8, 18.6, 14.3; MS (TOF) *m*/*z*: 441.3 $[M+H]^+$, 464.3 $[M+Na]^+$; Anal. Calcd. (%) for $C_{25}H_{39}N_5O_2$: C 67.99, H 8.90, N 15.86; found: C 68.49, H 9.05, N 15.93.

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