



Full paper/Mémoire

Photoinduced electron transfer in a triarylamine-organoboron-Ru(2,2'-bipyridine)₃²⁺ compound

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ARTICLE INFO

Article history:

Received 2 July 2015

Accepted 27 August 2015

Available online 7 January 2016

Keywords:

Electron transfer

Time-resolved spectroscopy

Donor–acceptor systems

Photochemistry

Voltammetry

Ruthenium

ABSTRACT

Long-range electron transfer reactions play a key role in biological photosynthesis, and they are likely to play an important role for future artificial photosynthetic endeavors as well. The possibility to control the rates for long-range electron transfer with external stimuli is of particular interest in this context. In the work presented herein, we explored a donor–bridge–acceptor compound in which intramolecular electron transfer from a triarylamine donor to a photoexcited Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine) acceptor occurs across an organoboron bridge over a distance of approximately 22 Å. Fluoride has a high binding affinity to the organoboron bridge in apolar solutions, and the resulting organo-fluoroborate has a significantly different electronic structure. We explored to what extent the change from an electron-deficient organoboron wire to an electron-rich organo-fluoroborate bridge affects long-range electron transfer between the distant triarylamine donor and the Ru(bpy)₃²⁺ acceptor.

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1. Introduction

Organoboron compounds have received significant attention in recent years as (fluoride) sensor materials [1–3], for opto-electronic applications [4–6], and for fundamental studies of charge transfer phenomena [7–9]. In the vast majority of these charge transfer studies, the boron center acted as a terminal electron acceptor, but the efficiency of organoboron compounds as molecular bridges (or “wires”) between a donor and a more potent acceptor has not been investigated until very recently. In a study published in 2015, we demonstrated that intramolecular electron transfer between the triarylamine unit and photoexcited Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine) across the organoboron bridge of the dyad in Scheme 1a can be controlled by fluoride anions [10]. Specifically, in the absence of F[−] intramolecular electron transfer occurred with a rate constant (k_{ET}) $\geq 10^8$ s^{−1}, but when two fluoride

anions were bound to the organoboron bridge, k_{ET} decreased to $\leq 10^6$ s^{−1}. Here, we present results that we obtained on the structurally similar TAA-B-Ru²⁺ dyad shown in Scheme 1b. We were curious to explore whether the *meta*-linkage in the new dyad permits an equally efficient switching of long-range electron transfer as in our previously studied dyad.

The possibility to control the rates of long-range electron transfer is of interest in the greater contexts of a future molecular electronics technology and artificial photosynthesis.

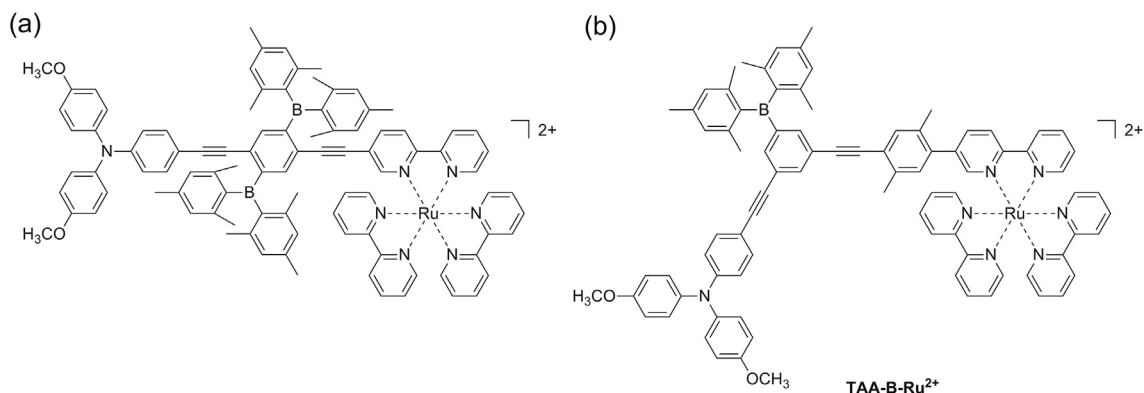
2. Results and discussion

2.1. Synthesis

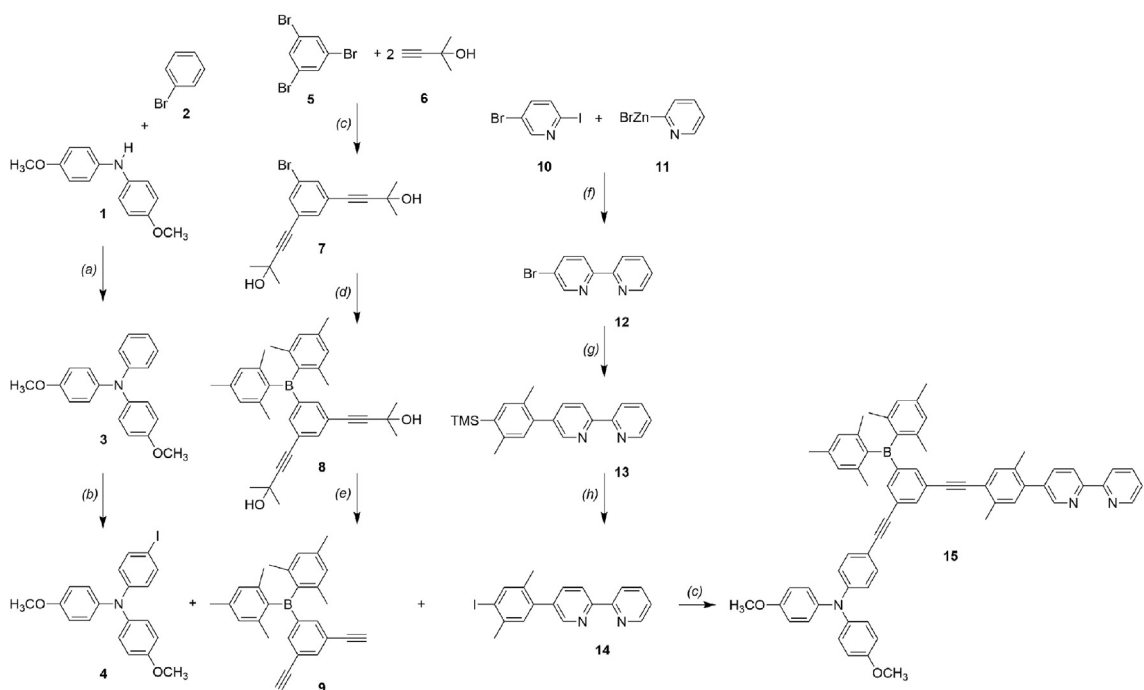
The synthesis of the key ligand of the TAA-B-Ru²⁺ compound is illustrated in Scheme 2. The triarylamine donor moiety was introduced into the TAA-B-Ru²⁺ dyad using the iodo-substituted triarylamine compound **4** which was prepared following previously published protocols [14,15]. The dimesitylboron-substituted bridging unit was

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Scheme 1. Chemical structures of two triarylamine-organoboron-Ru(bpy)₃²⁺ compounds: (a) Previously studied system [10]; (b) new system presented herein.



Scheme 2. Synthesis of the key ligand for the **TAA-B-Ru**²⁺ dyad from **Scheme 1b**: (a) P(^tBu)₃H⁺BF₄⁻, Pd(dba)₂, ^tBuOK, toluene; (b) C₆H₅I(CF₃COO)₂, I₂, CH₂Cl₂; (c) Et₃N, CuI, PdCl₂(PPh₃)₂; (d) *n*-BuLi, Bmes₂F, Et₂O; (e) NaH, toluene; (f) Pd(PPh₃)₄, THF [11]; (g) 2,5-dimethyl-4-trimethylsilyl-1-phenylboronic acid [12,13], Pd(PPh₃)₄, Na₂CO₃, THF/H₂O; (h) ICl, CH₃CN/CH₂Cl₂.

prepared starting from 1,3,5-tribromobenzene (**5**) which was reacted with 2 equivalents of 2-methyl-3-butyn-2-ol (**6**) to afford compound **7** [16]. The latter was reacted with dimesitylfluoroborane in order to obtain compound **8**. Subsequent deprotection with NaH gave the dialkynyl compound **9**. The iodo-xylene substituted bpy ligand unit **14** was prepared following our own published protocols [11,15]. Ligand **15** was obtained by reacting triarylamine compound **4**, dimesitylboron-substituted bridging unit **9**, and bpy ligand unit **14** in 1:1:1 molar ratio using standard Sonogashira coupling conditions. Subsequent reaction with Ru(bpy)₂Cl₂ afforded the **TAA-B-Ru**²⁺ dyad.

2.2. Electrochemistry

Cyclic voltammetry of the **TAA-B-Ru**²⁺ dyad was performed in CH₃CN containing 0.1 M TBAPF₆ as a supporting electrolyte. Oxidative and reductive potential sweeps with rates of 0.1 V/s were conducted separately because this gave higher quality results. Typical scans are shown in Fig. 1. Oxidation of the triarylamine unit is detected at 0.20 V vs. Fc^{+/0} and oxidation of Ru(II) occurs at 0.77 V vs. Fc^{+/0}, both in line with expectations [10,17,18]. Based on previous studies, [18] we expect that the Ru(II/III) wave overlaps with the wave associated with the oxidation of the

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