

Homoleptic star-shaped Ru(II) complexes*

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Abstract: A series of homoleptic Ru(II) star complexes were synthesized and bound to semiconductor metal oxide nanoparticle films. In the nanosized, highly symmetrical “star”-shaped complexes, the Ru(II) center is coordinated to three identical bipyridine ligands carrying conjugated oligophenylethyne (OPE) rigid linker units terminating with carboxylic anchor groups. In this report, we describe how this concept is being applied toward the development of chromophoric units that are isolated from the surface of the semiconductor, and some possible advantages of this surface engineering strategy.

Keywords: dyes; homoleptic complexes; synthesis; ruthenium complexes; TiO₂.

INTRODUCTION

Chromophore-linker-anchor dyes have attracted increasing interest over the past decade as useful models to study the sensitization of semiconductors [1]. The linker-anchor unit makes the surface attachment more predictable in terms of surface binding geometries, distance, and orientation of the chromophore, thereby allowing some level of control over electron-transfer processes. Additionally, the linker-anchor unit can be used to tune the photophysical properties of the chromophore, as in the case, for instance, of the efficient push–pull organic sensitizers studied by Sun and co-workers [2]. As part of our interest in the study of this type of model dyes, we previously reported the charge injection study of a series of Ru(II) bipyridyl complexes with a rigid-rod oligophenylethyne (OPE) linker terminated with an isophthalic acid (Ipa) anchor unit for attachment to the surface, Fig. 1 [3]. The two anchoring COOH groups on the Ipa unit ensured fewer surface orientations and degrees of freedom [3c] when compared to structurally very similar rigid-rod model dyes with one COOH group that have been described by others [4].

Injection kinetics for **1–3** bound to TiO₂ (anatase) nanoparticles films cast on glass slides, following 532 nm excitation, clearly showed the anticipated trend, i.e., slower injection from the longer linker, see Fig. 1. A complex charge-transfer behavior, though, was also observed. First, the injection traces of **1–3** could be fitted with biexponential decays. Multiexponential injection behavior is frequently observed in charge transfer of dyes on metal oxides, and it is attributed to a combination of factors, including injection from ¹MLCT, ³MLCT, and nonthermalized excited states [5], as well as to the heterogeneity of the nanoparticle films [5d,6].

*Paper based on a presentation made at the XXIII^d IUPAC Symposium on Photochemistry, Ferrara, Italy, 11–16 July 2010. Other presentations are published in this issue, pp. 733–930.

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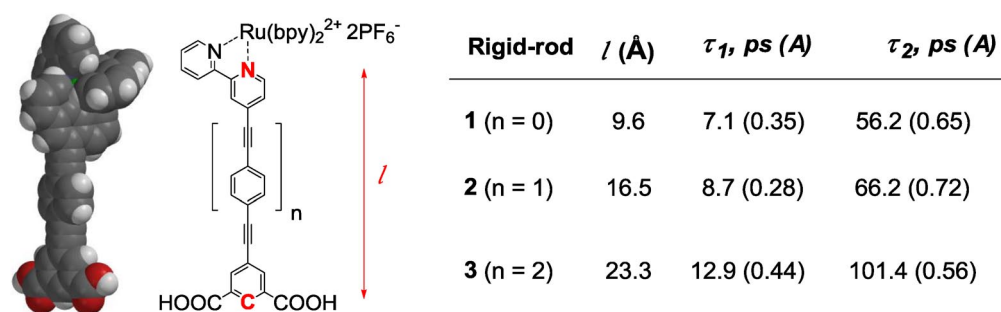


Fig. 1 Electron injection behavior of Ru-bpy rigid-rods bound to nanoparticle TiO_2 films. *Left*. Space filling model (AM1 optimization, Spartan '08, Wavefunction, Inc.) of **2** [3a].

Second, the charge recombination rate constants were found to be independent of the structure and linker length of the rigid rod [3b]. Finally, plots of the fast or slow component of the injection vs. the spacer length yielded a very low value for the attenuation factor (0.04 \AA^{-1}). This latter observation was in part attributed to the electronic and conformational properties of the OPE linker [3a], and in part was ascribed to direct contacts of the Ru complex units with nearby nanoparticles to which the rods are not directly attached, as schematically shown in Fig. 2 [7].

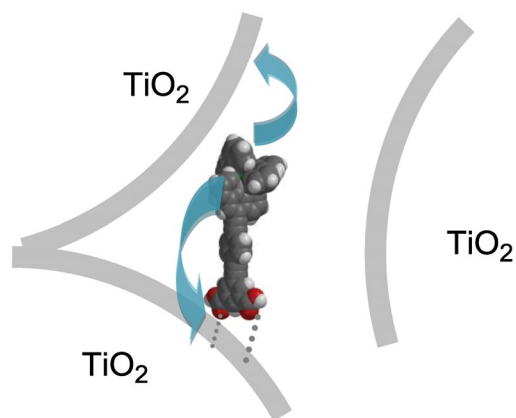


Fig. 2 Schematic representation of the challenges (orientations, “shorting” contacts, etc.) of the chromophore-linker-anchor design to prepare effective models for charge-transfer studies.

The influence of direct contacts on injection or recombination kinetics, and the suggestion that they may act as “short-circuits”, has been reported by others (Diao [6] and Willig [5d], e.g.) for rigid-rod or tripodal models dyes attached to TiO_2 through long linkers.

In summary, complex charge-transfer behavior has been observed in other dye-linker-anchor sensitizers designed in our group and by others [1,3,5], and it demonstrates that it is far from easy to design models where the positioning of a dye on a surface is effectively controlled. Uncertainty over the binding mode and orientation, and the heterogeneity of the surface can, in some cases, prevail over the molecular design.

In the past few years, there has been an interest in developing a new approach to dye/semiconductor interfaces, which could be useful to improve the control of binding geometry. In this approach, which has been recently reviewed [8], a dye is encapsulated in a host and the dye@host complex is

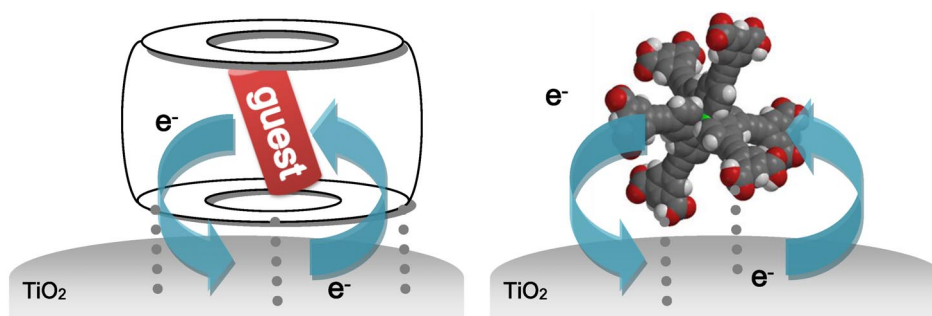


Fig. 3 Schematic representation of two methods for isolation of chromophores on semiconductor surfaces. *Left*: binding of a guest@host complex. *Right*: binding of a star-shaped symmetric homoleptic complex (AM1 optimization, Spartan '08, Wavefunction, Inc).

bound to the surface. This is schematically illustrated in Fig. 3 (left). As a result, the dye unit is shielded from the surface. Among the first examples of this strategy is the work of Piotrowiak and co-workers, who studied interfacial charge transfer in a hybrid assembly composed of an azulene@hemicarcerand complex covalently bound to nanoparticles of TiO_2 [9].

The effect of encapsulation on the photoinduced charge-transfer dynamics, after comparisons with a directly bound 1-carboxyazulene, was single exponential kinetics and slower recombination rates (from pico- to nanosecond scale). A remarkably similar trend was reported by Haque and Durrant in their study of azobenzene dyes encapsulated in cyclodextrins and bound to TiO_2 [10]. Other recent examples illustrate the implications of this surface engineering approach [8], including a recent report on methylviologens encapsulated in cucurbiturils (MV@CB[7]) for electrochromic windows [11].

In this paper, we describe the synthesis of a new class of Ru sensitizers as a second approach to isolate the chromophore from the heterogeneity of the semiconductor surface. Conjugated rigid OPE linkers on all three bpy ligands were used to separate the Ru metal center from the metal oxide semiconductor surface, Fig. 3 (right).

Homoleptic Ru complexes appear attractive highly symmetric dyes that may offer orientation control, distance control, and isolation of the Ru(II) center from the surface. There are several examples of studies involving homoleptic Ru complexes of bipyridines, including cation sensors [12], oxygen sensors [13], and as dendrimers for protein surface recognition [14]. Otsuki and co-workers synthesized Ru homoleptic complexes with bpy ligands substituted with OPE groups, that are structurally close to the ones presented here [15]. The complexes were bound onto gold by thiol anchoring groups. Single molecules were observed by using scanning tunneling microscopy (STM). To the best of our knowledge, their use for the approach proposed in Fig. 3 is a new application of homoleptic Ru complexes.

HOMOLEPTIC Ru(II) COMPLEXES: AN APPROACH TO ISOLATION OF METAL CENTERS ON SEMICONDUCTOR SURFACES

Star-shaped Ru(II) complexes

The homoleptic, highly symmetric complexes SSC, LSC, and SLSC were synthesized and compared with reference compounds $\text{Ru}(\text{bpy})_3^{2+}$, without any anchor groups, 3SSC, which is homoleptic but not symmetrical, and to $\text{Ru}(\text{deeb})_3^{2+}$, which has COOH anchor groups directly attached to the bpy ligands, Charts 1 and 2. The counterion was PF_6^- in all cases.

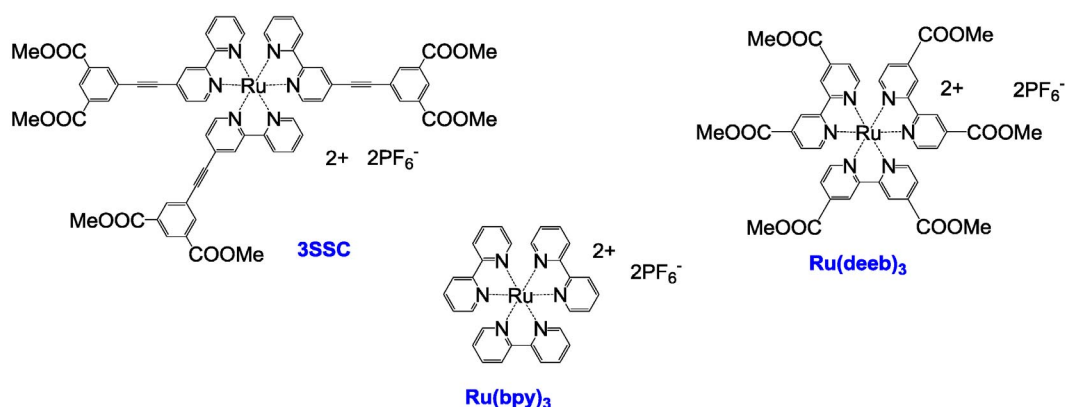


Chart 1

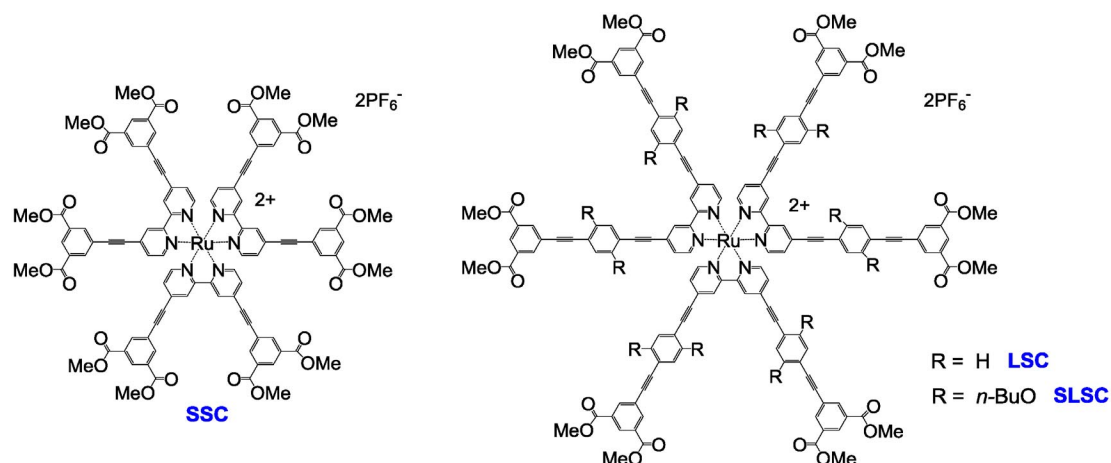


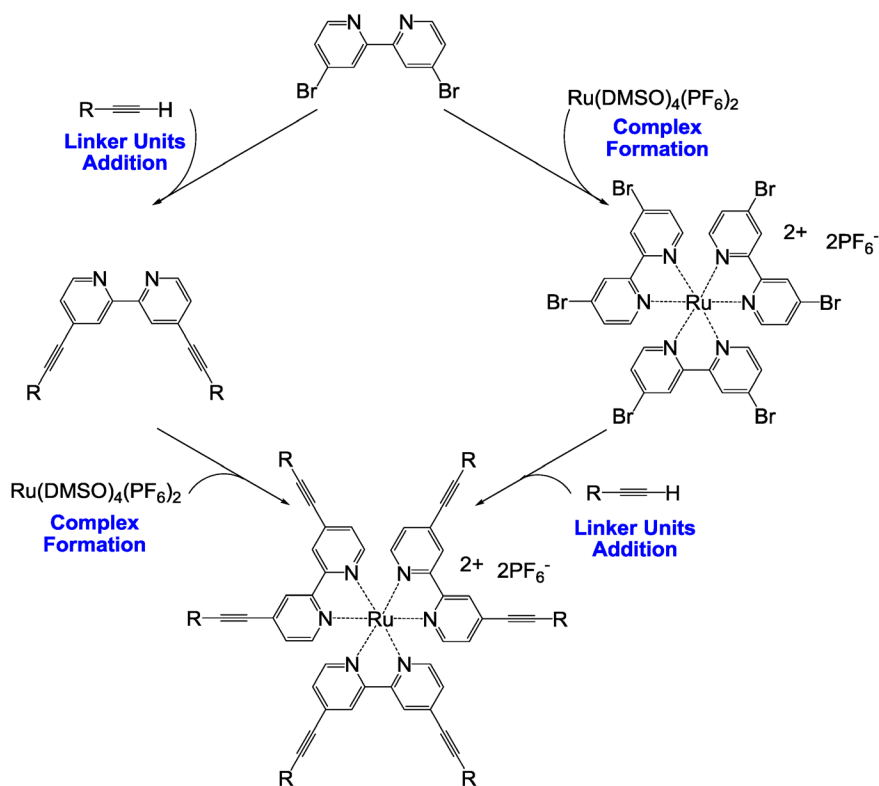
Chart 2

The star complexes have two rigid linkers attached onto the 4 and 4' position of each bipyridine unit. Star complexes SSC and LSC were synthesized to make direct comparisons with rods **1** and **2**, respectively. The solubility of SSC and LSC in organic solvents was low. This is potentially a problem, as the binding onto TiO₂ nanoparticles is done by immersing the films in solutions of the dyes. Because of the low solubility of the ester derivatives, these were not converted to carboxylic acids prior to binding. To increase the solubility of the star complex, a *n*-butoxy group was selected as the side chain group attached onto the central phenylene unit of the OPE bridge for the SLSC as a comparison with the LSC. All of the complexes had Ipa anchoring units to assure the binding to the metal oxide semiconductor nanoparticle surfaces. The diameter of the complexes was approximately 2.5 nm (for SSC) and 4 nm (for LSC).

Synthesis and properties

The classical method to synthesize homoleptic Ru(bpy)₃²⁺ derivatives, involving the reaction between RuCl₃ and a bipyridine ligand in the presence of hypophosphorous acid, was not successful in this case. After coordination of two bipyridine ligands, the resulting complexes precipitated from the reaction mixture, preventing further coordination. Thus, two alternative synthetic routes were used to synthesize

the target complexes, as shown in Scheme 1. Both routes involved reaction with $\text{Ru}(\text{DMSO})_4(\text{PF}_6)_2$, a soluble complex utilized by Otsuki and co-workers [15]. In the first method, the linker units were added to the bpy ligand, and the modified ligand reacted with $\text{Ru}(\text{DMSO})_4(\text{PF}_6)_2$ to form SLSC. In the second approach, particularly successful for the synthesis of LSC, a brominated complex precursor was formed first, followed by Sonogashira Pd-catalyzed coupling with an excess of linker units. The complex $\text{Ru}(\text{DMSO})_4(\text{PF}_6)_2$ was prepared by refluxing commercially available $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ and AgPF_6 in ethanol under nitrogen atmosphere. The precipitation of insoluble silver chloride drove this reaction to completion. The use of PF_6^- as a non-coordinating anion increased the solubility of Ru polypyridine complexes. The synthesis of the complexes in Chart 2, which proceeded in yields ranging from 15 to 66 %, will be published elsewhere. UV-vis absorption was used to monitor the progress of the complexation reaction, as the absorption spectra of the dichelated and trichelated complexes are rather different. A purple color ($\lambda_{\text{MLCT}} \sim 515 \text{ nm}$) indicated the presence of the partially chelated Ru bis(bipyridine) complex, and the typical orange color of the $\text{Ru}(\text{bpy})_3^{2+}$ complex ($\lambda_{\text{MLCT}} \sim 452 \text{ nm}$) indicated completion of the complexation reaction.



Scheme 1 Synthetic routes to the star complexes.

Ru polypyridine complexes are classical photosensitizing dyes for DSSCs application due to their intense MLCT (metal-to-ligand charge transfer) absorption band in the visible region, long-lived (micro to millisecond) excited states, and long-term stability in the ground, excited, and oxidized states [1d]. The solution photophysical properties of the star-shaped complexes SSC and LSC were, as expected, fairly similar to those reported for the Ru(II) rigid rods **1–3** and exhibited a trend observed for complexes substituted with the conjugated OPE units. When compared to the ground-state reduction poten-

tial value of Ru(bpy)₃ (1260 mV) and rigid rods (1300 mV), the $E_{1/2}$ value of 3SSC (1400 mV) and SLSC (1557 mV) was shifted to more positive potential in both cases. Due to their low solubility, the cyclic voltammetry (CV) data for SSC and LSC were not obtained. The excited-state reduction potentials $E_{1/2}(\text{Ru}^{\text{III/II}^*})$ for 3SSC (-760 mV) and the soluble-rod SLSC (-523 mV) were considerably less negative than the value of reference sensitizers **1–3** and Ru(deeb)₃ (-820 to -860 mV) [3], indicating that the star complexes may be less effective photosensitizers than the rods on TiO₂ films. Compared to the rigid rods (1.9 and 2.3 μs) [3], all star complexes exhibited slightly shorter excited-state lifetime τ (1.6–1.8 μs) and fluorescence emission bands centered at 643–648 nm.

The UV–vis absorption spectra of star complexes in acetonitrile solution exhibited the π, π^* transition band of the OPE units at ~370 nm [3], and the MLCT band at ~490 nm, was considerably red-shifted compared to the MLCT of Ru(bpy)₃²⁺ (~450 nm) and the rigid rods (~465 nm). The spectrum of the SLSC complex exhibited an additional π, π^* transition band at ~400 nm assigned to the electron donation of the oxygen on the butoxy side-chain group. This band was observed in the spectrum of the soluble ligand used to synthesize SLSC.

Preliminary binding studies were done binding the esters on TiO₂ nanoparticle thin films. In this preliminary work, all compounds were bound as esters. Previous research indicate that the carboxylic ester can be a strong binding group for Ru polypyridine complexes, but the binding of the carboxylic acid is preferable as it forms a stronger bond with the semiconductor surface [3b]. The hydrolysis of the soluble methyl ester SLSC and the study of the carboxylic acid derivative is forthcoming. Although the solubility of SSC in acetonitrile was low, Fig. 4, the compound did bind to TiO₂ films, upon long immersion times (2 days), Fig. 4.

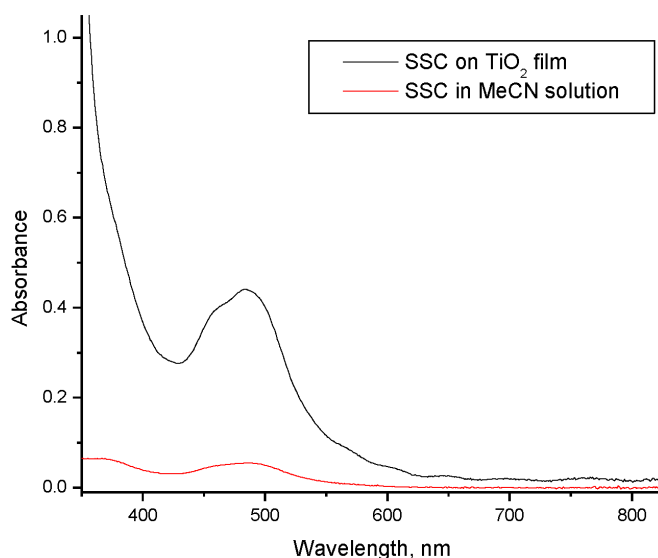


Fig. 4 Absorption spectra of SSC on TiO₂ film and in acetonitrile (~10⁻⁵ M).

The binding to TiO₂ for compounds 3SSC, SSC, LSC, and SLSC was studied by Fourier transform-infrared-attenuated total reflectance (FT-IR-ATR) spectroscopy. All the spectra of the esters showed the presence of intense bands at ~1720 cm⁻¹ ($\nu_{\text{C=O}}$) for the carbonyl group and at ~1610 cm⁻¹ ($\nu_{\text{C=C}}$) for the phenylene (Ph) group. Upon binding to the TiO₂ films, the IR spectra showed a ~8 cm⁻¹ shift of the carbonyl stretch band, while the Ph band was unchanged, Fig. 5. The presence of unbound carbonyl bands indicated that not all the anchoring groups were bound on the TiO₂ films. This was

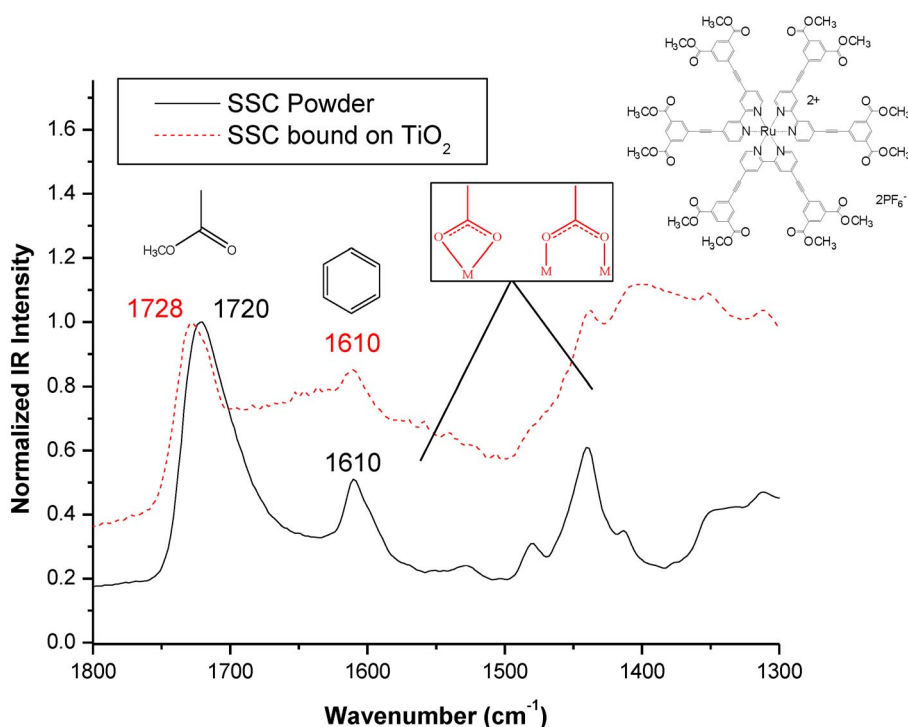


Fig. 5 FT-IR-ATR spectra of SSC before and after binding on TiO_2 films.

expected, as it is not possible for all COOMe group to bind. The new, broad bands at $\sim 1640 \text{ cm}^{-1}$ (ν_s) and 1400 cm^{-1} (ν_{as}), were consistent with bidentate coordination modes of carboxylate groups, presumably the result of surface hydrolysis or other interactions between the COOMe groups and the TiO_2 surface [3b].

In preliminary studies upon binding onto the TiO_2 thin films, the excited state was clearly observed with only a small yield of what appears to be charge-separated products, suggesting that the elongated bridges effectively suppress excited-state injection. The sensitization of TiO_2 films and the studies of charge injection and recombination processes are in progress. Of particular interest will be a comparison of injection vs. recombination rates and the charge-transfer kinetics.

SUMMARY

Homoleptic, nano-sized star-shaped Ru(II) complexes carrying OPE rigid linkers capped with anchor groups were synthesized as a novel type of chromophore-linker-anchor model dyes to study the interfacial charge-transfer processes which are at the basis of dye-sensitized solar cells. Preliminary studies indicate that the methyl esters of the complex compounds bind to TiO_2 films, and that injection occurs on TiO_2 films. The photophysical and charge-transfer properties for the star complexes are in progress. The compounds were designed to test the concept of highly symmetrical chromophoric units that, isolated from the surface of the semiconductor, may offer a better control of the interface between a dye and a semiconductor. This approach may offer a novel surface engineering method, as illustrated in Fig. 3.

ACKNOWLEDGMENTS

This work was funded by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-FC02-01ER15256 (E.G.) and DE-FG02-96ER14662 (G.J.M.). E.G. is grateful to Prof. Mendelsohn and Dr. Guangru Mao for the IR measurements.

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