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Synthesis of Homoleptic Ruthenium “Star” Complexes by Click Reaction for TiO_2 Sensitization

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Homoleptic Ru^{II} complexes carrying rigid linkers for attachment to semiconductor surfaces were synthesized by using the click reaction. Star-shaped complexes KStar-TzC-pBn (**1a**) and KStar-TzC-Ipa (**1b**), composed of 2,2′-bipyridine ligands 4,4′-disubstituted with 1,2,3-triazole rings connected to the Ru complex through the C4 of the 1,2,3-triazole (Tz) ring and capped with *p*-benzoic (pBn) and isophthalic (Ipa) methyl esters, respectively, as well as KStar-TzN-pBn (**1c**), connected to the Ru complex through the N1 of the Tz ring, were studied in solution and bound to semiconducting TiO_2 and insulating ZrO_2 nanoparticle films.

Introduction

Chromophores attached through rigid linker-anchor units to nanostructured TiO_2 or other semiconductor surfaces are of interest for the development of dye-sensitized solar cells,[1] photocatalysts,[2] and other applications. Synthetic modifications of the linkers can be used to tune the properties of the chromophore unit,[3] to modify surface binding, and to control charge-transfer processes.[4] Over the years, the linker strategy has led to a better understanding of interfacial charge transfer[5] and to improved devices.[6] However, the surface heterogeneity of nanostructured semiconductors can prevail over molecular design, and preventing binding disorder remains a significant challenge.[7]

Recently, we reported that “shielding” strategies for the adsorption of photo- or redox-active molecules on semiconductors result in improved binding control.[8] One approach involved the development of homoleptic Ru^{II} complexes (Star complexes) with octahedral symmetry,[9] in which the chromophore unit is shielded from direct contacts with the surface through the symmetrical arrangement of oligophenylenethynylene linkers. The initial Star complexes exhibited very low injection yields;[9b] however, recent computational studies suggest that judicious variations of the linker and anchor could improve the electronic coupling with the surface.[10]

In this paper we report the first Star complexes prepared by using the click reaction, that is, Cu-catalyzed azide–alkyne cycloaddition to form a 1,2,3-triazole ring.[11] The click approach, which is only very recently being applied to the synthesis of inorganic complexes,[12] has two advantages. First, the linker can be “clicked” to different anchor units, and, second, it will be possible to probe the electron-mediating function of triazole rings, changes in the dipole moment, and the structural conformation effects of the linker in relation to the ring connectivity with the Ru complex moiety.[13] Here we describe the synthesis of compounds **1a**, **1b**, and **1c** shown in Figure 1. Compounds **1a** and **1b** have C-connectivity to the $Ru(bpy)_3$ core but differ in the anchor group (R = pBn and Ipa, respectively), whereas **1c** is attached through N-connectivity to the $Ru(bpy)_3$ core and can be compared with **1a**, which has the same pBn anchor group.

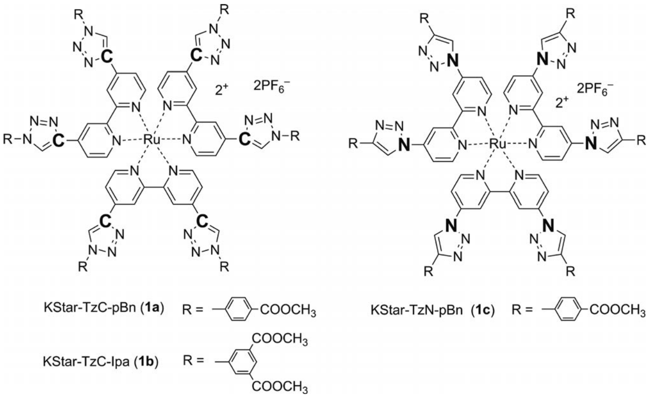

Figure 1. Molecular structure of **1a**, **1b**, and **1c**.

Results and Discussion

The synthesis of KStar-TzC-pBn (**1a**) and KStar-TzC-Ipa (**1b**) was carried out as shown in Scheme 1. Azides **3a**

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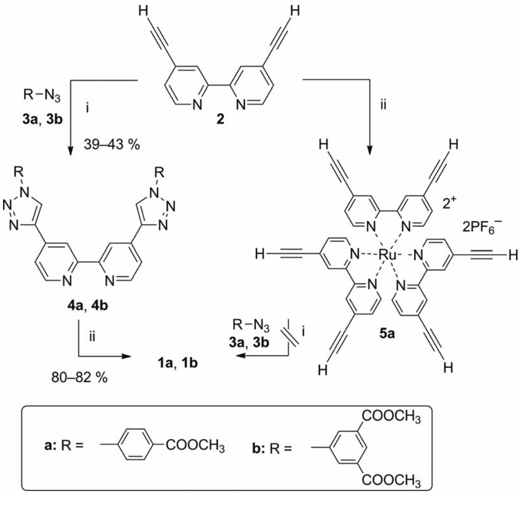
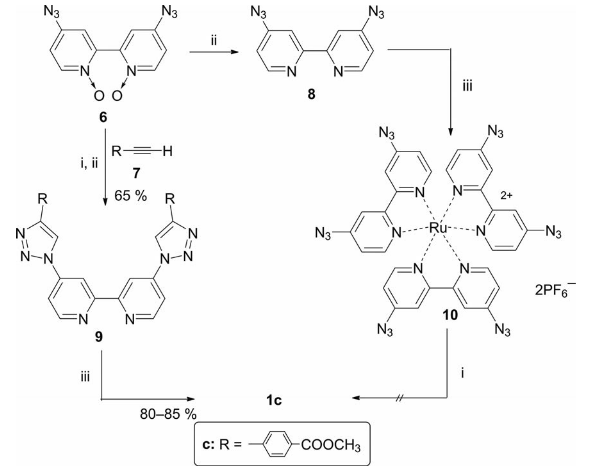
and **3b** were prepared in about 80% yield by conversion of the corresponding amines into diazonium salts and reaction with sodium azide.[14] Ligands **4a** and **4b** were synthesized by the click reaction[12a,15] between azides **3a** or **3b** and 4,4′-diethynyl-2,2′-bipyridine (**2**) in 43 and 39% yields, respectively, with use of catalytic Cu^{II} in the presence of sodium ascorbate to generate Cu^{I} in situ. The modest yields may be due to complexation of Cu^{I} with bipyridine. The reaction was carried out in the presence of small amounts of $(i\text{Pr})_2\text{EtN}$ to promote the formation of the copper acetylide intermediate.[16] In the absence of base, the reaction yielded mainly the monosubstituted product. A more attractive approach, involving the click reaction of the hexaethynyl-substituted Ru complex **5a** with the azide-substituted anchors (Scheme 1), was unsuccessful.[17] Possible explanations include the occurrence of alkyne homocoupling in the presence of copper salts or the formation of copper acetylide complexes on one or more of the alkynes (Cu^{I} saturation),[18] a process that would prevent cyclization with the azide.



Scheme 1. Click synthesis of C-connectivity Star complexes. Reagents and conditions: (i) $CuSO_4{\cdot}5H_2O$, sodium ascorbate, $(i\text{Pr})_2\text{EtN}$, H_2O, *t*BuOH, MeOH, room temp., 18 h; (ii) $\text{Ru(DMSO)}_4\text{Cl}_2$, ethylene glycol, MeOH, H_2O, 120 °C, 3 d.

Similarly, the synthesis of KStar-TzN-pBn **(1c)**[19] was carried out as shown in Scheme 2. 4,4′-Diazido-2,2′-bipyridine 1,1′-dioxide (**6**) was prepared from the nitro precursor in 97% yield and was then reacted with the corresponding alkyne **8** for the click reaction to obtain the *N*,*N*′-dioxide form of ligand **9**, which was reduced with phosphorus trichloride to obtain ligand **9** in 65% overall yield. However, the approach involving click reaction on diazidobipyridyl-substituted Ru complex **11** was unsuccessful because of the instability of **11** in a variety of reaction conditions.[17]



Scheme 2. Click synthesis of N-connectivity Star complexes. Reagents and conditions: (i) $CuSO_4{\cdot}5H_2O$, sodium ascorbate, $(i\text{Pr})_2\text{EtN}$, H_2O, *t*BuOH, MeOH, room temp., 18 h; (ii) PCl_3, acetonitrile, reflux, 4 h; (iii) $\text{Ru(DMSO)}_4\text{Cl}_2$, ethylene glycol, MeOH, H_2O, 120 °C, 3 d.

FTIR-ATR spectra of azides **3a**, **3b**, and **6** showed the characteristic N_3 stretching bands at about 2100 (ν_{as}) and 1250 (ν_{sym}) cm^{-1} (Figures S2, S3, and S6). Bipyridine **2** and alkyne **7** showed a strong $\nu_{as}(\equiv C\text{–}H)$ band at 3100 cm^{-1} and a weak $\nu_{sym}(C\equiv C)$ band at about 2100 cm^{-1} (see Supporting Information). The FTIR-ATR spectra of ligands **4a**, **4b**, and **8**, as well as the corresponding Ru complexes **1a**, **1b**, and **1c** show the $\nu_{as}(C{=}O)$ stretch characteristic of the ester group at 1728, 1733, and 1710 cm^{-1}, respectively. The spectra of **1a** and **1b** bound to TiO_2 films (Figures 2 and S9) show broad bands characteristic of the carboxylate group in the 1500–1650 cm^{-1} region. The observed spectral changes are consistent with chelating and/or bidentate binding modes of the carboxyl group to TiO_2, presumably as a result of surface hydrolysis or other interactions between the ester groups and the TiO_2 surface.[9] The presence of the carbonyl band assigned to free COOMe indicates that, as expected, not all the anchor groups bind to TiO_2.

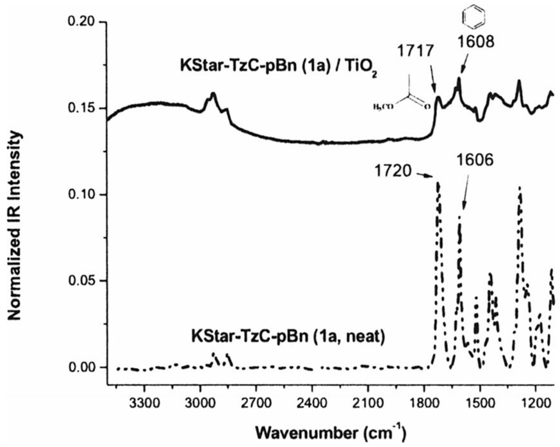


Figure 2. FTIR-ATR spectra of KStar-TzC-pBn (**1a**) neat (bottom) and bound to nanoparticle TiO_2 films (top). The broad band above 3100 cm^{-1} is assigned to water adsorbed on the film.

The solution (THF, 0.9 mM) UV/Vis absorption and steady-state photoluminescence (PL) spectra of **1a**, **1b**, and **1c** are shown in Figures S24 and S26, and selected photophysical properties are listed in Table 1. The UV/Vis absorption spectra for all complexes exhibit bands in the 280–310 nm region assigned to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions of the bpy and triazole moieties. The broad, structureless

MLCT band typical of $Ru(bpy)_3^{2+}$ complexes is centered at about 450 nm. The values of the molar extinction coefficients ($\varepsilon_{1a} = 2.3 \times 10^4$ M^{-1} cm^{-1}, $\varepsilon_{1b} = 2.1 \times 10^4$ M^{-1} cm^{-1}, and $\varepsilon_{1c} = 0.2 \times 10^4$ M^{-1} cm^{-1}) are close to those observed for typical bpy complexes of Ru^{II}.[9] The steady state PL spectra for **1a** and **1b** show a broad emission centered at 637 nm, but the emission quantum yields (Φ_{1a} = 0.7% and Φ_{1b} = 0.4%) are about one order of magnitude lower than that observed for $Ru(bpy)_3^{2+}$.[20] Compound **1c** is not photoluminescent. To probe the possibility that electron donation from the triazole ring may quench the emission, particularly in the N-connectivity Star compound **1c**, acid was added to the solution. Protonation of the triazole ring resulted in a twofold increase in PL, and titration of the acidic solution with base led to reversible behavior, with an approximately twofold decrease in PL for complexes **1a** and **1b**,[21] as shown in Figures 3 and S23. Surprisingly, no photoluminescence was observed for **1c** under acidic conditions, although the UV/Vis spectra of acidic solutions of **1c** showed increased intensity (Figure S26). Additionally, titration of $Ru(bpy)_3^{2+}2Cl^-$ with 4-phenyl-1*H*-1,2,3-triazole did not result in intermolecular photoluminescence quenching, suggesting that the role of the triazole ring on the emissive properties of **1a**–**c** is complex and needs to be further investigated.

Table 1. Selected photophysical properties in THF at room temp.

Complex	λ_{abs}[a] (ε [M^{-1} cm^{-1}])	λ_{PL}[a]	Φ_{em} ($\times 10^{-2}$)
KStar-TzC-pBn (**1a**)	485 (2.3×10^4)	637	0.7
KStar-TzC-Ipa (**1b**)	485 (2.1×10^4)	638	0.4
KStar-TzN-pBn (**1c**)	ca. 500 (0.2×10^4)	–	–
$Ru(bpy)_3^{2+}$[b]	450 (1.2×10^4)	610	6.2

[a] Wavelengths in nm. [b] Data from ref.[9]

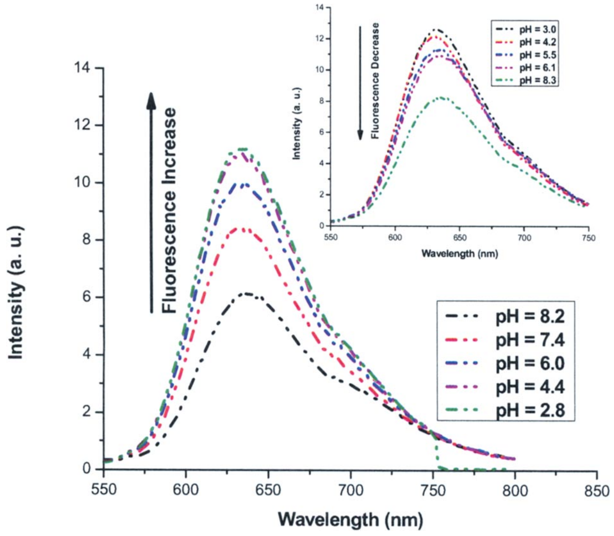


Figure 3. Photoluminescence spectrum of a 9×10^{-4} M THF solution of **1a** upon titration with aliquots of 6 N HCl. Inset: PL spectrum of a 9×10^{-4} M THF solution of **1b** upon titration with aliquots of 6 N NaOH. λ_{exc} = 485 nm.

These interesting observations suggest that the photoluminescence properties could be the result of multiple factors (different linker conformations or electronic delocalization influencing the excited state electronic structure, for instance). While this is beyond the scope of this communication, we will probe the origin of this behavior in our future studies.

Star complexes **1a** and **1b** were bound onto TiO_2 and ZrO_2 nanoparticle mesoporous films. The **1a**/TiO_2 and **1b**/TiO_2 films showed the characteristic MLCT band in the UV/Vis spectra (Figure S25) and full quenching of the PL emission (Figure 4). Since ZrO_2 has a wider band gap ($E_{bg} \approx 5$ eV) compared to TiO_2 ($E_{bg} \approx 3$ eV), it behaves as an insulator, and the PL emission was observed on films prepared from this material (Figure 4).

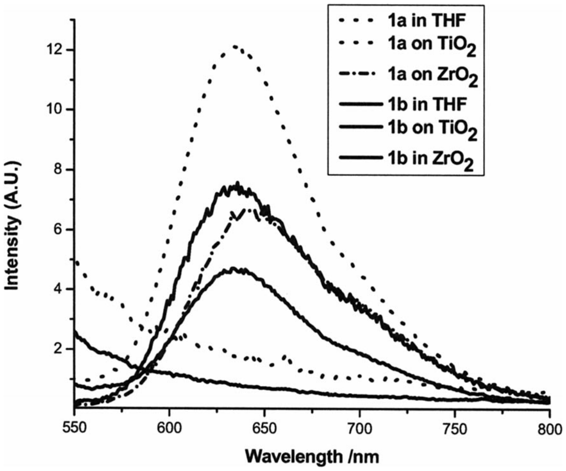


Figure 4. PL spectra of **1a** and **1b** in solution and bound on TiO_2 and ZrO_2 nanoparticle thin films.

Conclusions

Three star-shaped ruthenium complexes, KStar-TzC-pBn (**1a**), KStar-TzC-Ipa (**1b**), and KStar-TzN-pBn (**1c**), containing the triazole unit were synthesized by the click reaction and characterized. Titration with acid and base showed reversible behavior with twofold increase in the PL emission and vice-versa for C-connectivity complexes **1a** and **1b**. FTIR, UV/Vis, and photoluminescence studies of the compounds in solution and bound on metal oxide semiconductor nanoparticle thin films (TiO_2 and ZrO_2) showed that the complexes bind to the semiconductors. On TiO_2 the photoluminescence was completely quenched, whereas the functionalized ZrO_2 films showed a broad emission band. Ongoing studies include studying interfacial charge transfer and theoretical calculations for **1a**–**c** to assess the structural and electron-mediating function of 1,2,3-triazole rings and the role of the anchor group.

Supporting Information (see footnote on the first page of this article): Synthesis and characterization of **1a**, **1b**, and **1c**. ^1H and ^{13}C-NMR spectra for **4a**, **4b**, **9**, **1a**, **1b**, and **1c**. FTIR-ATR spectra for **2**, **6**, **3a**, **3b**, **8**, **4a**, **4b**, **9**, **1b** neat and adsorbed on TiO_2, PL spectra of **1b** upon titration with acid, UV/Vis and PL spectra of **1a** and **1b**, UV/Vis spectrum of **1c** in solution and upon titration with acid.

Acknowledgments

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[1] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, *110*, 6595–6663.

[2] a) A. Kubacka, M. Fernandez-Garcia, G. Colon, *Chem. Rev.* **2012**, *112*, 1555–1614; b) W. J. Youngblood, S. H. Lee, K. Maeda, T. E. Mallouk, *Acc. Chem. Res.* **2009**, *42*, 1966–1973; c) D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2009**, *42*, 1890–1898.

[3] A. Mishra, M. K. Fischer, P. Bäuerle, *Angew. Chem.* **2009**, *121*, 2510; *Angew. Chem. Int. Ed.* **2009**, *48*, 2474–2499.

[4] a) A. Kopecky, E. Galoppini in *Specialist Periodical Report on Photochemistry, Vol. 37* (Ed.: A. Albini), The Royal Society of Chemistry, Cambridge, **2009**, pp. 362–392; b) E. Galoppini, *Coord. Chem. Rev.* **2004**, *248*, 1283–1297.

[5] a) R. Ernstorfer, L. Gundlach, S. Felber, W. Storck, R. Eichberger, F. Willig, *J. Phys. Chem. B* **2006**, *110*, 25383–25391; b) N. A. Anderson, X. Ai, D. T. Chen, D. L. Mohler, T. Q. Lian, *J. Phys. Chem. B* **2003**, *107*, 14231–14239.

[6] D. P. Hagberg, J. H. Yum, H. Lee, F. De Angelis, T. Marinado, K. M. Karlsson, R. Humphry-Baker, L. Sun, A. Hagfeldt, M. Grätzel, M. K. Nazeeruddin, *J. Am. Chem. Soc.* **2008**, *130*, 6259–6266.

[7] a) S. Thyagarajan, E. Galoppini, P. Persson, J. M. Giaimuccio, G. J. Meyer, *Langmuir* **2009**, *25*, 9219–9226; b) C.-W. Chang, L. Luo, C.-K. Chou, C.-F. Lo, C.-Y. Lin, C.-S. Hung, Y.-P. Lee, E. W.-G. Diau, *J. Phys. Chem. C* **2009**, *113*, 11524–11531.

[8] a) M. Porel, A. Klimczak, M. Freitag, E. Galoppini, V. Ramamurthy, *Langmuir* **2012**, *28*, 3355–3359; b) M. Freitag, E. Galoppini, *Energy Environ. Sci.* **2011**, *4*, 2482–2494.

[9] a) Y. Zhang, E. Galoppini, P. G. Johansson, G. J. Meyer, *Pure Appl. Chem.* **2011**, *83*, 861–868; b) P. G. Johansson, Y. Zhang, M. Abrahamsson, G. J. Meyer, E. Galoppini, *Chem. Commun.* **2011**, *47*, 6410–6412.

[10] P. Persson, in private communication (publication in preparation).

[11] M. Meldal, C. W. Tornoe, *Chem. Rev.* **2008**, *108*, 2952–3015.

[12] a) S. Cicchi, P. Fabbrizzi, B. Cecconi, *Synlett* **2011**, 223–226; b) A. Baron, C. Herrero, A. Quaranta, M. F. Charlot, W. Leibl, B. Vauzeilles, A. Aukauloo, *Inorg. Chem.* **2012**, *51*, 5985–5987.

[13] a) G. de Miguel, M. Wielopolski, D. I. Schuster, M. A. Fazio, O. P. Lee, C. K. Haley, A. L. Ortiz, L. Echegoyen, T. Clark, D. M. Guldi, *J. Am. Chem. Soc.* **2011**, *133*, 13036–13054; b) C. Katan, M. Blanchard-Desce, S. Tretiak, *J. Chem. Theory Comput.* **2010**, *6*, 3410–3426.

[14] S. W. Kwok, J. R. Fotsing, R. J. Fraser, V. O. Rodionov, V. V. Fokin, *Org. Lett.* **2010**, *12*, 4217–4219.

[15] S. Paek, C. Baik, M. S. Kang, H. Kang, J. Ko, *J. Organomet. Chem.* **2010**, *695*, 821–826.

[16] a) P. Mobian, J. P. Collin, J. P. Sauvage, *Tetrahedron Lett.* **2006**, *47*, 4907–4909; b) G. Zhang, L. Fang, L. Zhu, D. Sun, P. G. Wang, *Bioorg. Med. Chem.* **2006**, *14*, 426–434.

[17] a) C. D. Hein, X. M. Liu, D. Wang, *Pharm. Res.* **2008**, *25*, 2216–2230; b) V. D. Bock, H. Hiemstra, J. H. van Maarseveen, *Eur. J. Org. Chem.* **2006**, 51–68.

[18] E. H. Ryu, Y. Zhao, *Org. Lett.* **2005**, *7*, 1035–1037.

[19] A. Baron, C. Herrero, A. Quaranta, M. F. Charlot, W. Leibl, B. Vauzeilles, A. Aukauloo, *Chem. Commun.* **2011**, *47*, 11011–11013.

[20] D. Wang, R. Mendelsohn, E. Galoppini, P. G. Hoertz, R. A. Carlisle, G. J. Meyer, *J. Phys. Chem. B* **2004**, *108*, 16642–16653.

[21] a) M. Atmeh, N. R. Russell, R. J. Forster, T. E. Keyes, *J. Inclusion Phenom. Macrocyclic Chem.* **2007**, *57*, 607–612; b) H. A. Nieuwenhuis, J. G. Haasnoot, R. Hage, J. Reedijk, T. L. Snoeck, D. J. Stufkens, J. G. Vos, *Inorg. Chem.* **1991**, *30*, 48–54; c) S. Fanni, T. E. Keyes, C. M. O'Connor, H. Hughes, R. Y. Wang, J. G. Vos, *Coord. Chem. Rev.* **2000**, *208*, 77–86.

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