Inorganic Chemistry
Communication
pubs.acs.org/IC

Click Chemistry on a Ruthenium Polypyridine Complex. An Efficient and Versatile Synthetic Route for the Synthesis of Photoactive Modular Assemblies

Aurélie Baron,[†] Christian Herrero,[†,‡] Annamaria Quaranta,[†] Marie-France Charlot,[‡] Winfried Leibl,[†] Boris Vauzeilles,*[,‡] and Ally Aukauloo*[,†,‡]

[†]CEA, iBiTecS, UMR 8221, Service de Bioénergétique, Biologie Structurale et Mécanismes, F-91191 Gif-sur-Yvette, France
[‡]Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR 8182, Université Paris-Sud and CNRS, F-91405 Orsay, France

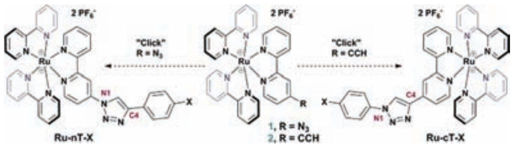
Supporting Information

ABSTRACT: In this Communication, we present the synthesis and use of $[Ru(bpy)_2(bpy\text{-}CCH)]^{2+}$, a versatile synthon for the construction of more sophisticated dyads by means of click chemistry. The resulting chromophore−acceptor or −donor complexes have been studied by flash photolysis and are shown to undergo efficient electron transfer to/from the chromophore. Additionally, the photophysical and chemical properties of the original chromophore remain intact, making it a very useful component for the preparation of visible-light-active dyads.

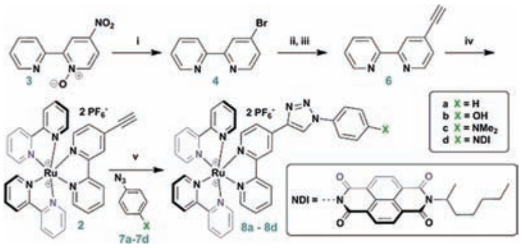
In recent years, a considerable amount of work has been published in the fields of artificial photosynthesis,[1,2] molecular sensing,[3,4] and molecular electronics.[5] The molecular approach in these fields involves the synthesis of increasingly complex molecules that can act as sensitizer−catalyst, reporter−host, or push−pull dyads.[6−9] Most of these molecules incorporate light-active components designed to perform different functions such as electron-transfer reactions, signaling via changes in the emission properties, and formation of charge-separated states. In a previous work,[10] we synthesized a series of molecules starting from an organic ligand bearing a bipyridine group attached to different electron acceptor/donor groups through a triazole moiety to which $[Ru(bpy)_2Cl_2]$ was coordinated in the last step. Although the molecules studied showed that the triazole group can act as an efficient linkage for electron-transfer reactions, the necessity of using sequential synthesis for their preparation could represent a drawback when trying to make more sophisticated systems. Herein, we report on our attempts to find a more versatile way to prepare molecular assemblies starting from ruthenium trisbypiridine analogues modified with either an azide or an alkyne at one of the 4′ positions of one coordinating byipiridine (Chart 1).

While the synthesis of an azide-derived complex (**1**, **Ru−N$_3$**) proved unviable (see Supporting Information, SI), the alkyne-derived complex (**2**, **Ru-CCH**)[11] was obtained in good yield (Chart 1, Scheme 1). **Ru-CCH** shows properties very similar to those of $[Ru(bpy)_3]^{2+}$, namely, absorption in the visible region with a maximum around 450 nm, a strong triplet state emission at 620 nm with a lifetime of 1.40 μs, and oxidation and reduction potentials of $Ru^{III/II}$ and $Ru^{II/I}$ of about 1.30 and −1.30 V vs SCE.

Chart 1. Structures of Azide- and Alkyne-Derived Chromophores and Proposed Strategies



Scheme 1. Synthetic Pathway for Compounds 8a−8d



Reagents and Conditions: (i) CH_3COBr, CH_3CO_2H, PBr_3, $CHCl_3$ (75%);[12] (ii) $(CH_3)_3SiCCH$, $[PdCl_2(PPh_3)_2]$, CuI, DIPA, THF (98%);[13,14] (iii) K_2CO_3, CH_3OH (68%);[13,14] (iv) $[Ru(bpy)_2Cl_2]$, $AgNO_3$, CH_3OH, NH_4PF_6 aq. (91%);[15] (v) **7a−7d**,[16−18] $CuSO_4$ (15 mol %), sodium ascorbate (45 mol %), 1:1 CH_2Cl_2/H_2O (58−81%).[19]

Ru-CCH is shown to react with a series of electron-donor and -acceptor moieties bearing an azido group (**7a−7d**) via click chemistry[20−22] in very good yields (Scheme 1). Complexes **Ru-cT-H**, **Ru-cT-OH**, **Ru-cT-NMe$_2$**, and **Ru-cT-NDI** (NDI = naphthalenediimide) were isolated as the corresponding hexafluorophosphate salts (**8a−8d**).

The electrochemical properties of this series of complexes were studied by cyclic voltammetry and show typical features of ruthenium complexes, namely, a reversible oxidation potential at +1.30 V vs SCE for the Ru^{II} to Ru^{III} process and three quasi-reversible reduction waves in the range of −1.20 to −1.74 V attributed to the one-electron reduction of each of the bipyridines in the coordination sphere. Additional redox features are observed for **Ru-cT-OH**, **Ru-cT-NMe$_2$**, and **Ru-cT-NDI** derivatives (Table S1, SI). A quasi-reversible oxidation wave is observed at +0.96 V for **Ru-cT-NMe$_2$** assigned to

Received: January 31, 2012
Published: May 16, 2012

oxidation of the tertiary amine, while **Ru-cT-NDI** presents two reversible reduction waves at −0.54 and −0.82 V corresponding to the singly and doubly reduced states of the NDI moiety. No additional electrochemical process was observed for reference compound **Ru-cT-H**, indicating that the triazole is electrochemically silent within the potential window used.

Ground-state absorption spectra of all complexes exhibit a metal-to-ligand charge-transfer (MLCT) band peaking at 458 nm and a $\pi-\pi^*$ (bpy) transition at 290 nm. In addition to these features, **Ru-cT-NDI** also presents $\pi-\pi^*$ transitions at 340, 360, and 378 nm characteristic of this family of complexes (Figure S1, SI). For all of the complexes studied the emission is red-shifted by about 10−20 nm compared to that of $[Ru(bpy)_3]^{2+}$ (Table 1). The emission quantum yields (Φ_{em}) were generally in good agreement with the observed emission lifetimes, except for **Ru-cT-NDI** and **Ru-CCH**, for which Φ_{em} seems to be respectively higher and lower than that expected from the observed lifetimes. The shortened emission lifetime observed for **Ru-cT-NDI**, together with the increased quantum yield, indicates an energy-transfer process from the ruthenium to the NDI moiety, as observed in other **Ru-NDI** complexes.[23] As in the case of **Ru-cT-NMe$_2$** (see below), the degree of quenching seems to depend strongly on the orientation of the triazole group. The latter presumably modulates the relative energy level of excited states on the chromophore and ligand.

Table 1. Emission Data on the Complexes Studied

complex	λ_{max}/nm	t/ns	Φ_{em}
Ru-cT-H	620	1300	0.089
Ru-cT-OH	620	1200	0.077
Ru-cT-NMe$_2$	620	450	0.038
Ru-cT-NDI	618	100 (95%); 840 (5%)	0.049
Ru-CCH	631 (535)[a]	1400 (<15)	0.054

[a]The emission spectrum in MeCN exhibits two band maxima, to which correspond two different lifetimes. All experiments were done with solvents deaerated with argon at 297 K. λ_{ex} = 460 nm.

The case of **Ru-cT-NMe$_2$** is striking because, in a previous study on an analogous complex,[10] we observed the complete quenching of the ^{3}MLCT emission due to the formation of a nonemissive intraligand charge-transfer (^{3}ILCT) state. Density functional theory (DFT) studies suggest that the lowest unoccupied molecular orbital (LUMO) is developed on the modified bipyridine ligand rather than on the ruthenium center. The fact that the emission is recovered in **Ru-cT-NMe$_2$** indicates that substitution via the C4 of the triazole rather than through its N1 on the periphery of the coordinated bipyridine leads to a reshuffling of the frontier molecular orbitals with probable destabilization of the ligand-based LUMO above the metal-centered LUMOs. Preliminary DFT calculations performed on the ligand already support this finding (Figure S7, SI). The transient absorption spectrum of the excited state is very similar for all complexes studied and shows an absorption maximum at 375 nm, a depletion maximum at 455 nm, and a broad featureless absorption between 500 and 800 nm.

Laser flash photolysis experiments with the **Ru-CCH** complex in the presence of methyl viologen (MV^{2+}) as an electron acceptor, or ascorbate as an electron donor, showed behavior similar to that of $[Ru(bpy)_3]^{2+}$ and reference compound **Ru-cT-H** (Figure S2, SI). In the presence of 10 mM MV^{2+}, features associated with reduced methyl viologen ($MV^{\bullet+}$) (peaks at 390 and 605 nm) are observed, together with bleaching at 400−500 nm due to Ru^{II} disappearance. The Ru^{III} formed recombines with $MV^{\bullet+}$, as indicated by the similar kinetics of the respective absorption decays. In the presence of 10 mM ascorbate, absorption at 510 nm, typical for Ru^{I} formation, and at 360 nm, attributed to the oxidized form of ascorbate, is observed, and kinetic measurements indicate recombination of the geminate charges. It can be concluded that in **Ru-cT-H** the triazole ring does not perturb the electron-transfer properties of the excited state of the ruthenium chromophore. In the case of the chromophore−donor complex **Ru-cT-NMe$_2$**, excitation in the presence of hexaamineruthenium(III), $[Ru(NH_3)_6]^{3+}$, shows the disappearance of the excited state of the chromophore (160 ns phases in transient absorption; Figure 1, inset) and formation of a long-lived species characterized by absorption maxima at 530 and 353 nm, which can be identified as $[-C_6H_4NMe_2]^{\bullet+}$ (Figure 1).[24,25] The fact that the rate for recovery of Ru^{II} absorption is indistinguishable from the rate of quenching of the excited state indicates that internal electron transfer from the $-NMe_2$ donor group to Ru^{III} occurs in less than 100 ns. The same behavior was observed with MV^{2+} as an acceptor (Figure S3, SI).

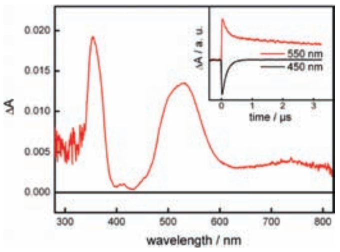


Figure 1. Transient absorption spectrum 2 μs after the flash obtained for **Ru-cT-NMe$_2$** in MeCN/H_2O (50:50) in the presence of 20 mM $[Ru(NH_3)_6]^{3+}$. Inset: kinetics at 550 and 450 nm. Ar, 297 K. λ_{ex} = 460 nm.

In the photodriven oxidation of **Ru-cT-OH** in the presence of MV^{2+}, formation of $MV^{\bullet+}$ was accompanied by a fast recovery of the initially oxidized Ru^{II} and formation, in ~15 μs, of a species absorbing at 410 nm, which we identify as the phenoxyl radical (Figure 2).

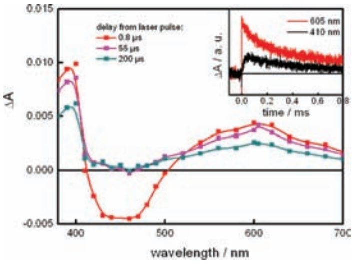


Figure 2. Transient absorption spectra in MeCN for **Ru-cT-OH** in the presence of 10 mM MV^{2+} at different delays from laser pulse. Inset: kinetics at 605 and 410 nm. Ar, 297 K. λ_{ex} = 460 nm.

When these results are compared with those obtained with **Ru-cT-NMe$_2$**, the slower rate of oxidation of phenol versus amine might be explained by the difference in the driving force ΔG between the $Ru^{III/II}$ couple and the oxidation of the different donor groups (50 vs 350 mV, respectively), although other factors such as deprotonation of phenol coupled to oxidation might also be of importance.

Excitation at 460 nm of the **Ru-cT-NDI** complex in the presence of 10 mM ascorbate reveals the appearance of several $NDI^{\bullet-}$ radical features within ca. 100 ns, as shown by the appearance of absorption bands at 487, 532, and 612 nm (Figure 3). No spectral features of a Ru^{I} intermediate were observed, and therefore direct interaction of ascorbate with an excited state delocalized over the ruthenium and NDI moieties cannot be excluded as a possible mechanism for reduction of the NDI group. By studying the effect of various donor concentrations on the rate of NDI reduction, we observed that the yield of NDI radical formation decreases with decreasing concentration of ascorbate. However, the fact that the rate of $NDI^{\bullet-}$ formation does not drop below the rate of decay of the fast phase of emission demonstrates that it is the quenching of this fast phase by the external donor that is responsible for $NDI^{\bullet-}$ formation (Figure S4, SI). Assuming that this fast phase is due to Ru*, which is quenched by energy transfer from Ru to NDI,[23] these results show that it is the ruthenium excited state that reacts with ascorbate, and the absence of a Ru^{I} intermediate suggests a very fast (<20 ns) electron transfer from Ru^{I} to the NDI acceptor. The resulting reduced state (**Ru-cT-NDI**$^{\bullet-}$) lasts for a few milliseconds.

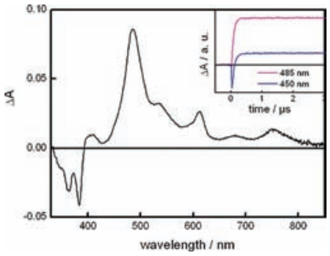


Figure 3. Transient absorption spectrum in MeCN/H_2O (50:50) for **Ru-cT-NDI** in the presence of 10 mM ascorbate, 150 ns after laser pulse. Inset: kinetics at 485 and 450 nm. Ar, 297 K. λ_{ex} = 460 nm.

We have presented a new and versatile method to construct complexes made up of a chromophore and different acceptor or donor groups. The heteroleptic ruthenium chromophore used as a starting synthon has properties similar to those of the well-known $[Ru(bpy)_3]^{2+}$ parent complex and can be easily incorporated via click chemistry into dyads. Light-driven electron-transfer studies in the presence of either a reversible electron acceptor or donor show efficient bidirectional intramolecular electron transfer through the triazole ring, both from or to the electron-donating/accepting groups, respectively. The synthetic methodology allows for the incorporation of visible-light sensitizers into more complex molecules while maintaining their original photophysical and chemical properties. This "modular" approach should be of great use in the synthesis of more sophisticated molecules, especially those incorporating different metals, such as chromophore–catalyst and chromophore–host complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterizations, as well as NMR and absorption spectra and flash photolysis. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: boris.vauzeilles@u-psud.fr, ally.aukauloo@u-psud.fr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by the ANR (Project ANR 2010 BLAN 0926), the EU/Energy SOLAR-H2 project (FP7 Contract 212508), and the Conseil Général de l'Essonne.

■ REFERENCES

(1) Magnuson, A.; Anderlund, M.; Johansson, O.; Lindblad, P.; Lomoth, R.; Polivka, T.; Ott, S.; Stensjö, K.; Styring, S.; Sundström, V.; Hammarström, L. *Acc. Chem. Res.* **2009**, *42*, 1899–1909.

(2) Herrero, C.; Quaranta, A.; Leibl, W.; Rutherford, A. W.; Aukauloo, A. *Energy Environ. Sci.* **2011**, *4*, 2353–2365.

(3) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516.

(4) Lau, Y. H.; Price, J. R.; Todd, M. H.; Rutledge, P. J. *Chem.—Eur. J.* **2011**, *17*, 2850–2858.

(5) Balzani, V. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: New York, 2001; Vol. 3, pp 337–408.

(6) Kato, S.-i.; Kivala, M.; Schweizer, W. B.; Boudon, C.; Gisselbrecht, J.-P.; Diederich, F. *Chem.—Eur. J.* **2009**, *15*, 8687–8691.

(7) Kato, S.-i.; Diederich, F. *Chem. Commun.* **2010**, *46*, 1994–2006.

(8) Kato, S.-i.; Beels, M. T. R.; La Porta, P.; Schweizer, W. B.; Boudon, C.; Gisselbrecht, J.-P.; Biaggio, I.; Diederich, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6207–6211.

(9) de Miguel, G.; Wielopolski, M.; Schuster, D. I.; Fazio, M. A.; Lee, O. P.; Haley, C. K.; Ortiz, A. L.; Echegoyen, L.; Clark, T.; Guldi, D. M. *J. Am. Chem. Soc.* **2011**, *133*, 13036–13054.

(10) Baron, A.; Herrero, C.; Quaranta, A.; Charlot, M.-F.; Leibl, W.; Vauzeilles, B.; Aukauloo, A. *Chem. Commun.* **2011**, *47*, 11011–11013.

(11) Hissler, M.; Ziessel, R. *J. Chem. Soc., Dalton Trans.* **1995**, 893–896.

(12) Mizuno, T.; Takeuchi, M.; Hamachi, I.; Nakashima, K.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2281–2288.

(13) Grosshenny, V.; Romero, F. M.; Ziessel, R. *J. Org. Chem.* **1997**, *62*, 1491–1500.

(14) Ziessel, R.; Suffert, J.; Youinou, M. T. *J. Org. Chem.* **1996**, *61*, 6535–6546.

(15) Quaranta, A.; Lachaud, F.; Herrero, C.; Guillot, R.; Charlot, M.-F.; Leibl, W.; Aukauloo, A. *Chem.—Eur. J.* **2007**, *13*, 8201–8211.

(16) Kurumi, M.; Sasaki, K.; Takata, H.; Nakayama, T. *Heterocycles* **2000**, *53*, 2809–2819.

(17) Andersen, J.; Madsen, U.; Björkling, F.; Liang, X. F. *Synlett* **2005**, 2209–2213.

(18) Zhang, H.; Podoprygorina, G.; Brusko, V.; Böhmer, V.; Janshoff, A. *Chem. Mater.* **2005**, *17*, 2290–2297.

(19) Lee, B.-Y.; Park, S. R.; Jeon, H. B.; Kim, K. S. *Tetrahedron Lett.* **2006**, *47*, 5105–5109.

(20) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.

(21) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599.

(22) Tornøe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057–3064.

(23) Borgström, M.; Shaikh, N.; Johansson, O.; Anderlund, M. F.; Styring, S.; Akermark, B.; Magnuson, A.; Hammarström, L. *J. Am. Chem. Soc.* **2005**, *127*, 17504–17515.

(24) Miyasaka, H.; Itaya, A.; Rotkiewicz, K.; Rechthaler, K. *Chem. Phys. Lett.* **1999**, *307*, 121–130.

(25) Pan, Y.; Fu, Y.; Liu, S. X.; Yu, H. Z.; Gao, Y. H.; Guo, Q. X.; Yu, S. Q. *J. Phys. Chem. A* **2006**, *110*, 7316–7322.