Inorg. Chem. **2008**, *47*, 9131−9133

Inorganic Chemistry

Communication

Tuning Emission Properties of Iridium and Ruthenium Metallosurfactants in Micellar Systems

Andrés Guerrero-Martínez, Yolanda Vida, David Domínguez-Gutiérrez, Rodrigo Q. Albuquerque, and Luisa De Cola*

Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Mendelstrasse 7, 48149 Münster, Germany

Received May 9, 2008

Ruthenium metallosurfactant forms micelles that show efficient electronic energy-transfer processes in the presence of an analogous iridium complex. Modulation of the process is achieved upon incorporation of these amphiphiles into cetyltrimethylammonium bromide micelles, allowing a tuning of the two emissions.

Transition-metal complexes have been used as an alternative to organic dyes as luminescent probes in the analysis of colloidal and biological systems.[1] They offer significant advantages such as long-lived luminescent excited states, high chemical and photochemical stabilities, and tunability of the excited-state energies.[2] Additionally, they can be employed as energy donor or acceptor units in energy-transfer (ET) processes.[3] Among the molecular architectures in which photoinduced processes can be investigated, micelles are particularly interesting because their composition can be easily modified, and their formation is a reversible and dynamic process.[4] Furthermore, it is possible to get high local concentrations and spatial proximity between donor and acceptor molecules in their structures. Toward this goal, we propose the use of different luminescent metallosurfactants as a new class of probes in soft aggregated systems. These novel surfactants, which are made of a polar transition-metal-complex headgroup and a hydrophobic tail, have gained attention because of their interesting applications in diverse subject areas such as the templating of mesoporous materials,[5] thin-film optoelectronics,[6] or formation of monolayers.[7]

Herein, we highlight the self-aggregation and ET processes between two different metallosurfactants both containing dialkylbipyridine, with 17 methylene units, as the hydrophobic part of the structure. The electronic energy acceptor metallosurfactant, bis(2,2′-bipyridine)(4,4′-diheptadecyl-2,2′-bipyridine)ruthenium(II) dichloride (**1**), was prepared according to a literature procedure[8] and the energy donor iridium complex with two fluorinated phenylpyridines, bis[2-(2,4-difluorophenyl)pyridine](4,4′-diheptadecyl-2,2′-bipyridine)iridium(III) chloride (**2**), by a modified procedure.[9] The complexes and a schematic micelle formation are depicted in Scheme 1. The photophysical properties of both metallosurfactants have been investigated in an air-equilibrated aqueous solution and 295 K. Absorption and emission data for compounds **1** and **2** were compared to their reference analogues $[Ru(bpy)_3]Cl_2$ (**1a**) and $[Ir(ppyFF)_2(bpy)]Cl$ (**2a**), where bpy = 2,2′-bipyridine and ppy = 2-phenylpyridine. Finally, the emission properties of complexes **1** and **2** were analyzed in the presence of a conventional cationic surfactant.

The photophysical properties of metallosurfactant **1** in water resemble those of the analogous compound **1a** when the concentration is lower than 0.05 mM, which has been

---

* To whom correspondence should be addressed. E-mail: decola@uni-muenster.de.

(1) (a) Friedman, A. E.; Chambron, J. C.; Sauvage, J. P.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4960–4962. (b) Arkin, M. R.; Stemp, E. D. A.; Turro, C.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 2267–2274. (c) Wu, L. Z.; Cheung, T. C.; Che, C. M.; Cheung, K. K.; Lam, M. H. W. *Chem. Commun.* **1998**, 1127–1128. (d) Minoofar, P. N.; Hernandez, R.; Chia, S.; Dunn, B.; Zink, J. I.; Franville, A. C. *J. Am. Chem. Soc.* **2002**, *124*, 14388–14396. (e) Liang, X. Y.; Campopiano, D. J.; Sadler, P. J. *Chem. Soc. Rev.* **2007**, *36*, 968–992.

(2) Evans, R. C.; Douglas, P.; Winscom, C. J. *Coord. Chem. Rev.* **2006**, *250*, 2093–2126.

(3) (a) Grätzel, M. *Inorg. Chem.* **2005**, *44*, 6841–6851. (b) Welter, S.; Salluce, N.; Belser, P.; Groeneveld, M.; De Cola, L. *Coord. Chem. Rev.* **2005**, *249*, 1360–1371. (c) De Cola, L.; Belser, P. *Electron Transfer in Chemistry: Photonic Wires Containing Metal Complexes*; Wiley/VCH Verlag GmbH: Weinheim, Germany, 2001.

(4) (a) Turro, N. J.; Garibay, M. G. *Photochemistry in Organized and Constraint Media*; VCH Publishers: New York, 1991. (b) Behera, G. B.; Mishra, B. K.; Behera, P. K.; Pandal, M. *Adv. Colloid Interface Sci.* **1999**, *82*, 1–42. (c) Capek, I. *Adv. Colloid Interface Sci.* **2002**, *97*, 91–149.

(5) (a) Griffiths, P. C.; Fallis, I. A.; Chuenpratoom, T.; Watanesk, R. *Adv. Colloid Interface Sci.* **2006**, *122*, 107–117. (b) Jervis, H. B.; Raimondi, M. E.; Raja, R.; Maschmeyer, T.; Seddon, J. M.; Bruce, D. W. *Chem. Commun.* **1999**, 2031–2032.

(6) Chu, B. W. K.; Yam, V. W. W. *Inorg. Chem.* **2001**, *40*, 3324.

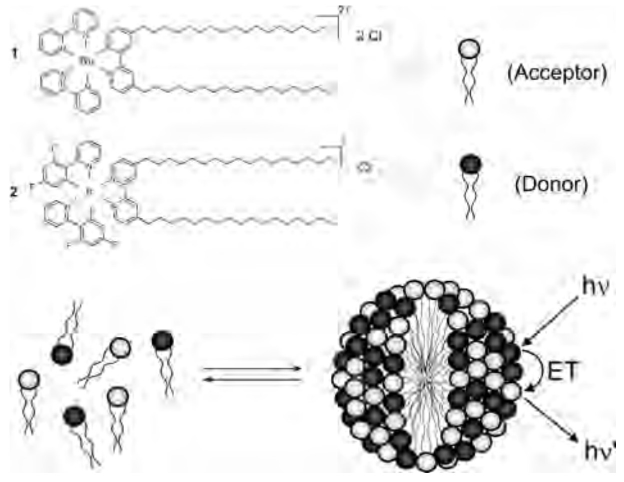
(7) (a) Dominguez-Gutierrez, D.; Surtchev, M.; Eiser, E.; Elsevier, C. J. *Nano Lett.* **2006**, *6*, 145–147. (b) Shakya, R.; Keyes, P. H.; Heeg, M. J.; Moussawel, A.; Heiney, P. A.; Verani, C. N. *Inorg. Chem.* **2006**, *45*, 7587–7589. (c) Li, X. D.; Zhang, S. R.; Zhao, P. Y.; Kovacs, Z.; Sherry, A. D. *Inorg. Chem.* **2001**, *40*, 6572–6579.

(8) Anderson, S.; Constable, E. C.; Seddon, K. R.; Turp, J. E.; Baggott, J. E.; Pilling, M. J. *J. Chem. Soc., Dalton Trans.* **1985**, *11*, 2247–2261.

(9) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647–6653.

10.1021/ic800849y CCC: $40.75

Scheme 1. Schematic Representation of Complexes **1** and **2** and Their Self-Aggregation into Mixed Aggregates[a]



[a] ET from donor to acceptor moieties is also schematically shown.

assigned to its critical micelle concentration (CMC).[10] The absorption band of compound **1** with a maximum at 455 nm is due to the spin-allowed singlet metal-to-ligand charge-transfer (^{1}MLCT) transition. The bands in the UV are mostly $\pi-\pi$ transitions involving the bpy ligands. Under excitation at 350 nm and below the CMC, compound **1** shows a broad and rather intense emission with a maximum at 635 nm that corresponds to the triplet MLCT (^{3}MLCT) transition (Figure 1).[11] The excited-state lifetime of the monomeric state of complex **1**, $\tau_1 = 360$ ns, was very similar to that measured for the parent **1a** ($\tau_{1a} = 390$ ns). At 0.15 mM (above the CMC), the emission lifetime becomes biexponential, with a short component due to the nonaggregated form, $\tau_{1,\mathrm{mon}} = 400$ ns (20%), and a longer decay due to the assembled species, $\tau_{1,\mathrm{mic}} = 860$ ns (80%) (Figure 2).[12]

For complex **2**, the absorption spectrum in air-equilibrated water is shown in Figure 1. The intense bands between 250 and 300 nm can be assigned to spin-allowed singlet ligand-centered (^{1}LC) transitions involving fluorinated phenylpyridines and bipyridines. The room-temperature emission spectrum of compound **2** under excitation at 350 nm exhibits a maximum at 544 nm. The emission results from the mixing of the ^{3}MLCT and ^{3}LC excited states (Figure 1).[13] Analogous to the study of complex **1**, the CMC of the metallosurfactant **2** in water has been observed around 3 μM by analyzing the lifetimes at different concentrations of amphiphile ($\tau_{2,\mathrm{mon}} = 175$ ns, 12%, and $\tau_{2,\mathrm{mic}} = 405$ ns, 88%, at 0.01 mM) and comparing these values with the lifetime of the parent complex **2a** ($\tau_{2a} = 160$ ns).

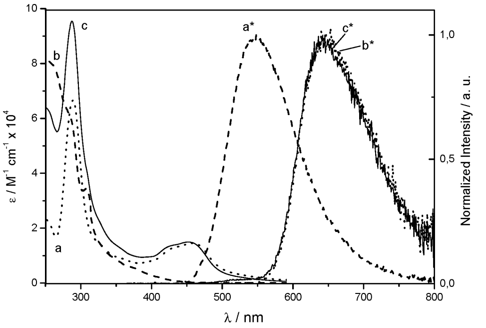


Figure 1. Absorption and normalized emission spectra of **1** (a), **2** (b), and a mixture of **1** (0.025 mM) and **2** (0.025 mM) (c) in dilute aqueous solutions at room temperature ($\lambda_{\mathrm{exc}} = 350$ nm). The emission spectra are indicated with asterisks.

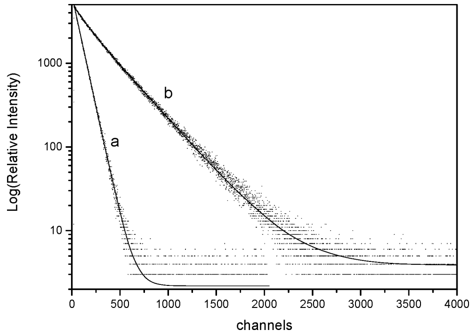


Figure 2. Time-resolved intensity decays and fits for **1** at (a) 0.01 mM and (b) 0.10 mM in aqueous solutions at room temperature ($\lambda_{\mathrm{exc}} = 431$ nm).

The appearance of long-lifetime components in both metallosurfactant systems above their CMCs shows that the aggregation brings the headgroups closer in proximity, reducing the nonradiative decays due to vibrational modes and most likely also the oxygen diffusion. This explanation is evidenced by the enhancement of the quantum yields of metallosurfactants **1** at 0.15 mM ($\phi_1 = 0.045$) and **2** at 0.015 mM ($\phi_2 = 0.033$), with respect to complexes **1a** ($\phi_{1a} = 0.030$) and **2a** ($\phi_{2a} = 0.025$), which are in good agreement with reported values for quantum yields of compounds **1a** and **2a** in water and acetonitrile, respectively, air-equilibrated solutions.[14]

The absorption and luminescence spectra of a 1:1 mixture of metallosurfactants **1** (0.025 mM) and **2** (0.025 mM) are shown in Figure 1. The absorption resembles the sum of the individual spectra of the mononuclear units at these concentrations. However, upon excitation at 350 nm, the characteristic emission from the excited state of the iridium complex is not observed, and the only emission present at 645 nm is attributed to the ^{3}MLCT emission of the ruthenium-based moiety ($\tau_{1,\mathrm{mon}} = 375$ ns, 25%, and $\tau_{1,\mathrm{mic}} = 890$ ns, 75%). Therefore, we can conclude that the observed quenching of metallosurfactant **2** is attributed to a very efficient ET that takes place from the excited iridium-based complex to the ruthenium moieties. These results indicate that the energy donor iridium(III) complex and the energy acceptor ruthenium(II) metallosurfactant form a mixed ag-

---

(10) (a) Bowers, J.; Amos, K. E.; Bruce, D. W. *Langmuir* **2005**, *21*, 1346–1353. (b) Bowers, J.; Amos, K. E.; Bruce, D. W. *Langmuir* **2005**, *21*, 5696–5706.

(11) Domínguez-Gutiérrez, D.; De Paoli, G.; Guerrero-Martinez, A.; Ginocchetti, G.; Ebeling, D.; Eiser, E.; De Cola, L.; Elsevier, C. J. *J. Mater. Chem.* **2008**, *18*, 2762–2768.

(12) Rack, J. J.; McCleskey, T. M.; Birnbaum, E. R. *J. Phys. Chem. B* **2002**, *106*, 632–636.

(13) (a) Colombo, M. G.; Hauser, A.; Güdel, H. U. *Inorg. Chem.* **1993**, *32*, 3088–3092. (b) Lafolet, F.; Welter, S.; Popovic, Z.; De Cola, L. *J. Mater. Chem.* **2005**, *15*, 2820–2828. (c) Flamigni, L.; Barbieri, A.; Sabatini, C.; Ventura, B.; Barigelletti, F. *Top. Curr. Chem.* **2007**, *208*, 143–203.

(14) (a) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697–2705. (b) Welter, S.; Lafolet, F.; Cecchetto, E.; Vergeer, F.; De Cola, L. *ChemPhysChem* **2005**, *6*, 2417–2427.

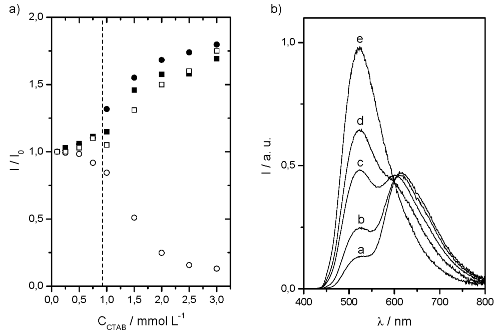


Figure 3. (a) Intensity ratio emission, I/I_0 (I_0 is the intensity in the absence of CTAB), of **1** (■), **2** (●), **1** (□), and **2** (○) in a 1:1 (2mM:2mM) mixture, at different concentrations of CTAB (the dashed line shows the CMC of CTAB; $\lambda_{exc} = 350$ nm for all of the experiments). (b) Emission spectra of a 1:1 mixture, at different amounts of CTAB. [CTAB] (mM): (a) 0.0, (b) 1.0, (c) 1.5, (d) 2.0, (e) 3.0 ($\lambda_{exc} = 350$ nm).

gregate. No quenching effects have been observed for analogous mixtures of complexes **1a** + **2a**, **1** + **2a**, and **1a** + **2**, ruling out bimolecular quenching processes and pointing the relevance in the ET process to the fact that complexes **1** and **2** are amphiphilic molecules with long alkyl chains.

Owing to the low value of the CMC of the mixed system, the tunability of the ET process in these metallomicelles is difficult. In order to overcome this limitation, we used micelles of a conventional surfactant with a higher value of the CMC as cetyltrimethylammonium bromide (CTAB; CMC = 0.9 mM),[15] in which small amounts of compounds **1** and **2** were dissolved. We found that the emission properties of complexes **1** and **2** and a 1:1 mixture of both metallosurfactants are dramatically altered in CTAB micelles, whereas the absorption properties are not affected. The concentration of both metallosurfactants was kept constant at 2 μM in these experiments.

The addition of different amounts of CTAB to complex **1** led to an enhancement of the emission intensity and lifetime of the ruthenium unit, when the concentration of the surfactant was above 1 mM, which points to the encapsulation of the ruthenium complex when the CMC of CTAB is reached (Figure 3a). In particular, we found biexponential values of the lifetime for complex **1**, $\tau_{\mathbf{1},\mathrm{mon(CTAB)}} = 380$ ns (60%) and $\tau_{\mathbf{1},\mathrm{mic(CTAB)}} = 650$ ns (40%), in the presence of 3.0 mM CTAB, which suggests that ruthenium−metal-complexed headgroups may reside inside the micellar core and that they are not completely subjected to quenching by the solvent or dioxygen molecules.

Analogous results were obtained for complex **2**. The aggregation of CTAB leads to enhancements of the emission (Figure 3a), and two different lifetimes were observed, $\tau_{\mathbf{2},\mathrm{mon(CTAB)}} = 145$ ns (35%) and $\tau_{\mathbf{2},\mathrm{mic(CTAB)}} = 450$ ns (65%) at 3.0 mM CTAB. The short component is in good agreement with the value obtained for monomers of compound **2** in water. The appearance of a long lifetime points to solubilization in the CTAB micelles. We argue that these aggregates create a protecting environment for the metallosurfactant, reducing the nonradiative decays of the iridium excited state. Protection of the ^{3}MLCT excited state of organometallic complexes against interactions with solvent and O_2 has also been reported to be responsible for similar trends in the lifetimes.[12] Nonsignificant enhancements of the emission were observed in the case of the reference complexes **1a** and **2a**.

Figure 3b shows the emission spectra of a 1:1 mixture (2mM:2mM) of **1** and **2** recorded at different concentrations of CTAB. The addition of CTAB increases the intensity of the ruthenium(II) emission at 635 nm, in accordance with the results observed previously for compound **1** alone. On the other hand, the emission of iridium(III) gradually decreases as the concentration of CTAB increases (Figure 3a). This behavior suggests that, with an increase in the amount of CTAB above its CMC, the concentration of complexes **1** and **2**, which are dissolved in the conventional micelles, increases. When the two complexes are located in the same micelle, the triplet−triplet ET between the donor and acceptor moieties can be effective. In fact, the maximum distance, which corresponds to the micellar dimensions (34 Å sphere for CTAB at 3.0 mM),[15] allows for an efficient Förster-type ET. Nonsignificant changes were observed for the biexponential values of the lifetime for complex **1**. In contrast, the excited-state lifetimes of the iridium emission, $\tau_{\mathbf{2},\mathrm{mon(CTAB)}} = 140$ ns (20%) and $\tau_{\mathbf{2},\mathrm{mic(CTAB)}} = 47$ ns (80%) at 3.0 mM of CTAB, differ from the previous results. The new short component, which is associated with quenching of the metallosurfactant **2** inside the CTAB micelle, can be explained by taking into account the large driving force characteristic for the ET process between ruthenium(II) and iridium(III) complexes ($\Delta G = -0.5$ eV).[14b] Micellization equilibrium of CTAB ensures the reversibility of the intramicellar ET between the complexes (see the isoemissive point in Figure 3b). No effective ET was observed for the analogous systems **1a** + **2a**, **1** + **2a**, and **1a** + **2**, in CTAB micelles. This indicates that the tails play a major role for the entrapment of the emitters inside the micelles.

This is the first time that such a behavior has been observed for self-assembled ruthenium(II) and iridium(III) metallosurfactants used as donor/acceptor components for ET processes. Thus, these assemblies represent an interesting way to obtain luminescent soft structures, avoiding complicated chemical synthesis. Interestingly, the ET process can be triggered by a change in the concentration of an "innocent" component, CTAB, without modification of any other parameter.

Acknowledgment. Financial support by the Ministerio de Educación y Ciencia (A.G.-M.), Fundación Ramón Areces (Y.V.), and Alexander von Humboldt Foundation (R.Q.A.) is gratefully acknowledged.

Supporting Information Available: Detailed description of spectroscopic data, the synthesis, and photophysical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

IC800849Y

---

(15) Mandal, A. B.; Nair, B. U. *J. Phys. Chem.* **1991**, *95*, 9008–9013.