



Luminescent multiruthenium metallocyclodextrins: Synthesis, fluorescence and electrochemiluminescence properties based on host–guest recognition



Yantao Qi^{a,b}, Xiuhua Wang^a, Hong Chen^a, Jie Tang^b, Fan Yang^b, Pingang He^{a,*}

^a Department of Chemistry, East China Normal University, Shanghai 20062, China

^b Shanghai Engineering Research Center of Molecular Therapeutics and New Drug Development, East China Normal University, Shanghai 200062, China

ARTICLE INFO

Article history:

Received 11 September 2013

Accepted 25 October 2013

Available online 14 November 2013

Keywords:

Cyclodextrins

Metallocyclodextrin

Host–guest recognition

Binding

ABSTRACT

We describe herein the synthesis of supramolecular metallocyclodextrins containing multiruthenium centers. These compounds exhibit especially strong fluorescence and electrochemiluminescence (ECL), as well as excellent quenching efficiency because of their ability to perform host–guest recognition.

© 2013 Elsevier B.V. All rights reserved.

In recent years, supramolecular systems based on metallocyclodextrins have increasingly attracted the interest of researchers from many fields [1]. The elegance with which cyclodextrins (CDs) bind to guest molecules, and the electronic and photoactive properties of metal centers such as ruthenium, make metallocyclodextrins appropriate for the development of sophisticated supramolecular devices [2]. Most of the metallocyclodextrins prepared up till now contain only a single metal center. It is noteworthy that polynuclear metal complexes, especially polypyridine ruthenium have been successfully applied in the construction of photovoltaic molecular devices; for instance, fluorescence switches, electrochemiluminescence (ECL) luminophores and biosensors [3]. Herein, we report the synthesis of a series of luminescent metallocyclodextrins containing monoruthenium (**Ru-CD**), diruthenium (**2Ru-CD**) and triruthenium (**3Ru-CD**) centers (Fig. 1), and a preliminary investigation of their fluorescence and ECL characteristics based on host–guest recognition.

We chose β -CD as the starting material. Three β -CD derivatives were synthesized [4], as key precursors, via the synthesis of the mono-, di- and trisubstitution of β -CD with phenylamino ligands (a, b and c in Fig. 1). The attachment of the ligands onto the primary side of β -CD was achieved by the Mitsunobu reaction in good yield.

The complexes (**Ru-CD**, **2Ru-CD** and **3Ru-CD**) were synthesized by reaction of their corresponding ligands **a**, **b** and **c** with a slight excess of the ligand *cis*-Ru(bpy)₂Cl₂ with refluxing in a mixed solvent of ethanol and distilled water (Scheme S1 in the SI). Because of the

strong polarity of all these complexes, their purification by general column chromatography is very difficult. We achieved their separation by eluting them through a C-18 reversed-phase column many times. The structures of these compounds were characterized by NMR, high-resolution MALDI-TOF MS, and UV–vis absorption spectroscopy.

To investigate the photoactive properties of these metallocyclodextrins, their fluorescence (Fig. 2a) upon excitation in their metal–ligand charge transfer (MLCT) band was monitored and compared with that of the model compound Ru(bpy)₃Cl₂. The emission maximum of all three metallocyclodextrins was red shifted versus that of the model compound. This phenomenon can be attributed to the influence of the electron withdrawing amide groups on the bipyridines [5]. The increase in the fluorescence intensity of **Ru-CD**, **2Ru-CD** and **3Ru-CD** was attributed to the influence of multiple bipyridine–ruthenium chromophore centers.

To study the potential of these complexes to participate in host–guest interactions involving energy transfer or electron transfer, we selected 4-dimethylaminoazobenzene-4'-carboxylic acid (dabcyl), as an organic guest [6]. The changes in the emission spectra of **Ru-CD**, **2Ru-CD** and **3Ru-CD** upon addition of the guest are shown in Fig. 2b, c and d, respectively. Addition of 1 equiv of guest quenched the emission of the three compounds to various degrees. The quenching occurred via photoinduced electron transfer from the excited ruthenium moiety to the guest [7]. The absolute and relative differences of the emission intensity, before and after the addition of the guest, were obtained by calculation and listed as follows: for **Ru-CD**, 251.1 (absolute) and 33% (relative), for **2Ru-CD**, 446.2 and 45%, and for **3Ru-CD**, 763.8 and 47%. The absolute difference showed that the number of ruthenium ions in the metallocyclodextrins dominated the extent of quenching. The

* Corresponding author.

E-mail addresses: fyang@chem.ecnu.edu.cn (F. Yang), pghe@chem.ecnu.edu.cn (P. He).

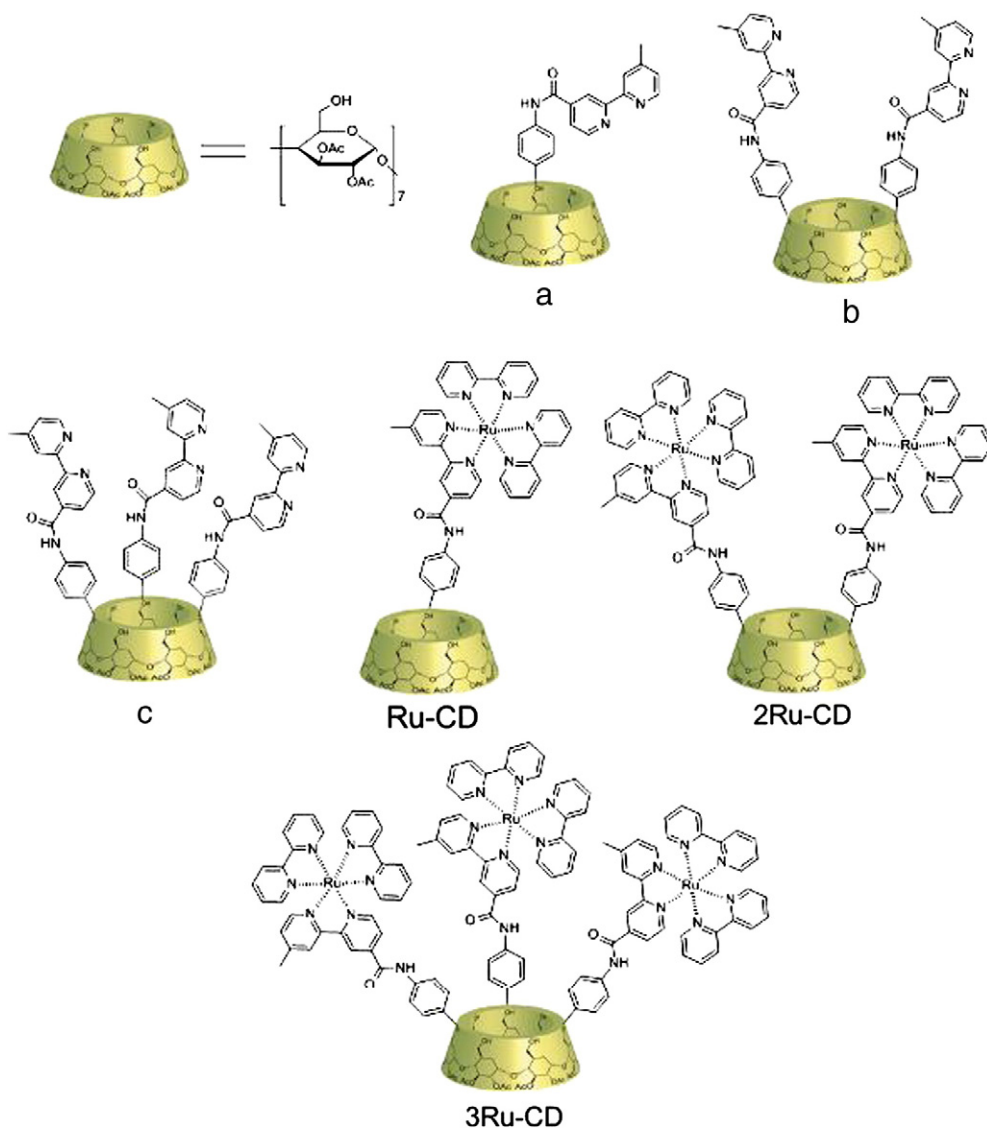


Fig. 1. Structures of luminescent metalocyclodextrins and their ligands.

relative differences showed less change for the emission intensity. This can be explained by noting that the three metalocyclodextrins have different binding capability for the guest under the same conditions. To gain insight into the binding capacity of the three metalocyclodextrins for dabcyI, we calculated their binding constant based on the emission quenching data according to the Benesi–Hildebrand equation (Table 1). As we expected, the binding constant of **3Ru-CD** is higher than that of **Ru-CD** and **2Ru-CD**. This may be attributed to the larger number of metal ions in **3Ru-CD**, which provides more opportunities for the guest to transfer energy and electrons. The dabcyI binding constant of each compounds is remarkably higher, by at least one order of magnitude, than that of natural β -CD ($K = 4.91 \times 10^4$) [8]. This significant information about this new multiruthenium metalocyclodextrin indicates its great potential for photovoltaic supramolecular devices.

To quantify the emission of these metalocyclodextrins, we calculated their relative fluorescence quantum yield using Rhodamine B as a standard (Table 2). The emission quantum yield of the three metalocyclodextrins was similar to that of $\text{Ru}(\text{bpy})_3\text{Cl}_2$; in other words, the emission efficiency of these metalocyclodextrins is not enhanced by increasing the number of metal Ru centers. On the contrary, **3Ru-CD** had the lowest emission quantum yield despite its higher emission intensity that stemmed from the presence of three Ru centers.

In contrast to fluorescence, ECL is the process in which electrodes undergo high-energy electron transfer to form excited states that emit light [10]. Applications of ECL range from biochemical diagnostics to detection of hazardous chemicals to light-emitting devices in liquid waste [11]. Research on ECL primarily aims to find new luminophores with higher efficiency. Towards this end, we investigated the effect of host–guest recognition on the ECL behavior of **Ru-CD**, **2Ru-CD** and **3Ru-CD**. The ECL intensity showed the same trend as the fluorescence, where that of **3Ru-CD** was the highest. This trend results from the oxidation of multiple metal centers on **3Ru-CD**. The ECL intensity of **3Ru-CD** is one order of magnitude higher than that of **Ru-CD**, while the ECL intensity of **Ru-CD** does not surpass that of $\text{Ru}(\text{bpy})_3\text{Cl}_2$. The latter results from the steric hindrance of cyclodextrin, which decreases the electron-transfer rate of the luminescent center on the surface of the electrode [8]. Because of the relatively weak ECL intensity of single-ruthenium metalocyclodextrins, few reports exist concerning their ECL behavior. The higher luminescence efficiency of multiruthenium metalocyclodextrins will lead to excellent applications as new luminophores exhibiting ECL.

Fig. 3b, c and d shows the ECL of the three metalocyclodextrins before and after adding the guest, dabcyI, in solution. Just similarly to the fluorescence quenching, more efficient ECL quenching from the three host compounds was observed. The absolute and relative

Download English Version:

<https://daneshyari.com/en/article/7749605>

Download Persian Version:

<https://daneshyari.com/article/7749605>

[Daneshyari.com](https://daneshyari.com)