

Quantum dot-ruthenium complex based energy transfer. Potentiality for theranostic applications

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Introduction

Quantum dots (QDs), have been extensively discussed in the field of energy, molecular diagnostics and nanotherapeutics^[1]. In all studied processes charge transfer and/or energy transfer mechanisms exist within this type of assembly, special with coordination compounds. Among them ruthenium compounds have received particular attention due possible inclusion in solar energy conversion. Generally exciplex is taken as pre-association process before energy transfer mechanism. There is currently a limited understanding of the underlying photophysical processes in such conjugates. The main goal in this work is to understand the effect of the back-bonding on energy transfer process between CdTe QD and pentaamine(pyridine)ruthenium complexes with special attention paid to the promise and challenges towards the use as theranostic agents.

Results and Discussion

Water-soluble cadmium telluride (CdTe) quantum dots were synthesized using 3-mercaptopropionic acid as capping agent. Effects of various factors on synthesis and fluorescent properties of CdTe quantum dots were studied. Generally the reaction was carried out in several pH's and refluxed at 100°C in variable time. It was shown that variation of pH, stabilizer and concentration of precursors brings to obtaining of CdTe QD with various fluorescent properties (Figure 1).

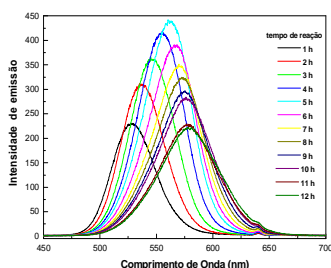


Figure 1. Fluorescence spectrum of CdTe QD at different reaction times.

UV-visible correlation spectroscopy was applied to measure the size of water-soluble QDs, based on the Stokes–Einstein equation. Particles size are in the range of 1 to 3 nm with the emission wavelength of a quantum dot strongly dependent on its size. The fluorescence wavelength increase by increasing the size of nanocrystals due Ostwald ripening.

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Energy-transfer dynamics has been demonstrated in CdTe QD using $[\text{Ru}(\text{NH}_3)_5(\text{py}-x)](\text{PF}_6)_2$ complex {py-x = pyridine (py), 4-picoline (4-pic), isonicotinamide (isn) and 4-acetylpyridine (4-acpy)}. The back-bonding increases in 4pic > py > isn > 4-acpy, resulting in an increase in the reduction potential (Table 1). Notably, the substituents of the pyridine ligand have a greater effect on the photophysical properties as observed bellow (Fig 2).

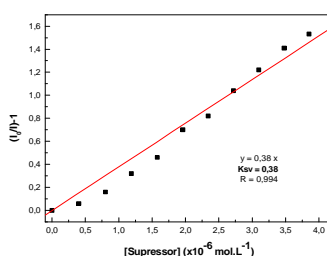


Figure 2. Quenching of fluorescence of CdTe by $[\text{Ru}(\text{NH}_3)_5(\text{py})](\text{PF}_6)_2$.

The quenching of fluorescence of QD by $[\text{Ru}(\text{NH}_3)_5(\text{py}-x)]^{2+}$ obeys the Stern-Volmer equation, which was described by a linear process except for 4-pic. Quenching constants were evaluated and described on Table 1. The K_{SV} is dependent on lifetime at excited state and slightly dependent on the back bonding $\{\text{Ru}^{\text{II}}-\text{py}-x\}^{2+}$ (Table 1).

Table 01. Lifetime and K_{sv} to interaction between CdTe QD and ruthenium complexes.

Compound	K_{sv}	$\tau(\text{ns})$
CdTe	--	8,3; 24,5; 55,1
Ru-py	$3,8 \cdot 10^5$	5,4; 44,6; 20,0
Ru-4-pic	$5,1 \cdot 10^4$	4,4; 19,3; 43,1
Ru-4-acpy	$2,1 \cdot 10^5$	5,7; 46,0; 20,7
Ru-isn	$6,3 \cdot 10^4$	3,7; 15,9; 39,5

Conclusions

The well established back bonding character of pyridine ligands provides a simpler format for exploiting the energy transfer process of QD and ruthenium complexes. The former exciplex is consistent with electrostatic interaction QD-ruthenium complex. The Stern-Volmer constant is dependent on the lifetime of the exciplex.

Acknowledgments

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1) Franco, L.P.; Cicillini, S.A.; Biazzotto, J.C.; Schiavon, M.A.; Mikhailovsky, A.; Burks, P.; Garcia, J.; Ford, P.C.; da Silva, R.S. *The Journal of Physical Chemistry A* **2014**, 118, 12184-12191.