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Two-Photon Fluorescence Property of Tris(4,7-Diphenyl-1,10-phenanthroline)ruthenium(II)perchlorate

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The two-photon absorption (TPA) characteristics of an octupolar metal complex; i.e., tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II)per-chlorate ($Ru(dpp)_3$), have been investigated. The TPA cross-section was evaluated by means of a fluorescence-based technique. As a result, the TPA cross-section of $Ru(dpp)_3$ was estimated to be 210 cm^4s/photon at the wavelength of 830 nm.

Keywords: two-photon absorption; two-photon emission; octupolar molecule; metal complex; tris(4,7-diphenyl-1,10-phenanthroline)-ruthenium(II)perchlorate

INTRODUCTION

A great deal of effort is being placed in developing materials with large two-photon absorption (TPA) cross sections. A material with a large TPA cross-section is potentially utilized for various photonics applications such as 3D-fluorescence imaging, 3D optical data storage, 3D lithographic microfabrication, photodynamic cancer therapy, optical limiting, and so forth[1]. A metal complex has been considered to

exhibit a large nonlinear optical (NLO) effect owing to its metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) interaction[2]. Since the TPA phenomena is one of the NLO effects, the TPA cross-section of a metal complex is expected to be considerably large. It is recently reported that the TPA cross-section of an octupolar molecule is large[3]. Therefore, we have undertaken to study the TPA characteristics of an octupolar metal complex. As for the means for evaluating TPA cross-section, a fluorescence-based technique is known to provide accurate results in an easy fashion[4]. Thus, in this study, we have designed an octupolar metal complex fluorophore, i.e., tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II)-perchlorate ($Ru(dpp)_3$; Figure 1). Then the TPA cross-section of $Ru(dpp)_3$ has been evaluated by means of a fluorescence-based technique. As a result, the TPA cross-section of $Ru(dpp)_3$ was estimated to be 210 cm^4s/photon at the wavelength of 830 nm.

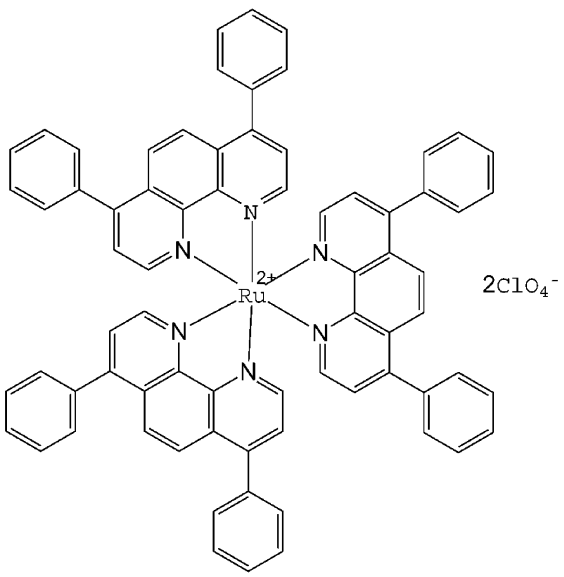

FIGURE 1 Chemical Formula of $[Ru(dpp)_3](ClO_4)_2$.

EXPERIMENT

$Ru(dpp)_3$ was prepared by the same way reported in the literature[5]. The TPA cross-section of $Ru(dpp)_3$ was determined in a way similar to the one reported in the literature[4]. $Ru(dpp)_3$ was solved in chloroform at the concentration of 10^{-2}M. A relative magnitude of TPA cross-section of $Ru(dpp)_3$ was determined by comparing the observed TPA spectrum with that of a reference sample of ethanol solution of rhodamine-B. An optical parametric amplifier (LAMBDA, Scan-Mate OPA) with a pulse duration of 2 nsec, a repetition rate of 10 Hz and an energy of 0.5 mJ was employed for excitation.

RESULTS AND DISCUSSION

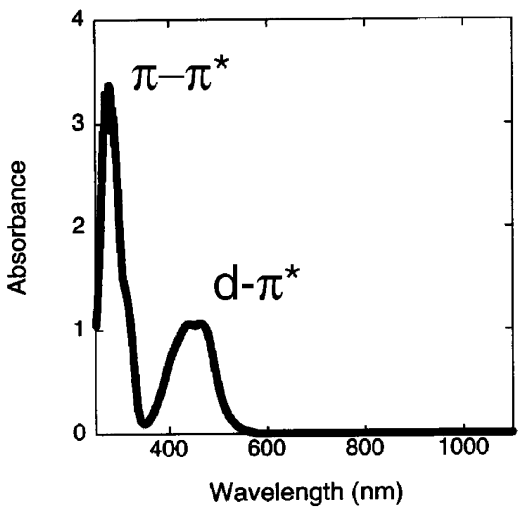

FIGURE 2 The absorption spectrum (10^{-6} M chloroform solution) of $Ru(dpp)_3$.

The absorption spectrum (Figure 2) shows that $Ru(dpp)_3$ is transparent at the excitation wavelength range. Nevertheless, as shown in Figure 3, emission was observed. As can be seen from Figure 2, weak d-π^* transition absorption band is observed at the half of the wavelength we have excited. This fact indicates that the observed emission is the two-photon emission related to the d-π^* transition.

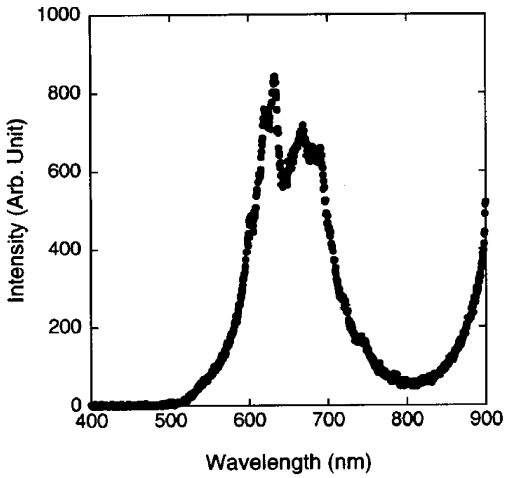

FIGURE 3 The two-photon emission spectrum (excited at the wavelength of 900 nm, 10^{-2} M chloroform solution) of $Ru(dpp)_3$.

We measured the dependence of the two-photon emission spectra on excitation wavelength. The result was shown in Figure 4. The TPA cross-section peak is blue shifted with respect to the one-photon absorption peak at twice the wavelength. This behavior is typical for a noncentrosymmetric molecule. The cause of the blue shift is considered that the parity selection rules favor excitation to higher energy levels than do the respective one-photon induced transitions[6].

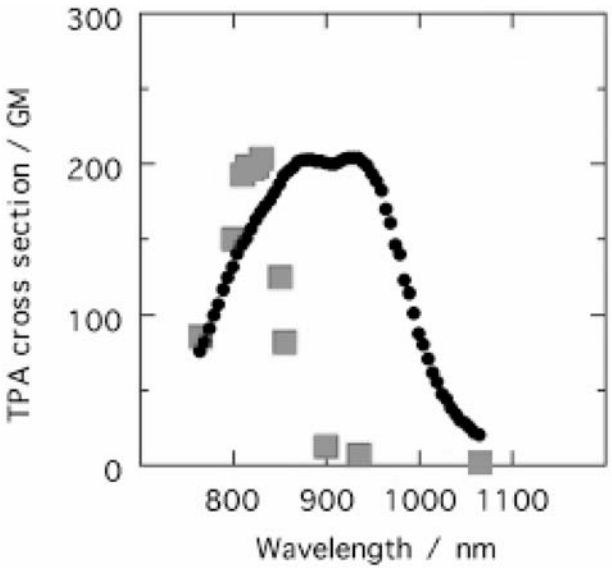

FIGURE 4. Plot of the TPA cross-section (■) compared with the one photon absorption spectra (●) of $Ru(dpp)_3$ dissolved in chloroform. Vertical-axis units: arbitrary for one photon absorption spectra and GM (1 GM = 1 X 10^{-50} cm^4s/photon) for the TPA spectra. Horizontal-axis units: wavelengths as shown for the TPA spectra; the one-photon absorption spectra wavelengths have been doubled as plotted.

The maximum value of the TPA cross-section of $Ru(dpp)_3$ was estimated to be 210 X 10^{-50} cm^4s/photon at the excitation wavelength of 830 nm. As shown in Figure 2, the absorbance concerning the d-π* transition is quite smaller than that of the π–π* transition. This fact indicates that the degree of MLCT of $Ru(dpp)_3$ is not so large. Nevertheless, the TPA cross-section of $Ru(dpp)_3$ observed at the twice wavelength of the d-π* transition is larger than that of the well-known TPA compounds[4]. It is often pointed out that a molecule with large

CT degree exhibits large NLO effects[2]. Thus, it is natural to consider that an octupolar metal complex which has a large MLCT or LMCT exhibits very large TPA cross-section. Consequently, it should be concluded that an octupolar metal complex like $Ru(dpp)_3$ exhibits promising TPA characteristics.

CONCLUDING REMARKS

We evaluated the two-photon absorption (TPA) cross-section of the octupolar metal complex fluorophore (Ru-$(dpp)_3$) by means of a fluorescence-based technique. As a result, we have found that an octupolar metal complex like $Ru(dpp)_3$ exhibits promising TPA characteristics. In order to obtain a metal complex with a larger TPA cross-section than that of $Ru(dpp)_3$, enhancement of the oscillator strength should be effective. The further research along with the above principle is now in progress.

References

[1.] M. Rumi, J. E. Ehrlich, A. A. Heikal, J. W. Perry, S. Barlow, Z. Hu, D. McCord-Maughon, T. C. Parker, H. Rockel, S. Thayumanavan, S. R. Marder, D. Beljonne and Jean-Luc Bredas, *J. Am. Chem. Soc.*, **122,** 9500 (2000).
[2.] D. S. Chemla and J. Zyss, ed. Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, New York, (1987).
[3.] B. Derkowska, J. C. Mulatier, I Fuks, B. Sahraoui, X. Nguyen Phu and C. Andraud, *J. Opt. Soc. Am. B,* **18,** 610(2001).
[4.] C. Xu and W. W. Webb, *J. Opt. Soc. Am. B,* **13,** 481 (1996).
[5.] K. Okamoto, M. Taniguchi, M. Takahashi and A. Yamagishi, Langmuir, **17,** 195 (2001).
[6.] M. A. Alobata, C. Xu and W. W. Webb, Appl. Opt., **31,** 7352 (1998).