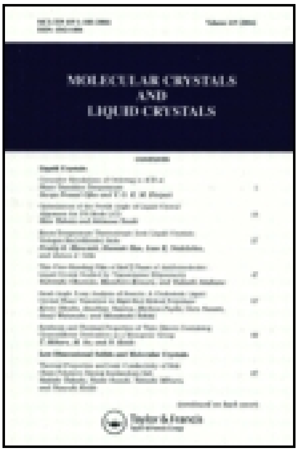
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 11:07
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

New Heteroleptic Ruthenium Complex with quqo Derivative for DSSCs

Dong Min Chang [a], Dong Yuel Kwon [a] & Young Sik Kim [a b]

[a] Department of Information Display, Hongik University, Seoul, Korea

[b] Department of Science, Hongik University, Seoul, Korea

Published online: 02 Sep 2013.

To cite this article: Dong Min Chang, Dong Yuel Kwon & Young Sik Kim (2013) New Heteroleptic Ruthenium Complex with quqo Derivative for DSSCs, Molecular Crystals and Liquid Crystals, 578:1, 104-110, DOI: 10.1080/15421406.2013.804782

To link to this article: http://dx.doi.org/10.1080/15421406.2013.804782

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Mol. Cryst. Liq. Cryst., Vol. 578: pp. 104–110, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.804782

New Heteroleptic Ruthenium Complex with quqo Derivative for DSSCs

DONG MIN CHANG,[1] DONG YUEL KWON,[1]
AND YOUNG SIK KIM[1,2,*]

[1]Department of Information Display, Hongik University, Seoul, Korea
[2]Department of Science, Hongik University, Seoul, Korea

In this study, heteroleptic ruthenium complex Ru(dcbpy)(quqo)(NCS)$_2$ (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) where the quqo was 2-(2-quniolinyl)quinoxaline, was designed and studied theoretically. To gain insight into their structural, electronic and optical properties using DFT calculations were performed on Ru(dcbpy)(quqo)(NCS)$_2$ derived from the N3 dye. Molecular orbitals analysis confirmed that HOMOs of Ru(dcbpy)(quqo)(NCS)$_2$ are localized over the NCS ligand orbitals and the LUMO is localized over the quqo moiety. For N3, HOMOs are localized over the NCS moiety, however LUMO is localized over the dcbpy moiety. The TDDFT calculations showed that the new heteroleptic complex had more panchromatic absorption spectra in the region above 600 nm compared to N3 dye. Absorption bands around 600 nm are due to the conjugated length of quqo ligand.

Keywords DFT; DSSCs; heteroleptic; ruthenium; TD-DFT

1. Introduction

In recent years, many progresses have been developed aiming at preparing new sensitizer for efficient conversion of light to electricity in the Dye-sensitized solar cells (DSSCs) [1, 2]. Some ruthenium (II) complexes have been used as efficient sensitizers because they have an intense MLCT transition in the visible region to absorb the solar radiation. With the feature of charge-transfer, ruthenium polypyridine and polypyridined-derivative complexes are commonly used as sensitizers, such as the famous N3 and black dyes [3, 4]. As the electronic absorption spectrum of sensitizer complexes play an important role on the capability of their efficiency, many efforts has been done on the new ruthenium complexes the determinations of their electronic spectra [5, 6]. But only a few theoretical studies deal with the ruthenium complexes, and limit the potentially wide application of these complexes.

Therefore, the investigation of DSSCs generally works on practical applications [7–10]. Modification of the dye is one of the strategies to improve the performance of DSSCs.

---

[*]Address correspondence to Young Sik Kim, Department of Information Display, Hongik University, Seoul 121–791, Korea. Tel.: +82-2-320-1607; Fax: +82-2-3142-0335. E-mail: youngkim@hongik.ac.kr

A possible way of finding new ruthenium complexes with good conversion efficiencies was investigated by attaching a π-conjugated group to the heteroleptic ruthenium complex.

In this study, a heteroleptic ruthenium complex [Ru(dcbpy)(quqo)$(NCS)_2$] (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) containing a quqo ligand was 2-(2-quniolinyl)quinoxaline (quqo) with the conjugated length was designed and studied theoretically. This report is focused on the effect on the photophysical property of substituent of bipyridine ligand. Compared with N3, the conjugated length of quqo ligand can significantly influence the photophysical property.

2. Computational Methods

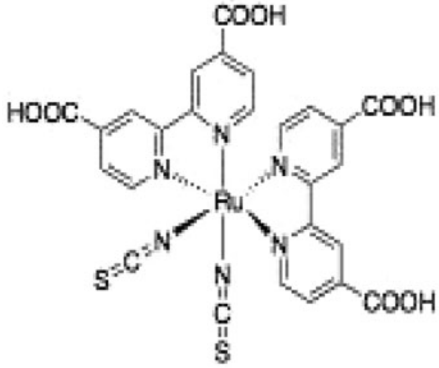
The geometries and energy levels of molecular orbital of the ruthenium (II) complexes were calculated by the density functional theory (DFT) method using the Gaussian 03 program package. For the calculated ground state geometries, the electronic structure was examined in terms of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs). The Hatree-Fork method with a 3-21G (d) basis set and the Becke-Lee-Young-Parr composite exchange correlation functional (B3LYP) method with the larger DGDZVP basis set were used for the geometry optimization and the energy level calculation of the ground state of those ligands, respectively. HOMOs and LUMOs were calculated to show the position of the localization of electron populations along with the calculated molecular orbital energy diagram. Solvation effects were included by means of the conductor-like polarizable continuum model (C-PCM) with the water solvent. time-dependent density functional theory(TD-DFT) calculations with a B3LYP/3-21G (d) level of theory were performed at the ground state optimized geometries by means of the C-PCM algorithm, as implemented in the G03 program package. Absorption spectrum was calculated at optimized ground state geometries for the 40 lowest singlet-singlet excitations (up to 350 nm). The simulation of the absorption spectra was performed by a Gaussian convolution with a full width at half maximum (fwhm) of 0.37 eV.

3. Results and Discussion

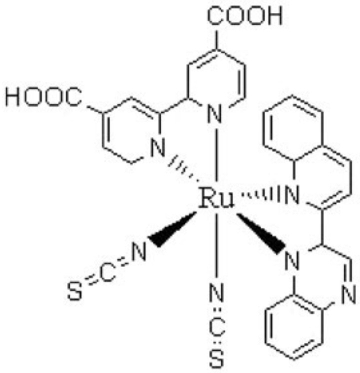
We have designed and characterized Ru(dcbpy)(quqo)$(NCS)_2$ based upon N3 as shown in Fig. 1. The substitution of the quqo ligand with the bipyridine ligand was expected to increase the power conversion efficiency, due to the extension of the π-conjugation system of quqo ligand. The π-conjugation system and heteroleptic ligand would lead to red-shifted and broadened absorption band. Therefore, [Ru(dcbpy)(quqo)$(NCS)_2$] is respected to better performance in J_{sc} than N3.

These dyes with their isodensity surface plots of the frontier MOs are shown in Fig. 2. It shows that the HOMO orbitals for both of N3 and [Ru(dcbpy)(quqo)$(NCS)_2$] are delocalized on the ruthenium center and the NCS ligands. In case of N3, LUMO orbitals are localized homogeneously on the two dcbpy ligands. However, the LUMO of [Ru(dcbpy)(quqo)$(NCS)_2$] is delocalized on the quqo, which would lead to decrement difference between HOMO and LUMO energy gap due to extension of the π-conjugation of quqo ligand.

Figure 3 shows the calculated molecular orbital energy diagram for these dyes. Overall, energy gaps between the HOMO and the LUMO of [Ru(dcbpy)(quqo)$(NCS)_2$] were



N3



[Ru(dcbpy)(quqo)(NCS)$_2$]

Figure 1. Structure of N3 and [Ru(dcbpy)(quqo)(NCS)$_2$].

decreased with an additional quqo ligand than that of N3. Specifically, the LUMO energy level decrements of [Ru(dcbpy)(quqo)(NCS)$_2$] are mainly due to characteristics of quqo moiety(see Fig. 2). The reduction of the energy gap of the dye would show more red-shifted band in the absorption spectrum. The degeneracy of LUMO would result in HOMO → LUMO, LUMO+1 and LUMO+2 simultaneous transitions of [Ru(dcbpy)(quqo)(NCS)$_2$], enabling more panchromatic absorption band in the long wavelength region.

Figure 4 shows the experimental UV-Vis absorption spectra of N3 in ethanol [11]. N3 presents two bands at 385 nm and 532 nm, respectively, while Fig. 5 shows the calculated UV-Vis absorption spectra of N3 and [Ru(dcbpy)(quqo)(NCS)$_2$] dyes by TDDFT calculations. The good agreements between he experimental and calculated absorption spectra of N3 allowed us to investigate dye. [Ru(dcbpy)(quqo)(NCS)$_2$] shows broad and red-shifted absorption band around 600nm than that of N3. The major absorption peak of N3 is at 447 nm and second major peak is at 556 nm, which are ascribed to the HOMO → LUMO+3 and the HOMO-2 → LUMO transition, respectively (see Table 1). The

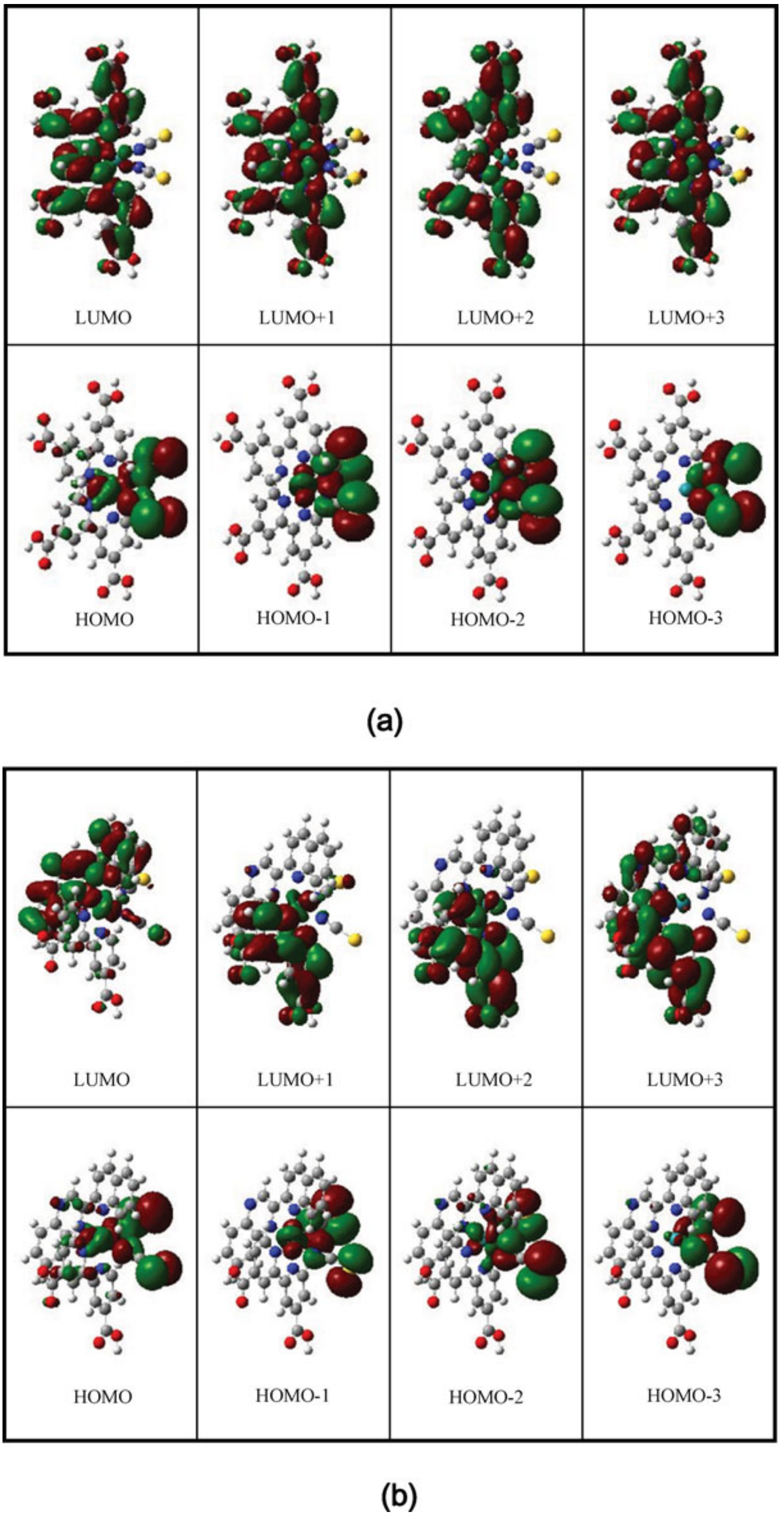


Figure 2. Frontier molecular orbitals : (a) N3 (b) [Ru(dcbpy)(quqo)$(NCS)_2$].

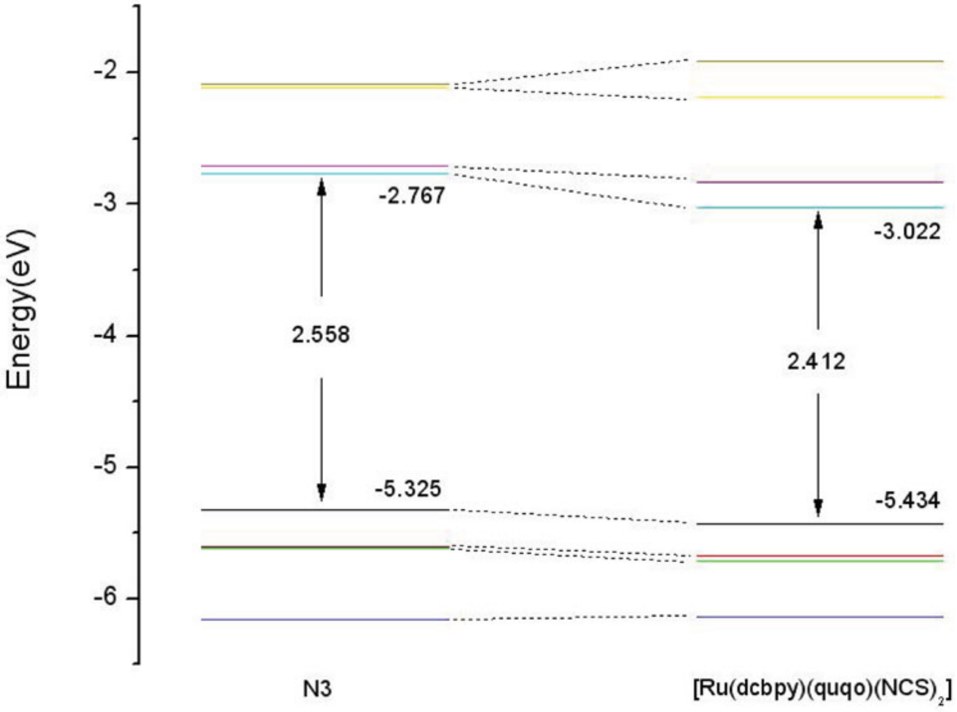


Figure 3. Schematic energy diagram for N3 and [Ru(dcbpy)(dpbpz)(NCS)$_2$].

major absorption peak of [Ru(dcbpy)(quqo)(NCS)$_2$] is at 419 nm and second major peak at 604 nm, which are ascribed to HOMO-4 → LUMO and HOMO-1 → LUMO transition, respectively. Especially, second major peak was red-shifted about 48 nm than that of N3. As shown in Fig. 2, the LUMO was delocalized on the quqo moiety. Therefore, by

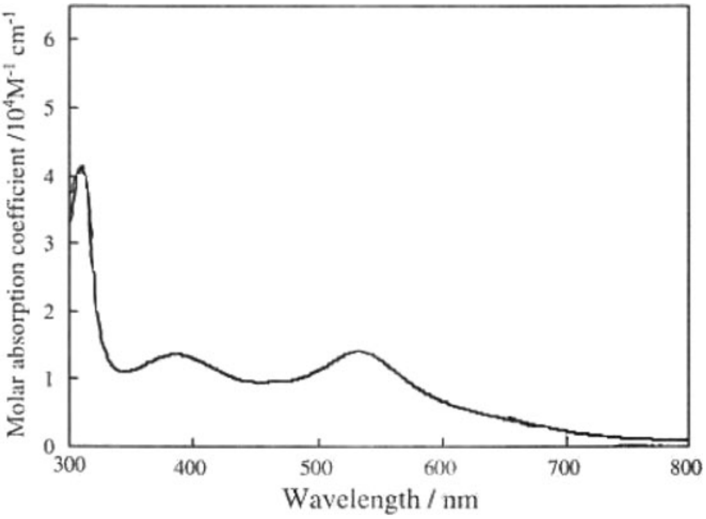


Figure 4. The experimental absorption spectra of N3 in ethanol.

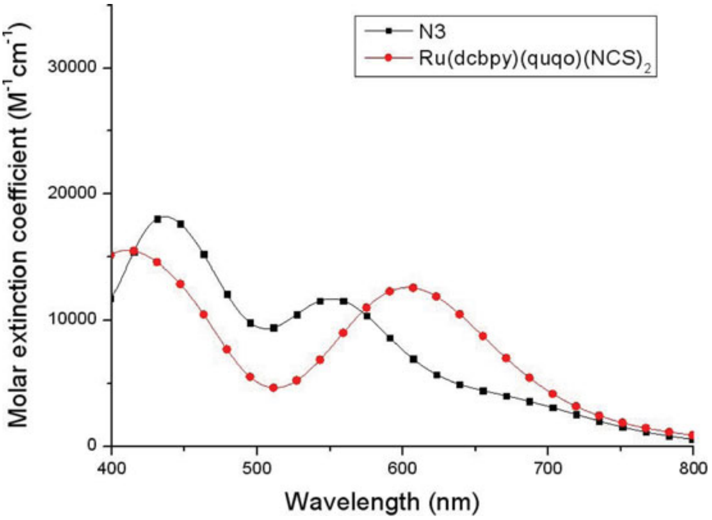


Figure 5. The calculated absorption spectra of N3 and [Ru(dcbpy)(dpbpz) $(NCS)_2$].

introducing quqo ligand, absorption energy bands of the [Ru(dcbpy)(quqo)$(NCS)_2$] were red-shifted around 600 nm and showed broad absorption bands in the long wavelength region, compared with N3. These results is due to the the π-conjugation of quqo ligand and heteroleptic structure of [Ru(dcbpy)(quqo)$(NCS)_2$].

Table 1. Calculated TDDFT excitation energies (eV, nm), oscillator strengths (f) and composition in terms of MO contributions: N3 and [Ru(dcbpy)(quqo)$(NCS)_2$].

Dye	# of excited state	Calculated energy (eV, nm)	Oscillator strengh (f)	Major composition
[Ru(ppd)(tctpy)]+	1	2.9711 (417.35)	0.1831	H-1->L+2 (80%)
	2	2.6718 (464.09)	0.1065	H-2->L+1 (53%), H-1->LUMO (22%)
	3	2.1998 (563.68)	0.0312	H-2->LUMO (65%), H-2->L+1 (33%)
[Ru(ppd-TPA)(tctpy)]+	1	2.9753 (416.76)	0.2313	H-2->L+2 (69%), HOMO->L+5 (16%)
	2	2.6784 (462.95)	0.1544	H-3->L+1 (50%), H-2->LUMO (16%)
	3	2.3596 (525.50)	0.1046	H-2->L+1 (91%)
[Ru(CF_3-ppyd-TPA)(tctpy)]+	1	3.0824 (402.28)	0.2238	HOMO->L+5 (62%), HOMO->L+4 (18%)
	2	2.9739 (416.95)	0.2335	H-2->L+3 (74%), H-1->L+4 (10%)
	3	2.9056 (426.76)	0.2013	H-1->L+3 (91%)
	4	2.5384 (488.49)	0.1577	H-1->L+1 (20%), H-1->L+2 (63%)
	5	2.3824 (520.48)	0.0805	H-2->L+1 (67%)

4. Conclusions

Novel heteroleptic sensitizer [Ru(dcbpy)(quqo)(NCS)$_2$] with an added heteroleptic π-conjugated group was designed and studied theoretically in order to determine the potential devices of DSSCs. Specifically, structural, electronic and optical properties of the [Ru(dcbpy)(quqo)(NCS)$_2$] were investigated with the introduction of the conjugated quqo ligand. The LUMO level was decreased due to the introduction of the quqo ligand. In contrast, HOMOs were not nearly changed. The absorption spectra of the [Ru(dcbpy)(quqo)(NCS)$_2$] showed more broad and red-shifted band in the long wavelength region, compared with the standard N3 dye by the additional quqo ligand. The red-shifted and broadened absorption band were arised from extension of the π conjugation of quqo lingand and heteroleptic structure of [Ru(dcbpy)(quqo)(NCS)$_2$], respectively, which would lead to efficient light harvesting in the long wavelength region and high performance in J_{sc}. Therefore, we suggest that the newly designed [Ru(dcbpy)(quqo)(NCS)$_2$] heteroleptic ruthenium complex will be a good candidate as a dye sensitizer of DSSCs, comparable to N3.

Acknowledgment

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0021668).

References

[1] Regan, B. O., & Grätzel, M. (1991). *Nature*, *353*, 737.

[2] Kuang, D., Ito, S., Wenger, B., Klein, C., Moser, J. E., Humphry-Baker, R., Zakeeruddin, S. M., & Grätzel, M. (2006). *J. Am. Chem. Soc.*, *128*, 4146.

[3] Kuang, D., Klein, C., Ito, S., Moser, J. E., Humphry-Baker, R., Zakeeruddin, S. M., & Gratzel, M. (2007). *Adv. Funct. Mater.*, *17*, 154.

[4] Kuang, D., Klein, C., Ito, S., Moser, J. E., Humphry-Baker, R., Evans, N., Duriaux, F., Gratzel, C., Zakeeruddin, S. M., & Gratzel, M. (2007). *Adv. Mater.*, *19*, 1133.

[5] Nazeeruddin, M. K., Angelis, F. D., Fantacci, S., Selloni, A., Viscardi, G., Liska, P., Ito, S., Takeru, B., & Gratzel, M. (2005). *J. Am. Chem. Soc.*, *127*, 16835.

[6] Wang, P., Klein, C., Humphry-Baker, R., Zakeeruddin, S. M., & Gratzel, M. (2005). *Appl. Phys. Lett.*, *86*, 123508.

[7] Horiuchi, T., Miura, H., Sumioka, K., & Uchida, S. (2004). *J. Am. Chem. Soc.*, *126*, 12218.

[8] Tian, H., Yang, X., Cong, J., Chen, R., Liu, J., Hao, Y., Hagfeldt, A., & Sun, L. (2009). *Chem. Commun.*, *6288*.

[9] Osamu Kitao, Hideki Sugihara. (2008). *Inorganica Chimica Acta*, *301*, 712.

[10] Christiana, A., Mitsopoulou, Irene Veroni, Athanassios, I., Philippopoulos, Polycarpos Falaras. (2007). *Journal of Photochemistry and Photobiology A : Chemistry*, *191*, 6.

[11] Ke-Jian, J., Jiang-bin, X., Naruhiko, M., Shuji, N., & Shozo, Y. (2008). *Inorganica Chimica Acta*, *361*, 783.