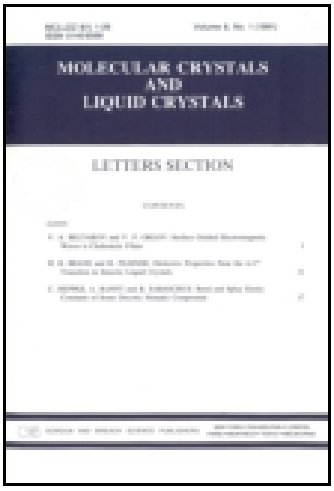

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Novel Ru(II) Complex with ppy Derivative for Dye-Sensitized Solar Cell

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Novel heteroleptic ruthenium(II) complex was designed and investigated theoretically, [Ru(F_2HexOppy)(NCS)(tctpy)] with ppy derivative for heteroleptic donor to increase molar absorptivity compared to N749 (tctpy = 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine, F2HexOppy = 2-(2',4'-difluorophenyl)-4-oxyhexylpyridine). Generally, absorption spectrum of dyes with ppy derivative was red-shifted and broadened compared to N749, especially, in the region above 650nm. This is attributed to the heteroleptic donor system of these dyes. According to the molecular orbital analysis, we observed the LUMO mainly localized on tctpy (4,4′,4″-tricarboxy-2-2′:6′.2″-terpyridine) moiety in N749. In case of HOMOs were localized on NCS moiety. However, HOMO of [Ru(F_2HexOppy)(NCS)(tctpy)] were delocalized over Ru-F_2HexOppy-NCS and HOMO-1 were delocalized on Ru-NCS moiety, respectively. These results, new type Ru(II) complex would show higher photovoltaic efficiency compared to N749 as dye sensitizers.

Keywords Dye-sensitized solar cells(DSSCs); Ruthenium; Heteroleptic donor; TD-DFT; DFT

1. Introduction

Recently much attention has focused on dye-sensitized solar cells (DSSCs), as possible low-cost photovoltaic devices [1]. The performance and the stability of DSSC devices have been studied and significantly improved over the past decade [2–4]. Among the components of DSSCs, the sensitizer is a crucial element, which significantly influences on the power conversion efficiency as well as the stability of the device. Up to now, the record for DSSC efficiency was held by a polypyridyl ruthenium (Ru) sensitizer (11%), which used a voltaic iodide/triiodide electrolyte mixture [5]. However, the conversion efficiency of DSSCs is still lower than that of the silicon-based photovoltaic cells. To obtain a high conversion efficiency, optimization of the short-circuit photocurrent (Jsc) and open-circuit potential (Voc) of the cell is essential. The value of Voc depends on the edge of the conduction band in TiO_2 and the redox potential of I^-/I_3^-, Jsc is related to the interaction between TiO_2 and the sensitizer as well as the absorption coefficient of the sensitizer [6]. Furthermore, Jsc

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is closely related to the metal-to-ligand charge transfer (MLCT) transition of immobilized dye molecules, which could be improved significantly by means of the enrichment electron-donating ability of the ancillary ligand [7].

To enhance the power conversion efficiencies of DSSCs, it is imperative to design novel sensitizers that exhibit an enhanced molar extinction coefficient in combination with a red-shifted absorption band compared to the standard N749 dye ($[Ru(tctpy)(NCS)_3]^-$). Dyes with heteroleptic donor systems of the dye for DSSCs can improve the light-harvesting ability of corresponding ruthenium sensitizers [8–10]. Extension of the π-conjugation of the ancillary ligand and/or the anchoring ligand can improve the spectral response of corresponding ruthenium sensitizers [11]. Therefore, efforts have been made recently to increase the molar extinction coefficients of ruthenium dyes in order to improve their light-harvesting abilities. In this work, we designed a novel heteroleptic [Ru(F_2HexOppy)(NCS)(tctpy)] complex with a 2-(2′,4′-difluorophenyl)-4-oxyhexylpyridine (F_2HexOppy) as the heteroleptic donor to increase the absorption ability in the long wavelength region. Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) were syidied to estimate the photovoltaic properties of the dyes [12].

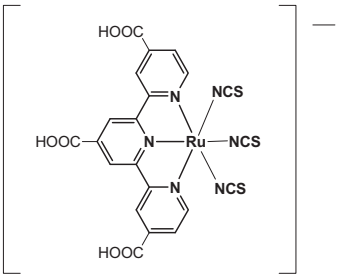
2. Experiment Details

To gain insight into the factors responsible for the absorption spectral response and the conversion efficiency of ruthenium dyes, the geometries and the energy levels of the molecular orbitals were calculated by the DFT method and the absorption spectrum was calculated at optimized ground state geometries by the TD-DFT method. The geometries in the gas phase were optimized by the DFT method using the B3LYP/DGDZVP in the Gaussian 03 program package. Possible isomers of the ruthenium complex with a F_2HexOppy (2-(2′,4′-difluorophenyl)-4-oxyhexylpyridine) were calculated by the DFT. Among the conformations, the present conformation had the lowest energy conformation, which was optimized by the molecular structure of the dyes in the gas phase.

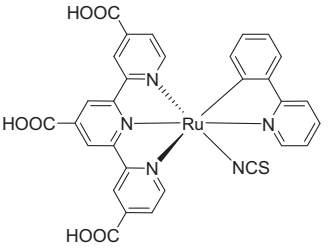
The TD-DFT calculation using the Coulomb attenuating B3LYP (CAM-B3LYP) approach with DGDZVP basis set was performed at the ground state optimized geometries. Solvation effect was taken into account in water solution using the conductor-like polarizable continuum model (C-PCM) as implemented in the G09 program package. The absorption spectrum was calculated at optimized ground state geometries for the lowest 20 singlet-singlet excitations up to wavelengths of 300 nm. The simulation of the absorption spectra was performed by a Gaussian convolution with fwhm = 0.3 eV.

3. Results and Discussion

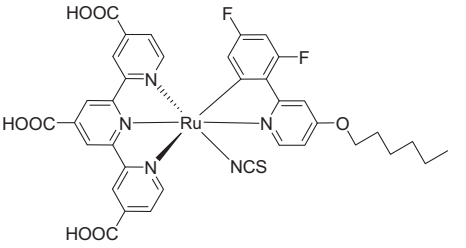
The chemical structures of the dyes studied herein are shown in Fig. 1. The [Ru(ppy)(NCS)(tctpy)] has the heteroleptic donor system. The heteroleptic donor system would lead to increase power conversion efficiency and broad absorption spectrum due to the dual electronic transitions from the Ru-ppy moiety to tctpy and from the Ru-NCS moiety to the tctpy. However, the HOMO energy level of the ppy ligand is too high, which lead to reduction of the Voc. Therefore, the [Ru(F_2HexOppy)(NCS)(tctpy)] was designed by adding the fluorine on the ppy ligand. The adding fluorine atoms on ppy ligand lead to stabilization HOMO energy level of ppy ligand due to the electron-withdrawing characteristic of the fluorine atoms. Thus the [Ru(F_2HexOppy)(NCS)(tctpy)] is expected to better performance



N749



[Ru(ppy)(NCS)(tctpy)]



[Ru(F_2HexOppy)(NCS)(tctpy)]

Figure 1. Molecular structure of the dyes: N749, [Ru(ppy)(NCS)(tctpy)] and [Ru(F_2HexOppy)(NCS)(tctpy)].

in Jsc than the N749 and increase Voc than that of the [Ru(ppy)(NCS)(tctpy)]. To elucidate the molecular orbitals and the electronic structures of the N749, [Ru(ppy)(NCS)(tctpy)], and [Ru(F_2HexOppy)(NCS)(tctpy)] dyes, DFT calculations at the B3LYP/DGDZVP level and geometry optimization were performed.

These dyes with their isodensity surface plots of the frontier MOs are shown in Fig. 2. It shows that the HOMO orbitals of the N749 are localized over the Ru-NCS moiety and that the LUMO orbitals are mainly localized on the tctpy moiety. However, the HOMO and HOMO-1 of the [Ru(ppy)(NCS)(tctpy)] are localized over the Ru-ppy-NCS moiety and HOMO-2 is localized over the Ru-NCS moiety, demonstrating that an anionic chelating ligand, such as ppy perform as a donor due to the electron-donating characteristic. The LUMO orbitls are mainly localized over the tctpy moiety. Therefore, the dual electronic transitions may possible from the Ru-ppy-NCS moiety to tctpy and from the Ru-NCS

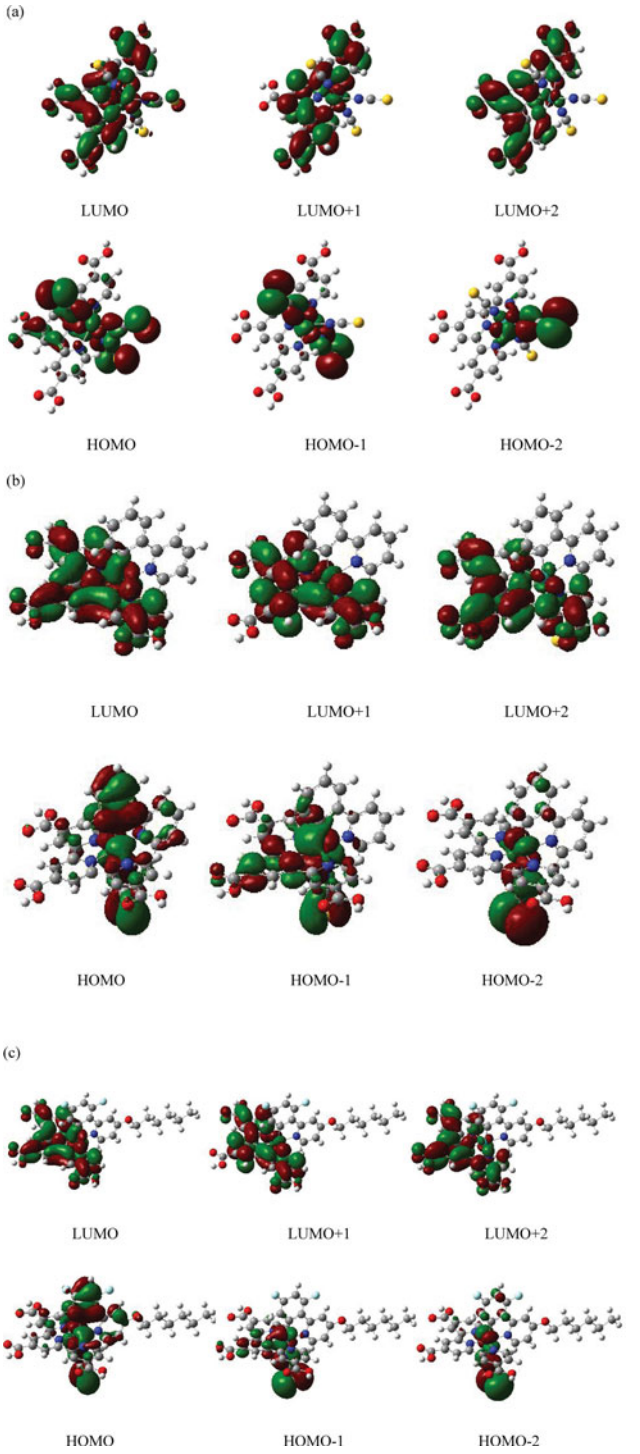


Figure 2. Frontier molecular orbitals (HOMOs, LUMOs): (a) N749, (b) [Ru(ppy)(NCS)(tctpy)], (c) [Ru(F_2HexOppy)(NCS)(tctpy)].

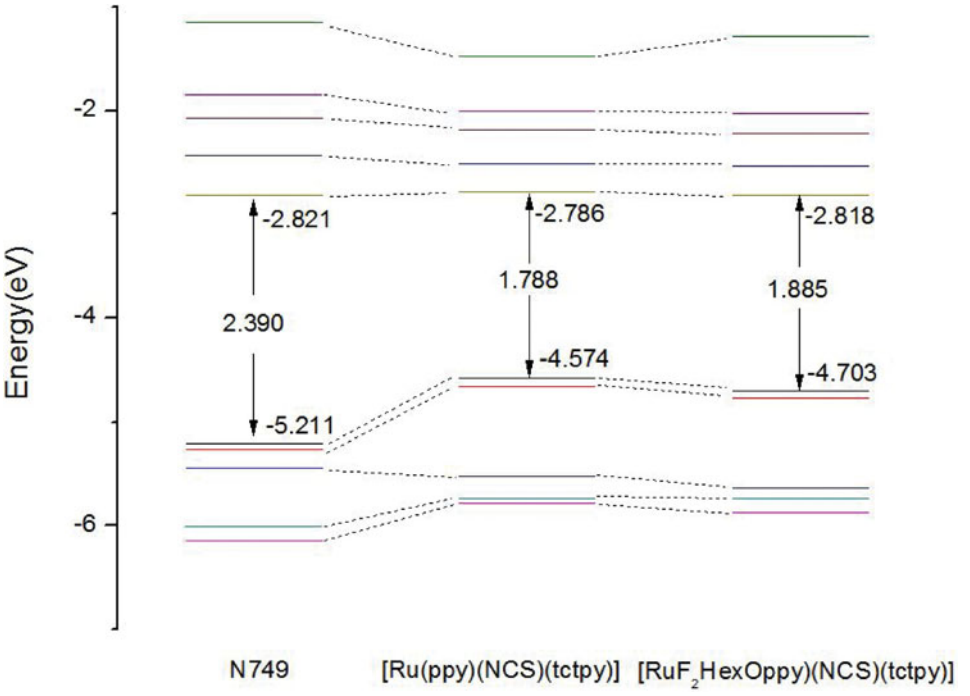


Figure 3. Schematic energy diagrams for N749, [Ru(ppy)(NCS)(tctpy)] and [Ru(F_2HexOppy)(NCS)(tctpy)].

moiety to the tctpy in the [Ru(ppy)(NCS)(tctpy)] dye. Similarly, the HOMO, the HOMO-1 and the HOMO-2 of the [Ru(F_2HexOppy)(NCS)(tctpy)] are delocalized over the Ru-F_2HexOppy-NCS, the Ru-NCS and the Ru-NCS moieties, respectively. Therefore, the F_2HexOppy and the NCS ligand would perform as a heteroleptic donor system leading to a broad absorption spectrum in the visible wavelength region. The LUMOs of the [Ru(F_2HexOppy)(NCS)(tctpy)] are mainly localized on the tctpy moiety.

Figure 3 shows the calculated molecular orbital energy diagram for these dyes. The energy gaps between HOMO and LUMO levels of the [Ru(ppy)(NCS)(tctpy)] was decreased with additional ppy ligand. However, the HOMO energy level of the [Ru(ppy)(NCS)(tctpy)] is too much high, which leads to reduction in the Voc. The HOMO energy levels of [Ru(F_2HexOppy)(NCS)(tctpy)] were stabilized by the electron-withdrawing characteristic of fluorine atoms than that of the [Ru(ppy)(NCS)(tctpy)]. The absorption spectrum would be blue-shifted due to the stablilized the HOMO energy level of the [Ru(F_2HexOppy)(NCS)(tctpy)] than that of the [Ru(ppy)(NCS)(tctpy)], however the Voc would be increased by stablilized the HOMO energy level due to the electron-withdrawing characteristic of fluorine atoms. Furthermore, [Ru(F_2HexOppy)(NCS)(tctpy)] would show the panchromatic absorption band in the long wavelength region due to the heteroleptic donor system than that of the N749.

Figure 4 shows the UV-Vis absorption spectra of the N749, the [Ru(ppy)(NCS)(tctpy)] and the [Ru(F_2HexOppy)(NCS)(tctpy)] dyes according to the TD-DFT calculations. The red-shift and the broad absorption band between 400 nm and 650 nm of [Ru(F_2HexOppy)(NCS)(tctpy)] are in agreement with the decreased energy gap between the HOMO and LUMO level than that of the N749 (see Fig. 3). The Molar extinction

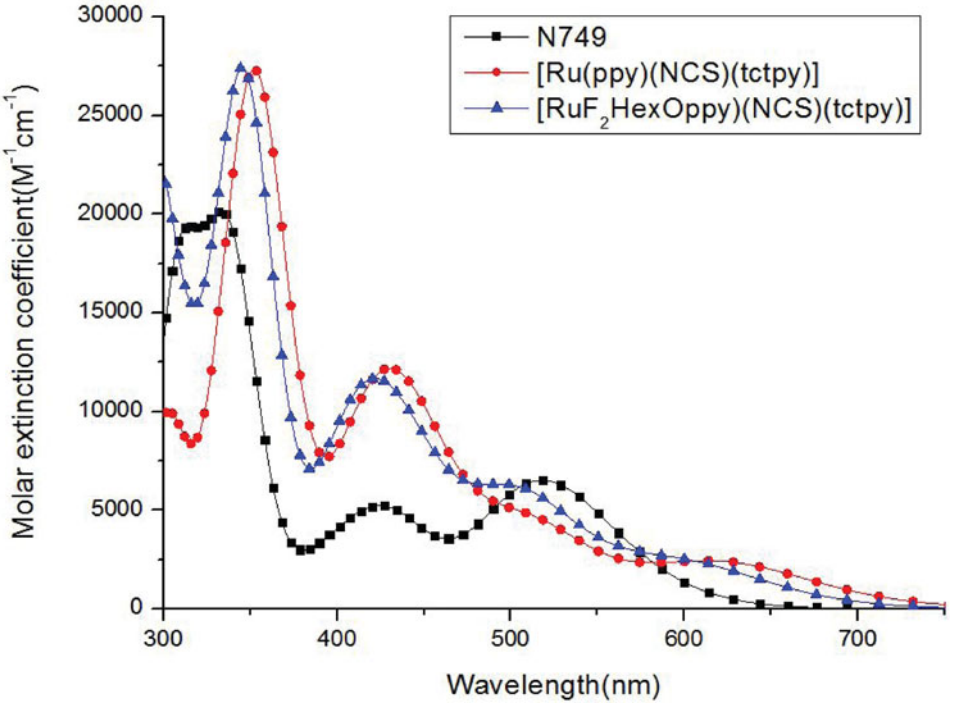


Figure 4. Absorption spectra of the dyes: N749, [Ru(ppy)(NCS)(tctpy)] and [Ru(F_2HexOppy)(NCS)(tctpy)].

coefficient of the [Ru(ppy)(NCS)(tctpy)] was enhanced from 350 nm to 500 nm in the absorption spectrum than that of the N749. It is due to the heteroleptic donor system of the [Ru(ppy)(NCS)(tctpy)]. Moreover, the extra peak was observed in the long wavelength region compared to the N749. The peak at 621 nm with [Ru(ppy)(NCS)(tctpy)] originated from HOMO → LUMO (87%) MLCT transition. (see Fig. 2 and Table 1). In the case of the [Ru(F_2HexOppy)(NCS)(tctpy)], the absorption spectrum was blue-shifted than that of the [Ru(ppy)(NCS)(tctpy)] due to the stabilized HOMO energy level by adding fluorine atoms. Nevertheless, the stabilized HOMO energy level would lead to the increase Voc than that of the [Ru(ppy)(NCS)(tctpy)]. The peak at 597 nm with [Ru(F_2HexOppy)(NCS)(tctpy)] originated from HOMO → LUMO (87%) MLCT transition. The HOMO of the [Ru(ppy)(NCS)(tctpy)] and the [Ru(F_2HexOppy)(NCS)(tctpy)] were located on the Ru-ppy-NCS and the Ru- F_2HexOppy-NCS, respectively. Therefore, the extra peaks in the long wave length region compared to the N749 were originated from additional ppy groups. The absorption spectrum of the [Ru(F_2HexOppy)(NCS)(tctpy)] between 350 nm and 500 nm was broader than that of N749. The 406 nm peak was originated from HOMO → LUMO+1 (71%) and the 504 nm peak was originated from HOMO-1 → LUMO (75%) transition. The HOMO and the HOMO-1 of [Ru(F_2HexOppy)(NCS)(tctpy)] were located on the Ru- F_2HexOppy-NCS and Ru-NCS moiety, respectively. Therefore, the broad absorption spectrum between 350 nm and 500 nm is due to the heteroleptic donor system of the [Ru(F_2HexOppy)(NCS)(tctpy)]. Particularly, the tansitions of HOMO → LUMO+1 and HOMO-1 → LUMO were estimated of MLTC transitions. These results reveal that the presence of the F_2HexOppy ligand can reinforce the electron-donating ability of the

Table 1. Calculated TDDFT excitation energies (eV, nm), oscillator strengths (f), and composition in terms of MO contributions for N749, [Ru(ppy)(NCS)(tctpy)] and [Ru(F_2HexOppy)(NCS)(tctpy)].

Dye	# of excited state	Calculated energy(eV, nm)	Oscillator strength(f)	Major composition
N749	1	2.4309(510.09)	0.0713	HOMO->LUMO (87%)
	2	2.8818(430.28)	0.0618	HOMO->L+1 (92%)
	3	3.6972(335.38)	0.1547	H-1->L+2 (81%)
[Ru(ppy)(NCS) (tctpy)]	1	1.9971(620.91)	0.0319	HOMO->LUMO (87%)
	2	2.4273(510.85)	0.0567	H-1->LUMO (70%), HOMO->L+1 (20%)
	3	2.7907(444.33)	0.1045	H-1->L+1 (92%)
	4	3.4576(358.63)	0.2115	HOMO->L+2 (87%)
[Ru(F_2HexOppy) (NCS)(tctpy)]	1	2.0736(597.91)	0.0312	HOMO->LUMO (87%)
	2	2.4590(504.20)	0.0769	H-1->LUMO (75%), HOMO->L+1 (16%)
	3	3.0506(406.42)	0.101	HOMO->L+1 (71%), H-1->LUMO (15%)
	4	3.6065(343.78)	0.1344	H-1->L+2 (84%)

ancillary ligand and the stabilized HOMO energy level by adding fluorine atoms leads to increase Voc than that of the [Ru(ppy)(NCS)(tctpy)], thereby enhancing the spectral response of the corresponding ruthenium sensitizer. Therefore, the [Ru(F_2HexOppy)(NCS)(tctpy)] dye can be expected to exhibit high light-harvesting and conversion efficiency in photovoltaic devices.

4. Conclusion

A novel ruthenium complex [Ru(F_2HexOppy)(NCS)(tctpy)] was designed and its potential application in DSSCs was studied theoretically. Specifically, the structural, electronic and optical properties of the [Ru(F_2HexOppy)(NCS)(tctpy)] complex were investigated following the introduction of the F_2HexOppy ligand as a hrteroleptic donor. In electronically, compared with [Ru(ppy)(NCS)(tctpy)], the level of the HOMO was stabilized by adding fluorine atoms due to the electron-withdrawing characteristic of fluorine. The absorption spectrum of the [Ru(F_2HexOppy)(NCS)(tctpy)] was broader and more red-shifted by the addition of the F_2HexOppy ligand than that of N749. The HOMO of the [Ru(F_2HexOppy)(NCS)(tctpy)] was located on the Ru-F_2HexOppy-NCS, therefore the [Ru(F_2HexOppy)(NCS)(tctpy)] showed the strong MLCT around 650 nm in the absortion spectrum compared to the N749. The broad absorption spectrum between 350 nm and 500 nm is due to the heteroleptic donor system of the [Ru(F_2HexOppy)(NCS)(tctpy)]. The [Ru(F_2HexOppy)(NCS)(tctpy)] can be expected to exhibit more efficient light harvesting and better performance in J_{sc} than the N749. Therefore, we suggest that the newly designed [Ru(F_2HexOppy)(NCS)(tctpy)] heteroleptic ruthenium complex would be a good candidate as a dye sensitizer of DSSCs, comparable to N749.

Acknowledgments

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References and Notes

[1] O'Regan, B., & Grätzel, M. (1991). *Nature (London)*, *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., & Grätzel, M. (2007). *Adv. Funct. Mater.*, *17*, 154.
[4] Kuang, D., Klein, C., Ito, S., Moser, J. E., Humphry-Baker, R., Evans, N., Duriaux, F., Grätzel, C., Zakeeruddin, S. M., & Grätzel, 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., & Grätzel, M. (2005). *J. Am. Chem. Soc.*, *127*, 16835.
[6] Wang, P., Klein, C., Humphry-Baker, R., Zakeeruddin, S. M., & Grätzel, M. (2005). *Appl. Phys. Lett.*, *86*, 123508.
[7] Li, J., Chen, C., Chen, J., Tan, C., Lee, K., Wu, S., Tung, Y., Tsai, H., Ho, K., & Wu, C. (2010). *J. Mater. Chem.*, *20*, 7158.
[8] Chang, D. M., Kim, J. Y., & Kim, Y. S. (2012). *Mol. Cryst. Liq. Cryst.*, *567*, 63.
[9] Pogozhev, D. V., Bezdek, M. J., Schauer, P. A., & Berlinguette, C. P. (2013). *Inorg. Chem.*, *52*, 3001.
[10] Huang, W., Wu, H., Lin, P., & Diau, E. W. (2013). *J. Phys. Chem. C*, *117*, 2059.
[11] Horiuchi, T., Miura, H., Sumioka, K., & Uchida, S. (2004). *J. Am. Chem. Soc.*, *126*, 12218.
[12] Tian, H., Yang, X., Cong, J., Chen, R., Liu, J., Hao, Y., Hagfeldt, A., & Sun, L. (2009). *Chem. Commun.*, 6288.