Convenient synthesis and purification of $[Bu_4N]_2[Ru(4\text{-carboxy-}4\text{-carboxylate-}2,2'\text{-bipyridine})_2(NCS)_2]$: a landmark DSC dye.

Tristan Rawling, Florian Buchholz, Andrew M. McDonagh*

Institute of Nanoscale Technology, University of Technology Sydney, Sydney, NSW 2007, Australia.

*Corresponding author. Tel.: +61 2 95141035

Email address: andrew.mcdonagh@uts.edu.au

Abstract

We present here a convenient synthesis to the landmark DSC dye $[Bu_4N]_2[Ru(4\text{-carboxy-}4\text{-carboxylate-}2,2'\text{-bipyridine})_2(NCS)_2]$ (N719). Key to this synthetic procedure is the protection of the carboxyl functionalities with *iso*-butyl ester groups. This strategy allows the use of silica chromatography to remove the less efficient S-bound isomers and significantly reduces the time and difficulty of the synthesis.

Keywords: Dye sensitised solar cells, N719, ruthenium

Dye sensitised solar cells (DSCs) based on nanocrystalline titania sensitised by light-absorbing dyes have been the subject of increasing attention over the past two decades.[1-4] A major breakthrough in the development of DCSs was the discovery of the sensitising dyes *cis*-[Ru(dcbpy)$_2$(X)$_2$] (where dcbpy = 4,4′-dicarboxylic acid-2,2′-bipyridine and X = Cl^-, Br^-, I^-, CN^-, or NCS^-).[5] In this series of dyes, the complex with X = NCS^- gives the highest cell efficiency. Furthermore, replacement of two of the carboxy protons with two tetrabutylammonium cations, [Bu_4N]$_2$[Ru(4-carboxy-4-carboxylate-2,2′-bipyridine)$_2$(NCS)$_2$] (often reported in an abbreviated form, N719) leads to even greater cell efficiency.[6] The improvement in performance is related to changes in the titania Fermi level by transfer of the optimum number of protons to the titania upon anchoring of the dye.[7,8] Currently, the N719 dye remains commercially important and in a research context is often used as a standard for comparison of new sensitising dyes.

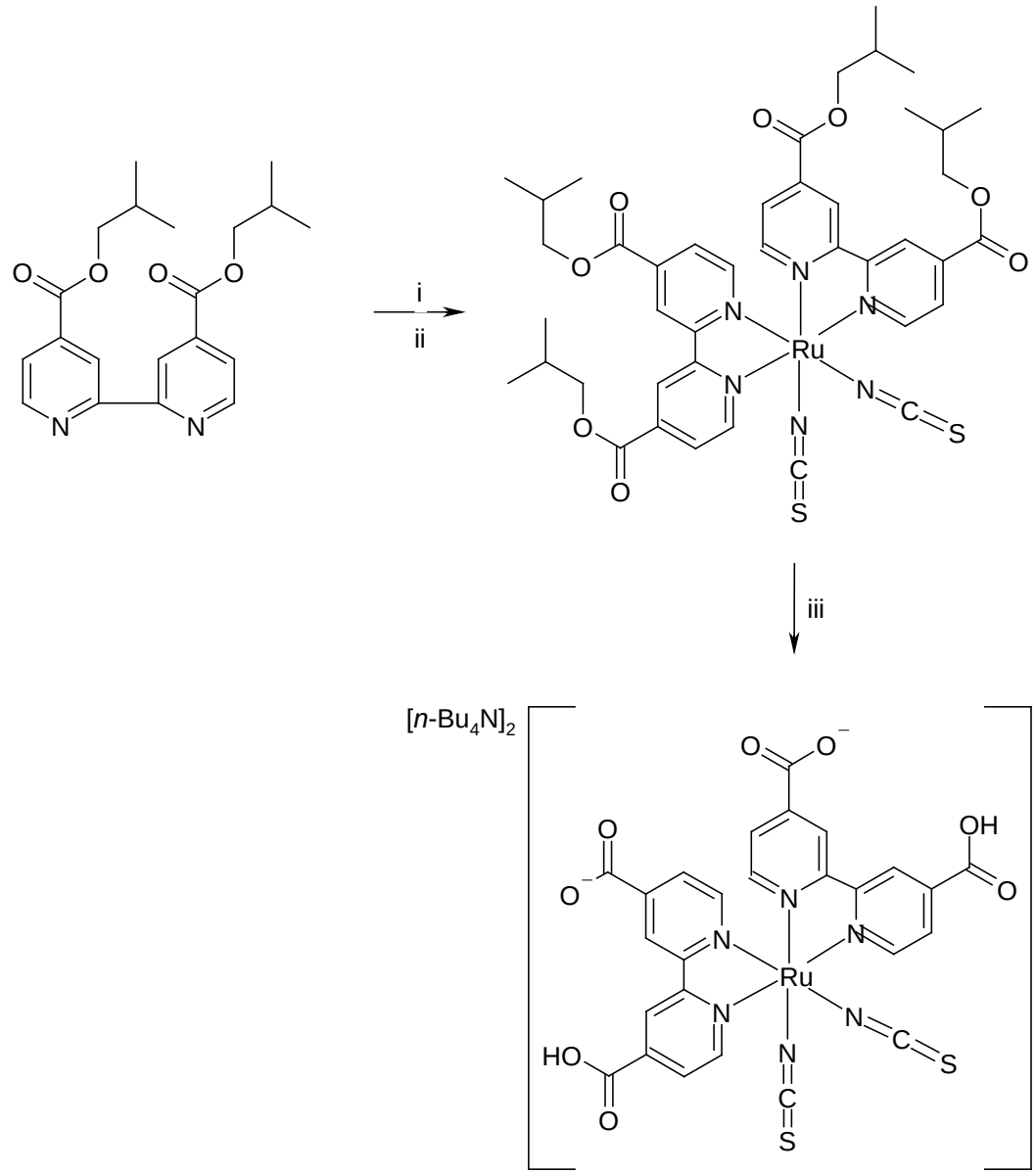
There are several reports describing the synthesis of N719 and the intermediate compounds *cis*-[Ru(dcbpy)$_2$Cl$_2$] and *cis*-[Ru(dcbpy)$_2$(NCS)$_2$]. Some reports describe the preparation of pure complexes without the use of chromatographic purification procedures,[5,6,9-11] while other reports suggest the need for chromatography.[8,12-14] In our hands, the preparation of *cis*-[Ru(dcbpy)$_2$Cl$_2$] (using the method reported in reference[9]) without subsequent chromatography procedures yielded a mixture of products. Wolfbauer and co-workers found that *cis*-[Ru(dcbpy)$_2$(NCS)$_2$] prepared without chromatography contained ≤ 4% of the mixed N-,S- linkage isomer[15] and Grätzel and co-workers noted the necessity of chromatography to remove the less efficient S-bound isomers from reaction mixtures.[14] However, where chromatography is employed, the carboxyl functionalities associated with the complexes necessitate the use of costly and time-consuming techniques using the Sephadex LH20 stationary phase. Some reports even state that multiple elutions are required to obtain pure products.[8,14]

In this work we present a straightforward alternative synthesis of the landmark sensitising dye, N719, using ethanol as solvent and utilising a protection/deprotection strategy which permits the use of conventional silica gel chromatography to conveniently afford an isomerically pure product.

Scheme 1 shows the synthetic procedure used to prepare the dye $[Bu_4N]_2$[Ru(4-carboxy-4-carboxylate-2,2′-bipyridine)$_2$(NCS)$_2$]. In a two-step one-pot procedure, the reaction of $RuCl_3.3H_2O$ with the new isobutyl-protected ligand, *i*Bu$_2$dcbpy, formed the complex *cis*-[Ru(*i*Bu$_2$dcbpy)$_2$Cl$_2$] (characterized by ^{1}H NMR, UV-Vis and ESI-MS experiments). Reaction with ammonium thiocyanate yields a mixture of N- and S-bound linkage isomers (observed using thin layer chromatography), which may be separated using silica gel column chromatography. The ^{1}H NMR spectrum of *cis*-[Ru(*i*Bu$_2$dcbpy)$_2$(NCS)$_2$] contains six resonances in the aromatic region between δ 9.47 and 7.62 arising from the six non-equivalent ring protons. The chemical shifts of these resonances confirm that the complex is the fully N-bonded isomer and are in good agreement with those reported by Wolfbauer *et al* for an analogous complex *cis*-[Ru(Et$_2$dcbpy)$_2$(NCS)$_2$] (where Et$_2$dcbpy = diethyl-2,2′-bipyridine-4,4′-dicarboxylate).[16] Generally, ^{1}H NMR spectroscopy is a useful tool for distinguishing N- and S-bonded isomers in complexes of the type [Ru(L)$_2$(NCS)$_2$] (where L = 2,2'-bipyridine analogues). Wolfbauer *et al* found that S-bound thiocyanate ligands induce a down field shift of ~0.4 ppm for the 6-H proton signal in the spectrum of *cis*-[Ru(Et$_2$dcbpy)$_2$(*N*CS)(*S*CN)] compared to the exclusively N-bound isomer.[16]

Each step of the one-pot reaction was monitored to determine the optimal reaction times. For the initial step, the reaction of *i*Bu$_2$dcbpy with $RuCl_3.3H_2O$, the *i*Bu$_2$dcbpy was consumed within three hours (as monitored by TLC) affording *cis*-[Ru(*i*Bu$_2$dcbpy)$_2$Cl$_2$] in 64 % yield after purification by column chromatography. Extending the reaction time (up

to nineteen hours) gave no improvement to the yield. Similarly, in the reaction of *cis*-[Ru(*i*Bu_2dcbpy)$_2Cl_2$] with [NH_4]NCS, complete disappearance of the chloride-containing complex was evident after 2.5 hours. The resulting yield of 73 % was not improved by extending the reaction time.



Scheme 1. Synthesis of [Bu_4N]$_2$[Ru(4-carboxy-4-carboxylate-2,2′-bipyridine)$_2$(NCS)$_2$]. Conditions: (i) $RuCl_3.3H_2O$, ethanol, reflux, 3.5 h; (ii) [NH_4]NCS, ethanol, reflux, 2.5 h; (iii) [*n*-Bu_4N]OH, acetonitrile, 20 m.

Addition of tetra-*n*-butylammonium hydroxide to *cis*-[Ru(*i*Bu$_2$dcbpy)$_2$(NCS)$_2$] hydrolysed the protecting ester groups at room temperature within 20 minutes. We note that a similar ethylester complex prepared by Shklover *et al*. was converted to the corresponding carboxylate by refluxing in triethylamine and water for 8 h.[11] Following de-esterification, N719 was precipitated from aqueous solution by adjustment of the pH to 3.8 following literature procedure[6,8,14] for the isolation of the bis(tetra-*n*-butylammonium) complex. The ^{1}H NMR spectrum and CHN analysis of the precipitated product are consistent with ~1.8 tetra-*n*-butylammonium cations / complex molecule. The presence of slightly less than the stoichiometric two tetra-*n*-butylammonium cations has been previously noted.[15] The ^{1}H NMR spectrum (Figure 1) shows six resonances in the aromatic region in agreement with the literature assignment of the all N-bound complex.[6] The absence of signals at lower field indicates that no S-bound isomers were present in the isolated product.[14]

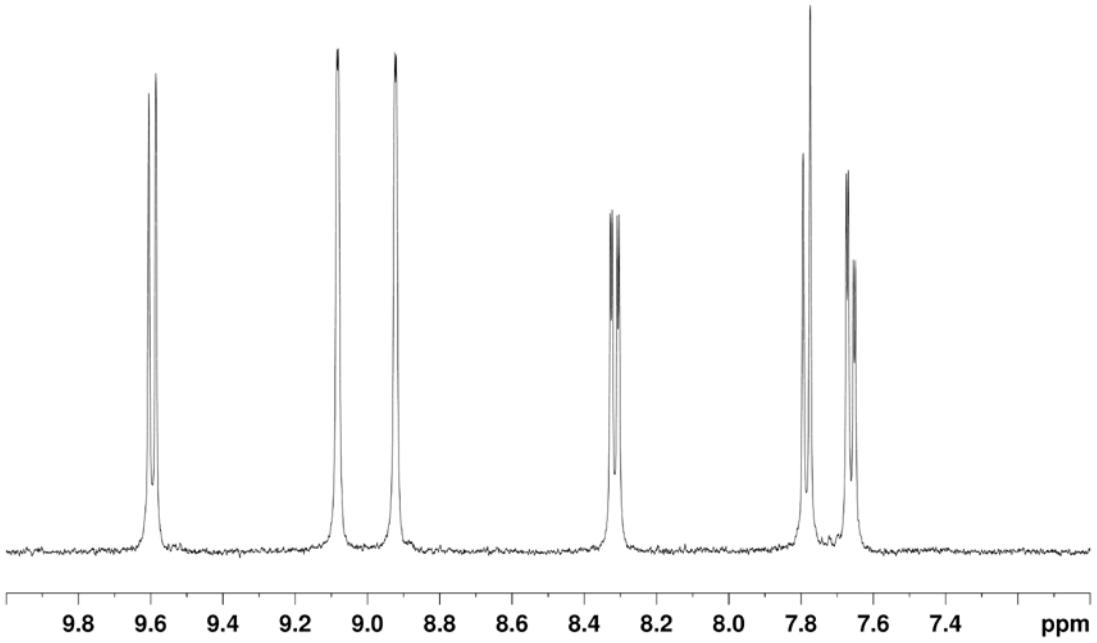


Figure 1. Aromatic region of the ^{1}H NMR spectrum of the isothiocyanate complex N719 (solvent: methanol-d_4).

An important aspect of this synthesis is the choice of ester protecting group. The synthesis was initially attempted using the methyl ester, however the solubility of *cis*-$[Ru(Me_2dcbpy)_2(NCS)_2]$ was found to be poor, thus limiting the quantity of complex that could be purified by column chromatography. Inclusion of the branched *iso*-butyl groups greatly increased solubility and made it possible to prepare larger batches (up to 260 mg could be purified on a 3 x 14 cm silica gel column in 20 minutes). Another important aspect of the synthesis was the choice of solvent. DMF, currently the most commonly used solvent in the preparation of N719 and related complexes, gave poor yields of $[Ru(iBu_2dcb)_2(NCS)_2]$ (< 15%). This was attributed to hydrolysis of the ester protecting groups by dimethylamine generated from decomposition of the DMF solvent.[17] Using ethanol as a solvent significantly increased the yield of $[Ru(iBu_2dcb)_2(NCS)_2]$ without increasing the reaction time. Using ethanol also avoided the difficulties associated with removal of DMF from the reaction product.

We have also found this strategy useful in the preparation of heteroleptic ruthenium(II) polypyridyl complexes of the type [RuL(4-carboxy-4-carboxylate-2,2′-bipyridine)$(NCS)_2]^{2-}$ where L is a functional bipyridyl ligand that does not bear carboxylate groups. These complexes will be reported elsewhere.

In conclusion, we have developed a synthetic procedure to conveniently and reliably prepare isomerically pure N719 sensitising dye. Key to the procedure is protection of the carboxyl functionalities providing good solubility in organic solvents and allowing the use of silica gel chromatography to separate the complexes bearing S-bound thiocyanate ligands from the more efficient all N-bound isomer. The protecting groups are conveniently removed with tetra-*n*-butyl ammonium hydroxide, which also provides the appropriate cations for the dye.

Experimental

Chemicals

The following were purchased commercially and used as received; $RuCl_3 \cdot 3H_2O$ (Precious Metals Online), 4,4′-dimethyl-2,2′-bipyridine (Aldrich), potassium chromate (Ajax), ammonium thiocyanate (Ajax), tetra-*n*-butylammonium hydroxide (1 M solution in methanol, Aldrich). 4,4′-Dicarboxylic acid-2,2′-bipyridine was prepared from 4,4′-dimethyl-2,2′-bipyridine by the method of Hoertz *et al* [18].

Physical measurements.

^{1}H NMR spectra were recorded using a BVT 3000 Bruker Spectrospin instrument operating at 300.13 MHz. Spectra are referenced internally to residual protic solvent ($CDCl_3$, δ 7.26, DMSO-d_6, δ 2.49, and MeOH-d_4, δ 2.85) except for spectra obtained using D_2O where 3-(trimethylsilyl)propanoic-2,2,3,3-d_4 acid, sodium salt is used (δ 0.00). UV-visible spectra were recorded using an Agilent 8453 UV-Visible spectrophotometer with ethanol as solvent. Electrospray ionization mass spectra (ESI-MS) were recorded using a Perkin-Elmer SCIEX API300 Triple Quadrupole Mass Spectrometer. The general conditions were: ion spray voltage = 5000V, drying gas temperature = 50 °C, orifice voltage = 30V, ring voltage = 340V, and injection via syringe pump. Spectra were averaged over 10 scans. GC mass spectra were recorded using an Agilent 6890 Series GC coupled to an Agilent 5973 Network mass spectrometer. Elemental microanalyses were carried out by the Microanalytical Service Unit at the Research School of Chemistry, Australian National University.

Synthesis

Preparation of *bis*(2-methylpropyl)-2,2′-bipyridine-4,4′-dicarboxylate (*i*Bu_2dcbpy). The following procedure is an adaptation of a literature method.[19] 2,2′-bipyridine-4,4’-

dicarboxylic acid (1.50 g, 6.15 mmol) was suspended in a mixture of isobutyl alcohol (60 mL) and conc. sulfuric acid (1 mL). The mixture was heated at reflux for 4 h, during which time the solution became clear. The solution was cooled and the remaining isobutyl alcohol was removed using a rotary evaporator. The residue was taken up in water (30 mL) and saturated aqueous Na_2CO_3 was added until a pH of 8-9 was obtained. The precipitate was collected by filtration, washed with water and dried under vacuum to yield 2.01 g (92 %) of a beige powder, mp = 128 – 130 ^oC. ^1H NMR (δ, 300 MHz, $CDCl_3$): 8.95 (dd, J_{HH} = 0.9, 1.5 Hz, 2 H), 8.87 (dd, J_{HH} = 0.9, 5.0 Hz, 2 H), 7.90 (dd, J_{HH} = 1.5, 4.8 Hz, 2 H), 4.19 (d, J_{HH} = 6.9, 4H), 2.15 (sep, J_{HH} = 6.9 Hz, 2H), 1.05 (d, J_{HH} = 6.9, 12H). MS (m/z): 356 (M^+), 283, 256, 200, 172, 152.. Anal. Calcd. for $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86. Found: C, 67.23; H, 6.56; N, 7.60.

Preparation of *cis*-[Ru(*i*Bu_2dcbpy)$_2$(NCS)$_2$]. Bis(2-methylpropyl)-2,2′-bipyridine-4,4′-dicarboxylate (0.400g, 1.12 mmol) and $RuCl_3.3H_2O$ (0.147g, 0.56 mmol) were dissolved in deoxygenated ethanol (120 mL). The resulting solution was refluxed under a nitrogen atmosphere for 3.5 hours and the reaction vessel shielded from light. Ammonium thiocyanate (1.712g, 22.49 mmol) was then added to the reaction mixture and heating at reflux continued for a further 2.5 hours. The solvent was then removed by rotary evaporation and the residue suspended in water (10 mL). The solid was collected by filtration and purified by silica gel column chromatography eluting with acetone: dichloromethane (3:97). After removal of the solvent, 0.260g (49 %) of the desired compound was obtained as a dark red solid. (Found: C 53.66, H, 5.12, N, 9.04%. $C_{42}H_{48}N_6O_4RuS_2$ requires C 54.24, H, 5.20, N, 9.04%.) ^1H NMR (δ, 300 MHz, d_6-DMSO): 9.47 (d, J_{HH} = 5.7 Hz, 2 H), 9.16 (d, J_{HH} = 1.2 Hz, 2 H), 8.99 (d, J_{HH} = 1.5, Hz, 2 H), 8.45 (dd, J_{HH} = 1.8, 6.0 Hz, 2H), 7.82 (d, J_{HH} = 6.0 Hz, 2H), 7.62 (dd, J_{HH} = 1.6, 6.0 Hz, 2H), 4.26 (d, J_{HH} = 6.6, 4H), 4.10 (d, J_{HH} = 6.6, 4H), 2.16 (sep, J_{HH} = 6.6 Hz, 2H),

2.02 (sep, J_{HH} = 6.6 Hz, 2H), 1.07 (d, J_{HH} = 6.6, 12H), 0.96 (d, J_{HH} = 6.9, 12H). λ_{max}/nm (ε,10^4 $M^{-1}cm^{-1}$) 547 (1.11), 406 (1.05), 318 (3.56). *m/z* (ESI): 930 (M^+, 100%).

Preparation of $[(Bu_4N)_2][Ru(4\text{-carboxy-4-carboxylate-2,2'-bipyridine})_2(NSC)_2]$ (N719). To a solution of $[Ru(i Bu_2dcbpy)_2(NCS)_2]$ (0.260g, 0.28 mmol) in acetonitrile (60 mL) was added 2.80 mL (2.80 mmol) of 1 M tetra-*n*-butylammonium hydroxide solution. The resulting mixture was stirred at room temperature for 20 minutes. The solvent was removed by rotary evaporation and the residue dissolved in water (10 mL). The pH of the solution was adjusted to 3.8 using 0.1 M nitric acid, at which point precipitation occurred. The suspension was left in a refrigerator at -3 °C overnight, then the solid collected by filtration to yield 0.316 g (93 %) of the desired compound. (Found: C 55.36, H 5.95, N 9.67%. $[TBA]_{1.8}(H)_{2..2}[Ru(NCS)_2$ (4,4′-dicarboxylate-2,2'-bipyridine)$_2]\cdot 4(H_2O)$: $C_{54.8}H_{86.8}N_{7.8}O_{12}RuS_2$ requires C 54.30, H, 7.21, N, 9.01%.) ^{1}H NMR (δ, 300 MHz, D_2O + 0.05 M NaOD): 9.48 (d, J_{HH} = 6.0 Hz, 2H), 8.87 (d, J_{HH} = 1.2 Hz, 2H), 8.71 (d, J_{HH} = 1.2 Hz, 2H), 8.16 (dd, J_{HH} = 1.6, 6.0 Hz, 2H), 7.76 (d, J_{HH} = 6.0 Hz, 2H), 7.47 (dd, J_{HH} = 1.6, 6.0 Hz, 2H), 3.12 (t, J_{HH} = 8.2 Hz, 14.12H), 1.59 (pen, J_{HH} = 7.8, 14.30H), 1.32 (sep, J_{HH} = 7.5, 14.22H), 0.91 (t, J_{HH} = 7.5, 21.31H). ^{1}H NMR (δ, 300 MHz, MeOD): 9.59 (d, J_{HH} = 5.7 Hz, 2 H), 9.08 (d, J_{HH} = 1.2 Hz, 2 H), 8.92 (d, J_{HH} = 1.2 Hz, 2 H), 8.31 (dd, J_{HH} = 1.6, 5.7 Hz, 2H), 7.79 (d, J_{HH} = 6.0 Hz, 2H), 7.66 (dd, J_{HH} = 1.6, 6.0 Hz, 2H), 3.26 (t, J_{HH} = 8.2 Hz, 14.08H), 1.67 (pen, J_{HH} = 8.1,13.96H), 1.43 (sep, J_{HH} = 7.3, 14.17H), 1.04 (t, J_{HH} = 7.3, 21.06H). λ_{max}/ nm (ε/10^4 $M^{-1}cm^{-1}$) 530 (1.29), 390 (1.15), 312 (4.30). *m/z* (ESI): 930 (M^+, 100%).

References

[1] *Michael Graetzel Festschrift, a tribute for his 60th Birthday, Dye Sensitized Solar Cells, Coord. Chem. Rev.* **2004**, *248*, Issues 13 and 14.

[2] H. Tributsch, *Coordination Chemistry Reviews* **2004**, *248*, 1511.

[3] B. Li, L. Wang, B. Kang, P. Wang, Y. Qiu, *Solar Energy Materials & Solar Cells* **2006**, *90*, 549.

[4] M. Graetzel, *Inorganic Chemistry* **2005**, *44*, 6841.
[5] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos, M. Grätzel, *Journal of the American Chemical Society* **1993**, *115*, 6382.
[6] M. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C.-H. Fischer, M. Grätzel, *Inorganic Chemistry* **1999**, *38*, 6298.
[7] S. Pelet, J.-E. Moser, M. Grätzel, *Journal of Physical Chemistry B* **2000**, *104*, 1791.
[8] R. Buscaino, C. Baiocchi, C. Barolo, C. Medana, M. Grätzel, K. Nazeeruddin Md, G. Viscardi, *Inorganica Chimica Acta* **2007**, *doi:10.1016/j.ica.2007.07.016*.
[9] M. K. Nazeeruddin, M. Grätzel, D. P. Rillema, *Inorganic Syntheses* **2002**, *33*, 185.
[10] P. Liska, N. Vlachopoulos, M. K. Nazeeruddin, P. Comte, M. Grätzel, *Journal of the American Chemical Society* **1988**, *110*, 3686.
[11] V. Shklover, M. K. Nazeeruddin, S. M. Zakeeruddin, C. Barbe, A. Kay, T. Haibach, W. Steurer, R. Hermann, H. U. Nissen, M. Grätzel, *Chemistry of Materials* **1997**, *9*, 430.
[12] P.-H. Xie, Y.-J. Hou, T.-X. Wei, B.-W. Zhang, Y. Cao, C.-H. Huang, *Inorganica Chimica Acta* **2000**, *308*, 73.
[13] O. Kohle, S. Ruile, M. Grätzel, *Inorganic Chemistry* **1996**, *35*, 4779.
[14] M. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru, M. Grätzel, *Journal of the American Chemical Society* **2005**, *127*, 16835.
[15] G. Wolfbauer, A. M. Bond, G. B. Deacon, D. R. MacFarlane, L. Spiccia, *Journal of the American Chemical Society* **2000**, *122*, 130.
[16] G. Wolfbauer, A. M. Bond, D. R. MacFarlane, *Inorganic Chemistry* **1999**, *38*, 3836.
[17] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals. 3rd Ed*, **1988**.
[18] P. G. Hoertz, A. Staniszewski, A. Marton, G. T. Higgins, C. D. Incarvito, A. L. Rheingold, G. J. Meyer, *Journal of the American Chemical Society* **2006**, *128*, 8234.
[19] G. Maerker, F. H. Case, *Journal of the American Chemical Society* **1958**, *80*, 2745.