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Note

Controlled microwave synthesis of Ru^{II} synthons and chromophores relevant to solar energy conversion

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ABSTRACT

Here we describe the efficient high yield atmospheric pressure microwave-assisted synthesis for seven distinct Ru^{II} coordination complexes relevant to solar energy conversion schemes and dye sensitized solar cells. In all instances, the reaction times have been markedly shortened, concomitant with higher yields with little or no need for subsequent purification and several multi-step reactions proceeded flawlessly in a single pot. Importantly, we observed no evidence for the decarboxylation of the essential metal oxide surface-anchoring 4,4′-diethylester-2,2′-bipyridine or 4,4′-dicarboxy-2,2′-bipyridine ligands as long as open reaction vessel conditions were utilized; these functionalities are not tolerant to sealed microwave reaction (superheated solvent/pressurized) conditions. The combined results suggest that microwave-assisted chemistry is indeed a valuable tool as far as Ru^{II} coordination chemistry is concerned and can likely be applied in the combinatorial pursuit of new dyes bearing sensitive functionalities.

1. Introduction

The application of microwave-assisted synthesis in organic, organometallic, and coordination chemistry continues to develop at an astonishing pace [1,2]. The general advantages to microwave heating include greatly accelerated heating to reflux in atmospheric pressure (open vessel) reactions, the ability to superheat solvents in pressurized (closed vessel) reactions, the maintenance of fixed reaction temperature by varying microwave power, the existence of the inhomogeneities producing "hot spots" in addition to non-thermal effects, and rapid temperature quenching of the reaction mixture through compressed air streams [1,3]. These combined attributes generally lead to extremely short reaction times, typically minutes as opposed to hours or days, with significantly higher reaction yields and narrow product distributions leading to minimal time-consuming purification procedures. When applied to substitutionally inert transition metal ions, such as d^6 Ru^{II} centers, microwave reactors have proven to be quite valuable [2,4–12]. For example, in the earliest report by Greene and Mingos [4], it is truly impressive that $[Ru(bpy)_3]^{2+}$, $[Ru(tpy)_2]^{2+}$, $[Ru(phen)_3]^{2+}$, and $[Ru(dbbpy)_3]^{2+}$ (dbbpy is 4,4′-di-*t*-butyl-2,2′-bipyridine) could be produced in a Teflon autoclave under microwave irradiation, generating purified yields ranging between 60% and 94% with the minuscule reaction time of 40 s. Since this original report, many other research groups have exploited microwave heating to rapidly produce a variety of desirable Ru^{II} coordination complexes featuring high yields with brief workups and minimal purification [5–12].

As our interests lie in the development of rapid and efficient synthetic procedures for producing Ru^{II} dyes of relevance to solar energy conversion and dye sensitized solar cells (DSSCs) in particular [13], a necessary structural feature within the diimine/triimine ligand structure is the metal oxide compatible surface-anchoring carboxylic acid functionality. Recently, Durham and coworkers observed complete decarboxylation of $[Ru(deeb)_3]^{2+}$, deeb is 4,4′-diethylester-2,2′-bipyridine, within the confines of their microwave reactor operating in the pressurized, sealed vessel mode [14]. This result suggested that the ester group is not tolerant to microwave synthesis conditions, at least not in ethylene glycol heated to 225 °C in the presence of Lewis acidic $RuCl_3$. We postulated that employing milder atmospheric pressure conditions in concert with lower boiling point solvents would likely eliminate the decarboxylation chemistry in those dyes bearing esters or carboxylic acids, paving the way for the widespread application of microwave-assisted synthesis in DSSC-relevant Ru^{II} chromophores. In parallel to our current investigation, Rau and coworkers have noted that open vessel microwave reactions operating at reflux in methanol/water preserve the methyl ester functionalities in a variety of heteroleptic Ru^{II} complexes bearing the 4,4′-dimethylester-2,2′-bipyridine ligand [12]. Their observations are completely consistent with that of the ethyl ester and carboxylic acid derivatives currently being explored in our laboratory, some of which are reported herein.

In the present contribution, we have investigated the microwave synthesis of seven distinct Ru^{II} coordination compounds that

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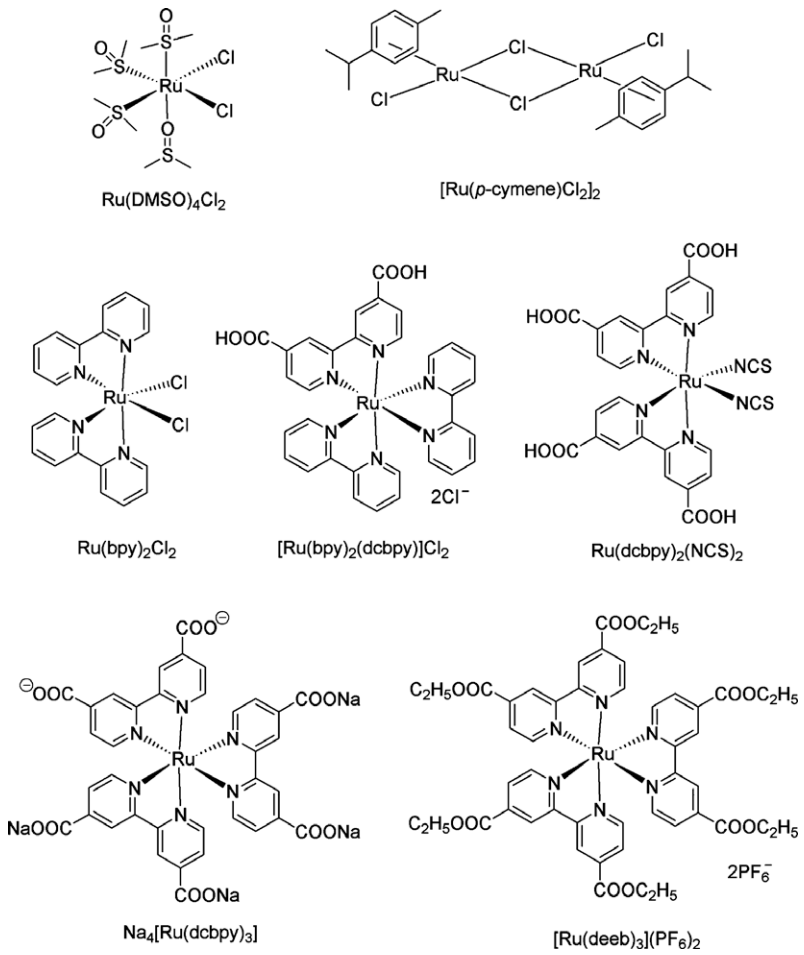

Fig. 1. Chemical structures of the various Ru^{II} synthons and chromophores produced through atmospheric pressure microwave-assisted chemistry.

serve either as synthons or dyes routinely employed in DSSCs (Fig. 1), including an efficient one-pot reaction of the pivotal $Ru(dcbpy)_2(NCS)_2$ dye, widely popularized as "N3" [13b,15]. Our intention here was to demonstrate the plausibility of applying scalable, economical, and "green" microwave-assisted chemistry to each and every step of Ru^{II} dye synthesis yielding high purity complexes that can be prepared in minutes with minimal or no purification required. The success realized here suggests that the entire synthetic process can indeed be combinatorialized using appropriate microwave reactors to rapidly prepare large arsenals of new dyes to be tested as sensitizers in DSSCs.

2. Experimental

2.1. General

All solvents and chemicals were of the highest possible commercially available grade and were used without further purification. The ligands, 4,4′-dicarboxy-2,2′-bipyridine (dcbpy) [16] and 4,4′-diethylester-2, 2′-bipyridine (deeb) [17], were prepared following published literature procedures. Each Ru^{II} synthon or dye was prepared both conventionally following the mildest possible established procedures [15,18–23] and under microwave irradiation using a CEM Discover system operating in atmospheric pressure (open vessel) mode. In the latter preparations, a 125 mL round-bottomed flask (ChemGlass) was used in concert with a water-cooled reflux condenser and each reaction was stirred with a Teflon-coated stir bar. The structural characterizations of all seven complexes were mutually consistent between microwave and conventional heating methods. Select ^1H NMR and ^{13}C NMR spectra recorded with a Bruker Advance 300 (300 MHz) spectrometer have been provided in some instances. MALDI-TOF mass spectra were measured using a Bruker-Daltonics Omniflex spectrometer using a dithranol matrix. Elemental analyses were performed by Atlantic Microlab, Norcross, GA, USA.

3. Microwave syntheses

3.1. $Ru(DMSO)_4Cl_2$

To 15 mL of DMSO was added $RuCl_3$ (1.4 g, 6.75 mmol). The solution was brought to reflux in the CEM system (open vessel mode) and maintained at 180 °C for 3 min. After cooling to RT in the reactor, 25 mL of acetone was added to the solution, producing solid yellow granules immediately. This precipitate was filtered and washed with ether and dried (2.0 g, 69% yield). MALDI-MS (TOF): 552.24 ($M^+ + 6H_2O - Cl^-$). *Anal.* Calc. for $C_8H_{24}Cl_2O_4RuS_4$: C, 19.83; H, 4.99. Found: C, 20.04; H, 5.06%.

3.2. $[Ru(p\text{-}cymene)Cl_2]_2$

To 20 mL of EtOH was added $RuCl_3$ (0.5 g, 2.41 mmol) and excess *p*-mentha-1,5-diene (68% technical grade, 4.83 g (3.28 g reagent), 24.1 mmol). The mixture was refluxed for 15 min in the CEM system at 1 atm. After cooling to RT, the solvent was removed under vacuum, the remaining diene removed by washing with ether, and the red solid product was collected by filtration and washed again with ether and dried (405 mg, 65% yield). ^1H NMR

(300 MHz, $CDCl_3$): 5.47 (d, J = 6 Hz, 4H), 5.33 (d, J = 6 Hz, 4H), 2.92 (septuplet, J = 6.9 Hz, 2H), 2.16 (s, 6H), 1.27 (d, J = 6.9 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): 101.25, 96.75, 81.30, 80.55, 30.63, 22.14, 18.91. MALDI-MS (TOF): 578.10 ($M^+ - Cl^-$).

3.3. $Ru(bpy)_2Cl_2 \cdot 4H_2O$

To 10 mL water was added NaCl (250 mg), sucrose (250 mg), L-ascorbic acid (500 mg), 2,2′-bipyridine (650 mg, 4.16 mmol), $RuCl_3$ (435 mg, 2.1 mmol) and 3 mL conc. HCl. The mixture was refluxed for 5 min in the CEM system at 1 atm. After cooling to RT, the precipitate was vacuum filtered to dryness, obtaining the title compound (776 mg, 72% yield). MALDI-MS (TOF): 484.08 ($M^+ - 4H_2O$), 449.09 ($M^+ - 4H_2O - Cl^-$). *Anal.* Calc. for $C_{20}H_{24}Cl_2N_4O_4Ru$: C, 43.17; H, 4.35, N, 10.07. Found: C, 43.04; H, 3.74; N, 10.16%.

3.4. $[Ru(bpy)_2(dcbpy)]Cl_2 \cdot 2H_2O$

To 32 mL acetic acid and 8 mL water was added dcbpy (288 mg, 1.2 mmol) and *cis*-$Ru(bpy)_2Cl_2$ (520 mg, 1 mmol). The mixture was maintained at 90 °C for 30 min in the CEM system at 1 atm. After completion of the reaction, the solvents were removed on a rotary evaporator under reduced pressure. The residue was taken up in methanol and filtered through Celite. The filtrate was collected; the methanol stripped under reduced pressure, and the product was dried under vacuum at 40 °C overnight (713 mg, 93% yield). ^1H NMR (300 MHz, DMSO-d_6): 9.24 (s, 2H), 8.86 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 4H), 8.17 (m, 4H), 7.95 (d, J = 5.7 Hz, 2H), 7.87 (dd, J_1 = 1.5 Hz, J_2 = 6 Hz, 2H), 7.73 (d, J = 5.4 Hz, 2H), 7.69 (d, J = 5.1 Hz, 2H), 7.55 (t, J = 6.6 Hz, 2H), 7.50 (t, J = 6.6 Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): 165.35, 157.70, 156.79, 156.76, 152.68, 152.05, 151.50, 140.22, 138.79, 128.51, 127.31, 125.11, 124.39. MALDI-MS (TOF): 658.24 ($M^+ - 2H_2O - 2Cl^-$).

3.5. $Ru(dcbpy)_2(NCS)_2$

To 40 mL DMF was added $Ru(DMSO)_4Cl_2$ (300 mg, 0.62 mmol) and one equivalent of dcbpy (151.6 mg, 0.62 mmol). The mixture was heated at 105 °C for 8 min in the CEM system at 1 atm. Subsequently, a second equivalent of dcbpy (151.6 mg, 0.62 mmol) was added to the solution which was maintained at 105 °C for 16 min in the microwave. Finally, an excess amount of NH_4NCS (708 mg, 9.3 mmol) was added to the solution. The temperature was then increased to 115 °C and maintained for 8 min. After cooling to RT in the reactor, the DMF was removed under vacuum. Water (100 mL) was added to dissolve the soluble impurities. The remaining solid was collected by filtration. Finally, methanol was used to dissolve the collected product, which was subsequently filtered. This process was repeated two additional times to yield the title compound (300 mg, 69% yield). ^1H NMR (300 MHz, DMSO-d_6): 9.42 (d, J = 5.7 Hz, 2H), 9.16 (s, 2H), 9.00 (s, 2H), 8.36 (dd, J_1 = 1.2 Hz, J_2 = 5.7 Hz, 2H), 7.78 (d, J = 5.7 Hz, 2H), 7.59 (dd, J_1 = 1.2 Hz, J_2 = 5.7 Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): 165.77, 165.34, 159.16, 157.70, 153.67, 153.39, 139.12, 138.35, 135.11, 126.82, 125.75, 123.58, 123.26. MALDI-MS (TOF): 706.10 (M^+).

3.6. $Na_4[Ru(dcbpy)_3] \cdot 6H_2O$

To a mixture of dcbpy (250 mg, 1.02 mmol) and $Ru(DMSO)_4Cl_2$ (121.5 mg, 0.25 mmol) was added a minimal amount of aqueous 2 M sodium hydroxide to dissolve these solids. Subsequently, hydrochloric acid (2 M) was added to this solution until it became slightly cloudy. This mixture was subjected to microwave irradiation in the CEM system for 60 min at the maintained temperature of 110 °C. After cooling to RT, the mixture was rotary evaporated until only ~2–3 mL water remained. This compound was purified on a Sephadex LH-20 column eluting with water to obtain the title compound (155 mg, 60% yield). ^1H NMR (300 MHz, D_2O): 8.70 (d, J = 1.5 Hz, 6H), 7.70 (d, J = 5.7 Hz, 6H), 7.5 (dd, J_1 = 1.5 Hz, J_2 = 5.7 Hz, 6H). ^{13}C NMR (75 MHz, D_2O): 170.99, 157.28, 151.82, 145.51, 126.09, 123.09. MALDI-MS (TOF): 834.29 ($M^+ - 6H_2O - 4Na^+$).

3.7. $[Ru(deeb)_3](PF_6)_2$

To a 10 mL aqueous solution of NaCl (32 mg), sucrose (32 mg), L-ascorbic acid (63 mg), 370 μL conc. HCl and $RuCl_3$ (54.4 mg, 0.263 mmol) was added deeb (158 mg, 0.525 mmol) dissolved in 5 mL $CHCl_3$. Finally, 35 mL EtOH was added to this mixture, producing a homogenous solution. The mixture was refluxed for 15 min in the CEM system at 1 atm. After completion of the reaction, the solvent was evaporated under vacuum. Subsequently, the solid residue was washed with water, removing the soluble reagents. The intermediate product $Ru(deeb)_2Cl_2$ was collected by vacuum filtration. To a 5 mL $CHCl_3$ solution containing $Ru(deeb)_2Cl_2$ was added deeb (95 mg, 0.32 mmol) along with a 5 mL aqueous solution of $AgNO_3$. Then 32 mL of acetic acid was added to the mixture, which was refluxed for 60 min in the CEM reactor at 1 atm. After cooling to RT, the reaction mixture was filtered through Celite, removing the AgCl precipitate. The filtrate was extracted with $CHCl_3$ and the collected organic fractions evaporated under reduced pressure. Water (5 mL) was added to dissolve the crude product which was subsequently vacuum filtered, removing additional precipitates. To the red filtrate was added 5 mL saturated aqueous NH_4PF_6, immediately producing a red precipitate which was collected by vacuum filtration and dried with ether (60 mg, 18% yield). ^1H NMR (300 MHz, acetone-d_6): 9.35 (d, J = 1.2 Hz, 6H), 8.36 (d, J = 5.7 Hz, 6H), 7.96 (dd, J_1 = 1.8 Hz, J_2 = 5.7 Hz, 6H), 4.46 (quart, J = 7.2 Hz, 12H), 1.37 (t, J = 7.2 Hz, 18H). ^{13}C NMR (75 MHz, acetone-d_6): 163.11, 157.59, 153.21, 139.69, 127.06, 124.12, 62.51, 13.46. MALDI-MS (TOF): 1002.42 ($M^+ - 2PF_6^-$), 988.43 ($M^+ - 2PF_6^- - CH_2$), 974.43 ($M^+ - 2PF_6^- - 2CH_2$).

4. Results and discussion

Table 1 summarizes the time duration and temperatures utilized along with reaction yields obtained in the present atmospheric pressure microwave-assisted chemistry compared to that achieved by conventional heating methods. In all cases, we selected and independently confirmed the literature procedures most comparable to the present microwave preparations. As can be generally inferred from the tabulated entries, in every instance the microwave reactions generated the desired products in higher or equivalent yields relative to the significantly more lengthy conventional heating procedures. Of the seven reactions performed in this study, only $Na_4[Ru(dcbpy)_3] \cdot 6H_2O$ required column chromatography over Sephadex LH-20 for purification. The remaining complexes were purified by simple workup, i.e. precipitation and washing with appropriate solvents which produced materials whose purity was confirmed by a variety of select analytical methods including elemental analysis, ^1H and ^{13}C NMR, and mass spectrometry.

The important synthons $Ru(DMSO)_4Cl_2$ [18], $[Ru(p\text{-cymene})Cl_2]_2$ [19], and *cis*-$Ru(bpy)_2Cl_2$ [20] were chosen as microwave synthesis candidates as they represent chief Ru^{II} source materials used in the production of a variety of homoleptic and heteroleptic complexes, including many popular dye sensitizers. While there is no significant advantage to the microwave preparation of $Ru(DMSO)_4Cl_2$, substantial resource and time-saving benefits are

Table 1
Comparison of reaction times and yields using the open vessel microwave methods *vs.* conventional heating methods.

Compound	μ-Wave	% Yield	Conventional method	% Yield
$Ru(DMSO)_4Cl_2$	180 °C, 3 min	69	DMSO reflux, 5 min[18]	72
$[Ru(p\text{-cymene})Cl_2]_2$	90 °C, 15 min	65	EtOH reflux, 4 h[19]	65
cis-$Ru(bpy)_2Cl_2$	110 °C, 5 min	72	Aqueous reflux, 30 min[20]	61
$[Ru(bpy)_2(dcbpy)]Cl_2{\cdot}2H_2O$	90 °C, 30 min	93	$AcOH/H_2O$ reflux, 5 h[21]	94
$Ru(dcbpy)_2(NCS)_2$	105 and 115 °C, 32 min total, one-pot reaction	69	DMF reflux, ~2 days, two-step reaction[15b]	74 overall
$Na_4[Ru(dcbpy)_3]{\cdot}6H_2O$	110 °C, 60 min	60	Aqueous reflux, 4 h[22]	50
$[Ru(deeb)_3](PF_6)_2$	110 °C, 15 min + 60 min	18	EtOH reflux, 1 week[23]	15

realized in both $[Ru(p\text{-cymene})Cl_2]_2$, and *cis*-$Ru(bpy)_2Cl_2$. We note that the commercially available $[Ru(p\text{-cymene})Cl_2]_2$ has previously been synthesised using both open and pressurized vessel microwave chemistry [24]. Although we did not explore this in the present work, a closed microwave vessel can be used generate the Ru^{II} cymene dimer in high yield in less than 1 min [24]. This precursor is of utmost importance for the synthesis of a variety of the most promising next generation heteroleptic dyes including Z907 [25], N-845 [26], Z-910 [27], and K-19 [28]. *cis*-$Ru(bpy)_2Cl_2$ is a well established precursor for the synthesis of a variety of photophysically interesting complexes which can be readily combined with a plethora of chelating N^N ligands in addition to complexes of mixed denticity, i.e. *cis*-$Ru(bpy)_2L_2$, where L can be selected from a variety of monodentate structures [29]. In the present work, *cis*-$Ru(bpy)_2Cl_2$ was used as a synthetic precursor for the preparation of $[Ru(bpy)_2(dcbpy)]Cl_2{\cdot}2H_2O$, a dye commonly used to study interfacial charge transfer at the metal oxide/solution interface [30] and as a bioconjugate precursor for the corresponding amine-reactive NHS-ester [31]. The latter reagent is currently sold by Sigma Chemical Company (cat # 96632) in both 1 and 5 mg quantities. The synthesis of this prototypical chromophore was accomplished in 30 min using microwave irradiation and obtained in 93% yield.

Probably the most significant finding of the present study is the 32 min one-pot microwave preparation of $Ru(dcbpy)_2(NCS)_2$, otherwise known as N3 in the DSSC literature [13,15]. This chemistry relies on the fact that $Ru(DMSO)_4Cl_2$ can be substituted in a stepwise and controlled manner, permitting the sequential stoichiometric addition of dcbpy followed by a large excess of the ambidentate NCS^- ligand. The present method afforded N3 in 69% yield and most importantly required no significant purification as the only major impurities could be simply washed away with water and methanol. $Ru(DMSO)_4Cl_2$ was also used as a synthon in the present work to prepare the homoleptic sensitizer $Na_4[Ru(dcbpy)_3]{\cdot}6H_2O$. Notably, this complex has also been employed in biophysics in its NHS-ester form [31a]. Finally, one of the most arduous synthetic targets in Ru^{II} chemistry is the high quantum yield photoluminescence emitter $[Ru(deeb)_3]^{2+}$. In the present study, we managed to produce this pure complex in 18% yield in 1.25 h using open vessel microwave-assisted conditions starting from $RuCl_3$ as opposed to 15% yield in 7 days through conventional heating [23]. Importantly, the current mild and atmospheric pressure-based synthetic routes lead to product formation without decarboxylation of the ester groups, consistent with the recent observations of Rau and coworkers who have prepared related structures [12]. Notably, analytically pure product was obtained through simple metathesis without the necessity for column chromatography which again highlights the advantages to using microwave-based synthetic approaches for Ru^{II} coordination compounds.

5. Conclusions

We have demonstrated efficient open vessel microwave synthesis of seven distinct Ru^{II} coordination compounds that serve either as synthons or dyes routinely employed in DSSCs, solar energy conversion schemes, and biophotonics. These compounds are prepared quite seamlessly in high yields, with the understandable exception of $[Ru(deeb)_3]^{2+}$, using microwave-assisted conditions at atmospheric pressure with correspondingly short reaction times and no significant purification necessary. Of particular importance is the one-pot reaction of the $Ru(dcbpy)_2(NCS)_2$ sensitizer, accomplished stepwise in 32 min departing from the labile $Ru(DMSO)_4Cl_2$ precursor. In all complexes incorporating ester or carboxylic acid functions, open vessel microwave reactions operated at relatively low temperatures maintain the integrity of these groups all the way through the synthesis, producing the desired isolated complexes. We believe that every procedure reported herein should be scalable by using larger volume microwave reactors that are currently available and new heteroleptic complexes of mixed denticity can likely be obtained using similar methodologies.

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References

[1] H.M. Kingston, S.J. Haswell (Eds.), Microwave-enhanced Chemistry: Fundamentals Sample Preparation and Applications, American Chemical Society, Washington, DC, 1997.
[2] D.M.P. Mingos, D.R. Baghurst, Chem. Soc. Rev. 20 (1991) 1.
[3] A. de la Hoz, A. Diaz-Ortez, A. Moreno, Chem. Soc. Rev. 34 (2005) 164.
[4] D.L. Greene, D.M.P. Mingos, Transition Met. Chem. 16 (1991) 71.
[5] T. Matsumura-Inoue, M. Tanabe, T. Minami, T. Ohashi, Chem. Lett. 12 (1994) 2443.
[6] E. Eskelinen, S. Luukkanen, M. Haukka, M. Ahlgrén, T.A. Pakkanen, J. Chem. Soc., Dalton Trans. (2000) 2745.
[7] F. Pezet, J.-C. Daran, I. Sasaki, H. A-Haddou, G.G.A. Balavoine, Organometallics 19 (2000) 4008.
[8] X. Xiao, J. Sakamoto, M. Tanabe, S. Yamazaki, S. Yamabe, T. Matsumura-Inoue, J. Electroanal. Chem. 527 (2002) 33.
[9] S. Rau, B. Schäfer, A. Grüßing, S. Schebesta, K. Lamm, J. Vieth, H. Görls, D. Walther, M. Rudolph, U.W. Grummt, E. Birkner, Inorg. Chim. Acta 357 (2004) 4496.
[10] H.J. Bolink, L. Cappelli, E. Coronado, M. Grätzel, M.K. Nazeeruddin, J. Am. Chem. Soc. 128 (2006) 46.
[11] D. Martineau, M. Beley, P.C. Gros, J. Org. Chem. 71 (2006) 566.
[12] M. Schwalde, B. Schäfer, H. Görls, S. Rau, S. Tschierlei, M. Schmitt, J. Popp, G. Vaughan, W. Henry, J.G. Vos, Eur. J. Inorg. Chem. (2008) 3310.
[13] (a) B. O'Regan, M. Grätzel, Nature 353 (1991) 737;
(b) A. Hagfeldt, M. Grätzel, Acc. Chem. Res. 33 (2000) 269;
(c) M. Grätzel, Nature 414 (2001) 338.
[14] T.J. Anderson, J.R. Scott, F. Millett, B. Durham, Inorg. Chem. 45 (2006) 3843.
[15] (a) M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382;
(b) M.K. Nazeeruddin, S.M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C.-H. Fischer, M. Grätzel, Inorg. Chem. 38 (1999) 6298.
[16] N. Garelli, P. Vierling, J. Org. Chem. 57 (1992) 3046.
[17] G. Sprintschnik, H.W. Sprintschnik, P.P. Kirsch, D.G. Whitten, J. Am. Chem. Soc. 99 (1977) 4947.
[18] I.P. Evans, A. Spencer, G. Wilkinson, J. Chem. Soc., Dalton Trans. (1973) 204.
[19] M.A. Bennett, A.K. Smith, J. Chem. Soc., Dalton Trans. (1974) 233.
[20] C. Viala, C. Coudret, Inorg. Chim. Acta 359 (2006) 984.
[21] (a) P.D. Beer, F. Szemes, V. Balzani, C.M. Sala', M.G.B. Drew, S.W. Dent, M. Maestri, J. Am. Chem. Soc. 119 (1997) 11864;
(b) L.H. Uppadine, F.R. Keene, P.D. Beer, J. Chem. Soc., Dalton Trans. (2001) 2188.

[22] S. Anderson, E.C. Constable, K.R. Seddon, J.E. Turp, J.E. Baggott, M.J. Pilling, J. Chem. Soc., Dalton Trans. (1985) 2247.
[23] H. Masui, R.W. Murray, Inorg. Chem. 36 (1997) 5118.
[24] D.R. Baghurst, D.M.P. Mingos, J. Organomet. Chem. 384 (1990) C57.
[25] P. Wang, S.M. Zakeeruddin, J.E. Moser, M.K. Nazeeruddin, T. Sekiguchi, M. Grätzel, Nat. Mater. 2 (2003) 402.
[26] N. Hirata, J.-J. Lagref, E.J. Palomares, J.R. Durrant, M.K. Nazeruddin, M. Grätzel, D. Di Censo, Chem. Eur. J. 10 (2004) 595.
[27] P. Wang, S.M. Zakeeruddin, J.E. Moser, R. Humphry-Baker, P. Comte, V. Aranyos, A. Hagfeldt, M.K. Nazeeruddin, M. Grätzel, Adv. Mater. 16 (2004) 1806.
[28] P. Wang, C. Klein, R. Humphry-Baker, S.M. Zakeeruddin, M. Grätzel, J. Am. Chem. Soc. 127 (2005) 808.
[29] Many examples of these topologies can be found in: A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.
[30] J.M. Stipkala, F.N. Castellano, T.A. Heimer, C.A. Kelly, K.J.T. Livi, G. Meyer, J. Chem. Mater. 9 (1997) 2341.
[31] (a) E. Terpetschnig, H. Szmacinski, H. Malak, J.R. Lakowicz, Biophys. J. 68 (1995) 342;
(b) H. Szmacinski, E. Terpetschnig, J.R. Lakowicz, Biophys. Chem. 62 (1996) 109.