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Synthesis of extended ethynylnaphthalene-based ruthenium(II) 2,2′:6′,2″-terpyridine complexes

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Abstract—A ‘synthesis-at-metal’ approach is described for the preparation of extended ethynylnaphthalene-based ruthenium(II) 2,2′:6′,2″-terpyridine complexes.

Efficient and directional transport of information at the nanoscale level is the basic concept behind research into molecular-scale photonic devices.[1] It is envisaged that in such devices input and output photonic signals are from well-separated terminals, with the organic connecting framework facilitating intramolecular communication (Fig. 1). Numerous input and output modules have been identified but some of the most popular are associated with ruthenium(II) and osmium(II) polypyridyl (e.g., 2,2′:6′,2″-terpyridine, 2,2′-bipyridine, etc.) complexes.[2] In examples to date, the ruthenium unit is the input centre, whereas the output signal is generated at the osmium-based terminal. An excitation energy transfer gradient ensures that photonic input at the ruthenium unit ends up at the osmium group. However, the proper choice of connector is vital for promoting communication between the two metal terminals, and so identification of the best unit is essential for the molecular device to work efficiently.

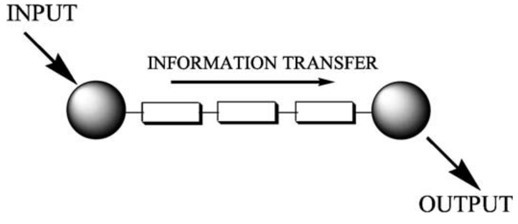

Figure 1. Simple illustration of the transport of information along a molecular conduit.

In previous work on ruthenium(II) complexes we identified an alkyl- or alkoxy-bridged biphenylynyl unit attached at the 4′-position of 2,2′:6′,2″-terpyridine as a connector that could facilitate/retard energy transduction.[3,4] However, for energy migration over unusually long distances the naphthalene unit has been targeted as a more promising conduit.[5] Thus, in this communication we describe an approach to produce extended ethynylnaphthalene-based arrays using a ‘synthesis at metal’ approach.[6] One particular advantage of this method is that the metal centre is introduced early in the synthesis and avoids isolation of the ligand; which is often rather insoluble and, therefore, difficult to purify.

The main synthetic approach to the targetted systems is illustrated in Scheme 1. The method relies on Sonogashira coupling protocols[7] but also uses the fact that in aromatics the iodo replacement reaction proceeds at lower temperatures when compared to the bromo derivative.[8] Thus, commercially available 4-bromonaphthylamine **1** was converted to the mixed halogenated naphthalene derivative **2** using simple Sandmeyer chemistry. Reaction of **2** with trimethylsilylacetylene at room temperature, followed by deprotection and column chromatography, (alumina, hexane) afforded **4** in 91% yield. Coupling of **4** with 1 equiv of **2**, again at room temperature, accordingly produced the dibrominated derivative **5** in an average 41% yield. Although Sonogashira coupling of **5** with **7** was possible, we found that conversion of **5** to the iodo derivative **6** prior to coupling

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Keywords: Ruthenium; Terpyridine; Naphthalene; Luminescence.

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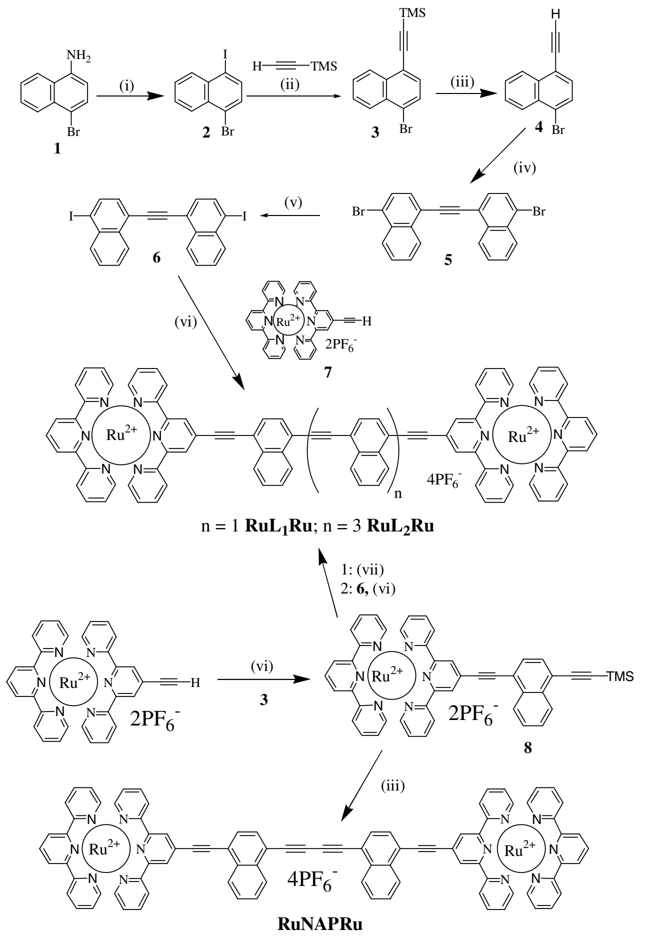

Scheme 1. Synthetic methodology used in the preparation of extended complexes. Reagents and conditions: (i) $NaNO_2$, KI, HCl; (ii) $PdCl_2(PPh_3)_2$, CuI, Et_3N, benzene, Δ, 18h; (iii) KF, MeOH, rt, 16h; (iv) **2**, $PdCl_2(PPh_3)_2$, CuI, Et_3N, benzene, rt, 21h; (v) *n*-BuLi, I_2, THF, −78°C, 4h; (vi) $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF/CH_3CN, Δ, 28h; (vii) K_2CO_3, MeOH.

gave the bis-ruthenium(II) 2,2′:6′,2″-terpyridine derivative **RuL_1Ru**[9] in an unoptimised 37% yield. In order to extend the molecular axis, **7**[10] was coupled to **3** and once again deprotected to afford derivative **8** in 51% yield. Surprisingly, removal of the tetramethylsilyl group from **8** using KF in MeOH gave not only the expected deprotected product but also the homodinuclear cross-coupled derivative **RuNAPRu** (17% yield).[11] Similar cross-coupling has been reported using KF on supported alumina under microwave irradiation but still required the presence of a copper catalyst.[12] It is not obvious at this stage what species acts as the catalyst in the formation of the dimeric complex. On the other hand, deprotection of **8** using K_2CO_3 in MeOH did produce the desired acetylene derivative, which was then coupled to **6** to afford **RuL_2Ru**[13] in an unoptimised yield of 7%. The rather low yield of this product can be attributed to the production of **RuNAPRu** as side product of the coupling reaction. Alternatively, it was found that in situ deprotection of **8** in the presence of **6** under Sonogashira conditions also afforded the desired bimetallic complex. The authenticity of all new compounds was checked by standard analytical techniques, including ^1H NMR spectroscopy, electrospray/MALDI mass spectrometry and elemental analysis.

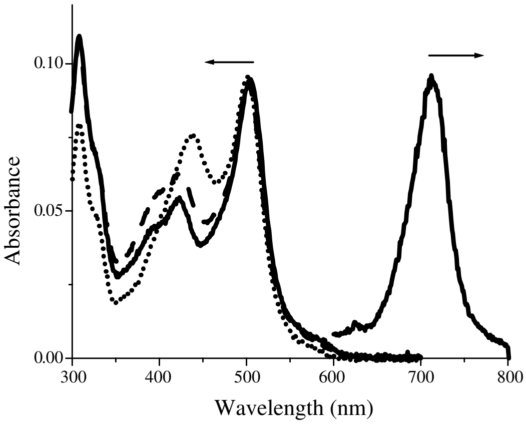

Figure 2. Absorption spectra recorded for **RuL_1Ru** (–), **RuNAPRu** (-·-·-·) and **RuL_2Ru** (···) in deoxygenated butyronitrile solution at 20°C. Also shown is the emission spectral profile recorded for **RuL_1Ru** at 20°C.

The absorption and luminescence spectra of the three complexes were recorded in butyronitrile (Fig. 2). Each complex displays the characteristic MLCT absorption band centred around 500nm; $\lambda_{MLCT} = 505$nm (**RuL_1Ru**), 501nm (**RuL_2Ru**) and 502nm (**RuNAPRu**). Additional bands are evident in the region 350–450nm for **RuL_1Ru** and **RuNAPRu**, which can be assigned to electronic transitions associated with the naphthalene units. It is noted that the main naphthalene absorption band for **RuL_2Ru** is lower in energy by ca. 15nm, indicating extended conjugation along the molecular bridge. Luminescence from the complexes is situated at the red-end of the visible spectral region, centred around 715nm. Similar low-energy luminescence has been observed in binuclear ruthenium(II) terpy complexes connected solely via acetylene bridges.[14] In general, the insertion of an aromatic residue between the alkynylene groups raises the energy of the luminescence profile. This is clearly not the case for naphthalene insertion. Long-wavelength emitters are currently under intense investigation[15] and, therefore, complexes based on multi-linked di(ethynyl)naphthalene units could find important applications in this area.

Preliminary variable temperature luminescence studies on the complexes are also very encouraging and suggest that the naphthalene bridge might play an active role in energy migration. At present, the synthesis of mixed Ru(II)/Os(II) complexes based on **L_1** and **L_2** is underway. Such complexes should enable the detailed investigation of long-range energy transfer processes and will be reported at a later date. It should be noted that the triplet manifold is likely to be crowded.

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