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Synthesis of bipyridine and terpyridine based ruthenium metallosynthons for grafting of multiple pyrene auxiliaries

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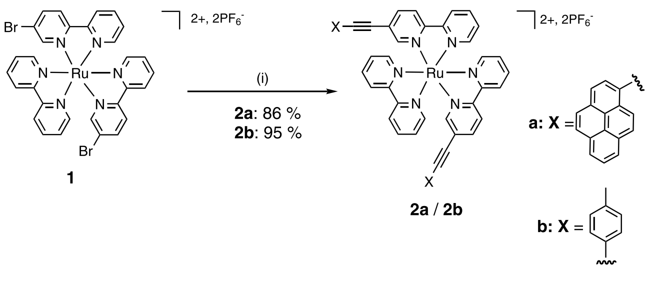
Abstract—The synthesis of novel ruthenium(II) bipyridine or terpyridine complexes bearing an increasing number of pyrene or toluyl moieties is described. The ruthenium complexes are constructed in a first step with ligands bearing the required bromine functions, followed in a second step by stepwise grafting of 1-ethynylpyrene or 4-ethynyltoluene promoted by Pd(0). A complex bearing a protected triethylsilylacetylene function was also prepared. In situ deprotection of this function with K_2CO_3 and cross-coupling with 1-bromopyrene afforded a soluble complex in which two pyrene moieties are linearly linked via ethynyl spacers to one of the bipyridine ligands. These highly coloured complexes exhibit well defined absorption and emission properties in solution at both rt and 77 K.

Tuning the optical properties of transition metal complexes by ligand tailoring is a fascinating research field which has generated highly colored pigments, very efficient triplet energy and electron transfer reactions, long-lived excited states, charge separated species, and singlet oxygen producers.[1] Along these lines pyrene modified bipyridines and phenanthrolines have previously been studied and exhibit interesting features connected to lifetime enhancement from the excited state manifold.[2–4] In most documented cases the long-lived room temperature luminescence of the excited state can be explained by excited state equilibrium or slow energy back transfer processes between energetically proximate ^{3}MLCT (metal to ligand charge transfer) and ^{3}IL (intra-ligand) excited states.[2–5] Alternatively, when the ^{3}IL state lies far below the ^{3}MLCT state, ^{3}IL phosphorescence is observed.[2,5]



Scheme 1. *Reagents and conditions*: (i) $[Pd(PPh_3)_4]$ 6 mol%, CH_3CN/C_6H_6 1/1, $i$$Pr_2NH$, 60°C.

Existing design strategies for the preparation of these advanced multicomponent molecules follow two principal methods based on the availability, stability and solubility of the starting materials. In one approach which is the more frequently used, the ligand is first constructed and subsequently coordinated to the appropriate metal. This method has the advantage of potentially allowing access to a variety of different complexes but has the drawback of requiring reasonably soluble ligands and well defined metal precursors. The other method, still far less common, exploits the use of metallo-synthons bearing reactive functions such as triflates, halides, carbonyls as the intermediates for producing the final species with the expected features. In both cases the quest for new and alternative approaches for easily building and organizing various photoactive partners around photoactive metals is one of the main aims of this field.

Keywords: ruthenium; bipyridine; terpyridine; pyrene; alkyne; palladium coupling.

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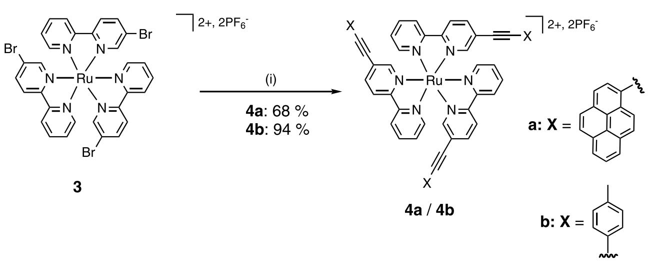
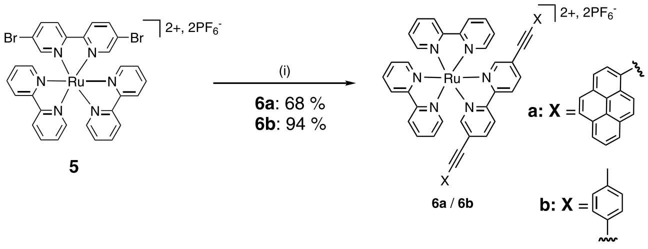
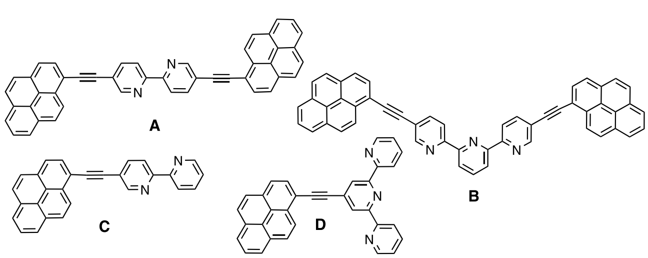


Scheme 2. *Reagents and conditions*: (i) [Pd(PPh$_3$)$_4$] 6 mol%, CH$_3$CN/C$_6$H$_6$ 1/1, *i*Pr$_2$NH, 60°C.

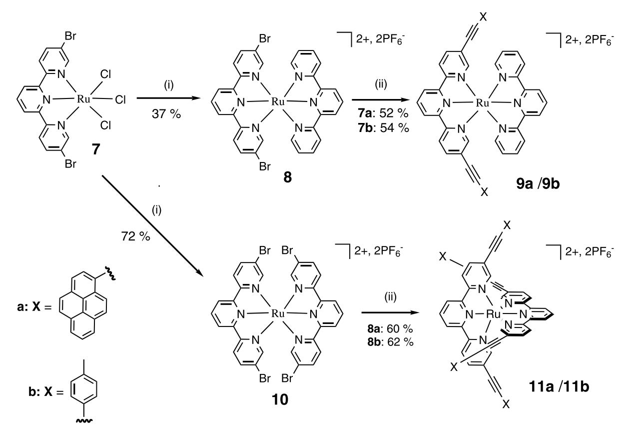


Scheme 3. *Reagents and conditions*: (i) [Pd(PPh$_3$)$_4$] 6 mol%, CH$_3$CN/C$_6$H$_6$ 1/1, *i*Pr$_2$NH, 60°C.



The strategy developed in this contribution was prompted by the fact that we were not able to prepare the ruthenium(II) complexes of ligands **A** and **B** by a classical procedure. These ligands **A** and **B** were prepared using the standard Pd-driven cross-coupling reaction between 1-ethynylpyrene and dibromo substituted bipyridine[6] and terpyridine[7] platforms. It is, however, worth pointing out that when a single pyrene fragment is present on the scaffold such as in **C** and **D**, the preparation of the corresponding ruthenium(II) is straightforward and not inhibited by ligand insolubility. As a matter of fact it was not possible to synthesize the Ru complexes with two such ligands. A nice solution was realized when we discovered that complex **1** bearing two bromine functions smoothly reacts under Sonogashira conditions with 1-ethynylpyrene to produce complex **2a** in good yield. By analogy and for comparative purposes the cross-coupling of **1** with 4-ethynyltoluene was also very effective, affording complex **2b** (Scheme 1). Complex **1** was successfully prepared in 73% yield from [Ru(5-bromo-2,2′-bipyridine)$_2$Cl$_2$] and free 2,2′-bipyridine.

Similarly, complex **4** was formed from complex **3** by cross-coupling with three equivalents of 1-ethynylpyrene (Scheme 2). Complex **3** was prepared in 41% yield from [Ru(5-bromo-2,2′-bipyridine)$_2$Cl$_2$] and free 5-bromo-2,2′-bipyridine.



Scheme 4. *Reagents and conditions*: (i) Step 1: AgBF$_4$, reflux, acetone, 2 h; step 2: DMF, 1 equiv. of terpyridine or dibromoterpyridine, reflux, 3 h, (ii) [Pd(PPh$_3$)$_4$] 6 mol%, CH$_3$CN/C$_6$H$_6$ 1/1, *i*Pr$_2$NH, 60°C.

Interestingly, it appears that the comprehensive convergent strategy described here is also applicable to the synthesis of appropriate complexes that could not be prepared by classical methodology using ligand **A**. Reaction of [Ru(2,2′-bipyridine)$_2$Cl$_2$] with 5,5′-dibromo-2,2′-bipyridine afforded complex **5** which was allowed to react with two equivalents of 1-ethynylpyrene or 4-ethynyltoluene to provide, respectively, compounds **6a** and **6b** (Scheme 3).

The generality of this synthetic methodology is exemplified in Scheme 4, where complexes **9** and **11** carrying respectively two and four ethynylpyrene or ethynyltoluyl auxiliaries were satisfactorily produced from the corresponding bromo derivatives. The pivotal bromo terpyridine complex **7** was prepared in a straightforward manner from RuCl$_3$·6H$_2$O and 5,5″-dibromo-terpy. This complex was allowed to react with terpy or 5,5″-dibromo-terpy to afford respectively complexes **8** and **10** in good yields. The cross-coupling procedure with 1-ethynylpyrene or 4-ethynyltoluene proceeded under similar conditions and gave the target complexes **9a**/**9b** and **11a**/**11b** in fair yields.

All complexes were unambiguously characterized by NMR, FT-IR and FAB$^+$ or ESI spectroscopy and all data were consistent with the proposed structures. A typical procedure is given in Ref. 8 and selected spectroscopic data are provided in Table 1.

The success achieved during the synthesis of these mononuclear complexes paved the way for the elaboration of more sophisticated structures where programmed grafting of successive modules onto a carefully designed core would provide auspicious cascade energy transfer or energy hopping events under photoexcitation. It has previously been shown that the construction of such intricate molecular structures is quite tedious and complex to realize on large scale owing to the low solubility of the molecules.[9] Here we demonstrate that the construction of a single ruthenium complex carrying two ethynyl-linked pyrene subunits is

Table 1. Selected spectroscopic and photophysical data at 300 K and 77 K for the Ru complexes

Complex	MS[a]	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm) 300 K[b,c]	ϕ_{em}[b,d] 10^4	λ_{em} (nm) 77 K[e]
2a	1163.2	420	54,000	671	110	669
2b	943.3	460	7,500	640	92	608
4a	1387.4	420	70,400	672	86	671
4b	1057.2	468	9,800	634	122	606
6a	1163.2	443	57,700	690	130	682
6b	943.2	440	9,800	675	0.7	639
9a	1161.2	428	38,300	674	1.2	672
9b	941.2	480	9,800	650	0.7	625
11a	1609.2	428	105,700	675	1.0	673
11b	1169.2	480	11,600	630	1.1	616
17a	466.1	430	48,000	715	100	715
18	510.1	428	37,200	680	8.0	678

[a] $[M-PF_6]^+$ for all complexes and $[M-2PF_6]^{2+}$ for complexes **17a** and **18**.

[b] Argon-saturated CH_3CN solution unless otherwise noted.

[c] Emission spectra were taken at ambient temperature with 450 nm excitation.

[d] Photoluminescence quantum yield was calculated using $[Ru(bpy)_3]^{2+}$ ($\Phi = 0.062$ in CH_3CN as quantum counter, ±10%).

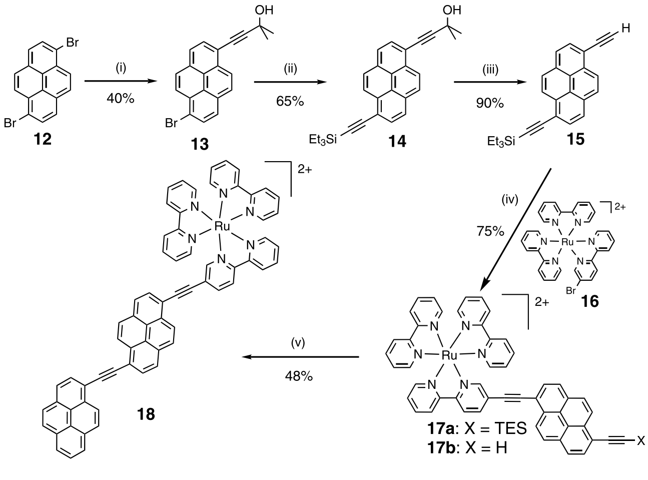
[e] Emission spectra were taken at 77 K in 4:1 EtOH:MeOH with 450 nm excitation.

feasible using [Ru(2,2′-bipyridine)$_2$(5-bromo-2,2′-bipyridine)]$^{2+}$ as starting material (Scheme 5). In order to achieve this synthesis we first needed to prepare a dissymmetrically substituted pyrene derivative **13**, which was prepared by monosubstitution of 1,6-dibromopyrene[10] with a propargylic alcohol in the presence of $[Pd(PPh_3)_4]$. Chromatographic separation of **13** from unreacted **12** (10%) and the disubstituted derivative is very easy owing to the high polarity induced by the alcohol function. Further functionalization of **13** with triethylsilylacetylene afforded the difunctionalized derivative **14** in 65% yield.

Interestingly, the reaction with trimethylsilylacetylene was very slow and gave the TMS-protected derivative in less than 30% isolated yield. Selective deprotection of the propargylic function leading to **15** was realized using NaOH in anhydrous toluene.[11] Grafting to the Ru complex **16** was made possible by using a Pd(0)-catalyzed cross-coupling reaction. The presence of acetonitrile was required to solubilize the complex and seems not to perturb the catalytic process. Complex **16** was prepared in 75% yield from [Ru(2,2′-bipyridine)$_2$Cl$_2$] and free 5-bromo-2,2′-bipyridine.

The release of the TES protecting group is easy to perform with K_2CO_3 in a protic solvent (ESI-OTF: 409.4 $[M-2PF_6]^{2+}$, $\delta_{C\equiv CH} = 3.82$ ppm), however the isolation of derivative **17b** was impossible due to its high tendency to polymerise. A convenient solution to this came up when we discovered that the deprotection is feasible in situ and mediated by K_2CO_3 and methanol, while the coupling reaction with 1-bromopyrene was made possible in the presence of Pd(0), CuI and iPr$_2$NH to quench the nascent acid. This procedure would maintain the concentration of the terminal alkyne on the ruthenium complex **17b**, to a very low concentration during the course of the reaction and would reduce the rate of polymeriztion. In fact, examination of TLC during the course of the reaction revealed the presence of small amounts of **17b** and the absence of polymerization. A similar procedure has recently been applied to porphyrin molecules in order to avoid the tedious purification of the alkyne intermediate.[12]

The photophysical properties of all the metal-organic structures are summarized in Table 1. The C≡C-pyrenyl substituted bipy-complexes (**2a**, **4a**, **6a**) display behaviour consistent with ^{3}IL excited states, yielding structured room temperature phosphorescence in the red which is only slightly variable with lowering temperature. Such small thermally induced Stokes shifts are consistent with excited state manifolds that are relatively nonpolar, whereas the C≡C-phenyl substituted



Scheme 5. *Reagents and conditions*: (i) propargylic alcohol (1.4 equiv.), $[Pd(PPh_3)_4]$ (6 mol%), iPrNH$_2$, 60°C, 5 days. (ii) (1.5 equiv.), $[Pd(PPh_3)_4]$ (6 mol%), nPrNH$_2$, 60°C, 16 h. (iii) NaOH (1.2 equiv.), toluene, 130°C, 8 h. (iv) $[Pd(PPh_3)_4]$ 6 mol%, CH_3CN/C_6H_6 1/1, iPr$_2$NH 60°C, 16 h. (v) **17a**, K_2CO_3 (5 equiv.), DMF, MeOH, pyr-Br, $[Pd(PPh_3)_4]$ (6 mol%), CuI (10% mol), 60°C. All counterions are PF_6^-.

bipy-complexes (**2b**, **4b**, **6b**) display static photoluminescence properties entirely consistent with a polar ^{3}MLCT parentage. In the $C\equiv C$-pyrenyl substituted terpy systems (**9a**, **11a**), the emission properties are consistent with nonpolar π,π^* ^{3}IL excited states while the opposite is observed in the $C\equiv C$-toluyl substituted terpy-complexes (**9b**, **11b**). The latter displays spectral properties typical of ^{3}MLCT Ru(II)-terpy excited states. In cases where there is effective conjugation from the diimine or triimine fragment to the pyrene chromophore(s) there is an effective lowering of the ligand-based triplet energy, yielding π,π^* ^{3}IL-based phosphorescence at room temperature.

In summary, we have prepared new ruthenium(II) complexes bearing a controlled number of pyrene fragments by using a modified procedure for Sonogashira couplings. Here we coordinate in a first step the ligand carrying the adequate reactive functions to the photoactive metal centre and then in a final step the pyrene moieties are linked to the complexes. When more sophisticated molecules are engineered one major modification of this metallo-synthon/cross-coupling procedure consists of in situ liberation of the terminal alkyne from the corresponding TES-protected complex. This variation avoids undesired polymerization of the Ru-bipy-pyrene-$C\equiv CH$ derivative **17b**. Furthermore, this method avoids the deprotection and subsequent purification steps. This is clearly a convenient and versatile protocol because of the mild conditions and the tolerance of various solvents, reactants and functions on the reactive complex. The extension of this methodology to more sophisticated molecular scaffolds, and the detailed study of the photophysical properties of the present complexes are currently under investigation in our laboratories.

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8. General procedure for the preparation of the ruthenium(II) complexes. In a Schlenk flask, to a stirred degassed 50/50 acetonitrile/benzene solution of the precursor complex were added progressively $Pd(PPh_3)_4$, diisopropylamine, and the acetylenic-ligand. The mixture was heated under argon for 16 h until complete consumption of the starting material. After the solution cooled to room temperature, potassium hexafluorophosphate in water was added and the solution was evaporated. The crude precipitate was washed twice with water, once with diethyl ether, and chromatographed. The fractions containing the pure complex were evaporated to dryness and recrystallized from CH_2Cl_2/hexane. Compound **9a** was prepared according to the general conditions, from 30 mg of **8** (0.029 mmol) in 1.5 mL of acetonitrile and 1.5 mL of benzene, 17 mg of 1-ethynyl-pyrene (2.5 equiv., 0.073 mmol), 2.1 mg of $[Pd(PPh_3)_4]$ (6 mol%), 1 mL of iPr$_2$NH. Chromatography was performed on alumina with CH_2Cl_2/MeOH (100/0 to 99/1) as eluant, and recrystallization gave 20 mg of **9a** (52%). ^{1}H NMR (CD_3CN, 400 MHz): $\delta = 8.91$ (d, 2H, $^3J = 8.5$ Hz), 8.84 (d, 2H, $^3J = 8.5$ Hz), 8.61–8.59 (m, 4H), 8.59 (t, 1H, $^3J = 8.0$ Hz), 8.50 (t, 1H, $^3J = 8.0$ Hz), 8.46 (d, 2H, $^3J = 9.0$ Hz), 8.40 (d, 2H, $^3J = 7.5$ Hz), 8.35 (d, 2H, $^3J = 7.5$ Hz), 8.29 (d, 2H, $^3J = 9.0$ Hz), 8.26–8.21 (m, 6H), 8.17–8.11 (m, 6H), 8.00 (td, 2H, $^3J = 9.0$ Hz, $^4J = 1.0$ Hz), 7.65 (d, 2H, $^4J = 1.5$ Hz), 7.47 (d, 2H, $^3J = 5.0$ Hz), 7.27 (td, 2H, $^3J = 7.5$ Hz, $^4J = 1.0$ Hz); $^{13}C\{^1H\}$ NMR (CD_3CN, 400 MHz): $\delta =$ 159.2, 157.7, 156.5, 156.1, 152.5, 153.7, 140.8, 139.2, 137.2, 136.8, 133.3, 132.9, 132.1, 131.8, 130.8, 130.1, 130, 128.5, 128.1, 127.8, 127.3, 127.2, 125.8, 125.7, 125.6, 125.1, 125.0, 124.9, 124.8, 124.6, 116.3, 96.7 ($CC_{ethynyl}$), 90.4 ($CC_{ethynyl}$); FT-IR (KBr, cm^{-1}): $\nu = 3437$ (m), 2925 (m), 2854 (m), 2193 ($C\equiv C$) (s), 1742 (s), 1620 (m), 1448 (s), 1261 (m), 1098 (m), 877 (m), 845 (s), 785 (m), 558 (s); UV–vis (CH_3CN): λ nm (ε, M^{-1} cm^{-1}): 426 (64400), 386 (54900), 365 (52000), 359 (52600), 305 (77000), 273 2 (75000), 241 (89700), 235 (98400); FAB, -m-NBA (CH_3CN): 1161.2 ($[M-PF_6]^+$), 508.2 ($[M-2PF_6]^{2+}$). Anal. calcd for $C_{66}H_{38}F_{12}N_6P_2Ru{\cdot}CH_3CN$: C, 60.63; H, 3.07; N, 7.28; found: C, 60.48; H, 2.97; N, 7.12.
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