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Stepwise construction of pyrene bridged polytopic ligands carrying acetylenic tethers

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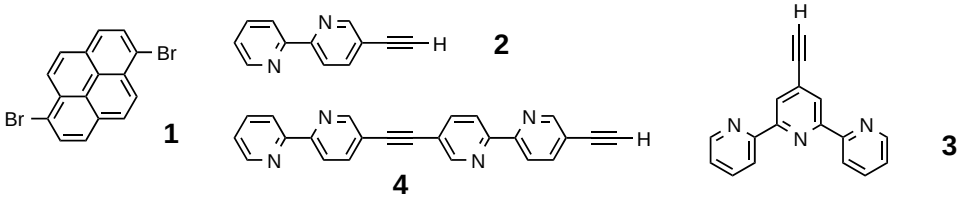
Abstract—Reliable and practical synthetic routes for the construction of polytopic bipyridine or terpyridine frameworks are presented. These ligands are prepared by sequential Pd-promoted cross-coupling reactions between selected ethynyl substituted bipyridine or terpyridine building blocks and 1,6-dibromopyrene. A convergent synthetic route for the preparation of Ru complexes bearing peripheral uncomplexed fragments has been established starting from preorganized building blocks carrying a bromide function. This protocol highlights the use of metallo-synthons in Sonogashira cross-coupling reactions and allows the synthesis of very soluble complexes. © 2002 Published by Elsevier Science Ltd.

As a result of the optical and redox significance of transition metal complexes of Re(I), Ru(II) and Os(II) in analytical and photophysical chemistry, the engineering of new ligands bearing useful functions is of great importance.[1] Due to the multiple possibilities in fine-tuning the electronic properties, polypyridine ligands have been widely studied. However, the future preparation of advanced multicomponent materials will be both more complicated and also more sophisticated than the current analogs and will require the development of new synthetic strategies.[2–4] In the classical procedure the ligand is exposed to a preformed metal precursor containing the adequate molecular fragments to complete the first coordination sphere of the metal. This procedure has extensively been used for the synthesis of symmetrical units but lacks the necessary specificity for the introduction of sequential electronic asymmetry into the molecular architecture. Furthermore, the tethering of suitable polyaromatic fragments dramatically decreases the solubility of the resulting molecules which strongly limits their use in coordination chemistry.

However, it has recently been shown that short covalent linkage of pyrene subunits to ruthenium(II) diimine complexes induces a significant increase of the excited state lifetime emission from the MLCT state resulting from reversible intramolecular energy transfer between the $^3S_1^*$ of the Ru fragment and the $^3S_1^*$ state of the pyrene fragment.[5–7] We have recently investigated in some details the photophysical behaviour of ruthenium complexes bearing a mono-substituted pyrene fragment.[8,9]

We herein describe novel ligands constructed from 1,6-disubstituted-pyrene, connected to the chelating part of the molecule by an acetylenic linkage. The strategy provides access to complexes retaining various chromophoric units and vacant coordination sites. Access to this family of ligands requires the key building blocks **1**–**4**, prepared according to literature procedures.[10–12] The homo-ditopic and homo-tetratopic ligands **5**–**7** are readily prepared in a 'one pot' reaction via a Sonogashira–Hagihara cross-coupling reaction between, respectively, 5-ethynyl-2,2′-bipyridine **2**,[10] 4′-ethynyl-2,2′:6′,2″-terpyridine



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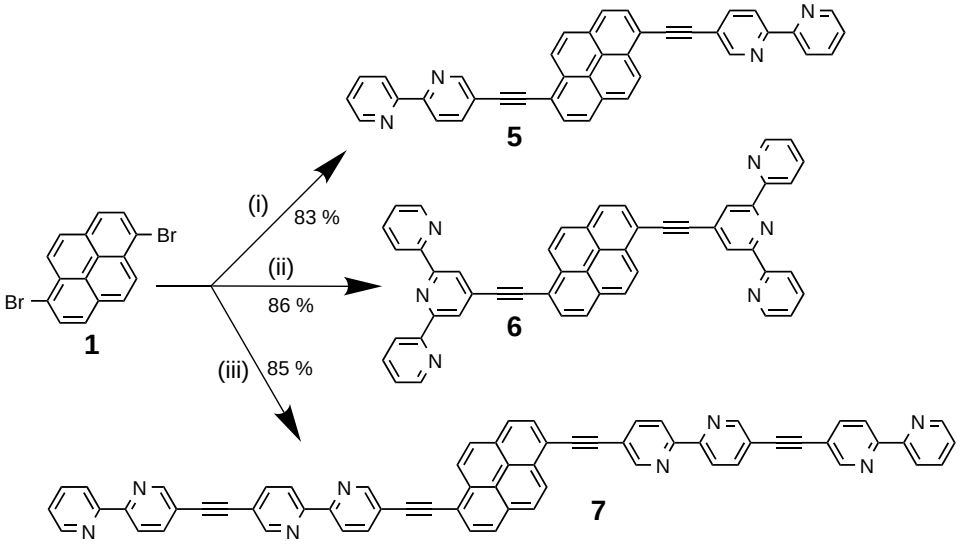
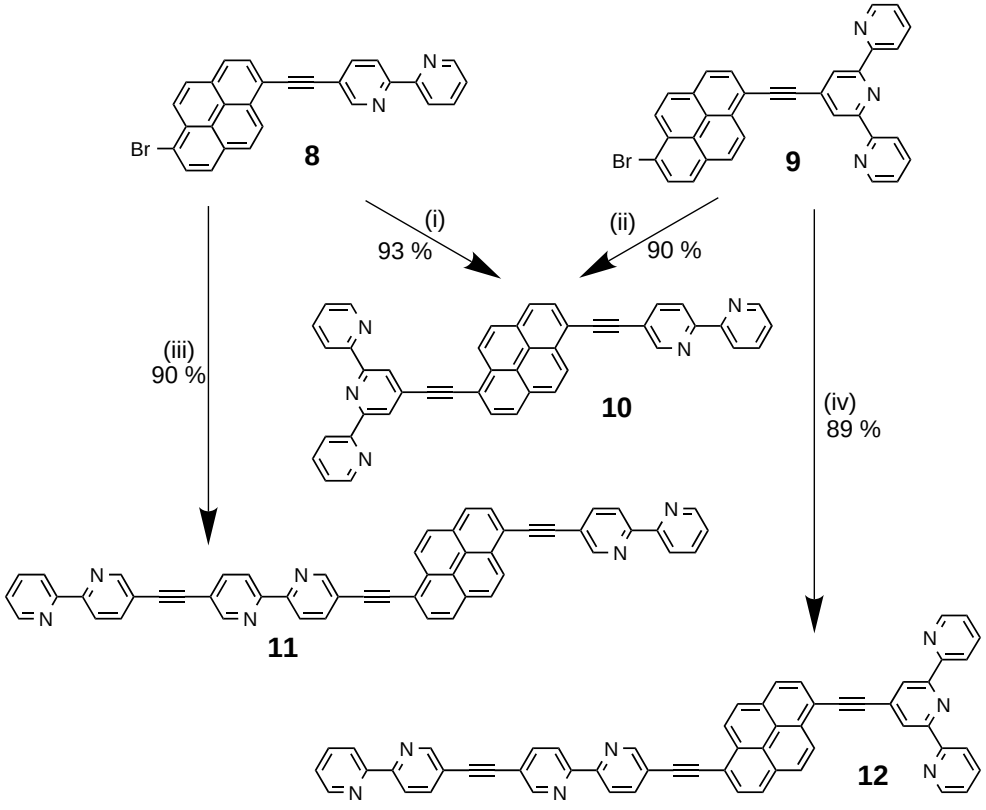
3,[10] 5-ethynyl-5′-(5-ethynyl-2,2′-bipyridine-yl)-2,2′-bipyridine **4**[11] and substoichiometric amounts of 1,6-dibromopyrene,[12] as sketched in Scheme 1.

These desired products obtained in good yields were photostable and characterized by ^{1}H, $^{13}C\{^{1}H\}$ NMR for the most soluble compounds, FAB^{+}-MS, UV–vis, IR spectroscopies and all data were consistent with the proposed structures. Selected data are given in Refs. 13–17.

This is a convenient and versatile method because the required ligands precipitate during the reaction. The use of higher temperature for the synthesis of compound **7**



Scheme 1. *Reagents and conditions*: (i) $[Pd(PPh_3)_4]$ (6 mol%), compound **2** (2.1 equiv.), benzene, $^{i}Pr_2NH$, 80°C; (ii) $[Pd(PPh_3)_4]$ (6 mol%), compound **3** (2.2 equiv.), benzene, $^{i}Pr_2NH$, 80°C; (iii) $[Pd(PPh_3)_4]$ (6 mol%), compound **4** (2.2 equiv.), toluene, $^{i}Pr_2NH$, 110°C.



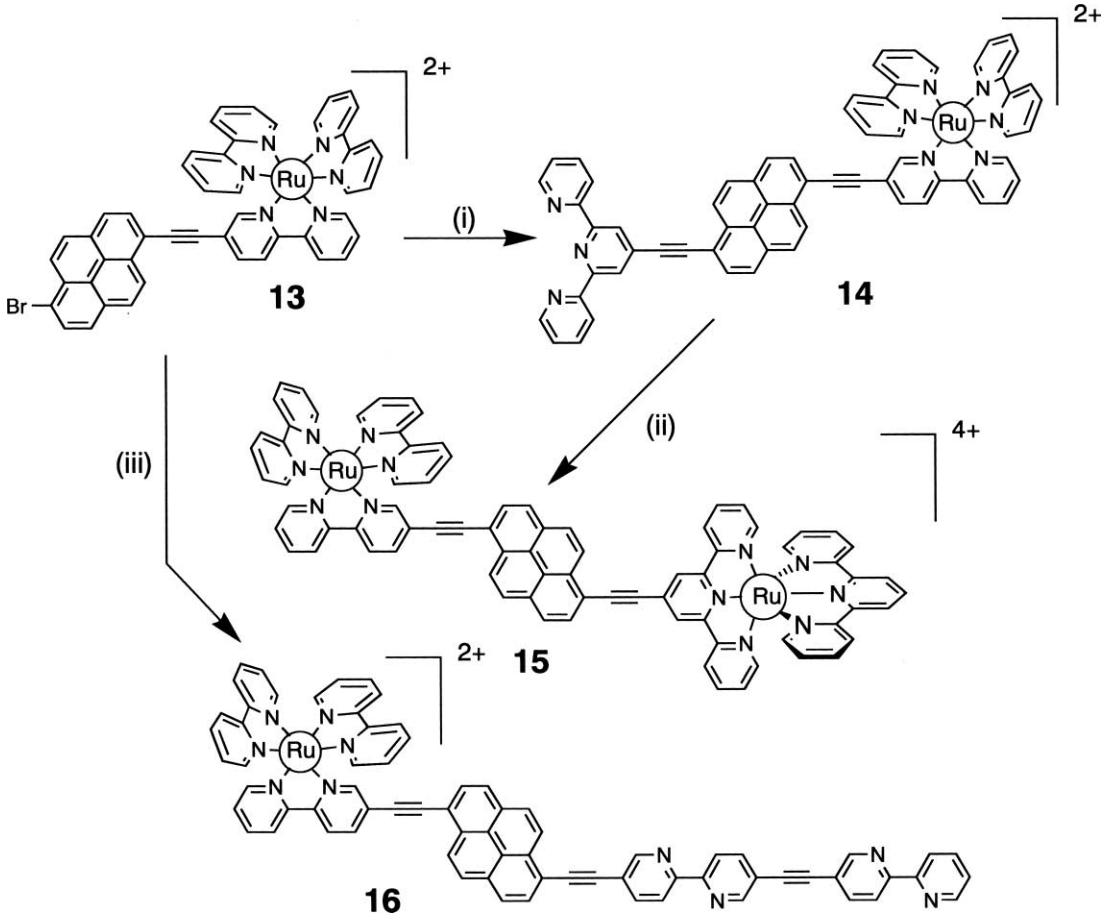
Scheme 2. *Reagents and conditions*: (i) $[Pd(PPh_3)_4]$ (6 mol%), compound **3** (1.2 equiv.), benzene, $^{i}Pr_2NH$, 80°C; (ii) $[Pd(PPh_3)_4]$ (6 mol%), compound **2** (1.3 equiv.), benzene, $^{i}Pr_2NH$, 80°C; (iii) $[Pd(PPh_3)_4]$ (6 mol%), compound **4** (1.0 equiv.), toluene, $^{i}Pr_2NH$, 110°C; (iv) $[Pd(PPh_3)_4]$ (6 mol%), compound **4** (1.0 equiv.), toluene, $^{i}Pr_2NH$, 110°C.

limits the formation of a mixture of compounds observed when milder experimental conditions are used. During these reactions, it was soon established by thin layer chromatography that the mono substituted derivatives are preferentially formed at the early stage of the reaction. This was auspicious for the future preparation of molecules bearing different coordination sites (e.g. bipy versus terpy) or empty coordination sites (vide infra). The use of rt conditions and the in situ formation of the Pd(0) precursor from Pd(II) and Cu(I) salts was unsatisfactory since deeply coloured solutions are formed from which only polymeric products were observed.

Following the successful synthesis of a number of pyrene bridged multitopic ligands, we have closely examined the monosubtitution reaction of 1,6-dibromopyrene with derivatives **2** and **3** (Scheme 2). In our hands, under a variety of conditions, e.g. using different bases, solvents and catalysts precursors, we found that the use of substoichiometric quantities of the terminal alkynes afforded the target compounds **8**[14] and **9** within an average yield of 75%. However, under similar conditions the use of **4** only provides the disubstituted derivative **7** and the excess starting 1,6-dibromopyrene **1** was always recovered.

The high reactivity of **4** and the very low solubility of the final ligand **7** might account for this observation. Interestingly, the mixed ligands can be synthesized in a straightforward manner in good yields (ca. 90%) from the pivotal mono substituted derivatives **8** and **9** (Scheme 2). Ligands **10**–**12** precipitate during the reaction and were recovered by centrifugation. These ligands, despite their low solubility, are interesting by themselves due to their high absorption and strong luminescence properties but they will also serve to prepare homonuclear complexes which are interesting test complexes for the study of forthcoming photophysical and redox properties.

However, a common problem encountered which these ligands, apart from their weak solubility, is the lack of selective complexation behaviour of one chelating fragment versus the other. In order to bypass this problem, we designed a two-step protocol based on the complexation of the free vacant site in **8** by, e.g. a Ru centre, providing the metallo-synthon **13**,[15] which is then used as a building block in the Pd-promoted cross-coupling reaction with metal free bipyridine or terpyridine templates. A sampling of these reactions is given in Scheme 3.



Scheme 3. *Reagents and conditions*: (i) $[Pd(PPh_3)_4]$ (6 mol%), compound **3** (1.0 equiv.), CH_3CN/THF, $^iPr_2NH$, 80°C; (ii) $[Ru(terpy)(DMSO)Cl_2]$, $AgBF_4$ (2 equiv.), methanol, 80°C, filtration, addition of compound **14**; (iii) $[Pd(PPh_3)_4]$ (6 mol%), compound **4** (1.1 equiv.), CH_3CN/THF, $^iPr_2NH$, 80°C. All conterions are PF_6^-.

Interestingly, the mononuclear complexes **14**[16] and **16** exhibit, respectively, one uncomplexed terpyridine or two uncomplexed bipyridine fragments which are potential candidates for further complexation with various metal precursors such as Os(II) or Re(I). Finally, it is demonstrated that complex **14** reacts smoothly with a second metal centre to provide a hybrid complex **15** bearing Ru tris-bipy and Ru bis-terpy subunits.[17]

The possible Ru translocation of one site to the other, in complexes **14** and **15**, was discarded thanks to the use of UV–vis absorption spectroscopy. Complex **14** exhibited a MLCT absorption band at $\lambda_{max}=422$ nm ($\varepsilon=24{,}500$ M^{-1} cm^{-1}), while complex **15** has two absorption bands at $\lambda_{max}=425$ nm ($\varepsilon=29{,}700$ M^{-1} cm^{-1}) and $\lambda_{max}=474$ nm ($\varepsilon=20{,}300$ M^{-1} cm^{-1}). This is clear evidence that the absorption of Ru-terpy fragment lies at lower energy versus the Ru-bipy fragment. This has also previously been observed in related samples[18] and is clear evidence that no scrambling of the Ru occurs in complex **14** and **15**.

From the above results, we conclude that the mono-substituted bromo-pyrene derivatives **8** and **9** can be usefully elaborated in a manner analogous to the homo-ditopic ligands **5**–**7**. This synthetic utility is further reinforced in the following paper by the use of their ruthenium analogues **13** and **14** in the construction of novel pyrene bridged scaffoldings. This convergent synthetic strategy en route to multinuclear transition metal complexes paves the way for a new generation of luminophoric species in which directional information transfer is targeted.[19]

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13. Compound **5**: FT-IR (KBr, cm^{-1}) 3142 (s), 2905 (s), 2513 (m), 2201 (w, C≡C), 2137 (w), 1796 (w), 1656 (m), 1456 (s), 1434 (s), 1364 (s), 1166 (s), 1115 (s), 1012 (s), 898 (m); FAB^+ m/z (nature of peak, relative intensity) 559.2 ($[M+H]^+$, 100). Anal. calcd for $C_{40}H_{22}N_4$: C, 86.00; H, 3.97; N, 10.03. Found: C, 85.89; H, 3.83; N, 9.62%.
14. Compound **8**: ^1H NMR ($CDCl_3$) δ 7.36 (m, 1H), 7.87 (td, $^3J_{H-H}=7.8$ Hz, $^4J_{H-H}=1.9$ Hz, 1H), 8.20 (m, 7H), 8.48 (m, 3H), 8.72 (m, 2H), 9.00 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 91.1 (C≡C), 93.8 (C≡C), 118.0, 118.7, 120.5, 124.1, 125.8, 126.4, 127.1, 128.5, 128.9, 130.6, 137.1, 139.5, 149.4, 151.8; FT-IR (KBr, cm^{-1}) 2958 (s), 2920 (s), 2851 (s), 2195 (w, C≡C), 1656 (m), 1570 (m), 1459 (s), 1433 (m), 1381 (m), 1123 (s), 1060 (s), 846 (s); UV–vis (CH_3CN): λ nm (ε, M^{-1} cm^{-1}) 279 (12.100) 378 (5.300), 402 (5.100); FAB^+ m/z (nature of peak, relative intensity) 461.1 ($[M+H]^+$, 100), 459.1 ($[M+H]^+$, 98). Anal. calcd for $C_{28}H_{15}N_2Br$: C, 73.21; H, 3.29; N, 6.10. Found: C, 72.83; H, 2.98; N, 5.89%.
15. Compound **13**: ^1H NMR (acetone-d_6) δ 7.58–7.74 (m, 5H), 8.04–8.38 (m, 18H), 8.42–8.54 (m, 2H), 8.84–8.97 (m, 6H); FT-IR (KBr, cm^{-1}) 3405 (m), 2927 (s), 2729 (s), 2196 (m, C≡C), 1790 (m), 1621 (m), 1459 (s), 1401 (m), 1259 (m), 1098 (s), 1005 (m), 837 (s); UV–vis (CH_3CN): λ nm (ε, M^{-1} cm^{-1}) 287 (29.200), 372 (10.600), 390 (13.600), 422 (14.600); FAB^+ m/z (nature of peak, relative intensity) 1019.2 ($[M-PF_6]^+$, 100), 874.2 ($[M-2PF_6]^+$, 30), 793.2 ($[M-2PF_6-Br]^+$, <5). Anal. calcd for $C_{48}H_{31}N_6BrRuP_2F_{12}$: C, 49.58; H, 2.69; N, 7.23. Found: C, 49.44; H, 2.57; N, 7.08%.
16. Compound **14**: FT-IR (KBr, cm^{-1}) 3425 (m), 2920 (m), 2749 (m), 2191 (w, C≡C), 1733 (m), 1624 (w), 1567 (m), 1488 (m), 1455 (m), 1400 (s), 1262 (s), 1207, (m), 1186 (m), 891 (m), 794 (s); UV–vis (CH_3CN): λ nm (ε, M^{-1} cm^{-1}) 288 (74.200), 398 (24.400), 422 (24.500); FAB^+ m/z (nature of peak, relative intensity) 1194.3 ($[M-PF_6]^+$, 100), 1049.3 ($[M-2PF_6]^+$, 30). Anal. calcd for $C_{65}H_{41}N_9RuP_2F_{12}$: C, 58.30; H, 3.09; N, 9.41. Found: C, 58.06; H, 2.89; N, 9.23%.
17. Compound **15**: FT-IR (KBr, cm^{-1}) 2970 (m), 2936 (m), 2205 (m, C≡C), 1712 (m), 1613 (m), 1458 (s), 1456 (s), 852 (s); UV–vis (CH_3CN): λ nm (ε, M^{-1} cm^{-1}) 296 (57.600), 425 (29.700), 474 (20.300); FAB^+ m/z (nature of peak, relative intensity %) 1819.3 ($[M-PF_6]^+$, 100), 1674.2 ($[M-2PF_6]^+$, 30), 1115.2 ($[M-Ru(bipy)_2-3PF_6]^+$, <5). Anal. calcd for $C_{80}H_{52}N_{12}Ru_2P_4F_{24}$: C, 48.94; H, 2.67; N, 8.56. Found: C, 48.78; H, 2.53; N, 8.39%.
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