

Synthesis and characterization of π -conjugated oligomers that contain metal-to-ligand charge transfer chromophores†

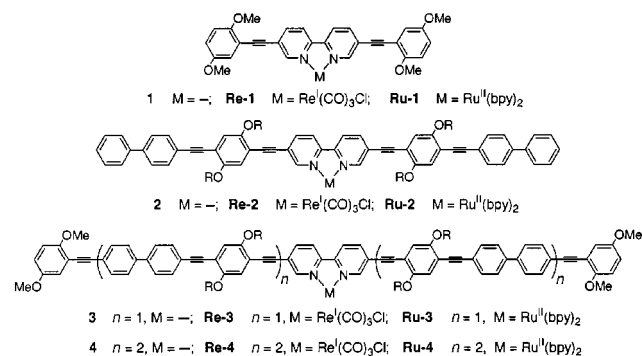
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The synthesis and characterization of a series of *p*-phenyleneethynylene oligomers that contain the 2,2'-bipyridine-5,5'-diyl moiety is reported; metallation of the oligomers with $\text{Re}(\text{CO})_5\text{Cl}$ and $\text{Ru}(\text{bpy})_2\text{Cl}_2$ yields the corresponding $(\text{L})\text{Re}(\text{CO})_3\text{Cl}$ and $(\text{L})\text{Ru}(\text{bpy})_2^{2+}$ complexes.

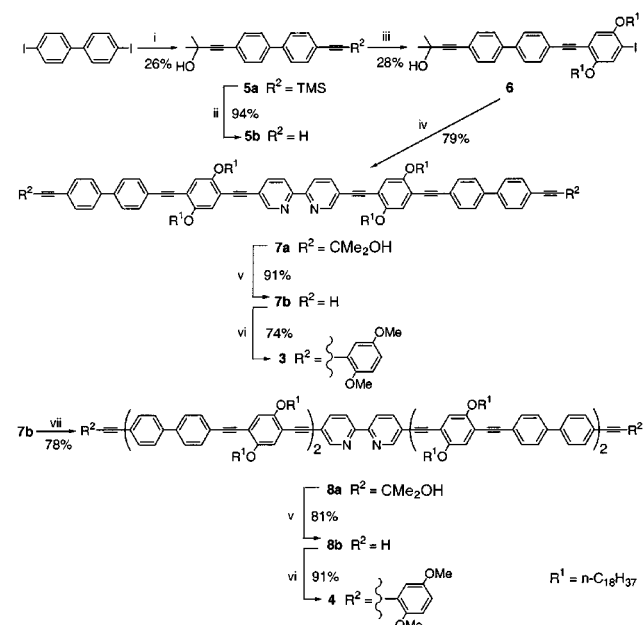
π -Conjugated oligomers and polymers are of interest due to unique optical and electronic properties which enable their use as the active medium in optical, electronic, optoelectronic and chemical sensing devices.^{1,2} We recently synthesized and characterized the photophysical properties of a series of π -conjugated polymers that incorporate a metal-bipyridine (bpy) chromophore directly into the backbone of a poly(phenyleneethynylene) (PPE) polymer.³ The metal-organic polymers exhibit several interesting properties, including a decreased band-gap compared to the unmetallated polymer and a long-lived photoluminescence believed to arise from the metal-to-ligand charge transfer (MLCT) state. In an effort to better understand the optical properties of the metal-organic π -conjugated materials, we set out to prepare a series of mono-disperse PPE-based metal-organic oligomers as models for the structurally related polymers.⁴ Accordingly we have synthesized oligomers **1–4**, along with the corresponding metal complex derivatives, **Re-1–Re-4** and **Ru-1–Ru-4**. The present report describes the synthesis and optical absorption data for this new series of oligomers.



Preparation of series **1–4** required an iterative strategy that uses Pd-mediated (Sonogashira)⁵ coupling chemistry to extend the PPE backbone outward from a 2,2'-bipyridine-5,5'-diyl 'core'. In order to implement this strategy a suitably functionalized 'monomer' unit that contains a protected terminal acetylene or a protected (or masked) aryl iodide was required. Other groups had previously reported application of the TMS group to protect terminal acetylenes and/or the 1-aryl-3,3-diethyltriazene function as a masked aryl iodide in the synthesis of mono-disperse PPE oligomers.^{2a–d} The 1-aryl-3,3-diethyltriazene masking group was deemed unsuitable for our needs owing to the possibility that the bipyridyl nitrogens would react with the electrophile (MeI) that is used in the aryltriazene to aryl

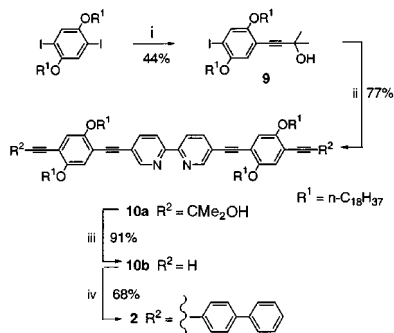
iodide conversion step. Although the TMS group seemed suitable for protecting the terminal acetylene, preliminary synthetic efforts aimed at preparing a monomer which contained an aryl iodide and a TMS-protected acetylene were thwarted due to the difficulty of separating the desired product from unreacted starting materials and by-products. The chromatographic separation is difficult (if not impossible) because the starting materials, the by-products and the desired product are all non-polar and therefore have similar solubility and comparable R_f values.

We finally discovered that the 2-hydroxypropan-2-yl (2-HP) protecting group⁶ would allow us to readily prepare and purify multigram quantities of monomer **6** (Scheme 1), which features a protected terminal acetylene and a reactive aryl iodide.‡ Thus, in a two-step, one-pot procedure 4,4'-diiodobiphenyl was reacted with $\text{TMSC}\equiv\text{CH}$ and then with 2-methylbut-3-yn-2-ol to afford **5a**. The 2-HP protecting group in **5a** allows this compound to be separated from the reaction by-products by silica chromatography. The separation is facile because the by-products have significantly higher R_f values compared to **5a** owing to the polar 2-HP protecting group. Selective removal of the TMS group from **5a** with $\text{KOH}-\text{MeOH}$ afforded mono-protected compound **5b**. Monomer **6** was obtained by coupling **5b** with 1 equiv. of 1,4-diiodo-2,5-dioctadecyloxybenzene. Here again the polarity of the 2-HP protecting group in **6** allowed this material to be easily separated from the reaction by-products, affording the pure compound in 28% yield after chromatography.



Scheme 1 Reagents and conditions: i, $\text{TMSC}\equiv\text{CH}$ (1 equiv.), Pd/Cu (cat.), heat, 3 h, then $\text{HC}\equiv\text{CCMe}_2\text{OH}$ (excess), heat, 3 h; ii, KOH , $\text{THF}-\text{MeOH}$; iii, 1,4-diiodo-2,5-dioctadecyloxybenzene (1 equiv.), Pd/Cu (cat.); iv, 5,5'-diethynyl-2,2'-bipyridine (0.5 equiv.), Pd/Cu (cat.); v, KOH , toluene, reflux; vi, 2-iodo-1,4-dimethoxybenzene (2 equiv.), Pd/Cu (cat.); vii, **6** (2 equiv.), Pd/Cu (cat.).

† Details of the synthesis and characterization of the oligomers is available from the RSC web site, see <http://www.rsc.org/suppdata/cc/1999/1749/>



Scheme 2 Reagents and conditions: i, $\text{HC}\equiv\text{CCMe}_2\text{OH}$ (1 equiv.), Pd/Cu (cat.); ii, 5,5'-diethynyl-2,2'-bipyridine (0.5 equiv.), Pd/Cu (cat.); iii, KOH, toluene, reflux; iv, 4-bromobiphenyl, Pd/Cu (cat.).

Once **6** was available in multigram quantities, synthesis of the desired oligomers proceeded rapidly. Thus, reaction of 2 equiv. of **6** with 5,5'-diethynyl-2,2'-bipyridine⁷ produces **7a**, which is subsequently deprotected by KOH, toluene and heat to afford **7b**. Endcapping of **7b** with 2-iodo-1,4-dimethoxybenzene affords **3**, and subsequent metallation of **3** with $\text{Re}(\text{CO})_5\text{Cl}$ in toluene or $\text{Ru}(\text{bpy})_2(\text{CF}_3\text{SO}_3)_2$ in THF-acetone yields **Re-3** and **Ru-3**, respectively. A further iterative sequence beginning with coupling of **7b** with 2 equiv. of **6** followed by deprotection and endcapping affords oligomer **4**.

As shown in Scheme 2, **2** was synthesized by a different approach that also relies upon the use of the 2-HP protecting group. First, 1,4-diiodo-2,5-dioctadecyloxybenzene was coupled with 1 equiv. of 2-methylbut-3-yn-2-ol to produce **9**. This compound was readily separated from unreacted starting material owing to the polar 2-HP function. Reaction of 2 equiv. of **9** with 5,5'-diethynyl-2,2'-bipyridine afforded **10a**, which was deprotected to **10b** by KOH, toluene and heat. Finally, **10b** was coupled with 4-bromobiphenyl to produce **2** which is subsequently metallated to afford **Re-2** or **Ru-2**.

Fig. 1 compares the UV-visible absorption spectra of the free oligomers with those of the corresponding (L)Re(CO)₃Cl and (L)Ru(bpy)₂²⁺ complexes. The free oligomers all feature two absorption bands in the 300–500 nm region. The lowest energy band is assigned to the long-axis polarized π,π^* (HOMO → LUMO) transition, while the second band is assigned to the short-axis polarized π,π^* transition. The low energy band red-shifts considerably from **1** to **2**, but the position and bandshape of the transition remains relatively constant in **2–4**, indicating that the bandgap of the oligomers is defined early in the series. This observation contrasts with observations made on PPE

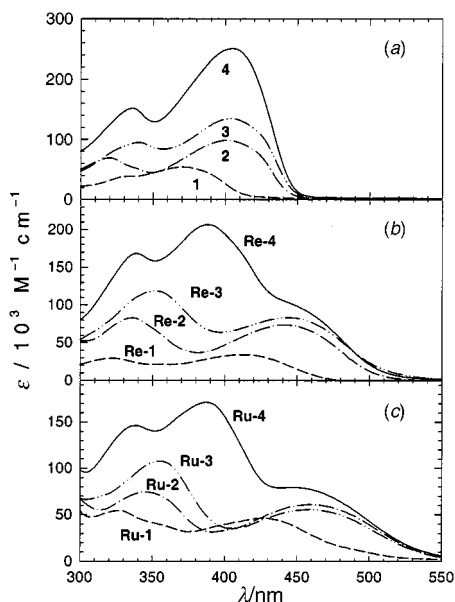


Fig. 1 Absorption spectra of oligomers: (a) **1–4** in THF solution; (b) **Re-1–Re-4** in THF solution; (c) **Ru-1–Ru-4** in CH_2Cl_2 solution.

oligomers that contain phenylene repeats (as opposed to the biphenyl and bipyridyl repeats present in **1–4**), in which the bandgap continues to decrease for 10 or more repeat units.^{2b,d,f} This suggests that the poor electronic coupling between the non-coplanar phenyl (and pyridyl) rings in the biphenyl and bipyridyl units in **2–4** restricts the conjugation length.

Comparison of the spectra of **Re-1–Re-4** with those of the corresponding free oligomers demonstrates that metallation induces a substantial red-shift of the lowest π,π^* absorption. The oscillator strength of the low energy band is large, but relatively constant throughout the series **Re-1–Re-4**. The low-energy band likely arises from a long-axis polarized π,π^* transition localized predominantly on the chromophore defined by the bis(dioctadecyloxyphenylethynyl)-capped bipyridine segment. The transition is red-shifted because metallation forces the bipyridyl unit into a planar conformation, thereby effectively increasing the conjugation length.^{4d} In addition to this effect, the electrophilic metal center likely decreases the LUMO energy and consequently decreases the HOMO–LUMO gap. An important point is that the $d\pi(\text{Re}) \rightarrow \pi^*$ (bpy-oligomer) MLCT transition, which is expected to arise in the 400–500 nm region (with $\epsilon \approx 10^3\text{--}10^4 \text{ M}^{-1} \text{ cm}^{-1}$), is likely buried under the considerably more intense ligand-centered π,π^* transition.

The spectra of the Ru^{II} complexes **Ru-1–Ru-4** are also dominated by the π,π^* transitions of the ligand; in fact, these bands have approximately the same λ_{max} and ϵ in the Ru^{II} and Re^I complexes. A distinct shoulder is observed ($\lambda \approx 485 \text{ nm}$, $\epsilon \approx 8000 \text{ M}^{-1} \text{ cm}^{-1}$) in the spectrum of **Ru-1** which is very likely the $d\pi(\text{Ru}) \rightarrow \pi^*$ (**1**) MLCT transition. A similar MLCT band is not observed in the spectra of **Ru-2–Ru-4** because it is obscured by the more intense π,π^* transition that occurs at a lower energy in these oligomers.

In conclusion, we have applied an iterative method to synthesize a series of mono-disperse PPE-based metal-organic oligomers. Ongoing spectroscopic and photophysical studies demonstrate that the oligomers are excellent models for structurally related bipyridine-containing poly(*p*-phenyleneethynylene) polymers.

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Notes and references

‡ Godt and co-workers recently reported the use of the hydroxymethyl (HM) moiety as a protecting group for terminal acetylenes in the synthesis of PPE oligomers [ref. 2(f)].

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