

One-pot synthesis of 2,5-diethynyl-3,4-dibutylthiophene substituted multitopic bipyridine ligands: redox and photophysical properties of their ruthenium(II) complexes

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A facile and original synthesis of four 2,2'-bipyridine (bipy) ligands grafted with thiophene subunits is described using phase transfer experimental conditions: related Ru(II) complexes exhibit well-defined redox and photophysical properties which were probed by cyclic voltammetry, UV-vis, steady-state emission and transient absorption spectroscopy.

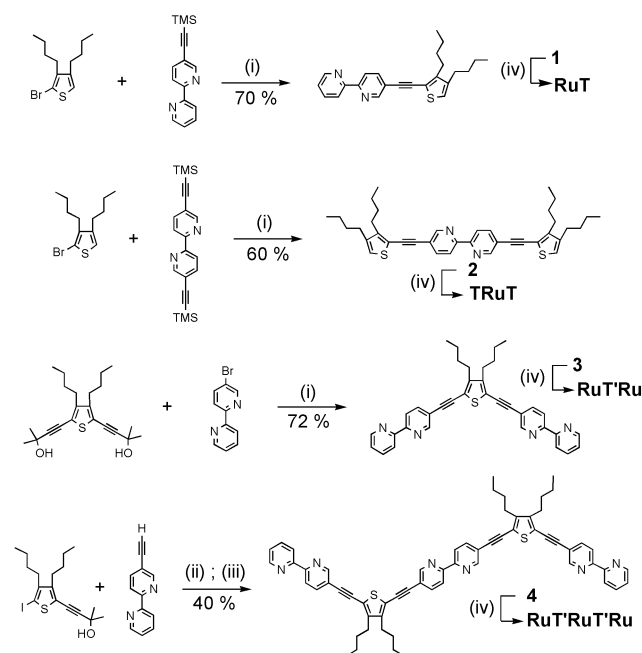
The design and characterization of well-defined transition metal complexes, particularly those containing Ru(II), Os(II), Re(I), Cu(I) and recently Pt(II)^{1,2} is a research area of widespread interest due to their potential application in solar cells,³ luminescence sensing,⁴ biotechnology⁵ and molecular electronics.⁶ One of the more important needs in this area is to identify convenient ways by which to interconnect these metal-based redox and chromophoric subunits so as to promote, long-lived excited states, efficient photon collection, and in some cases unidirectional electron or energy flow and photon hopping along the molecular axis. Bridging units and ligand substituents are subject to many prerequisites including such diverse demands as synthetic versatility, accessibility, rigidity, thermal and photostability, and good electronic conductivity for the spacers. In all these systems the lowest emitting excited states as well as the LUMOs or HOMOs resident on the emitting molecules have to be determined precisely. Many different unsaturated bridged systems have been tested and in some cases the spacers participate directly in the photoprocess.⁷ In order to avoid this complication, but to still expand the size of the molecular frame we design here new molecules where we kept the bridge short and asymmetry is insured by incorporating additional coordination sites. Along these lines various thiophene bridged architectures have recently been examined.^{8,9}

Here we report an original one-pot synthesis of new mono- and polytopic bipy ligands, each bipy being functionalized by either one or two 2-ethynyl-3,4-dibutylthiophene (T) substituents (in **1** and **2**, respectively) or the bipy sites are linked by one or two 2,5-diethynyl-3,4-dibutylthiophene (T') groups (in **3** and **4**, respectively). The *n*-butyl fragments ensure solubility, while the ethynyl spacers favour optimal electronic interactions.^{6,7}

The one-pot synthesis of unsymmetrical and symmetrical mono- and disubstituted bipy ligands is sketched in Scheme 1. The use of phase-transfer conditions with aqueous NaOH and a mixture of [Pd⁰(PPh₃)₄] and CuI as catalysts ensure the *in-situ* deprotection of the alkyne function (from trimethylsilyl or propargylic alcohol) and the cross-coupling reaction.¹⁰ It is interesting that this latter reaction is always operating at rt, while the deprotection step requires higher temperature. This is a very interesting procedure because it avoids the purification of the intermediate as well as the manipulation of weakly stable 5-ethynyl- and 5,5'-diethynyl-2,2'-bipyridine derivatives.¹¹ The preparation of the Ru(II) complexes is straightforward by the use of the required equivalents of the [Ru(bipy)₂Cl₂] \cdot 2H₂O precursor in refluxing EtOH. The purified complexes were characterized by NMR and ES-MS which shows in each case a

well defined molecular peak [M - PF₆]⁺ at *m/z* 933.3, 1151.3, 1815.3 and 1385.3, respectively, for **RuT**, **TRuT**, **RuT'Ru** and **RuT'RuT'Ru**. All complexes are redox active and exhibit a single reversible anodic wave typical of Ru(II) oxidation to Ru(III). Some anodic shifts ($\Delta E_{ox} \approx 50$ mV) are evidenced when two thiophenes are present on the bipy ligand reflecting its electron withdrawing character (Table 1). This effect is also highlighted by reduction where the doubly substituted bipy ligands are much easier to reduce compared with the mono-substituted bipy ligands or the unsubstituted ligands ($\Delta E_{red} \approx 380$ –460 mV). In all these complexes the first reduction is localized on the T-substituted bipy, which plays the role of the electron acceptor.

All of the new complexes display strong absorption in the range 360–425 nm and a weaker band (or shoulder) at lower energy in the range 460–500 nm. The higher energy band is due to the long-axis polarized π, π^* transition of the T-substituted bipy ligands¹² and its intensity increases with the length of the conjugated ligand. The metal-to-ligand charge transfer (MLCT) absorption appears as a well resolved band in **RuT** ($\lambda_{max} = 453$ nm), as a shoulder on the more intense π, π^* intraligand transition in **TRuT**, and **RuT'Ru** and is completely obscured by the intense intraligand band in **RuT'RuT'Ru**. The complexes are photoluminescent in solution at ambient temperature with emission bands red-shifted relative to [Ru(bipy)₃]²⁺, consistent



Scheme 1 Reagents and conditions: (i) Et₃BzNCl, [Pd⁰(PPh₃)₄] (6 mol%), CuI (10 mol%), benzene, aqueous NaOH, 80 °C; (ii) as in (i) but at rt; (iii) 5,5'-dibromo-2,2'-bipyridine (0.5 equiv.), 80 °C; (iv) coordination sites saturated with 'Ru(bipy)₂(PF₆)₂'.

Table 1 Selected electrochemical and photophysical properties of the ruthenium complexes^a

Complex	$E_{1/2, \text{ox}}^b/\text{V}$ ($\Delta E_p/\text{mV}$)	$E_{1/2, \text{red}}^c/\text{V}$ ($\Delta E_p/\text{mV}$)	$\lambda_{\text{em}}^d/\text{nm}$	$\tau_{\text{em}}/\mu\text{s}$	ϕ_{em} (%)
RuT	1.26 (70)	-1.18 (60)	647	1.05	8.2
TRuT	1.30 (70)	-1.02 (60)	677	0.88	3.5
RuT'Ru	1.31 (100)	-1.14 (90)	670	7.32	4.4
RuT'RuT'Ru	1.31 (100)	-1.16 (70)	701	1.35	2.1

^a Argon outgassed acetonitrile solutions at 298 K. ^b First oxidation potential standardized using ferrocene (Fc) as internal reference and are converted to SSCE scale assuming that $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.39$ V. Signal integrate for one electron for **RuT** and **TRuT**, two electrons for **RuT'Ru** and three electrons for **RuT'RuT'Ru**. ^c First reduction potential localized on the thiophene substituted bipy ligands. ^d Steady state luminescence maximum.

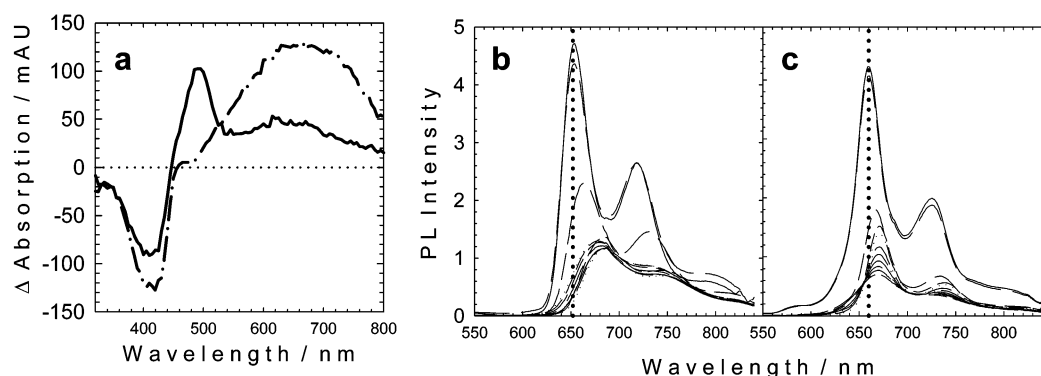


Fig. 1 (a) Transient absorption spectra of **TRuT** (—) and **RuT'Ru** (---) obtained in argon outgassed CH_3CN solution at 100 ns delay following 355 nm laser excitation. (b), (c): Variable temperature photoluminescence spectra of **TRuT** (b) and **RuT'Ru** (c) in EtOH–MeOH solution (4:1 v:v) at temperatures in the range 80–280 K (intensity decreases with increasing temperature).

with the easily reduced T-substituted bipy ligands (Table 1). A combination of transient absorption (TA) spectroscopy and temperature dependence of the steady state emission allows us to assign the lowest excited states as arising from MLCT or ${}^3\pi, \pi^*$ based on the conjugated bipy ligand. For **RuT** and **TRuT** the lowest excited state is safely assigned to a $d\pi \text{Ru} \rightarrow \pi^*$ (bipy-T MLCT). The TA spectra of these two complexes are characterized by strong ground state bleaching and a narrow but intense transient absorption band in the mid-visible region. This feature is typical of MLCT excited states in d^6 transition metal complexes that feature aryl-ethynyl fragments in the 5,5'-positions (Fig. 1(a)).¹² For **TRuT** decreasing the temperature increases the luminescence intensity and at the solvent fluid-to-glass temperature (≈ 130 K) the emission blue shifts by 70 meV and a well-resolved vibronic structure appears (Fig. 1(b)). The observed blue shift that occurs at the solvent glass point (luminescence rigidochromism) indicates that the emissive state is polar, and supports the MLCT assignment. A similar situation is found for **RuT**.

The situation is completely different for the polynuclear complexes **RuT'Ru** and **RuT'RuT'Ru**. In these complexes the TA spectrum exhibits strong ground state bleaching in the intraligand $\pi-\pi^*$ absorption band combined with a broad excited state absorption band that extends throughout the visible region (see Fig. 1(a)). Furthermore, the luminescence of these complexes exhibits well-defined vibrational structure at all temperatures and almost no luminescence rigidochromism. For example, as shown in Fig. 1(c), the emission of **RuT'Ru** shifts by only 30 meV at the solvent fluid-to-glass transition. By analogy with π -conjugated poly(3-octylthiophene) polymers containing Ru-luminophores¹² it is concluded that in the polynuclear complexes the lowest excited state is ${}^3\pi, \pi^*$ state localized on the bridging ligand. The ${}^3\pi, \pi^*$ assignment for **RuT'Ru** is also supported by its long emission lifetime (7 μs), which is a feature characteristic of metal complexes with lowest ${}^3\pi, \pi^*$ excited states.

In summary, we have found an interesting one-pot synthesis of new multitopic bipy based ligands bearing ethynyl-substituted dibutylthiophene fragments. The electrochemical and photochemical properties of the Ru(II) complexes allow us to conclude that the T-substituted bipy chelates act as electron

acceptor. The photophysical properties of the metal complexes are dominated by long-lived excited states with a ${}^3\text{MLCT}$ configuration for mononuclear complexes, whereas for the polynuclear complexes a ${}^3\pi, \pi^*$ low lying excited state based on the thiophene–bipyridine oligomer is dominant. These complexes will be used in photoinduced electron transfer reaction in order to determine a possible influence of the nature of the excited state on the oxidative quenching rates. Studies along these lines are in progress and will be reported in a subsequent full account.

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