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Tuning the Electronic Properties of Phenanthroline Ligands: 3,8-Bis(arylethynyl)-1,10-Phenanthrolines and their Ru(II) Complexes

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Abstract: Palladium-catalyzed cross-coupling reactions between 3,8-dibromo-1,10phenanthroline and substituted phenylacetylenes provide a novel family of highly conjugated metal chelators. The electronic transitions of the ligands and their Ru(II) complexes are affected by the nature of the substituents on the conjugated phenyl rings.

Self-assembling supramolecular systems capable of photo-induced electron and energy transfer, and molecular arrays displaying non-linear optical (NLO) properties, exemplify key design targets in materials chemistry.¹ Ruthenium coordination compounds play a central role in these systems; for example, ruthenium complexes of polypyridine ligands are potential building blocks for luminescent and redox active assemblies as well as for "molecular wires".² Tuning the electronic properties of the ligands can induce desirable changes in the physical properties of the resulting complexes. In particular, tris(2,2'-bipyridyl)ruthenium(II) exhibits NLO effects;^{3,4} however, tris([4,4'-dibutylaminostyryl]-2,2'-bipyridyl)-ruthenium(II) shows much larger optical non-linearities.⁵

The rigid framework of 1,10-phenanthroline ligands is an attractive feature for the construction of functional molecular assemblies. Yet, despite their advantageous metal binding properties, 1,10-phenanthroline ligands have rarely been employed for these purposes.^{6,7} This is largely due to the lack of synthetically accessible building blocks. In general, 1,10-phenanthroline ligands substituted at the 2,9 and 4,7 positions are available, while derivatives substituted along the strategic long axis of the molecule, (*i.e.*, along the 3-8 positions), are rare. Since the most intense electronic transitions of the phenanthroline ring are polarized along this axis,⁸ we were interested in preparing highly conjugated 3,8-disubstituted-1,10-phenanthrolines.⁹ Acetylenic linkages are attractive candidates for this purpose as they have previously been shown to effect substantial electron delocalization in aromatic compounds.¹⁰ In this letter, we describe the synthesis and spectral properties of a novel family of 3,8-bis(arylethynyl)-1,10-phenanthroline ligands (**3**). The electronic transitions of these ligands and their Ru(II) complexes are affected by the nature of the substituents on the conjugated phenyl rings.



The new ligands are synthesized by cross-coupling reactions between 3,8-dibromo-1,10-phenanthroline $(1)^{11}$ and substituted phenylacetylenes $(2)^{12}$ in the presence of $(Ph_3P)_2PdCl_2$ and CuI under sonication at room temperature (Scheme).¹³ Reactions performed at room temperature without sonication proceed much slower, and although reactions at elevated temperatures yielded the desired products, they were accompanied by the formation of undesired by products.¹⁴ Table 1 summarizes selected data for the new ligands.

Comparing the ultraviolet spectra of the new ligands 3 to that of the parent 1,10-phenanthroline shows a substantial red-shift of the π - π * transitions and a change in the relative intensity of the two major bands (Table 1). The higher energy transition in 3a is shifted by 54 nm compared to that of phenanthroline, while the lower energy transition is shifted by 76 nm.^{15,16} This is indicative of a substantial electron delocalization through the ethynyl groups. The lower energy absorption maximum of the methoxyphenyl derivative 3c is 6 nm red-shifted compared to the tolyl derivative 3b which is red-shifted by 6 nm compared to the phenyl derivative 3a. Clearly, the absorption maxima are affected by the remote ring substituents. This observation supports an extended conjugation.

Ligand	R	Yield ^a	MS ^b	UVC
1,10-ph ^d	-	-	_	230 (5.1), 264 (3.0), 280 (1.2)
3a	Н	90%	380.1302 (380.1313)	284 (5.3), 340 (5.7), 354 (4.1)
3 b	CH ₃	87%	408.1607 (408.1626)	286 (4.2), 346 (5.1), 360 (4.6)
3 c	OCH ₃	89%	440.1516 (440.1524)	290 (4.0), ^e 352 (5.5), 368 (4.9)
3d	CF ₃	43%	516.1060 (516.1061)	286 (5.4), 338 (6.4), 352 (5.5)

Table 1. Preparation and selected spectral data for 3.

^a Isolated yields of chromatographically pure products based on 1. ^b Observed and (in parenthesis) calculated EI high resolution mass spectrum. ^c UV spectra of 1×10^{-5} M solutions in acetonitrile. The absorption maxima are given in nm and $10^{-4}\varepsilon$ (in parenthesis) is given in M⁻¹cm⁻¹. Prominent shoulders are italicized. ^d The data for 1,10-phenanthroline is given for comparison. ^e A broad absorption between 268-290 nm is observed.

Scheme

Complex	R	Yielda	MS ^b	UV-vis ^c
 Ru(1,10-Ph)3	-	77 %	-	224 (7.2), 262 (9.6), 290 (2.0), 446 (1.6)
Ru(3a) ₃	Н	60 %	1242 (M+)	280 (6.3), 294 (5.8), 356 (6.5), 376 (5.0), 474 (0.72)
Ru(3b) ₃	CH ₃	86 %	1325 (м ²⁺ -н ⁺)	276 (8.7) , 296 (7.4), 364 (9.8) , 382 (8.2), 474 (0.97)
			1471 (M ²⁺ +PF ₆ ⁻))
Ru(3c)3	OCH ₃	94 %	1422 (M ⁺)	274 (9.3), 300 (5.7), 378 (8.2), 394 (7.7), 472 (0.97)

Table 2. Preparation and selected spectral data for Ru(II) complexes of ligands 3.17

^a Isolated yields of chromatographically pure complexes (based on 3) as their PF₆⁻ salts. ^b Positive FAB mass spectrum. ^c UV-vis spectra were taken in acetonitrile. Absorption maxima are given in nm and $10^{-4}\varepsilon$ (in parenthesis) is given in M⁻¹cm⁻¹. The major bands are bolded and prominent shoulders are italicized.

Upon complex formation, the electronic transitions of 1,10-phenanthroline remain largely unmodified except for a small hypsochromic effect of the two major transitions (Table 2). In contrast, the Ru(II) complexes of ligands **3** show a different behavior (Table 2). Although the higher energy transitions around 280 nm are blue-shifted upon Ru(II) complexation, the lower energy transitions at *ca*. 340 nm are red-shifted (compare Tables 1 and 2). The latter seem to be more sensitive to the nature of the substituent on the phenyl rings with the methoxy derivative Ru(**3c**)₃ suffering the largest shift of more than 25 nm. The visible metal to ligand charge transfer (MLCT) bands, while red-shifted by *ca*. 30 nm in Ru(**3**)₃ compared to Ru(1,10-phen)₃, appear at the same wavelength for all derivatives.¹⁸ Further analysis of the absorption and fluorescence spectra of the new derivatives will shed light on the nature of the electronic transitions of the new ligands and their complexes.

In summary, we have reported the synthesis of a novel series of highly conjugated 3,8-bis(arylethynyl)-1,10-phenanthroline ligands and the preliminary studies of their electronic spectra. It is possible to tune the ligand-centered electronic transitions in the free ligands and in their Ru(II) complexes by changing the substituents on the phenyl rings. We are currently investigating the photophysical properties of the new ligands and their complexation with various metal ions.

References and Notes

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- 12. Phenylacetylene and 4-ethynyltoluene are commercially available. Other aromatic acetylenes have been synthesized as reported: Nguyen, P.; Todd, S.; Van der Biggelaar, D.; Taylor, N.J.; Marder, T.B.; Wittmann, F.; Friend, R.H. *Synlett* **1994**, 299-301.
- 13. In a typical reaction, a degassed solution of phenylacetylene (0.26 ml, 2.5 mmol) in triethylamine (8 ml) and methanol (4 ml) was added under argon to a reaction flask containing 1 (0.1 g, 0.3 mmol), (Ph₃P)₂PdCl₂ (16 mg, 0.03 mmol) and CuI (10 mg, 0.05 mmol). The mixture was sonicated at room temperature under argon for 2-4 hr. The reaction mixture was dissolved in dichloromethane (50 ml), washed with aqueous KCN and water. Drying (MgSO₄) and evaporation afforded the crude product. Flash chromatography (1% methanol/dichloromethane) followed by recrystallization from chloroform afforded **3a**. ¹H NMR (CDCl₃) δ 9.31 (d, *J*=1.9 Hz, 2H, H2,9), 8.41 (d, *J*=1.9 Hz, 2H, H4,7), 7.83 (s, 2H, H5,6), 7.65 (m, 4H, phenyl-H2), 7.36 (m, 6H, phenyl-H3,4); ¹³C NMR (CDCl₃) δ 152.4, 144.3, 138.0, 131.9, 129.0, 128.5, 128.0, 126.8, 122.3, 119.8, 94.0, 86.3.
- 14. The effect of sonication has not been thoroughly investigated. We believe it promotes the reaction by facilitating the solubilization of 1 in the reaction medium.
- 15. The two major bands in the UV spectrum of phenanthroline have been assigned to the long-axis polarized β (230 nm) and β' (264 nm) transitions; see: Bray, R.G.; Ferguson, J.; Hawkins, C.J. Aust. J. Chem. **1969**, 22, 2091-2103. The major transitions of the new ligands are only tentatively assigned here. A careful study of the absorption and fluorescence spectra of the conjugated ligands under various conditions is required for a full analysis.
- 16. Similar effects have been observed in other phenylacetylene conjugated aromatic systems; for example, the major absorption band of 9,10-bis(phenylethynyl)anthracene is red-shifted by 73 nm compared to anthracene. See ref 10.
- 17. In a typical reaction, the ligand 3a (0.1 g, 0.26 mmol) in degassed DMF (10 ml) was treated under argon with a solution of K₂RuCl₅ (33 mg, 0.08 mmol) in water (4 ml) containing 1 drop of 6N HCl. The solution was refluxed for 1 h. Sodium hypophosphite (38 mg, 0.44 mmol) in water (1 ml) was added, and reflux was continued for 1 h. After cooling to 60°C, the reaction mixture was treated with potassium hexafluorophosphate (48 mg, 0.26 mmol) as a 10% aqueous solution, cooled to RT and concentrated *in vacuo*. Silica-gel chromatography using 1% aqueous 0.5 M KNO₃ in acetonitrile as eluent afforded Ru(3a)₃. ¹H NMR (CD₃CN) δ 8.75 (d, J=1.3 Hz, 2H, H2,9), 8.27 (s, 2H, H5,6), 8.18 (d, J=1.3 Hz, 2H, H4,7), 7.45 (m, 10H, phenyl).
- 18. MLCT bands in Ru(II) complexes of other substituted phenanthrolines have been shown *not* to be very sensitive to the nature of the substituents. See for example: Lin, C.-T.; Böttcher, W.; Chou, M.; Creutz, C.; Sutin, N. J. Am. Chem. Soc. 1976, 98, 6536-6544.

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