Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Non-Natural Peptide Containing Ru(II)- and Pd(II)- Bipyridine Complexes in the Main Chain

Taka-Aki Okamura [a], Taku Iwamura [a], Koichi Nozaki [b], Takeshi Ohno [b], Hitoshi Yamamoto [a] & Norikazu Ueyama [a]

[a] Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan

[b] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan

Version of record first published: 18 Oct 2010

To cite this article: Taka-Aki Okamura, Taku Iwamura, Koichi Nozaki, Takeshi Ohno, Hitoshi Yamamoto & Norikazu Ueyama (2003): Non-Natural Peptide Containing Ru(II)- and Pd(II)- Bipyridine Complexes in the Main Chain, Molecular Crystals and Liquid Crystals, 379:1, 431-436

To link to this article: http://dx.doi.org/10.1080/713738675

*Mol. Cryst. Liq. Cryst.*, Vol. 379, pp. 431-436

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290090840



# Non-Natural Peptide Containing Ru(II)- and Pd(II)- Bipyridine Complexes in the Main Chain

TAKA-AKI OKAMURA[a], TAKU IWAMURA[a], KOICHI NOZAKI[b], TAKESHI OHNO[b], HITOSHI YAMAMOTO[a] and NORIKAZU UEYAMA[a]

[a]*Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan and*
[b]*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*

Non-natural peptides containing Ru(II) and Pd(II)-bipyridine complexes in the main chain were synthesized and characterized by spectral measurements and element analysis. The 5,5'-disubstituted derivatives exhibit red-shifted π-π* transition bands, which suggest the presence of extended π-conjugated system. Emission spectra, electrochemical measurements and molecular dynamics (MD) calculations also support this suggestion.

Keywords: non-natural amino acid; peptide; metal complex; bipyridine; palladium; ruthenium

## INTRODUCTION

Polymer containing metal complex in the backbone is one of the most attractive compounds having considerable importance, e.g., magnetic, electronic and optical properties[1]. Many π-conjugated bipyridine derivatives have been synthesized and known to exhibit electric conductivity or photoconductivity when ruthenium ions coordinate to bipyridine units[2-5]. In these polymers, bipyridine units are

symmetrically linked by relatively rigid spacers. Introduction of electric potential orientation to the polymer will lead rectifier or finely designed electric devices. For this purpose, unsymmetrical unit and synergetic effect are necessary.

On the other hand, natural peptides form various secondary structures, which are determined by the contents and kinds of amino acids. Some peptides tend to form α-helix structure. In random conformation, once two amides interacts and then form a hydrogen bond, the *N*-terminus amide NH prefers the next formation of hydrogen bond. The formation is accelerated by large dipole moment and results ordered helix, this process is well-known as helix-coil transition.

We present here new approach to develop functional materials with well-defined structure and directivity. A conceptual combination of metal-containing polymer with peptides gives non-natural peptide containing metal complex in the main chain. For this purpose, a variety of amino acids is required. Previously, we have reported a non-natural amino acid containing a skeletal ferrocene that has freely rotated Fe-Cp (cyclopentadienyl) bond[6]. In this paper, 4,4'- or 5,5'-disubstituted bipyridine derivatives are shown, which have fixed bent angles (60° and 180°, respectively) as shown in Figure 1.

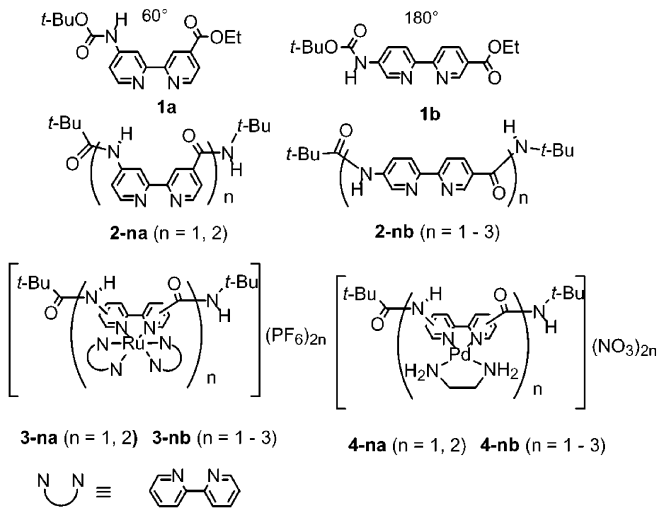


FIGURE 1 Non-natural amino acids and peptides containing 4,4'-and 5,5'-disubstituted bipyridine derivatives.

## EXPERIMENTAL

### Materials

$[Ru(bpy)_2Cl_2]$ (bpy = 2,2'-bipyridine)[7] and $[Pd(en)(H_2O)_2](NO_3)_2$ (en = ethylenediamine)[8] were prepared by the reported method. $[Ru(bpy)_2(OCMe_2)_2](BF_4)_2$ was synthesized in a similar way reported in the literature[9].

### Synthesis

The compounds **1a** and **1b** were prepared by a similar method described in the paper[10]. The ligands **2-na** (n = 1,2), **2-nb** (n = 1-3) were synthesized by a general procedure for liquid-phase peptide synthesis. The ruthenium and palladium compounds, **3-na**, **3-nb**, **4-na** and **4-nb** were obtained by the reaction of the ligand with $[Ru(bpy)_2Cl_2]$, $[Ru(bpy)_2(OCMe_2)_2](BF_4)_2$ and $[Pd(en)(H_2O)_2](NO_3)_2$. For the ruthenium derivatives were obtained as $PF_6^-$ salts by the anion-exchange reaction using an aqueous $NH_4PF_6$ solution. The products were characterized by $^1$H NMR, ESI-MS and elemental analysis.

## RESULTS AND DISCUSSION

### Palladium Derivatives

#### Absorption spectra

The 4,4'-disubstituted derivatives show MLCT band at ca. 310-320 nm in water as found for usual palladium-bipyridine complexes[11]. On the other hands, the 5,5'-disubstituted derivatives exhibit characteristic absorption at 344 (for **4-1b**), 361 (for **4-2b**) and 367 nm (for **4-3b**) due to $\pi$-$\pi^*$ transition. Significant red shift was observed with increasing the degree of polymerization (n). The results suggest the presence of expanded $\pi$-conjugated system in the oligomeric ligands. Molecular dynamics (MD) calculation and $^1$H NMR spectra support it. In the ligand, pyridine moieties are twisted by the repulsion of lone-pair electrons on the nitrogen atom. When the metal ion is coordinated to the nitrogen atoms, the ligand prefers to form a planner structure.

### Ruthenium Derivatives

Absorption spectra

The UV-visible spectra of the ruthenium complexes show a similar trend to the corresponding palladium compounds (Figure 2). The lowest energy π-π* transition was observed at 357 nm for **3-3b**. MLCT bands were observed at normal region (ca. 450-470 nm) for typical tris(bipyridine)ruthenium complexes. Proposed structure of **3-3b** is shown in Figure 3.

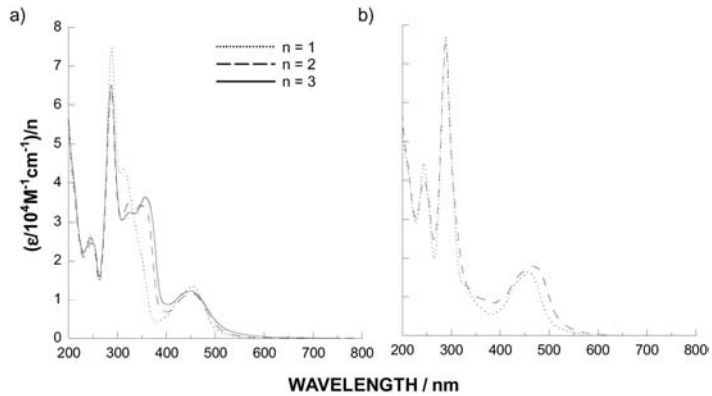


FIGURE 2 UV-visible absorption spectra of a) **3-nb** (n = 1-3) and b) **3-na** (n = 1,2 ) in acetonitrile. The vertical axis is normalized for the concentration of ruthenium ion or polymerization number (n). Absorption maxima: **3-1b**, 312, 452 nm; **3-2b**, 324, 346, 452 nm; **3-3b**, 326, 357, 450 nm; **3-1a**, 456 nm; **3-2a**, 467 nm.

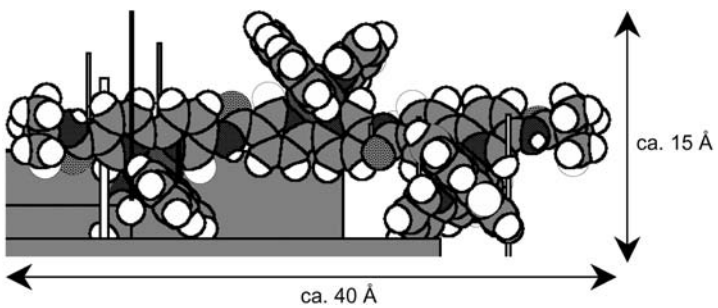


FIGURE 3 Proposed structure of **3-3b** (MD calculation).

Fluorescence spectra

The ruthenium compounds show characteristic emission from $^3$MLCT state at ca. 600-700 nm (Figure 4). In the comparison with $[Ru(bpy)_3](PF_6)_2$, the relatively intense peaks with lower energy show the stabilization of the excited state by the conjugation of bipyridine with amide groups. Emission spectrum (excited at 488 nm in $CH_3CN$) of each dimeric Ru(II) compound, **3-2a** and **3-2b**, show red-shifted maximum by *ca.* 30 nm compared with the corresponding monomeric compounds. The results suggested; the presence of low-lying π* orbital in oligomeric compounds. The low intensity of **3-2b** and **3-3b** indicates the presence of another quenching pathway that is probably intersystem crossing to $^3$π-π* state with lower energy[12].

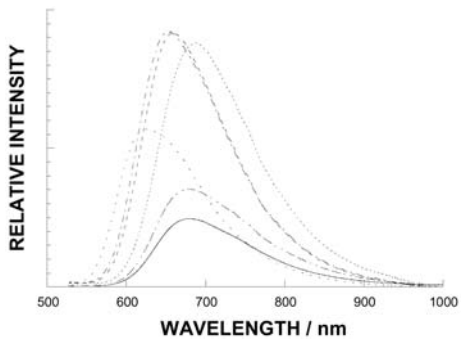


FIGURE 4 Emission spectra of **3-1a** (·····), **3-1b** (–·–·–) **3-2a** (-----), **3-2b** (–·–·–·–), **3-3b** (——) and $[Ru(bpy)_3](PF_6)_2$ (· · ·) excited at 488 nm in acetonitrile.

Electrochemical measurements

Each complex shows one reversible redox couple due to Ru(III/II) and some quasi-reversible couple due to ligand moieties in DMF (Table 1).

TABLE 1 Redox potentials (vs. SCE) of the complexes in DMF.

| | $E_{1/2}$ ($Ru^{III}/Ru^{II}$) | $E_{red}^{I\,a)}$ | $E_{red}^{II\,a)}$ | $E_{red}^{III\,a)}$ |
|---|---|---|---|---|
| **3-1a** | 1.25 | -1.23 | -1.43 | -1.69 |
| **3-2a** | 1.27 | -1.06, -1.29 | -1.44 | -1.70 |
| **3-1b** | 1.31 | -1.19 | -1.42 | -1.67 |
| **3-2b** | 1.32 | -1.04, -1.22 | -1.44 | -1.69 |
| **3-3b** | 1.29 | -0.98, -1.03, -1.28 | -1.45 | -1.68 |

[a)] Each potential corresponds to the reduction of each bipyridine moiety. $E_{red}^{I}$ is assigned to that of the disubstituted bipyridine.

The amide-substituted bipyridine ligand is reduced more easily than the normal bipyridine. $E_{red}^{I}$ separates into two peaks in the dimeric derivatives, **3-2a** and **3-2b**, and into three in the trimeric one, **3-3b**, whereas Ru(III/II) redox couple is found as only one peak. This result indicates that the LUMO (lowest unoccupied molecular orbital) of the current Ru-complexes is localized on the bipyridine ligands interacting each other through the amide bridges, without detectable delocalization onto the metal atoms.

Acknowledgements
This work is supported by a Grant-in-Aid for Encouragement of Young Scientists (No. 12740366).from Japan Society of the Promotion of Science

References

[1.] P. Nguyen, P. Gómez-Elipe and I. Manners, *Chem. Rev.,* **99**, 1515 (1999).
[2.] T. Yamamoto, T. Maruyama, Z.-h. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda and K. Kubota, *J. Am. Chem. Soc.,* **116**, 4832 (1994).
[3.] Q. Wang, L. Wang and L. Yu, *J. Am. Chem. Soc.,* **120**, 12860 (1998).
[4.] K. A. Walters, L. Trouillet, S. Guillerez and K. S. Schanze, *Inorg. Chem.,* **39**, 5496 (2000).
[5.] Z. Peng and L. Yu, *J. Am. Chem. Soc.*, **118**, 3777 (1996).
[6.] T. Okamura, K. Sakauye, N. Ueyama and A. Nakamura, *Inorg. Chem.,* **37**, 6731 (1998).
[7.] P. A. Lay, A. M. Sargeson and H. Taube, *Inorg. Synth.,* **24**, 291 (1986).
[8.] H. D. K. Drew, F. W. Pinkard, G. H. Preston and W. Wardlaw, *J. Chem.Soc.*, 1895 (1932).
[9.] S. C. Yu, X. Gong and W. K. Chan, *Macromolecules*, **31**, 5639 (1998).
[10.] G. R. Newkome, J. Gross and K. Patri, *J. Org. Chem.,* **62**, 3013 (1997).
[11.] P. M. Gidney, R. D. Gillard and B. T. Heaton, *J. Chem.Soc., Dalton Trans.,* 132 (1973).
[12.] J. R. Shaw, R. T. Webb and R. H. Schmehl, *J. Am. Chem. Soc.,* **112**, 117 (1990).