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Synthesis and Characterization of new D-π-D Type Schiff Base Ligands by 1,10-Phenanthroline Derivatives and its Complexes with Ruthenium(II)

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The Schiff base ligands L_1 and L_2 with D-π-D type have been synthesized from the reaction of 5-amino-1,10-phenanthroline and 5,6-diamino-1,10-phenanthroline with 2-(hexyloxy)benzaldehyde. The ruthenium(II) complexes of these ligands were prepared and characterized. The ligands L_1, L_2 and ruthenium complexes have been characterized by FTIR, UV-visible, ^{1}H NMR and fluorescence spectra, as well as, elemental analyses and mass spectra.

Key Words: Schiff base, D-π-D, TPA, Fluorescence spectra.

INTRODUCTION

The past few decades have witnessed an explosion in the field of organic-based conjugated materials. The structural moiety provides a rigidly planar 1,10-phenanthroline and 2,2'-bipyridyl unit with in the molecular backbone. The derivatives of 1,10-phenanthroline, which have excellent hole blocking and electron transporting properties, are likely to have interesting value in the construction of such molecular device too. Moreover, 1,10-phenanthroline compounds have been regarded as excellent fluorescent materials because of their ability to achieve high thermal stability as well as high photoluminescence efficiency. The photochemical and photophysical properties of compounds containing platinum d^6 configuration metals, particularly those based on Ru(II), continue to receive considerable attention[1-8].

As known, Schiff bases are a special class of ligands with a variety of donor atoms exhibiting coordination modes towards various metals. Schiff bases are reagents which are becoming increasingly important in the pharmaceutical, dye and plastic industries as well as for liquid-crystal technology. Schiff bases with donors (N, O, S) have structural similarities with natural biological systems and rasemination reaction in biological systems due to presence of imines (-N=CH-) group[9-16].

Moreover, Schiff base compounds have been regarded as excellent fluorescent materials because of their ability to achieve high thermal stability as well as high photoluminescent efficiencies. Conjugated Schiff base systems that contain electronically coupled photo- and/or redox-active sites across an unsaturated organic bridge are of considerable current interest[17-23].

Many complicated factors can affect the Two-Photon Excitation (TPA) properties of organic materials. So it is important to investigate the structure and the TPA effect relationships of organic materials. However, most of these compounds employ C=C bonds as the conjugation bridge, the compounds with C=N structure such as Schiff bases are less studied to our knowledge[24-26].

In this report, new synthetic procedures for the preparation of such multifunctional 1,10-phenanthrolines derivatives with different fluorescent characteristics with good yield are described. We have focused on the preparation of a new family of conjugated Schiff bases with D-π-D type, in which 1,10-phenanthroline unit are linked together by imine. In this paper, the synthesis and characterization of new Schiff base ligands are reported. The structure of the ligands were determined by elemental analysis, FTIR, UV-visible, ^{1}H NMR and LC-MS spectrometry. The fluorescence properties of the ligands were also examined.

EXPERIMENTAL

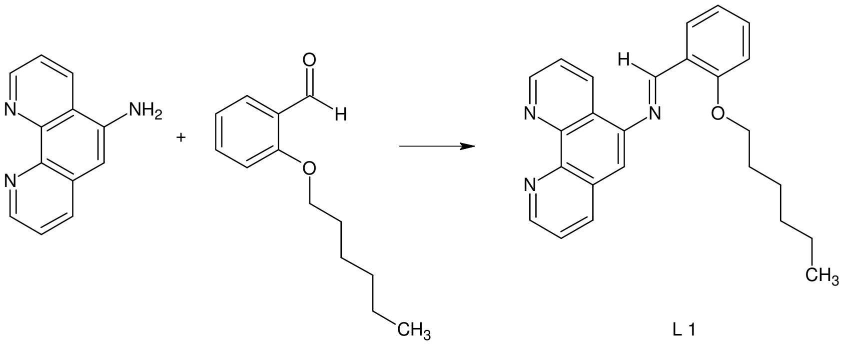
All chemicals were of the highest grade available. FTIR spectra were recorded as KBr disks on a Mattson 1000 FTIR spectrometer. ^{1}H NMR spectra were recorded on a Brucker AC-200 MHz ($CDCl_3$) spectrometer. Absorption spectra were recorded with an Agilent 8453 UV-visible spectrophotometer. The elemental analyses and mass spectra (LC-MS) were determined in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey). Fluorescence spectra were measured on a PTI time master C71 fluorescence spectrophotometer. Melting points were obtained with a BUCHI melting point B-540 apparatus in open capillaries.

The starting compounds, 5-nitro-1,10-phenanthroline, 5-amino-1,10-phenanthroline, 5-nitro-6-amino-1,10-phenanthroline, 5,6-diamino-1,10-phenanthroline, 2-(hexyloxy)benzaldehyde and $Ru(pby)_2Cl_2$ were prepared according the reported procedures[1-4].

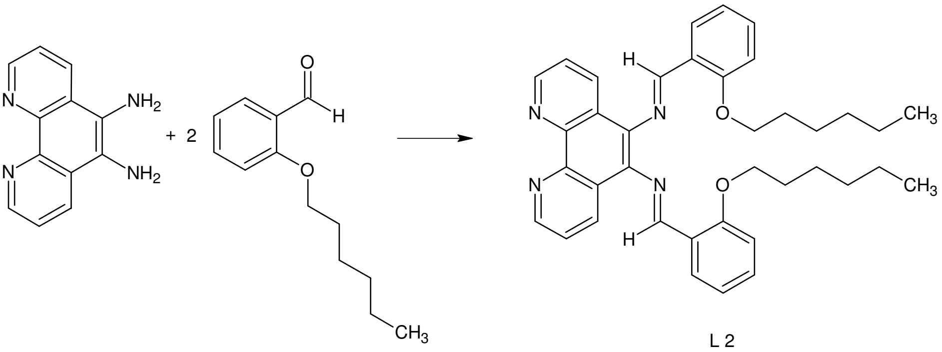
Synthesis of L_1: A solution of 5-amino-1,10-phenanthroline (0.050 g, 0.250 mmol) in 20 mL dry ethanol was added dropwise to a solution of 2-(hexyloxy)-benzaldehyde (0.04 g, 0.040 mmol) in 10 mL of dry ethanol and the mixture was stirred under argon for 9 h at 80 ºC and progress of the reaction was monitored by TLC on silica, ethyl acetate/chloroform 1:2. The solvent was evaporated to half of the initial volume and petroleum ether was added at room temperature. A yellow precipitate was obtained when the solution was cooled to room temperature. It was filtered off and then recrystallized from 1:2 *n*-hexane/ethyl acetate. Yield: 55 %, m.p. 203-205 ºC. IR(KBr, ν_{max}, cm^{-1}, discs): 3060-3032 (Ar, w), 2915-2852 (-CH_3-, m), 1642 ($C=N_{phen}$, s), 1624 (HC=N, s). ^{1}H NMR data (DMSO): δ 9.3 (s, H, HC=N), 9.0-8.4 (m, 7 H, Ar_{phen}-H), 7.8-7.2 (m, 4 H, Ar-H), 3.3 (t, 2H, CH_2), 2.8 (m, 8 H, CH_2) 1.8 (m, 3H, CH_3). LC-MS (APCI) m/z: 355.41 (M^+). ($C_{26}H_{27}N_3O$). Found: C 78.32; H 6.57; N 10.58. Anal. calcd. for: C 78.56; H 6.85; N 10.57 %.

Synthesis of L_2: A solution of 5,6-diamino-1,10-phenanthroline (0.05 g, 0.250 mmol) in 20 mL dry ethanol was added dropwise to a solution of 2-(hexyloxy)-

benzaldehyde (0.04 g, 0.250 mmol) in 10 mL dry ethanol and the mixture was stirred under argon for 12 h at 80 ºC and progress of the reaction was monitored by TLC on silica, ethyl acetate/chloroform 1:2. The solvent was evaporated to half of the initial volume and petroleum ether was added at room temperature. A yellow precipitate was obtained when the solution was cooled to room temperature. It was filtered off and then recrystallized from 2:1 *n*-hexane/ethyl acetate. Yield 45 %, m.p. 244-245 ºC. FTIR (KBr, ν_{max}, cm^{-1}): 3042-3064 (Ar, w), 2912-2855 (-CH_3-, m), 1640 (C=N_{phen}, s), 1620 (HC=N, s), ^{1}H NMR data ($CDCI_3$): δ 9.5-9.4 (d, 2H, HC=N), 9.1-8.3 (m, 7 H, Ar_{phen}-H), 7.7-7.1 (m, 4 H, Ar-H), 3.5 (m, 4H, CH_2), 2.5 (s, 16H, CH_2), 1.5 (s, 6H, CH_3). LC-MS (APCI) m/z: 586.33 (M^+), ($C_{38}H_{42}N_4O_2$). Found: C, 77.81; H, 7.15; N, 9.73 %. Anal. calcd. for: C, 77.78; H, 7.21; N, 9.55 %.



Scheme-I



Scheme-II

L_1-Ru(II) complex: In order to prepare the Ru(II) complex, the L_1 ligand (0.02 g, 0.022 mmol) was dissolved in dry ethanol (20 mL) and $Ru(pby)_2Cl_2$ (0.015 g, 0.022 mmol) in 10 mL of dry ethanol was added to this solution. After addition of 0.01 M KOH solution in ethanol to raise the pH to 7.0-7.5 the mixture was stirred at 80 ºC for 5 h. A dark-yellow precipitate was obtained when the solution was cooled room temperature. It was filtered off, washed with diethyl ether. Yield 0.025 g. (35 %);

m.p. > 350 ºC. IR (KBr, ν_{max}, cm^{-1}): 1608 (H-C=N$_{imine}$), 1622 (C=N$_{phen}$), 2955-2878 (CH$_{aliph}$), 1155 (-C-N). $C_{45}H_{41}N_7OCl_2Ru$ (867.82): Found: C, 62.30; H, 4.72; N, 11.41 %. Anal. calcd. for: C, 62.28; H, 4.76; N, 11.30 %.

L_2-Ru(II) complex: The above procedure was applied using Ru(pby)$_2$Cl$_2$ (0.02 g, 0.023 mmol) at pH to 7.0-7.5. Yield 0.021 g (40 %); m.p. > 350 ºC. IR (KBr, ν_{max} cm^{-1}): 1620 (H-C=N$_{imine}$), 1598 (C=N$_{phen}$), 2950-2884 (CH$_{aliph}$), 1158 (-C-N). $C_{58}H_{58}Cl_2N_8O_2Ru$ (1071.10): Found: C, 65.06; H, 5.44; N, 10.63 %. Anal. calcd. for: C, 65.04; H, 5.46; N, 10.46 %.

RESULTS AND DISCUSSION

The new Schiff base ligands was synthesized from the reaction of 5-amino-1,10-phenanthroline and 5,6-diamino-1,10-phenanthroline with 2-(hexyloxy)benzaldehyde, in a good yield. The IR spectra of the L_1 and L_2 ligands showed a strong band in the region 1642$_{(phen)}$-1624$_{(imine)}$ and 1640$_{(phen)}$-1620$_{(imine)}$ assignable to ν(C=N), respectively. This band disappeared completely in the new complexes indicating the absence of only -C=N$_{(phen)}$ group, because if coordination of the ligand has occurred through the 1,10-phenanthroline nitrogen then this band will undergo a bathochromic shift of 35-30 cm^{-1} and not completely disappear. The absorption band at 1635 cm^{-1} of the C=O in the 2-(hexyloxy)benzaldehyde disappeared in the infrared spectrum of the ligand, which indicate that the condensation has occurred. The alkyl and aryl bands of the ligands are observed at 2910-2850, 1470-1365 and 1155-1150, respectively.

The Schiff bases L_1 and L_2 are subjected to elemental analyses. The results of obtained are in good agreement with those calculated for the suggested formula. The ^{1}H NMR spectrum of the ligands L_1 and L_2 in DMSO solutions confirmed the proposed structure. The ^{1}H NMR spectra of the free ligands, showed besides the aromatic proton signals appearing at 7.2-7.8 and 7.1-7.7 ppm, the assignments of the protons are highly complicated in the region 2.2-2.6 ppm, where the signals are due to the protons of the alkyl, the azomethine proton at 9.3 and 8.5-8.2 ppm, in case of ligands L_1 and L_2, respectively[27-29].

The ligands are stable at room temperature but hygroscopic. The ligands are soluble in common polar organic solvents, such as ethanol, methanol and chloroform but partially soluble in non-polar organic solvents such as, benzene and hexane. The absorption spectrum of L_1 and L_2 extended into the visible region shown typical CT band around 250-290 nm and broad π-π^* transition band around 350-450 nm is a result of extended conjugation of the 1,10-phenanthroline moiety. The peaks recorded in the spectrum are broadened and slightly red-shifted[30-32].

In the mass spectra, the molecular ion peaks of the L_1 appeared at m/z 397.51 [M$^+$] in the LC/MS-APCI spectra. The most intense peaks at m/z 314.12, 298.23, 222.10 and 181.07 correspond to the fragments $[C_{20}H_{15}N_3O]^{2+}$, $[C_{19}H_{13}N_3O]^-$, $[C_{14}H_{11}N_3]^+$, $[C_{12}H_8N_2]$. The molecular ion peaks m/z 586.33 [M$^+$] of the L_2 ligand are present in the LC/MS-APCI spectra and support the proposed structures. The most intense peaks at m/z 419.15, 387.16, 209.09 correspond to the fragments $[C_{26}H_{16}N_4O_2]^{2+}$, $[C_{26}H_{16}N_4]^{3+}$, $[C_{12}H_8N_4]^{+}$, respectively. Mass spectral data confirmed the proposed structure of Schiff base ligands (Fig. 1).

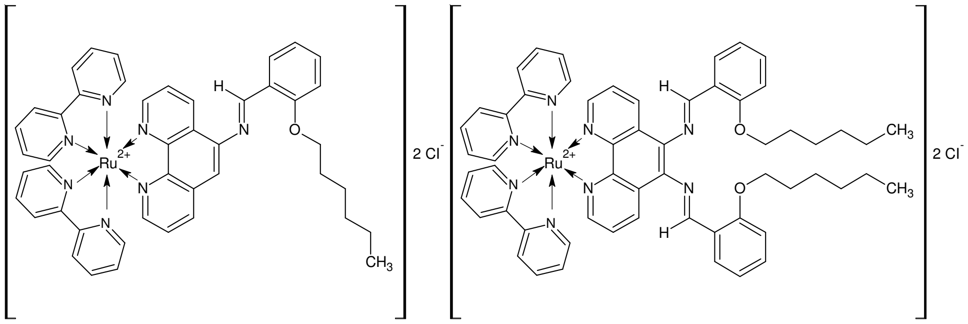


Fig. 1. Suggested structure of the $[Ru(L_1)(bpy)_2]Cl_2$ and $[Ru(L_2)(bpy)_2]Cl_2$ complexes

The solvents used in the fluorescence studies were spectrophotometric grade and were checked by fluorescence spectroscopy to make sure that they contain no fluorescence impurities before use. As a result of several experimental optimum fluorescence emissions of the L_1 and L_2 were obtained in ethanol, methanol and chloroform at room temperature. The emission band maxima of the L_1 were 580 nm in chloroform, 595 nm in methanol, 605 nm in ethanol. The emission band maxima of the L_1 were 585 nm in chloroform, 590 nm in methanol, 610 nm in ethanol. The lifetime of the L_1 and L_2 is measured in ethanol and selected excited-state lifetimes found to be 7.4 and 8.2 ns, respectively. It was found[7,21,32] that the optimum interval of concentration was between 1×10^{-4} and 1×10^{-5} M.

In conclusion, this report has described synthetic routes for the preparation of novel multifunctional 1,10-phenanthroline derivatives. The two compounds have different light-emitting characteristics but are both functional charge transporting materials. Further studies for the two compounds to be used as metal coordination ligand for multifunctional molecular materials are under investigation.

REFERENCES

1. E. Amouyal, A. Homsi, J.-C. Chambron and J.-P. Sauvage. *J. Chem. Soc. Dalton Trans*, 1841 (1990).
2. J. Bolger, A Gourdon, E Ishow and J.-P. Launay, *Inorg. Chem.*, **35**, 2937 (1996).
3. H. Camren, M.Y. Chang, L. Zeng and M.E. McGuire, *Synth. Commun.*, **26**, 1247 (1996).
4. M.S. Deshpande and A.S. Kumbhar, *J. Chem. Sci.*, **117**, 153 (2005).
5. H. Chao, B.-H. Ye, H. Li, R.-H. Li, J.-Y. Zhou and L.-N. Ji, *Polyhedron*, **19**, 1975 (2000).
6. I. Erden, N. Demirhan and U. Avciata, *Synth. React. Inorg. Met.-Org. Nano Met.-Chem.*, **36**, 559 (2006).
7. M.B. Roy, S. Samanta, G. Chattopadhyay and S. Ghosh, *J. Luminescence*, **106**, 141 (2004).
8. W.J. Finkenzeller, T. Hofbeck, M.E. Thompson and H. Yersin, *Inorg. Chem.*, **46**, 5076 (2007).
9. P.K. Sasmal, A.K. Patra and A.R. Chakravarty, *J. Inorg. Biochem.*, **102**, 1463 (2008).

10. H. Keypour, R. Azadbakht, S. Salehzadeh, H. Khanmohammadi, H. Khavasi and H. Adams, *J. Organomet. Chem.*, **693**, 2237 (2008).
11. W.-Y. Wong, G.-L. Lu, K.-F. Ng, C.-K. Wong and K.-H. Choi, *J. Organomet. Chem*., **637**, 159 (2001).
12. I. Erden, A. Erdogmus, N. Demirhan and U. Avciata, *Transition Met. Chem.*, **33**, 439 (2008).
13. Q.-L. Zhang, B.-X. Zhu, L.F. Lindoy and G. Wei, *Inorg. Chem. Commun.*, **11**, 678 (2008).
14. N.E. Borisova, M.D. Reshetova, T.V. Magdesieva, V.N. Khrustalev, G.G. Aleksandrov, M. Kuznetsov, R.S. Skazov, A.V. Dolganov, V.N. Ikorskiy, V.M. Novotortsev, I.L. Eremenko, I.I. Moiseev and Y.A. Ustynyuk, *Inorg. Chim. Acta*, **361**, 2032 (2008).
15. S. Sreedaran, K.S. Bharathi, A.K. Rahiman, K. Rajesh, G. Nirmala, L. Jagadish, V. Kaviyarasan and V. Narayanan, *Polyhedron*, **27**, 1867 (2008).
16. H.D. Leçe, K.C. Emregül and O. Atakol, *Corr. Sci.*, **50**, 1460 (2008).
17. C. Tang, F. Liu, Y.-J. Xia, J. Lin, L.-H. Xie, G.-Y. Zhong, Q.-L. Fan and W. Huang, *Org. Electro*., **7**, 155 (2006).
18. Y. Sun and K. Yasukawa, *Bioorg. Med. Chem. Lett.*, **18**, 3417 (2008).
19. F. Habrard, T. Ouisse, O. Stéphan, L. Aubouy, Ph. Gerbier, L. Hirsch, N. Huby and A. Van der Lee, *Synth. Metals*, **156**, 1262 (2006).
20. R.C. Evans, P. Douglas and C.J. Winscom, *Coord. Chem. Rev.*, **250**, 2093 (2006).
21. W.-Y. Wong, *Coord. Chem. Rev*., **249**, 971 (2005).
22. A.A.A. Emara and A.A.A. Abou-Hussen, *Spectrochim. Acta*, **64A**, 1010 (2006).
23. Z. Popovic, V. Roje, G. Pavlovic, D. Matkovic-Calogovic, M. Rajic and G. Giester, *Inorg. Chim. Acta*, **322**, 65 (2001).
24. A. Loaiza-Gil, M. Villarroel, J.F. Balbuena, M.A. Lacruz and S. Gonzalez-Cortés, *J. Mole. Catal. A: Chem.*, **281**, 207 (2008).
25. D.-H. Huang, C.-H. Hsu, Y.-C. Lin, C.-L. Chang, K.-W. Wong and W.-Y. Ho, *Surface Coat. Tech.*, **201**, 6681 (2007).
26. R. Ziessel, *Coord. Chem. Rev.*, **216**, 195 (2001).
27. H.J. Bolink, E. Barea, R.D. Costa, E. Coronado, S. Sudhakar, C. Zhen and A. Sellinger, *Org. Electr.,* **9**, 155 (2008).
28. L. Tian, Z. Hu, P. Shi, H. Zhou, J. Wu, Y. Tian, Y. Zhou, X. Tao, M. Jiang, *J. Luminescence*, **127**, 423 (2007).
29. D.S. Tyson, C.R. Luman, X. Zhou and F.N. Castellano, *Inorg. Chem*., **40**, 4063 (2001).
30. J.T. Warren, W. Chen, D.H. Johnston and C. Turro, *Inorg. Chem*., **38**, 6187 (1999).
31. J. Chen and F.M. MacDonnell, *Chem. Commun*., 2529 (1999).
32. C. Bonnefous, A. Chouai and R.P. Thummel, *Inorg. Chem*., **40**, 5851 (2001).

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