Scientific paper

Synthesis and Properties of two Cu^I Complexes Involving Tetrathia-fulvalene-Fused Phenanthroline Ligand

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Abstract

Two Cu^I complexes based on the π -conjugated tetrathiafulvalene-annulated phenanthroline ligands (TTF-Phen, \mathbf{L}_1 and \mathbf{L}_2), $[Cu^I(Xantphos)(\mathbf{L}_1)]BF_4$ (1, Xantphos = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene) and $[Cu^I(Binap)(\mathbf{L}_2)]BF_4$ (2, Binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl), have been synthesized. They have been fully characterized, and their photophysical and electrochemical properties are reported together with those of \mathbf{L}_1 and \mathbf{L}_2 for comparison. Both Cu^I complexes show metal-to-ligand charge transfer (MLCT) absorption bands, whereas the ³MLCT luminescence is strongly quenched.

Keywords: Copper(I) complexes; Tetrathiafulvalene ligands; Photoluminescence; Cyclic voltammetry

1. Introduction

In the recent study of TTF chemistry, multifunctional molecular material involving interplay and synergy between multiple physical properties have received considerable attention. An established strategy for the preparation of such molecular materials is the combination of functional groups and electro-active TTF moieties. Indeed, in the past years this strategy has led to materials exhibiting novel photofunctional properties, such as fluorescence switches, metal ion sensors, photovoltaic cells, and nonlinear optics. Following this strategy, we recently reported two TTF-based Cu^I complexes, [Cu^I(Binap)(TTF-TzPy)]BF₄ and [Cu^I(Xantphos)(TTF-Tz-Py)]BF₄, which exhibit interesting electrochemical and photophysical properties.

However, TTF-TzPy is a non-conjugated system with σ -bonded molecular bridge. Thus, in this paper, we

use more π -conjugated TTF-Phen ligand instead of TTF-TzPy ligand to form two Cu^I complexes, $[Cu^I(Xantphos)(L_1)]BF_4$ (1, Xantphos = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene) and $[Cu^I(Binap)(L_2)]BF_4$ (2, Binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl). The photophysical and electrochemical properties of these complexes are investigated.

2. Experimental

2. 1. Materials and Measurements

All air-sensitive and/or water-sensitive reactions were carried out under a dry nitrogen atmosphere. All commercial chemicals were used without further purification unless otherwise stated. Solvents were dried and degassed following standard procedures. Column chromatography was carried out using 200–300 µm mesh silica.

Scheme 1. Synthetic routes of Cu^I complexes 1–2.

4',5'-dimethyldithiotetrathiafulvenyl[4,5-f][1,10]phenanthroline ($\mathbf{L_1}$) and 4',5'-bis(methyloxycarbonyl)dithiotetrathiafulvenyl[4,5-f][1,10]phenanthroline ($\mathbf{L_2}$) were synthesized according to the literature. ¹⁴

¹H NMR spectra were recorded on a Bruker AM 400 MHz instrument. Chemical shifts were reported in ppm relative to Me₄Si as internal standard. ESIMS spectra were recorded on an Esquire HCT-Agilent 1200 LC/MS spectrometer. FT-IR spectra were taken on a Nicolet 6700 FTIR spectrometer (400–4000 cm⁻¹) with KBr pellets. The thermoanalytical anaysis (TG) was performed with a simultaneous NETZSCH STA 449C thermal analyzer. The elemental analyses were performed on a Vario EL Cube Analyzer system. UV-Vis spectra were recorded on a Hitachi U3900/3900H spectrophotometer. Fluorescence spectra were carried out on a Hitachi F–7000 spectrophotometer.

2. 2. Synthesis

2. 2. 1. Preparation of $[Cu^{I}(Xantphos)(L_1)]BF_4(1)$

To a solution of $\mathbf{L_1}$ (30 mg, 0.067 mmol) in degassed, dry DCM (5 mL) and MeOH (5 mL), was added [Cu¹(MeCN)₄]BF₄ (25 mg, 0.080 mmol) and Xantphos (42 mg, 0.074 mmol). Then the mixture was degassed by vacuum and charged with N₂ (three times). The mixture was stirred at room temperature for 5 h under nitrogen atmosphere. The resulting solution was concentrated and Et₂O was added to precipitate the product $\mathbf{1}$ (42 mg, yield: 53%) as a red solid. ¹H NMR (400 MHz, CDCl₃) δ 8.50 (d, J = 4.4 Hz, 2H), 8.15 (d, J = 8.0 Hz, 2H), 7.85 (dd, J₁ = 4.8 Hz, J₂ = 8.0 Hz, 2H), 7.69 (d, J = 7.6 Hz, 2H), 7.11~7.25 (m, 8H), 7.04~7.08 (m, 8H), 6.86~6.91 (m, 8H), 2.49 (s, 6H), 1.78 (s, 6H). FT-IR (KBr, cm⁻¹):

3056(w), 2922(w), 1578(w), 1405(s), 1228(m), 1058(s), 746(m), 696(m). MS (EI): m/z 1089.1 (M-BF₄). Anal. Calcd for $C_{57}H_{44}BCuF_4N_2OP_2S_6$ (%): C 58.14, H 3.77, N 2.38; Found: C 57.87, H 3.53, N 2.42.

2. 2. 2. Preparation of $[Cu^{I}(Binap)(L_2)]BF_4(2)$

[Cu^I(Binap)(MeCN)₂]BF₄ (60 mg, 0.070 mmol) and L_2 (30 mg mg, 0.063 mmol) were stirred in degassed, dry DCM (5 mL) and MeOH (5 mL) for 5 h under nitrogen atmosphere. The resulting solution was concentrated and Et₂O was added to precipitate the product **2** (38 mg, yield: 48%) as a red solid. ¹H NMR (400 MHz, CDCl₃) δ 8.74 (s, 2H), 8.12 (d, J = 6.8 Hz, 2H), 7.92 (s, 2H), 7.31~7.34 (m, 6H), 7.07~7.18 (m, 26H), 3.89 (s, 6H). FT-IR (KBr, cm⁻¹): 3056(w), 2925(w), 1727(s), 1576(m), 1433(s), 1269(s), 1060(s), 749(m), 697(m). MS (EI): m/z 1157.1 (M-BF₄). Anal. Calcd for $C_{64}H_{44}BCuF_4N_2O_4P_2S_4$ (%): C 61.71, H 3.56, N 2.25; Found: C 61.45, H 3.58, N 2.12.

2. 3. Cyclic Voltammetry

Cyclic voltammetry (CV) was performed on a CHI 1210B electrochemical workstation, with a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, an aqueous saturated calomel electrode (SCE) as the reference electrode, and 0.1 M n-Bu $_4$ NClO $_4$ as the supporting electrolyte.

3. Results and Discussion

The synthetic routes to complexes **1–2** are shown in Scheme 1. The TTF-fused ligands, copper(I) salt and PČP

ligands were added in dry DCM and MeOH, and coordinated to afford corresponding Cu^I complexes **1–2**. The crude product was recrystallized from dichloromethane and diethyl ether. Complexes **1–2** were characterized by IR, ESI-MS, elemental analysis, ¹H NMR, UV-vis, FL spectra and cyclic voltammetry.

3. 1. IR and ESI Spectra

In the IR spectrum of complexes 1 and 2 (Fig. S1 and Fig. S2), their spectra have almost the same tendency. The peaks at 3056, 2922, 1405 cm $^{-1}$ for 1 and 3056, 2925, 1433 cm $^{-1}$ for 2 are ν_{C-H} of CH_3 group and ν_{Ar-H} , and the strong absorption peak at 1058 cm $^{-1}$ for 1 and 1060 cm $^{-1}$ for 2 are attributed to B–F stretches of BF_4^- group. Moreover, the strong absorption peaks at 746 and 696 cm $^{-1}$ for 1 and 746, 696 cm $^{-1}$ for 2 are δ_{C-CH} . Particularly, the strong absorption peaks at 1727 cm $^{-1}$ for 2 are attributed to C=O stretches of CO_2Me group.

The structure of complexes **1** and **2** was also studied by electrospray ionization mass spectrometry (ESI-MS). A positive ion ESI-MS of complexes **1** and **2** (Fig. S3 and Fig. S4) were measured in methanol solution. The main peak at m/z 1089.1 of **1** is $[Cu^{I}(Xantphos)(L_{1})]^{+}$ ion and m/z 1157.1 of **2** is $[Cu^{I}(Binap)(L_{2})]^{+}$ ion, respectively.

3. 2. Photophysical Properties

3. 2. 1. Absorption Properties

The absorption spectra of the ligands $\mathbf{L_1}$ – $\mathbf{L_2}$ and complexes 1–2 were measured in dichloromethane solution at room temperature (Fig. 1), and the data are provided in Table 1. For complexes 1–2, absorption spectra are similar to that of the free ligand $\mathbf{L_1}$ – $\mathbf{L_2}$. Intense absorption bands from 250 to 350 nm at high energy are observed, which is attributed to spin-allowed intraligand (π - π *) transitions. Compared with $\mathbf{L_1}$ – $\mathbf{L_2}$, the absorption bands at

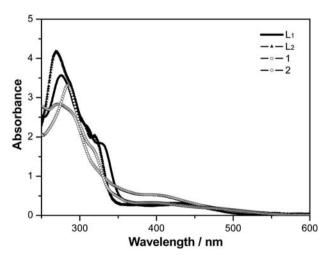


Fig. 1. Electronic absorption spectra of ligands L_1 – L_2 and complexes 1–2 in CH₂Cl₂ at room temperature.

Table 1. Photophysical data for compounds L₁-L₂ and 1-2

C1	Absorption	Emission	
Complex	$\lambda_{abs} (nm)^a$	$\lambda_{em} (nm)^a$	
$\mathbf{L_1}^b$	275, 308, 326, 435	382, 400	
$egin{array}{c} \mathbf{L_1}^b \ \mathbf{L_2}^b \end{array}$	268, 318, 436	381, 400	
1	271, 288, 406	383, 406	
2	284, 317, 406	381, 434	

^a Measured in degassed CH₂Cl₂ solution at room temperature. ^b Data from ref. 13.

low energy ($\lambda > 350$ nm) of complexes 1–2 are slightly blue shifted, and the intensities are increased around 400–410 nm, which may be related to metalation of the ligand.¹⁵

3. 2. 2. Emission Properties

The normalized emission spectra of the ligands $\mathbf{L_1}$ – $\mathbf{L_2}$ and complexes $\mathbf{1}$ – $\mathbf{2}$ in $\mathrm{CH_2Cl_2}$ solution are presented in Fig. 2. The emission data are also included in Table 1. In comparison to the related ligands, the emission spectra of complexes $\mathbf{1}$ – $\mathbf{2}$ exhibit similar emission. The emission maxima at 381–383 nm and a shoulder peak at 406–434 nm are observed resulting from the ligand-centered (LC) π – π * relaxations. However, no obvious emissions with 3 MLCT character are found. Similar observations are also found in other metal complex systems. $^{16-17}$

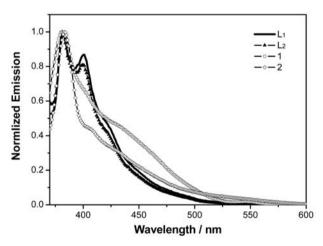


Fig. 2. Normalized emission spectra of ligands $L_1\!-\!L_2$ and complexes 1–2 in CH₂Cl, at room temperature.

3. 3. Electrochemical Properties

Electrochemical properties of the complexes 1-2 were investigated by cyclic voltammetry in CH_3CN/CH_2Cl_2 as illustrated in Fig. 3, and their electrochemical data are collected in Table 2. All compounds $(\mathbf{L_1}-\mathbf{L_2}, \mathbf{1}-\mathbf{2})$ exhibit two one-electron oxidation processes, which are associated with the successive oxidation of the

TTF unit to TTF⁺ and TTF²⁺. The redox potentials $E_{1/2}^{-1}$ and $E_{1/2}^{-2}$ for **1** are 0.79 and 0.98 V, and those for 2 are 0.93 and 1.15 V, respectively. Upon coordination, the two oxidation processes of TTF subunits for 1-2 are shifted to more positive potentials in comparison with the respective ligands (Table 2). This is attributed to the electron-withdrawing inductive effect of Cu^I core. 12 For the previously synthesized Cu^I complexes based on TTF-TzPy, redox potentials for the ligand and Cu^I complexes have no obvious change.¹³ These differences result is that we use different types of ligands. TTF-TzPy is a non-conjugated system with σ -bonded molecular bridge, which is unfavorable to the transmission of electrons. However, we use more π -conjugated TTF-Phen ligand and the phen unit is grafted on the TTF core through a conjugated spacer group, which is advantageous to intramolecular electron transfer and communications. Consequently, Cu^I complexes 1-2 possess better electron-withdrawing abilities than the free ligands.

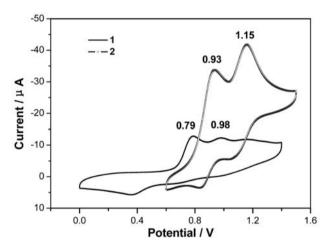


Fig. 3. Cyclic voltammogram of **1–2** measured in CH_3CN/CH_2Cl_2 (1:1) solution containing n-Bu₄NClO₄ (0.1 M), at a scan rate of 100 mV/s.

3. 4. Thermal Stability

The TG analyses were carried out from 30 °C to 700 °C in $\rm N_2$ atmosphere with a heating rate of 10 °C min⁻¹. As shown in Fig.4, complex 1 began to lose weight at approximately 295 °C and continuous decomposition is observed during 295 to 650 °C with the increase of temperature. The residue weight of 6.94% is due to CuO and is in agreement

with the calculated value of 6.76%. For complex **2**, no weight loss was observed up to 250 °C, indicating that it is stable below 250 °C. With the increase of temperature, the organic fragments start to decompose gradually in range of 250 to 640 °C. The residue weight of 6.68% is due to CuO and is in agreement with the calculated value of 6.38%.

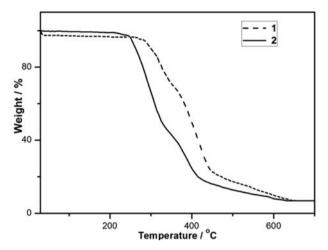


Fig. 4. TG curves of complexes 1 and 2

4. Conclusions

In summary, we have synthesized two new Cu^I complexes with TTF-Phen as the ligands, $[Cu^I(Xantp-hos)(L_1)]BF_4$ (1) and $[Cu^I(Binap)(L_2)]BF_4$ (2). Their thermal stability, photophysical properties and electrochemical behaviors have been investigated. The two new Cu^I complexes are stable below 250 °C. The emission of complexes 1–2 is no longer of 3MLCT but rather of ligand-centered (LC) nature. The interesting redox-active properties for complexes 1 and 2 have been evidenced by electrochemical studies. The association of the redox-active bridging TTF ligand to a variety of mixed-ligand transition-metal complexes may pave the way to obtain multifunctional materials, which are currently under investigation in our laboratory.

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Table 2. Electrochemical data for compounds L_1-L_2 and 1-2

Complex	$E_{1/2}^{1}(V)^{a}$	$E_{1/2}^{2}(V)^{a}$	Complex	$E_{1/2}^{-1}(V)^a$	$E_{1/2}^{2}(V)^{a}$
$\mathbf{L_1}^b$	0.48	0.75	1	0.79	0.98
$\mathbf{L_2^{'b}}$	0.64	0.94	2	0.93	1.15

^a Measured in CH₂Cl₂/CH3CN solution (1/1, v/v) containing 0.1 M n-Bu₄NClO₄ and the scan rate was 100 m-V/s. ^b Data from ref. 13.

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6. References

- H. Y. Wang, L. Cui, J. Z. Xie, C. F. Leong, D. M. D'Alessandro, J. L. Zuo, *Coord. Chem. Rev.* 2017, 345, 342–361. http://www.sciencedirect.com/science/article/pii/S00108545 16303563
- L. Cui, J. Y. Ge, C. F. Leong, D. M. D'Alessandro, J. L. Zuo, Dalton Trans. 2017, 46, 3980–3988. http://pubs.rsc.org/en/content/articlepdf/2017/dt/c6dt04903f
- 3. J. L. Segura, N. Martin, Angew. Chem. Int. Ed. 2001, 40, 1372–1409.
 - http://onlinelibrary.wiley.com/doi/10.1002/1521-3773 (20010417)40:8%3C1372::AID-ANIE1372%3E3.0.CO;2-I/pdf
- 4. (a) Z. G. Niu, H. Xie, L. R. He, K. X. Li, Q. Xia, D. M. Wu, G. N. Li, *Acta. Chim. Slov.* 2016, 62, 323–326. https://journals.matheo.si/index.php/ACSi/article/download/2246/951
 - (b) Z. G. Niu, L. R. He, L. Li, W. F. Cheng, X. Y. Li, H. H. Chen, G. N. Li, *Acta. Chim. Slov.* **2014**, *61*, 786–791.
- https://journals.matheo.si/index.php/ACSi/article/view/473
- I. N. Avarvari, K. Kiracki, R. Llusar, V. Polo, I. Sorribes, C. Vicent, *Inorg. Chem.* 2010, 49, 1894–1904. http://pubs.acs.org/doi/pdf/10.1021/ic902244m
- F. Riobé, N. Avarvari, Coord. Chem. Rev. 2010, 254, 1523– 1533.
 - http://www.sciencedirect.com/science/article/pii/S00108545 09003324
- A. Kobayashi, E. Fujiwara, H. Kobayashi, *Chem. Rev.* 2004, 104, 5243–5264.

- http://pubs.acs.org/doi/pdf/10.1021/cr0306561
- S. Wenger, P.-A. Bouit, Q. Chen, J. Teuscher, D. D. Censo, R. Humphry-Baker, J.-E. Moser, J. L. Delgado, N. Martín, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* 2010, 132, 5164–5169.
 - http://pubs.acs.org/doi/pdf/10.1021/ja909291h
- F. G. Brunetti, J. L. López, C. Atienza, N. Martín, *J. Mater. Chem.* 2012, 22, 4188–4205.
 http://pubs.rsc.org/en/content/articlelanding/2012/jm/c2jm 15710a
- D. Canevet, M. Sallé, G. X. Zhang, D. Q. Zhang, D. B. Zhu, Chem. Commun. 2009, 2245–2269. http://pubs.rsc.org/en/content/articlelanding/2009/cc/ b818607n
- 11. G. X. Zhang, D. Q. Zhang, X. F. Guo, D. B. Zhu, *Org. Lett.* **2004**, *6*, 1209–1212.
 - http://pubs.acs.org/doi/pdf/10.1021/ol036511i
- J. Qin, S. Y. Deng, C. X. Qian, T. Y. Li, H. X. Ju, J. L. Zuo, J. Organomet. Chem. 2014, 750, 7–12.
 http://www.sciencedirect.com/science/article/pii/S0022328 X1300781X
- G. N. Li, L. R. He, D. Xia, L. Li, W. F. Cheng, K. X. Li, F. Cui, Z. G. Niu, *J. Chin. Chem. Soc.* 2015, 62, 889–897.
 http://onlinelibrary.wiley.com/doi/10.1002/jccs.201500251/pdf
- J. Qin, L. Hu, G. N. Li, X. S. Wang, Y. Xu, J. L. Zuo, X. Z. You, *Organometallics*, 2011, 30, 2173–2179. http://pubs.acs.org/doi/pdf/10.1021/om101141h
- J.-C. Wu, S.-X. Liu, T. D. Keene, A. Neels, V. Mereacre, A. K. Powell, S. Decurtins, *Inorg. Chem.* 2008, 47, 3452–3459. http://pubs.acs.org/doi/pdf/10.1021/ic800138x
- R. Sahai, D.P. Rillema, R. Shaver, S. V. Wallendael, D. C. Jackman, M. Boldaji, *Inorg. Chem.* 1989, 28, 1022–1028. http://pubs.acs.org/doi/pdf/10.1021/ic00305a008
- 17. A. Vorler, J. Kisslinger, *Inorg. Chim. Acta.* **1986**, *115*, 193–196.
 - http://www.sciencedirect.com/science/article/pii/S00201693 00844138

Povzetek

Sintetizirali smo dva Cu^I kompleksa s π -konjugiranim tetratiafulvalen vsebujočim fenantrolinskim ligandom (TTF-Phen, $\mathbf{L_1}$ in $\mathbf{L_2}$) [$Cu^I(Xantphos)(\mathbf{L_1})$]BF $_4$ (1, Xantphos = 9,9-dimetil-4,5-bis(difenilfosfino)ksanten) in [Cu^I (Binap)($\mathbf{L_2}$)]BF $_4$ (2, Binap = 2,2'-bis(difenilfosfino)-1,1'-binaftil) ter ju okarakterizirali in določiti fotofizikalne in elektrokemijske lastnosti v primerjavi z ligandoma $\mathbf{L_1}$ in $\mathbf{L_2}$. Oba Cu^I kompleksa izkazujeta absorpcijski vrh za prenos naboja s kovine na ligand (MLCT), medtem ko je 3 MLCT luminescenca preprečena.