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Synthesis, photoluminescence and electrochemical properties of a series of carbazole-functionalized ligands and their silver(I) complexes

Jie-Ying Wu^{a,*}, Yue-Li Pan^a, Xuan-Jun Zhang^a, Tao Sun^a, Yu-Peng Tian^{a,b,*}, Jia-Xiang Yang^a, Zhong-Ning Chen^c

^a Department of Chemistry, Anhui University, Hefei, Anhui 230039, China

^b State Key Laboratory of Coordination Chemistry, Nanjing University, China

^c State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, China

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Abstract

A series of carbazole-functionalized carboxylate ligands (*N*-carbazolylacetic acid (**L1**), 4-carbazol-9-yl-benzoic acid (**L2**), and 3-(4-carbazol-9-yl-phenyl)-acrylic acid (**L3**)) and their corresponding silver complexes were designed and synthesized and the structures were determined by single crystal X-ray diffractions. The silver atoms in the complexes are in tetrahedral geometry coordinated with two oxygen from carboxylic and two phosphorous atoms from triphenylphosphine. The complexes exhibit excellent electrochemical characters in solution and strong photoluminescence in the solid state. The emission wavelengths of the compounds can be tuned (from ultraviolet to visible region) by introducing of the second coordinating ligand triphenylphosphine and by elongation of the conjugation moieties. © 2006 Elsevier B.V. All rights reserved.

Keywords: Coordination; Crystal structure; Carbazole; Photoluminescence; Ligand

1. Introduction

Luminescent coordination compounds have been an active research area for decades because of their various potential applications in material science, such as electroluminescent display and chemical sensors [1–4]. By carefully selecting the organic and inorganic components new or enhanced phenomena can arise [5]. For example, by changing metal ions or introducing second coordinating ligand, hybrids with enhanced emissions, tunable emission wavelengths, or enhanced thermo stabilities can be obtained [6].

Carbazole compounds are well known to exhibit good hole transporting properties and their charge transfer (CT) complexes can create free carriers in the visible region through the photocarrier generation process [7]. Several electroluminescence (EL) materials containing carbazole group have been used in light emitting diodes (LEDs) devices [8,9], most of which are pure organic compounds or polymers. We have previously demonstrated that hybrids materials with new emissions and enhanced thermal stability were obtained by introducing carbazole group and second ligand such as 1,10-phenanthroline or triphenylphosphine into coordination complexes [10]. In those work, ethanoic acid group was combined with carbazole group (Scheme 1, (L1)). The introduce of carboxylate groups is because of it's rich binding modes with metal ions, which can lead to complexes with versatile molecular structures. However, the emission wavelengths are less than 400 nm due to the relatively little conjugation moiety. In this work, two new ligands (L2 and L3) with relatively longer conjugation moieties and their corresponding silver complexes emitting in the visible region have been synthesized and characterized by single crystal X-ray diffraction. Herein, we report the design, synthesis, crystal structure, optical and electrochemical properties of these three ligands and corresponding silver complexes.

^{*} Corresponding authors. Address: Department of Chemistry, Anhui University, Hefei, Anhui 230039, China. Fax: +86 551 5107342 (Y.-P. Tian).

E-mail addresses: jywu1957@163.com (J.-Y. Wu), yptian@ahu.edu.cn (Y.-P. Tian).

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2. Experimental

2.1. Materials

All chemicals and solvents were dried and purified by usual methods. The ligand N-carbazolylacetic acid (L1) was synthesized by the method as we had reported [10]. Elemental analyses were performed with a Perkin-Elmer 240 instrument. IR spectra were recorded with a Nicolet FT-IR 170SX instrument (KBr discs) in the 4000- 400 cm^{-1} region. UV–Vis spectra were recorded with a UV-265 spectrophotometer and corrected by subtracting solvent backgrounds. TGA analyses were recorded with a Perkin-Elmer Pris-1 DMDA-V1 analyzer in a atmosphere of nitrogen at a heating rate of 5 °C min⁻¹. The luminescence spectra were recorded on a Perkin-Elmer LS50B spectrofluorimeter. Electrospray mass spectra (ES-MS) were determined with a Finnigan LCQ mass spectrograph; the concentration of the samples was about 1.0 mmol L^{-1} . The diluted solution was electrosprayed at a flow rate of 5×10^{-6} L min⁻¹ with a needle voltage of 4.5 kV. The mobile phase was an aqueous solution of methanol (1:1, v/v). The samples were run in the positive-ion mode.

Cyclic voltammograms were obtained on an EG&G PAR 283 potentiostat at 20 °C, using acetonitrile as solvent for the ligands and DMF for complexes, 0.1 M Bu₄NClO₄ as supporting electrolyte. The potentials were referred to an Ag–AgCl electrode separated from the solution by a medium-porosity fritted disk. A platinum-wire auxiliary electrode was used in conjunction with a platinum-disk-working electrode cyclic voltammograms of a freshly prepared (1 mM) solution of all compounds in solution recorded at 0.05 V s⁻¹ in the -1.5 to 2.0 V range, and the values of compounds and a measured potentials were afterward referred to Ag–AgCl.

3. Preparations

3.1. 4-Carbazol-9-ylbenzaldehyde (a)

The compound was prepared by modification of the previously reported method in a high yield [11]. Carbazole (8.40 g, 50 mmol), fresh potassium tert-butoxide (5.60 g, 50 m mol) and anhydrous dmf (200 mL) were mixed in a flask fitted with a magnetic stirrer and condenser. The mixture was heated at 110 °C for 0.5 h, 4-fluorobenzaldehyde (6.20 g, 50 mmol) was added dropwise into it with stirring for 36 h. The mixture was cooled to room temperature, and poured into ice water. After 30 min of stirring, the mixture was filtered, and evaporated. The crude residue was recrystallized by acetone/water (10:1). Pale yellow powder was obtained (9.49 g, 70%). Mp 163 °C. Anal. Calc. for C₁₉H₁₃ON: C, 84.13; H, 4.80; N, 5.17. Found: C, 84.40; H, 4.77; N, 5.12%. IR (KBr, pellet, cm^{-1}) 3419 (s), 3056 (w), 1597 (s), 1509 (m), 1480 (w), 1448 (s), 1360 (m), 1337 (m), 1220 (m), 1158 (m), 1125 (m), 830 (m) 753 (s). UV-Vis (dmf solution). λ/nm (log ε): 265.5 (4.13), 292.0 (4.35), 326.2 (3.70), 341.1 (3.40).

3.2. 4-Carbazol-9-yl-benzoic acid (L2)

4-Carbazol-9-ylbenzaldehyde (2.71 g, 10 mmol), H₂O₂ (11.32 mL) and NaOH (0.4 g, 10 mmol) were solved in the mixed solvent of dioxane (5 mL), the mixture was stirred at 0 °C for 2 h, then was heated to reflux overnight and filtered. The filtration was adjusted to pH = 2 with HCl solution, filtered again. The crude residue was re-crystallized in acetone/water (5:1) and dried in vacuum. Yield was 71% (2.04 g). *Anal.* Calc. for C₁₉H₁₃O₂N: C, 79.14; H, 4.38; N, 4.69. Found: C, 79.44; H, 4.53; N, 4.87%. ES-MS, *m*/*z* 286.3. IR (KBr, pellet, cm⁻¹) 3450 (s), 3076 (w), 1687 (s), 1600 (s), 1524 (m), 1483 (w), 1448 (s), 1421 (s), 1356 (m), 1287 (s), 1222 (m), 1165 (m), 1127 (w), 753 (s). UV–Vis (dmf solution). λ /nm (log ε): 265.5 (4.21), 292.0 (4.48), 326.2 (3.90), 341.1 (3.71). Weight loss at: 330 °C.

3.3. 3-(4-Carbazol-9-yl-phenyl)-acrylic acid (L3)

4-Carbazol-9-ylbenzaldehyde (2.71 g, 10 mmol), malonic acid malonic acid (2.16 g, 0.03 mol), in pyridine were mixed with four drops of piperidine. The reaction was stirred at 90 °C for 2 h, followed by adjustment of pH = 2 with HCl solution. A yellow crude product was obtained and re-crys-

tallized with toluene and dried in vacuum. Yield was 95% (2.97 g). *Anal.* Calc. for C₂₁H₁₅O₂N: C, 80.51; H, 4.791; N, 4.47. Found: C, 80.43; H, 4.8; N, 4.50%. ES-MS, *m/z* 312.0. IR (KBr, pellet, cm⁻¹) 3449 (s), 3056 (w), 1686 (s), 1628 (s), 1599 (s), 1514 (s), 1449 (s), 1424 (m), 1361 (w), 1313 (m), 1223 (s), 1169 (m), 753 (s). UV–Vis (dmf solution). λ /nm (log ε): 265.5 (4.83), 292.0 (4.65), 326.2 (3.70), 341.1 (3.40). Weight loss at: 344 °C.

AgL1: *N*-Carbazolylacetic acid (0.45 g, 2 mmol) was added into a solution of NaOH (0.08 g, 2 mmol) in water (80 mL). The mixture was stirred for 30 min and filtered. To the filtration silver nitrate (0.34 g, 2 mmol) in water (10 mL) was added with vigorous stirring. The white precipitate was filtered and washed exhaustively with water and ethanol and air-dried. Yield was 92% (0.66 g). *Anal.* Calc. for AgC₁₄H₁₀O₂N: C, 50.60; H, 3.01; N, 4.22. Found: C, 50.42; H, 2.95; N 4.11%.

AgL2: To a solution of NaOH (0.08 g, 2 mmol) in water (10 mL), 2 (0.58 g, 2 mmol) was added, the mixture was stirred for 30 min and filtered. To the filtration silver nitrate (0.34 g, 2 mmol) in water (10 mL) was added with vigorous stirring. The white precipitate was filtered and washed exhaustively with water and ethanol and air-dried. Yield was 90% (0.71 g). *Anal.* Calc. for $AgC_{19}H_{12}O_2N$: C, 57.87; H, 3.05; N, 3.55. Found: C, 57.65; H, 3.12; N, 3.73%.

AgL3: Acid 3 (0.63 g, 2 mmol) in ethanol (10 mL) was added to a solution of NaOH (0.08 g, 2 mmol) in ethanol (10 mL), the mixture was stirred for 30 min and filtered. To the filtration silver nitrate (0.34 g, 2 mmol) in ethanol (10 mL) was added with vigorous stirring. The white precipitate was filtered and washed exhaustively with water and ethanol and air-dried. Yield was 87% (0.73 g). *Anal.* Calc. for AgC₂₁H₁₄O₂N: C, 60.24; H, 3.33; N, 3.33. Found: C, 60.00; H, 3.31; N, 3.45%.

Complex 4: To a solution of AgL1 (0.33 g, 1 mmol) in dmf (10 mL), PPh₃ (0.52 g, 2 mmol) was added. The mix-

ture was heated to 100 °C for 10 min. A colorless solution was filtered and stood at room temperature. After 10 h colorless crystals were formed. Yield was 78% (0.67 g). *Anal.* Calc. for AgC₅₀H₄₀O₂NP₂: C, 70.09; H, 4.67; N, 1.64. Found: C, 69.82; H, 4.92; N, 1.58%. IR (KBr, pellet, cm⁻¹) 3076 (w), 1581 (s), 1481 (m), 1462 (m), 1429 (s), 1385 (m), 1350 (m), 1304 (w), 1261 (w), 1097 (m), 744 (s). UV–Vis (dmf solution). λ/nm (log ε): 265.5 (4.03), 292.0 (4.25), 326.2 (3.53), 341.1 (3.27). Weight loss at 271 °C.

Complex **5**: To a solution of **AgL2** (0.39 g, 1 mmol) in dmf (10 mL) PPh₃ (0.52 g, 2 mmol) was added. The mixture was heated to 100 °C for 10 min and then a colorless solution appeared, which was filtered and stood at room temperature. After 10 h colorless crystals were formed. Yield was 82% (0.75 g). Anal. Calc. for AgC₅₅H₄₂O₂NP₂: C, 71.90; H, 4.58; N, 1.53. Found: C, 71.87; H, 4.54; N, 1.55%. IR (KBr, pellet, cm⁻¹) 3076 (w), 1637 (m), 1591 (m), 1537 (s), 1516 (m), 1450 (m), 1381 (s), 1168 (m), 742 (s). UV–Vis (dmf solution). λ /nm (log ε): 265.1 (4.49), 290.3 (4.63), 323.0 (3.46), 339.5 (3.76). Weight loss at 280 °C.

Complex **6**: To a solution of **AgL3** (0.42 g, 1 mmol) in dmf (10 mL) PPh₃ (0.52 g, 2 mmol) was added. The mixture was heated to 100 °C for 10 min, a colorless solution appeared, which was filtered and stood at room temperature. After 8 h colorless crystals were formed. Yield was 90% (0.85 g). *Anal.* Calc. for AgC₅₇H₄₄O₂NP₂: C, 72.46; H, 4.66; N, 1.48. Found: C, 72.31; H, 4.70; N, 1.51%. IR (KBr, pellet, cm⁻¹) 3076 (w), 1632 (m), 1593 (s), 1539 (m), 1483 (m), 1439 (m), 1379 (s), 1165 (m), 1099 (w), 742 (s). UV–Vis (dmf solution). λ/nm (log ε): 271.4 (4.91), 295.3 (4.83), 322.0 (3.95), 338.5 (3.73). Weight loss at 286 °C.

3.4. X-ray crystal structure determinations

The crystallographic data for ligands and their silver complexes were collected on a Bruker Smart 1000 CCD

Table 1

The crystal data and parameters of the ligands and complexes

Compounds	L2	L3	4	5	6
Formula	C ₁₉ H ₁₃ NO ₂	C ₂₈ H ₂₃ NO ₂	C ₅₀ H ₄₀ AgNO ₂ P ₂	C55H42AgNO2P2	C ₅₇ H ₄₄ AgNO ₂ P ₂
Formula weight	287.30	405.47	856.64	918.71	944.74
Crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\overline{1}$	$P\bar{1}$	$P\overline{1}$
a (Å)	5.0955(5)	8.555(4)	12.3268(2)	10.638(2)	10.502(8)
$b(\mathbf{A})$	24.613(2)	34.440(15)	13.6246(2)	11.818(2)	13.226(10)
$c(\mathbf{A})$	11.5320(11)	7.884(4)	14.2818(3)	18.712(3)	17.198(13)
α (°)	90	90	110.873(1)	79.261(4)	96.072(11)
β (°)	90.818(2)	104.282(8)	91.914(1)	89.388(4)	93.687(12)
γ (°)	90	90	110.198(1)	80.157(3)	98.614(11)
$V(\text{\AA}^3)$	1446.1(2)	2251.1(17)	2069.63(6)	2276.8(7)	2341(3)
Z	4	4	2	2	2
$\mu (mm^{-1})$	0.086	0.075	0.605	0.555	0.542
$D_{\text{calc}} (\text{g cm}^{-3})$	1.320	1.196	1.375	1.340	1.340
F(000)	600	856	880	944	972
Unique reflections	2482	3950	7941	7933	8178
Reflections observed	4264	11 394	12741	12019	12350
R	0.0666	0.0627	0.0589	0.0265	0.0379
R_w	0.1455	0.1429	0.1516	0.0663	0.0596
$\Delta \rho_{\rm max,min} \ ({\rm e} \ {\rm \AA}^{-3})$	0.172, -0.258	0.239, -0.173	1.271, -2.312	0.333, -0.196	0.493, -0.320

Table 2 Selected bond distances (Å) and angles (°) for the six compounds

Compound 2			
O(1)–C(17)	1.274(4)	N(1)-C(22)	1.403(4)
O(2)-C(17)	1.261(4)	N(1)-C(32)	1.407(4)
C(22)-N(1)-C(14)	125.9(3)	C(13)-C(14)-N(1)	120.9(3)
C(32)–N(1)–C(14)	125.8(3)	O(2)-C(17)-O(1)	122.9(3)
C(15)-C(14)-N(1)	119.0(3)	O(2)-C(17)-C(11)	119.2(3)
Compound 3			
O(2) - C(1)	1.256(4)	N(1)-C(10)	1.403(4)
O(1) - C(1)	1.265(4)	N(1)–C(21)	1.380(4)
O(2)–C(1)–O(1)	123.1(3)	O(2)-C(1)-C(2)	119.1(3)
O(1)-C(1)-C(2)	117.8(3)	C(3)-C(2)-C(1)	123.4(3)
C(2)-C(3)-C(4)	128.5(3)	C(8)-C(7)-N(1)	119.6(3)
Compound 4			
Ag(1)–O(2)	2.419(3)	Ag(1) - O(1)	2.448(3)
O(1)-C(37)	1.215(5)	O(2)–C(37)	1.265(5)
P(2)-Ag(1)-O(2)	109.20(8)	O(2)-Ag(1)-P(1)	115.18(8)
P(2)-Ag(1)-O(1)	119.49(8)	P(1)-Ag(1)-O(1)	105.99(8)
O(1)-C(37)-O(2)	126.2(4)	O(2)-Ag(1)-O(1)	54.06(9)
C(37)–O(1)–Ag(1)	89.8(3)	C(37)-O(2)-Ag(1)	90.0(2)
Compound 5			
Ag(1)–O(1)	2.421(15)	Ag(1) - O(2)	2.490(14)
O(1)–C(1)	1.256(2)	O(2) - C(1)	1.255(2)
O(1)-Ag(1)-P(1)	105.51(5)	P(2)-Ag(1)-O(2)	109.69(4)
O(1)-Ag(1)-P(2)	117.08(5)	P(1)-Ag(1)-O(2)	112.92(4)
O(2)–C(1)–O(1)	123.63(18)	O(1)-Ag(1)-O(2)	53.55(5)
C(1)-O(1)-Ag(1)	92.96(12)	C(1)-O(2)-Ag(1)	89.81(11)
Compound 6			
Ag(1)–O(2)	2.400(2)	Ag(1) - O(1)	2.440(2)
O(2)–C(1)	1.258(3)	O(1) - C(1)	1.247(3)
P(1)-Ag(1)-O(1)	117.10(5)	O(2) - Ag(1) - P(2)	112.29(7)
O(1)-Ag(1)-P(2)	110.90(5)	O(2) - Ag(1) - P(1)	121.96(7)
O(1)-C(1)-O(2)	123.6(2)	O(2)-Ag(1)-O(1)	54.25(6)
C(1)-O(1)-Ag(1)	90.13(16)	C(1)-O(2)-Ag(1)	91.71(16)

area detector diffractometer. Equipped with Mo K α ($\lambda = 0.71073$ Å) radiation using *w*-scan mode. Empirical absorption correction was applied to the data. The structures were solved by direct methods and refined by full-matrix least-squares methods on *F* [2]. All non-hydrogen atoms were located from the trial structure and then refined anisotropically. All hydrogen atoms were generated in idealized positions. All calculations were performed with the SHELXL-97 programs [12]. Other relevant parameters of the crystal structure are listed in Table 1. Selected bond lengths and angles are given in Table 2. CCDC reference numbers 245219–245223. See http://www.rsc.org/supp-data/nj/b2/b203334h/ for crystallographic data in CIF or other electronic format.

4. Results and discussion

4.1. Synthesis and characterization

The three ligands were prepared in high yields. The structures of L2, L3 and three silver complexes 4, 5, and 6 have been confirmed by ¹H NMR, IR spectra and elemental analyses. The ¹H NMR spectra of compounds L2 and L3 display well resolved peaks, ranging from 7.3 to

8.2 ppm, which are characters of carbazolyl ring. The chemical shift above 10 ppm is a character of –COOH.

Thermogravimetric analysis (TGA) was used to study the thermal stabilities of the five compounds on the powder sample. All the compounds display high thermal stability since there was no weight loss below the temperature of 250 °C.

The main absorption peaks in the IR spectra of the six compounds are given in synthetic section. The difference between $v_{as}(COO)$ and $v_s(COO)$ (Δv) of the complexes compared to the corresponding carboxylates is currently employed to determine the coordination mode of carboxylate group [13,14]. The frequency differences between the asymmetric COO stretching and the symmetric stretching are 196 cm⁻¹, 210 cm⁻¹ and 214 cm⁻¹ for (4), (5) and (6), respectively. It suggests that the carboxylate group in the three complexes is coordinated to a silver atom via a bidentate mode, which agree well with the crystal structures analysis. For all of the three ligands, there is a shift of their stretching band towards lower frequency after the carboxylic group bonding to the metal ion.

4.2. Crystal structural description

In ligand L1, carbazolyl ring and –COO were linked though –CH₂– group. Ligand L2 (Fig. 1) has an extended π -delocalization through phenyl group. In ligand L3 (Fig. 2) the π -delocalization was further extended through a phenylethylene group. There are π – π stacking interactions in crystal of L2. The centroid-centroid distance between the carbazolyl rings is 3.679 Å. A classical O-H···O hydrogen bond $[O(1)-H(1 A)\cdots O(2)^a 2.6233 Å,$ 172.66°; symmetry code: 1 - x, 1 - y, 1 - z] exists between neighboring carboxylic acid. In the crystal of L3, O–H···O hydrogen bonds $[O(1)-H(1 A)\cdots O(2)^a 2.6473 Å$, 166.28°; symmetry code: -x, -y, 3 - z also exists between neighboring carboxylic acid. The two carboxylic groups from are connected by hydrogen bonds to form dimer unit.

In the crystals of the complex 4, 5 and 6 (Fig. 3), each Ag(I) atoms are in a distorted tetrahedral AgO_2P_2 environments coordinated by two oxygen atoms from one ligand and phosphorus atoms from two different PPh₃, respectively. Each carboxylate ligand adopts bidentate chelating coordination mode. Upon closer examination of the structures, none of the ligands are planar. The average dihedral angles between the carbazolyl ring planes and the Nreplacement plane are 79.1°, 46.1° and 54.4° for L1–L3; 67.3°, 59.9° and 67.0° for 4-6, respectively. In complex 4, the C(37)–O(1) bond length and C(37)–O(2) bond length are 1.2155 and 1.2655 Å, respectively. The O(1)-Ag(1)-P(1) and O(2)-Ag(1)-P(2) bond angles are 105.99° and 109.21°, respectively, indicating a slight distorted tetrahedral coordination environment. C37, O1, O2 and Ag1 atoms are almost in one plane (the largest deviation: (0.0017 Å) that forms a dihedral angle of (81.3°) with the carbazole ring. In complex 5, the C(1)-O(1) bond length and C(1)–O(2) bond length is 1.2562 and 1.2552 Å, respec-



Fig. 1. Molecular structure of L2.



Fig. 2. Molecular structure of L3. Solvent molecules have been omitted.

tively, which is slightly shorter than 1.2614 and 1.2744 Å of the C–O bond length in corresponding ligand L2. The O(1)–Ag(1)–P(1) and O(2)–Ag(1)–P(2) bond angles are 105.51° and 109.69°, respectively, indicating a slight distortion. All of the coordination environments were summarized in Table 3. Although the formation of a fourmember Ag–O–C–O ring, with the high angular strains involved, is not expected to be energetically favorable, this type of structure is more stable than the one in which carboxylato group adopts monodentate mode with three bulky triphenylphosphine ligands to complete four-coordination geometry of the Ag(I) ion.

There are a number of C–H···O interactions in complexes **4–6**. In complex **4**, there is a weak interaction between the carboxyl O(1) and H(18) on a adjacent PPh₃ ring (C(18)–O(1) 3.432(1) Å, 149.72°) and a slightly stronger interaction between the carboxyl O(2) and H(38) on a adjacent vinyl chain (C(18)–O(1) 3.377 Å, 164.23°). As well, there is a interaction between the carboxyl O(2) and H(40) on the adjacent carbazolyl ring (C(40)–O(2)



Fig. 3. ORTEP drawing of the complex 4, 5, and 6. The thermal ellipsoids are drawn at the 50% probability.

3.291(8) Å, 171.97°). In complex **5** and **6**, there are also a number of $C-H\cdots O$ interactions forming supramolecules.

4.3. UV–Vis absorbance

UV–Vis absorbance spectra was shown in Fig. 4. All of the compounds show similar peak position but the complexes showed relatively stronger absorbance than the ligands.

Table 3	
Structural comparison of the ligands and their complexes	

Compounds	∠P–Ag–P (°)	∠AgO ₂ (°)	Dihedral angle (°) (CO ₂ / carbazol)	∠CO ₂ (°)	Ag–O (Å)	C=O C-O Δd (Å)
1			79.1	125.1		1.193(3) 1.323(3) 0.13
2			46.1	122.9		1.261(4) 1.274(4) 0.013
3			54.4	117.8		1.256(4) 1.265(4) 0.009
4/Δα	129.37	54.06	67.3/11.8	126.2	2.419(3) 2.448(3)	1.215(5) 1.265(5) 0.05
5/Δα	132.08	53.55	59.9/ -13.8	123.63	2.421(1) 2.490(14)	1.255(2) 1.256(2) 0.001
6 /Δα	121.59	54.25	67/-12.6	123.6	2.400 2.440	1.247(3) 1.258(3) 0.011

 $\Delta \alpha$: Dihedral angle change comparing with its free ligand.

 Δd : Differences of the bond lengths between C=O and C–O bond in carboxylato group.

4.4. Solution photoluminescence

The single-photon fluorescence spectra for the ligands and their complexes were measured in different solvents. The emission maxima at $\lambda = 352$, 388 and 416 nm for L1–L3 and 353, 389 and 514 nm for 4–6 in dmf, respectively. There is a distinct red shift (36 nm) of the emission energy from compound L1 to L2, and there is a ca. 64 nm red shift from L1 to L3, which is due to the extended conjugation of the molecules. This phenomenon also exists in the corresponding complexes. As well, the fluorescent spectra of all the ligands and complexes show sensitivity to the polarity of the environments. The PL intensity is weak in acetonitrile compared with those in other solvents. In The represent fluorescent peak at 370–390 nm in hexane,



Fig. 4. UV–Vis spectra of ligands 1–3 and complexes 4–6 in DMF.



Fig. 5. The PL and excitation spectra of complex **6**: (a) PL in different solvents, (b) excitation spectra in different solvents, (c) PL spectra in DMF with different concentrations.



4.5. Solid state photoluminescence

The fluorescent emission spectrum of six compounds were also measured in the solid state at room temperature. The maximum emission peaks for ligands L1–L3 are at ca. 423, 460 and 465 nm, respectively (Fig. 6). For luminescence of compound 4, two peaks of emissions are shown in Fig. 7. The maximum is at 377 nm, which can be assigned to the intraligand π – π charge transfer similarly to the emission of carbazole in dmf solution. The other emission is at 418 nm with a shoulder at 439 nm, which can be assigned to the excimeric emissions due to the weak ligand–ligand interactions between the molecules in solid state. For the luminescence of 5, the emission of 377 nm disappears due to the delocalization of the benzene ring and carbazole group. Excimeric emissions at 412 and



Fig. 7. Emission spectra of 4-6 in the solid state at room temperature.



Fig. 6. The emission spectra of L1-L3 in solid state at room temperature.



Fig. 8. Cyclic voltammograms for (a) ligand L1; (b) ligand L2; (c) ligand L3.

435 nm were also observed. The luminescence of 6 is similar to that of 5, with some red shifts due to further elongation of the delocalization.

The reason of shift from L1 to L3 and 4 to 6 is similar to the solution fluorescence spectra. Here, we observed that the emission spectra of the complexes are remarkable blue-shifted compared to corresponding free ligands. This is reasonable according to their crystal structures. In these complexes, the two bulky PPh₃ ligands with six benzene rings almost perpendicular to one another significantly decrease the symmetry of the molecule. The strong emission at short wavelength is caused by the energy increase resulting from the symmetry decrease of 4, 5 and 6 compared to the free ligand and the high angular strain of the four-number chelating ring [10].

4.6. Electrochemical studies

The cyclic voltammogram of the ligands in MeCN was shown in Fig. 8. The initial oxidation wave of the three ligands is at +1.39, 1.36 and 1.31 V for ligand L1 to ligand L3, respectively, which appears to be the formation of cation radicals. The different oxidation wave is related to the conjugation of these ligands. Different oxidation wave of ligand L2 in different time are shown in Fig. 9. The oxidation route can be explained in Scheme 2, which indicates that the cation radical is unstable and produce dicarbazyl easily. The site 1 and site 8 carbons are somewhat sterically hindered due to the rather rigid structure of the *N*-substituted derivatives. Therefore, the formation of 1,1'-dicarbazyl from resonance form C seems unlikely and in fact, has not been observed. The 3,3'-dicarbazyl is more easily oxidized than before and loses two electrons (anodic peak at 1.50 V) to yield a moderately stable dication with extensive conjugation.

The cyclic voltammogram of the three complexes in DMF are similar and are related with the carbazole and

Table 4 The oxidation–reduction peak data for **4–6**

	1		
Compound	$\begin{array}{c} Ag(I) \rightarrow Ag(II) \\ (v) \end{array}$	$\begin{array}{c} Ag(II) \rightarrow Ag(I) \\ (v) \end{array}$	$\begin{array}{c} Ag(I) \rightarrow Ag(0) \\ (v) \end{array}$
4	0.232	-0.452	-0.926
5	0.155	-0.300	-1.009
6	0.218	-0.316	-0.968



Fig. 9. Cyclic voltammograms for ligand L2 (b), 10 min later (d), 30 min later (e) in CH₃CN/Bu₄NClO₄/Pt vs. SCE at 20 °C, scan rate = 50 mV s⁻¹.



Fig. 10. Cyclic voltammogram for complex **4** in dmf/Bu₄NClO₄/Pt vs. SCE at 20 °C, scan rate = 50 mV s^{-1} .



Scheme 2. Oxidation process of the ligands.

COO⁻ groups (Table 4). The cyclic voltammogram recorded in the anodic area exhibited an oxidation peak, which is assigned to the process of the $Ag(I) \rightarrow Ag(II)$. When the cyclic voltammogram was recorded in the cathodic area, two reductive peaks were detected (Fig. 10). In compound 5, the oxidation peak of the $Ag(I) \rightarrow Ag(II)$ is lowest and the process easily happened. The fact is that L2 was extended π -delocalization through phenylene, while ligand L3 through vinyl based on ligand L2. The Nreplacement plane are 67.3° , 59.9° and 67.0° for **4-6**, respectively, and thus compound 5 exhibit a rather rigid structure and the higher electron density around Ag(I). It is obvious that the process $Ag(I) \rightarrow Ag(0)$ rather difficultly happen in the three complexes, especially in complex 5 according to the reduction peak data. The oxidation peak of the N-substituted derivatives had completely disappeared. One explanation is the electron transfer from the 'carbazole' to the silver Ag(I), thus, the electron density of the carbazole decreases in the complexes.

5. Conclusions

A short series of carbazole-functionalized carboxylate ligands and corresponding silver complexes were synthesized and their structures were determined by single crystal X-ray diffractions analysis. The emission wavelengths of the compounds can be tuned (from ultraviolet to visible region) by introducing of the second coordination ligand and/or by elongation of the conjugation moieties. The excellent electrochemical characters, strong photoluminescence in the solid state, as well as reasonable thermal stability may enable them good candidates for electroluminescence devices. The study of the structure–property relationship may provide important information for further designing other useful emission materials.

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