

Blue Luminescent Rigid Molecular Rods Bearing *N*-7-Azaindoyl and 2,2'-Dipyridylamino and Their Zn(II) and Ag(I) Complexes

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To investigate the luminescent and thermal properties of organic compounds with rigid entities, a series of new blue/purple luminescent bridging ligands, 4,4'-(*N*-7-azaindoyl)diphenylacetylene (**5**), 4-(*N*-7-azaindoyl)-4'-(2,2'-dipyridylamino)diphenylacetylene (**6**), 4,4'-(2,2'-dipyridylamino)diphenylacetylene (**7**), and 4,4'-(dipyridylamino)-diphenylbutadiyne (**8**) have been synthesized through Pd-mediated Sonogashira coupling. The structures of compounds **6** and **8** were determined by single-crystal X-ray diffraction analyses. Compounds **5–8** are luminescent in solution at room temperature, with emission $\lambda_{\text{max}} = 361, 382, 386, \text{ and } 405 \text{ nm}$, respectively. At 77 K, compounds **5–8** exhibit both fluorescent and phosphorescent emission. The 2,2'-dipyridylamino symmetrically substituted ligand **7** forms a linear dinuclear complex **9** with zinc(II) ions, in which the two pyridyl rings of the dipyridylamino portion are chelated to the metal center. However, with Ag(I) ions, ligand **7** forms a dinuclear complex (**10**), which displays a macrocyclic structure with only one of the two pyridyl rings from each dipyridylamino portion being coordinated to the silver atom. Both **9** and **10** exhibit luminescence in the near-UV region in CH_2Cl_2 at room temperature with $\lambda_{\text{max}} = 385 \text{ and } 384 \text{ nm}$, respectively. The fluorescence of **7** can be partially quenched by either Zn^{2+} or H^+ . The behavior of ligands **8** toward Ag(I) and Zn(II) ions is similar to that of **7**.

Introduction

Luminescent compounds of highly π -conjugated systems are of great current interest due to their various applications in molecular optical or electronic devices and chemical sensors.¹ One of the most important considerations in light-

emitting devices (LEDs) is the design and synthesis of molecules capable of tuning luminescent properties through the modification of the ligand subunit.² In particular, π -conjugated organic compounds with aromatic nitrogen heterocycles, which can be receptors for metal ions, have attracted much attention because they are capable of performing useful light- and/or redox-induced tasks.³ For example, organic oligomers and polymers incorporating 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) have been demonstrated to have unique photophysical and photochemical features for the construction of materials with tunable luminescences.⁴ These oligomers can also function as efficient chemical sensors for small molecules with the

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integration of transition metals into their frameworks.⁵ Recently, nanoscale conjugated molecular rods of 1,10-phenanthroline and their derivatives, linked by an internal acetylene unit, have been shown to exhibit distinct emission energies depending on substituents, metal ions, protons, and solvent polarity.⁶ In addition, organic compounds with alternating acetylene groups and pyridine, phenanthrene, phenylene, or biphenylene groups have been shown to affect substantial electron delocalization through extended conjugation, which make them possible molecular electronic materials.⁷ Although much research on 2,2'-bipyridine (bpy), phenanthroline (phen), and their metal complexes has been well established for several decades, little attention has been paid to the derivatives of 2,2'-dipyridylamine.⁸ In the course of our investigation into luminescent organic and organometallic compounds, we have observed that 2,2'-dipyridylamine derivatives and their metal complexes not only are efficient blue emitters in electroluminescent devices but also can function as chemical sensors for specific organic molecules.⁹ Our interest in the design of highly conjugated organic spacers, incorporating 2,2'-dipyridylamine and internal ethynyl linkages, has prompted us to investigate the syntheses, luminescent properties, and coordination chemistry of their derivatives. Herein, we report a full account of a class of rigid molecular rods based on 2,2'-dipyridylamine and 7-azaindole. Preliminary results have been presented in a recent communication.¹⁰

Experimental Section

All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Benzene, hexane, and THF were freshly distilled over sodium and benzophenone. Dichloromethane was dried and distilled over P₂O₅. All starting materials were purchased from Aldrich and used without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300-

400-MHz spectrometer. UV/vis spectra were obtained on a Hewlett-Packard 8562A diode array spectrophotometer. All differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Pyris DSC6. A sample (5–10 mg) was placed in aluminum pan and the scan performed at a rate of 20 °C/min for the first heating and 5 °C/min for the second heating, under a N₂ gas flow rate of 50 mL/min. An empty aluminum pan was used as a standard. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster model 2 spectrometer. Emission lifetimes were measured on a Photon Technology International phosphorescent lifetime spectrometer, Timemaster C-631F equipped with a Xenon flash lamp, and digital emission photon multiplier tube using a band path of 2 nm for both excitation and emission. For phosphorescent measurement at 77 K, a delay time of 150–200 μs was used to obtain the spectra. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, BC, Canada. Melting points were determined on a Fisher-Johns melting point apparatus. The 4-bromophenyl-2,2'-dipyridylamine was synthesized by recently reported procedures.^{10,11}

General Procedure of Sonogashira Coupling. To the aryl bromides, Pd(PPh₃)₄ (5 mol %), CuI (5 mol %), and NEt₃ (10–15 mL), in a Schlenk flask equipped with stirring bar and rubber septum, under nitrogen, were added their corresponding terminal alkynes (small excess). The mixture was heated at 80–100 °C for 12–24 h. After cooling to room temperature, all volatiles were removed under reduced pressure. The mixture was dissolved in CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄ and filtered and the solvent removed under reduced pressure. Purification by column chromatography (silica gel) using ethyl acetate and hexane as eluent afforded the title compounds.

Synthesis of Intermediate 1-Trimethylsilyl-2-(N-7-azaindolyphenyl)ethyne (1). Yield: 86%. ¹H NMR in CDCl₃ (δ, ppm, 25 °C): 8.41 (dd, *J* = 4.5 Hz, 1.5 Hz, 2H), 8.01 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.79, 7.63 (AA'BB'', *J*_{AB} = 8.7 Hz, 4H, 4H), 7.54 (d, *J* = 3.9 Hz, 2H), 7.18 (dd, *J* = 7.8 Hz, 4.8 Hz, 2H), 6.68 (d, *J* = 3.6 Hz, 2H), 0.29 (s, C≡CSiMe₃, 9H). ¹³C NMR in CDCl₃ (δ, ppm, 25 °C): 148.3, 143.9, 133.7, 130.2, 128.2, 127.0, 123.8, 122.5, 117.6, 105.2, 103.6, 95.3, 77.1, 0.67.

Synthesis of Intermediate 1-Trimethylsilyl-2-(2,2'-dipyridylaminophenyl)ethyne (2). Yield: 80%. ¹H NMR in CDCl₃ (δ, ppm, 25 °C): 8.34 (ddd, *J* = 6.0, 2.1, 0.9 Hz, 2H), 7.58 (ddd, *J* = 15.6, 7.5, 2.1 Hz, 2H), 7.45, 7.11 (AA'BB'', *J*_{AB} = 8.7 Hz, 2H, 2H), 6.96–7.01 (m, overlap, 4H), 0.26 (s, C≡CSiMe₃, 9H). ¹³C NMR in CDCl₃ (δ, ppm, 25 °C): 158.4, 149.4, 146.1(Ph), 138.5, 134.4(Ph), 126.9, 119.4 (Ph), 119.3 (Ph), 118.1, 84.2, 77.7, –0.52.

Synthesis of 4,4'-(N-7-Azaindoly)diphenylacetylene (5). Yield: 60%. Mp: 175–178 °C. ¹H NMR in CDCl₃ (δ, ppm, 25 °C): 8.43 (dd, *J* = 4.5 Hz, 1.5 Hz, 2H), 8.01 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.87, 7.73 (AA'BB'', *J*_{AB} = 8.7 Hz, 4H, 4H), 7.58 (d, *J* = 3.9 Hz, 2H), 7.19 (dd, *J* = 7.8 Hz, 4.8 Hz, 2H), 6.69 (d, *J* = 3.6 Hz, 2H). ¹³C NMR in CDCl₃ (δ, ppm, 25 °C): 147.7, 144.0, 138.8, 133.4, 128.2, 126.0, 124.1, 122.7, 117.6, 103.1, 90.1. IR (KBr, pellet, cm⁻¹): 2206 ν(C≡C). Anal. Calcd for C₂₈H₁₈N₄: C, 81.95; H, 4.39; N, 13.66. Found: C, 82.20; H, 4.30; N, 13.65.

Synthesis of 4-(N-7-Azaindoly)-4'-(2,2'-dipyridylamino)-diphenylacetylene (6). Yield: 75%. Mp: 165–168 °C. ¹H NMR in CDCl₃ (δ, ppm, 25 °C): 8.40 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.38 (ddd, *J* = 6.0, 1.8, 0.9 Hz, 2H), 8.00 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.83, 7.68 (AA'BB'', *J*_{AB} = 8.7 Hz, 2H, 2H), 7.61–7.54 (m, overlap, 5H), 7.19 (m, overlap, 3H), 7.05 (d, *J* = 8.4 Hz, 2H),

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6.99 (ddd, $J = 7.2, 4.8, 0.9$ Hz, 2H), 6.68 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR in CDCl_3 (δ , ppm, 25 °C): 158.6, 149.4, 148.2, 145.8, 144.3, 138.9, 138.4, 133.6, 133.3, 129.9, 128.0, 127.0, 124.0, 122.5, 121.7, 120.4, 119.4, 118.1, 117.7, 103.0, 90.4, 89.7. IR (KBr, pellet, cm^{-1}): 2206 $\nu(\text{C}\equiv\text{C})$. Anal. Calcd for $\text{C}_{31}\text{H}_{21}\text{N}_5$: C, 80.34; H, 4.53; N, 15.12. Found: C, 80.07; H, 4.65; N, 15.16.

Synthesis of 4,4'-(2,2'-Dipyridylamino)diphenylacetylene (7). Yield: 68%. Mp: 238–240 °C. ^1H NMR in CDCl_3 (δ , ppm, 25 °C): 8.36 (ddd, $J = 6.0, 2.1, 0.9$ Hz, 4H), 7.59 (ddd, $J = 15.6, 7.5, 2.1$ Hz, 4H), 7.51, 7.15 (AA'BB'', $J_{\text{AB}} = 8.7$ Hz, 4H, 4H), 7.03 (d, $J = 8.1$ Hz, 4H), 6.97 (ddd, $J = 7.2, 4.8, 0.9$ Hz, 4H). ^{13}C NMR in CDCl_3 (δ , ppm, 25 °C): 158.2, 149.2, 145.2, 138.7, 133.7, 127.1, 119.4, 118.0, 110.2, 90.1. IR (KBr, pellet, cm^{-1}): 2206 $\nu(\text{C}\equiv\text{C})$. Anal. Calcd for $\text{C}_{34}\text{H}_{24}\text{N}_6$: C, 79.05; H, 4.68; N, 16.28. Found: C, 78.58; H, 4.62; N, 15.76.

General Procedures of Desilylation. A solution of **1** or **2** and saturated KOH in MeOH/THF (20 mL/10 mL, 2:1) was stirred for 20–30 min at ambient temperature. The reaction was monitored by TLC. The solvent was removed under reduced pressure. After addition of water, the mixture was extracted with diethyl ether. The extract was washed with water and brine, dried over MgSO_4 , and concentrated under reduced pressure. The product was isolated by using column chromatography with ethyl acetate/hexane as the eluent.

Synthesis of Intermediate 4-(*N*-7-Azaindolyl)phenylacetylene (3). Yield: 95%. ^1H NMR in CDCl_3 (δ , ppm, 25 °C): 8.42 (dd, $J = 4.5$ Hz, 1.5 Hz, 2H), 8.02 (dd, $J = 7.8, 1.5$ Hz, 2H), 7.81, 7.67 (AA'BB'', $J_{\text{AB}} = 8.7$ Hz, 4H, 4H), 7.55 (d, $J = 3.9$ Hz, 2H), 7.19 (dd, $J = 7.8$ Hz, 4.8 Hz, 2H), 6.69 (d, $J = 3.6$ Hz, 2H), 3.15 (s, $\text{C}\equiv\text{CH}$, 1H). ^{13}C NMR in CDCl_3 (δ , ppm, 25 °C): 148.3, 143.9, 133.7, 130.2, 128.2, 127.0, 123.8, 122.5, 117.6, 105.2, 103.6, 95.3, 77.1, 0.67.

Synthesis of Intermediate 4-(2,2'-Dipyridylamino)phenylacetylene (4). Yield: 93%. ^1H NMR in CDCl_3 (δ , ppm, 25 °C): 8.35 (ddd, $J = 6.0, 2.1, 0.9$ Hz, 2H), 7.59 (ddd, $J = 15.6, 7.5, 2.1$ Hz, 2H), 7.48, 7.13 (AA'BB'', $J_{\text{AB}} = 8.7$ Hz, 2H, 2H), 7.02 (d, $J = 8.4$ Hz, 2H), 6.97 (ddd, $J = 7.2, 4.8, 0.9$ Hz, 2H), 3.08 (s, $\text{C}\equiv\text{CH}$, 1H). ^{13}C NMR in CDCl_3 (δ , ppm, 25 °C): 158.4, 149.4, 146.1 (Ph), 138.5, 134.4 (Ph), 126.9, 119.4 (Ph), 119.3 (Ph), 118.1, 84.2, 77.7.

Synthesis of 4,4'-(Dipyridylamino)diphenylbutadiyne (8). To a flask containing compound **4** and a catalytic amount of CuCl was added oxygen-saturated pyridine over several minutes. The mixture was stirred at room temperature for 24 h. All volatiles were removed by reduced pressure. The mixture was dissolved in CH_2Cl_2 and washed with water until it reached pH 7. The organic layer was dried over MgSO_4 and filtered and the solvent removed under reduced pressure. Purification by column chromatography (silica gel) using ethyl acetate as eluent afforded compound **8** (yield 88%). Mp: 275–280 °C. ^1H NMR in CDCl_3 (δ , ppm, 25 °C): 8.37 (ddd, $J = 6.0, 2.1, 0.9$ Hz, 4H), 7.61 (ddd, $J = 15.6, 7.5, 2.1$ Hz, 4H), 7.51, 7.13 (AA'BB'', $J_{\text{AB}} = 8.7$ Hz, 4H, 4H), 7.05–6.98 (m, overlap, 8H). ^{13}C NMR in CDCl_3 (δ , ppm, 25 °C): 158.4, 149.5, 146.5, 138.5, 134.4, 126.5, 119.6, 118.6, 118.3, 82.3, 74.7. IR (KBr, pellet, cm^{-1}): 2206, 2142 $\nu(\text{C}\equiv\text{C})$. Anal. Calcd for $\text{C}_{36}\text{H}_{24}\text{N}_6$: C, 80.00; H, 4.44; N, 15.56. Found: C, 79.78; H, 4.48; N, 15.38.

Synthesis of [(ZnX₂)₂(L)] (L = 7, X = CF₃COO) (9). To a solution of $\text{Zn}(\text{CF}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (0.072 g, 0.248 mmol) in THF (10 mL) was added **7** (0.064 g, 0.124 mmol). The mixture was stirred overnight. After filtration, the yellow solution was concentrated to approximately 3 mL under reduced pressure. The solution was layered with benzene and hexane, yielding colorless crystals over several days at room temperature. Yield: 94%. Mp: 261–

263 °C. ^1H NMR in CD_2Cl_2 (δ , ppm, 25 °C): 8.68 (dd, $J = 4.8$ Hz, 1.5 Hz, 2H), 7.89–7.83 (m, overlap, 4H), 7.55 (AA'BB'', $J_{\text{AB}} = 5.4$ Hz, 2H), 7.32 (dd, $J = 8.7$ Hz, 4.8 Hz, 2H). ^{13}C NMR in CD_2Cl_2 (δ , ppm, 25 °C): 163.01 (d, $^2J_{\text{C-F}} = 38.5$ Hz), 156.5, 155.0, 148.2, 142.1, 135.2, 130.2, 120.4, 118.5, 117.3 (d, $^1J_{\text{C-F}} = 299.4$ Hz) 90.5. ^{19}F NMR in CDCl_3 (δ , ppm, 25 °C): –75.46. Anal. Calcd for $\text{C}_{42}\text{H}_{24}\text{N}_6\text{O}_8\text{F}_{12}\text{Zn}_2 \cdot \text{C}_6\text{H}_6$: C, 48.95; H, 2.55; N, 7.14. Found: C, 49.48; H, 2.80; N, 7.27.

Synthesis of [AgX(L)]₂ (L = 7, X = CF₃COO) (10). Compound **10** was prepared according to the same procedures used for compound **9**, except that either 1 or 2 equiv of silver trifluoroacetate was used instead of zinc trifluoroacetate. Yield: 85%. Mp: 205–207 °C (dec). ^1H NMR in CD_3CN (δ , ppm, 25 °C): 8.27 (ddd, $J = 6.0, 2.1, 0.9$ Hz, 2H), 7.70 (ddd, $J = 15.6, 7.5, 2.1$ Hz, 2H), 7.50, 7.11 (AA'BB'', $J_{\text{AB}} = 8.7$ Hz, 2H, 2H), 7.09–7.04 (m, overlap, 4H), ^{13}C NMR in CD_3CN (δ , ppm, 25 °C): 165.2, 149.2, 138.9, 133.1, 126.8, 122.2, 119.8, 118.6, 117.9, 114.2, 111.1, 108.2, 94.3 (The expected coupling patterns between ^{13}C and ^{19}F could not be resolved due to low solubility). ^{19}F NMR in CD_3CN (δ , ppm, 25 °C): –75.79. Anal. Calcd for $\text{C}_{72}\text{H}_{48}\text{N}_{12}\text{O}_4\text{F}_6\text{Ag}_2$: C, 58.62; H, 3.25; N, 11.39. Found: C, 58.54; H, 3.02; N, 10.96.

X-ray Crystallography Analysis. Single-crystals of **6** and **8** were obtained from ethyl acetate/hexanes. Single-crystals of compounds **9** and **10** were obtained from solvent diffusion of CH_2Cl_2 /benzene/hexanes, and CH_3CN /diethyl ether, respectively. All data were collected on a Siemens P4 X-ray diffractometer with a Bruker SMART CCD 1000 detector, with monochromated Mo K α radiation, operating at 50 kV and 30 mA at 298 K. The data for **6** and **8–10** were collected over 2θ ranges of 3.72–56.74°. No significant decay was observed during the data collection. Data were processed on a Pentium PC using the Bruker AXS Windows NT SHELXTL software package (version 5.10).¹² Neutral atom scattering factors were taken from Cromer and Waber.¹³ Empirical absorption correction was applied to all crystals. All structures were solved by direct methods. Benzene and CH_3CN molecules were found in the crystal lattices of compounds **9** and **10**, respectively. The disordering of CF_3 groups in **9** and **10** were modeled and refined successfully. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. The crystal data are summarized in Table 1. Selected bond lengths and angles for **6** and **8–10** are given in Table 2.

Results and Discussion

Syntheses and Properties of Ligands. Molecules **5–8** were designed for the following reasons: (i) stable, neutral organic compounds, which possess 2,2'-dipyridylamino and/or *N*-7-azaindolyl, have potential applications in electro-luminescent (EL) devices; (ii) the introduction of 2,2'-dipyridylamino groups can provide binding sites for metal ions, and the resulting complex may provide selective fluorescent sensing toward organic molecules; and (iii) incorporation of acetylene groups gives rigid entities, higher electrical conductivity, the ability to tune luminescent properties, and increased luminescent efficiency through extended π -orbital conjugations. The ligands for this purpose were prepared from the reaction of a terminal acetylene with

(12) SHELXTL NT Crystal Structure Analysis Package, version 5.10; Bruker AXS, Analytical X-ray System: Madison, WI, 1999.

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Table 1. Crystallographic Data for Compounds **6** and **8–10**

	6	8	9	10
formula	C ₃₁ H ₂₁ N ₅	C ₃₆ H ₂₄ N ₆	C ₄₂ H ₂₄ F ₁₂ - N ₆ O ₈ Zn ₂	C ₇₂ H ₄₈ F ₆ N ₁₂ - O ₄ Ag ₂
fw	463.53	540.61	1098.73	1473.64
space group	P2 ₁ /n	P2 ₁ /n	P $\bar{1}$	P2 ₁ /c
a, Å	9.6666(17)	5.833(10)	11.140(15)	21.686(6)
b, Å	9.9118(17)	16.952(3)	11.192(15)	8.772(2)
c, Å	25.086(4)	14.493(3)	11.500(15)	18.378(5)
α , deg	90	90	112.04(2)	90
β , deg	95.814(3)	99.643(3)	98.06(2)	101.773(4)
γ , deg	90	90	108.39(2)	90
V, Å ³	2391.2(7)	1413.0(4)	1205(3)	3422.6(16)
Z	4	2	2	4
D _{calc} , g cm ⁻³	1.288	1.271	1.622	1.511
μ , cm ⁻¹	0.78	0.77	11.02	6.51
2 θ _{max} , deg	56.56	56.56	56.74	56.62
no. of reflns measd	16958	10191	8657	24091
no. of reflns used	5692	3355	5539	8161
(R _{int})	(0.0437)	(0.0901)	(0.0763)	(0.0549)
no. of params	325	190	397	565
final R [I > 2 σ (I)]				
R1 ^a	0.0466	0.0544	0.0460	0.0471
wR2 ^b	0.1000	0.1065	0.1169	0.1003
R (all data)				
R1 ^a	0.1417	0.1994	0.0647	0.1024
wR2 ^b	0.1262	0.1427	0.1293	0.1168
GOF on F ²	0.828	0.842	1.043	0.886

^a R1 = $\sum |F_o| - |F_c| / \sum |F_o|$. ^b wR2 = $[\sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$.
w = $1/[\sigma^2(F_o^2) + (0.075P)^2]$, where P = $[\text{Max}(F_o^2, 0) + 2F_c^2]/3$.

a corresponding bromoarene by sequential Pd-mediated Sonogashira couplings,¹⁴ as shown in Scheme 1. A recent report has demonstrated that the procedure for the synthesis of arylacetylenes by Sonogashira coupling of aryl bromides with terminal alkynes can be improved by using THF as solvent.¹⁵ However, in the case of compounds **1–7**, we found that the use of triethylamine and Pd(PPh₃)₄ as the solvent and the catalyst, respectively, gives better yields than the use of THF and Pd(PPh₃)₂Cl₂. The oxidative homocoupling (Glaser coupling) of compound **4** was achieved successfully in the presence of oxygen and Cu(I), resulting in formation of the compound **8** in good yield. Compounds **1–8** are soluble in common organic solvents except pentane and hexane, and their structures have been confirmed by ¹H and ¹³C NMR spectra, IR spectra, and elemental analyses. The ¹H NMR spectra of compounds **5–8** display well-resolved peaks, ranging from 8.5 to 6.7 ppm, that are characteristic of *N*-7-azaindoyl and 2,2'-dipyridylamino groups with an AA'BB'' spin system of the aromatic ring. In the ¹³C NMR spectra of **5–8**, resonance at 80–90 ppm could be assigned to triply bound carbon atoms. Compounds **5–8** were also characterized by a stretching band 2206 cm⁻¹ in the IR spectra associated with the carbon–carbon triple bond. Both stretching bands at 2206 and 2142 cm⁻¹ for compound **8** are assigned to the asymmetric and symmetric modes of the ethynyl moieties. In order for molecular organic compounds to be useful in EL, they should be sufficiently thermally and morphologically stable.¹⁶ Therefore, we carried out DSC experiments to investigate the glass-forming properties and

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **6** and **8–10**

Compound 6			
N(1)–C(8)	1.427(2)	C(15)–C(16)	1.371(3)
N(5)–C(27)	1.408(2)	C(11)–C(14)	1.438(3)
N(5)–C(22)	1.415(2)	C(12)–C(13)	1.387(3)
N(5)–C(19)	1.439(2)	C(14)–C(15)	1.190(2)
C(7)–N(1)–C(8)	127.94(19)	C(9)–C(8)–N(1)	119.09(19)
C(1)–N(1)–C(8)	124.89(19)	C(13)–C(8)–N(1)	121.1(2)
C(27)–N(5)–C(22)	123.95(15)	C(10)–C(11)–C(14)	120.8(2)
C(27)–N(5)–C(19)	117.67(16)	C(15)–C(14)–C(11)	178.4(2)
C(22)–N(5)–C(19)	117.67(15)	C(14)–C(15)–C(16)	176.9(2)
Compound 8			
N(3)–C(11)	1.431(3)	C(17)–C(18)	1.196(3)
C(14)–C(17)	1.432(4)	C(18)–C(18')	1.371(5)
C(1)–N(3)–C(11)	119.0(2)	C(15)–C(14)–C(13)	118.2(3)
C(1)–N(3)–C(6)	121.9(2)	C(15)–C(14)–C(17)	120.1(3)
C(6)–N(3)–C(11)	119.1(2)	C(13)–C(14)–C(17)	121.7(3)
C(18)–C(17)–C(14)	176.9(3)	C(17)–C(18)–C(18')	179.0(4)
Compound 9			
Zn(1)–O(1)	1.928(3)	O(1)–C(18)	1.245(3)
Zn(1)–O(3)	1.958(3)	O(2)–C(18)	1.182(4)
Zn(1)–N(1)	1.995(3)	N(3)–C(11)	1.444(3)
Zn(1)–N(2)	2.000(3)	C(14)–C(17)	1.426(3)
C(17)–C(17')	1.171(5)		
O(1)–Zn(1)–O(3)	101.79(13)	C(20)–O(3)–Zn(1)	113.1(2)
O(1)–Zn(1)–N(1)	119.34(10)	C(1)–N(1)–Zn(1)	122.14(15)
O(3)–Zn(1)–N(1)	126.56(10)	C(6)–N(2)–Zn(1)	123.50(17)
O(1)–Zn(1)–N(2)	115.34(10)	C(6)–N(3)–C(1)	128.21(18)
O(3)–Zn(1)–N(2)	101.05(12)	C(17')–C(17)–C(14)	179.4(4)
N(1)–Zn(1)–N(2)	91.18(10)		
Compound 10			
Ag(1)–N(1)	2.248(3)	N(3)–C(11)	1.432(4)
Ag(1)–N(5')	2.274(3)	N(5)–Ag(1')	2.274(3)
Ag(1)–O(2)	2.416(3)	C(14)–C(17)	1.431(5)
C(17)–C(18)	1.196(5)		
N(1)–Ag(1)–N(5')	136.71(9)	C(1)–N(3)–C(6)	122.7(3)
N(1)–Ag(1)–O(2)	127.55(10)	C(1)–N(3)–C(11)	118.4(3)
N(5')–Ag(1)–O(2)	94.43(10)	C(6)–N(3)–C(11)	118.7(3)
C(35)–O(2)–Ag(1)	96.7(2)	C(15)–C(14)–C(17)	121.4(4)
C(30)–N(5)–Ag(1')	127.1(2)	C(18)–C(17)–C(14)	179.0(5)
C(34)–N(5)–Ag(1')	115.5(2)		

phase transition for compounds **5–8**. Well-defined melting points were observed for compounds **5–8** (Table 3). Compound **5** does not show glass formation during either the first or second heating cycle. Instead, the second heating cycle of **5** revealed a recrystallization exothermic peak (T_c) at 175 °C without any glass formation, followed by melting (186 °C). Compound **6** displays a glass transition (T_g) at 61 °C in the second heating cycle. Figure 1 shows the DSC trace of **7** in the first heating cycle, providing evidence of a glass transition (T_g) at approximately 130 °C. As heating continues, a well-resolved crystallization exothermic peak occurs at 216 °C. Finally, the sample melts at 239 °C. The crystallization exothermic peak is likely attributable to rigid moieties, a nonplanar structure, and polymorphism of crystalline materials.¹⁷ The high glass transition temperature of **7** makes it potentially useful for applications in EL devices.

To better understand the solid-state nature, single-crystal X-ray diffraction analysis was performed for compounds **6**

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Scheme 1

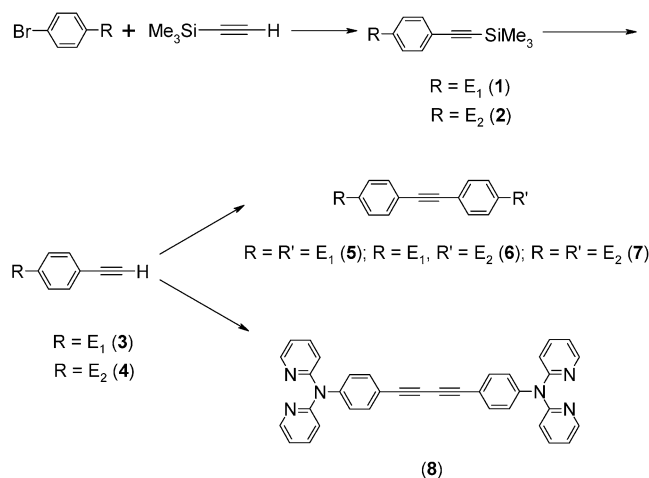
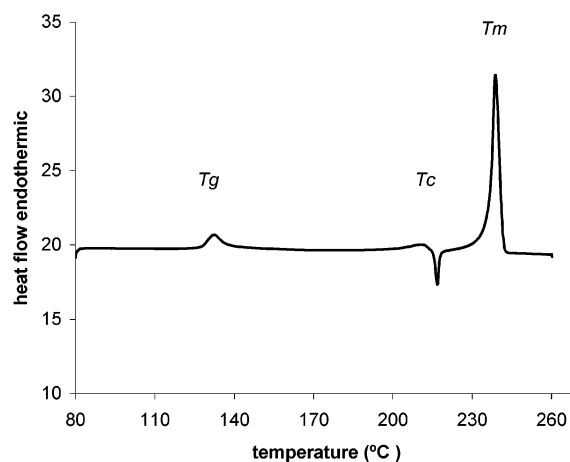
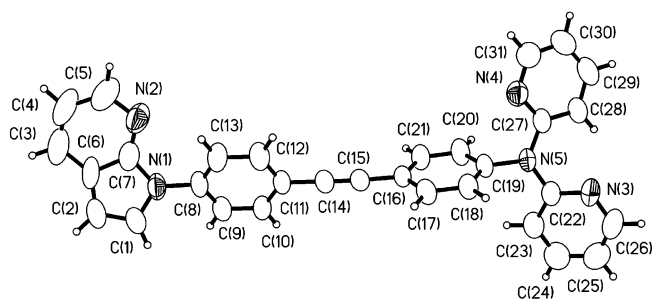
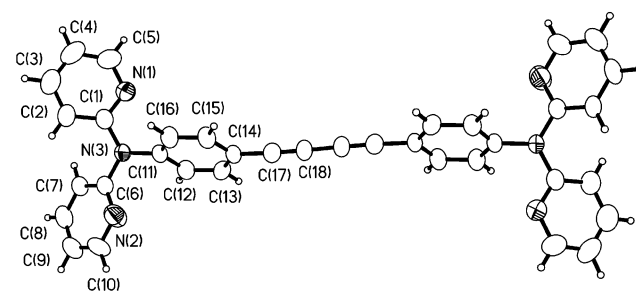


Table 3. Phase Transition Temperatures for 5–8

compd	$T_g/^\circ\text{C}$	$T_c/^\circ\text{C}$	$T_m/^\circ\text{C}$
5		175	186
6	61		164
7	130	216	239
8			278

and **8**. As shown in Figure 2, the two phenyl groups connected by the ethynyl link are perpendicular to each other. The pyridyl rings are not coplanar with the phenyl ring, as indicated by the dihedral angles of 76.65° between the N(3) ring and the phenyl and 77.08° between the N(4) ring and the phenyl, respectively. The nonplanarity of **6** is clearly caused by the steric hindrance between C–H groups. Compound **6** has several intermolecular interactions that appear to direct the extended packing of the solid-state structure. There are two symmetry-related, edge-to-face π – π stacking interactions between the phenylene rings (C(10) and C(16)) on adjacent molecules of **6**. The centroid-to-centroid distance is 4.91 \AA , and the angle between the ring planes is 78° . A weaker interaction also exists in the opposite direction, between symmetry equivalents of the same two rings, with a centroid-to-centroid distance of 5.06 \AA , and an angle also of 78° . There is also a face-to-face π – π stacking interaction between the C(30) pyridyl ring and the five-membered ring of an adjacent 7-azaindolyl moiety, with a centroid-to-centroid distance of 3.86 \AA , and an interplane angle of 16° . The six-membered ring of the 7-azaindolyl system also forms a somewhat weaker interaction with the C(16) phenylene ring of an adjacent molecule of **6**, with a centroid-to-centroid distance of 5.11 \AA and an interplane angle of 69° . The structure of compound **8** is shown in Figure 3. The bond lengths of C(17)–C(18) and C(18)–C(18') are $1.196(3)$ and $1.371(5) \text{ \AA}$ and are consistent with typical values for diynes. The bond angle of C(17)–C(18)–C(18') is $179.0(4)$, showing an almost ideal linear bond, with a deviation of only 1° . In contrast to **6**, the two phenyl rings linked by the diyne are coplanar. The extended structure of **8** exhibits a herring-

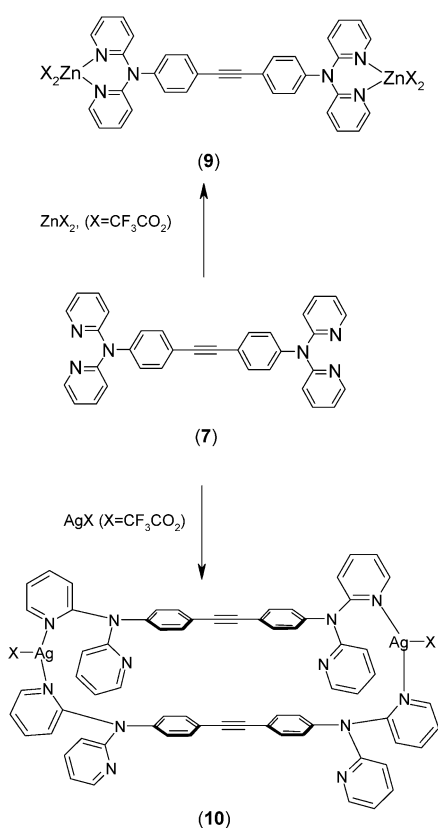
Figure 1. DSC diagram of **7** in the first heating.Figure 2. Molecular structure of **6** showing the atom-numbering scheme.Figure 3. Molecular structure of **8** showing the atom-numbering scheme.

bone packing motif (see Supporting Information) along the crystallographic c -axis, a pattern not uncommon to aromatic molecules, including benzene and naphthalene.¹⁸ To obtain this packing pattern, there are two important π – π stacking interactions present. The first is an edge-to-face interaction which occurs between the C(10)- and C(11)-containing rings of adjacent molecules of **8**, with a centroid-to-centroid distance of 4.93 \AA and an interplane angle of 77° . The second is a π – π interaction between the acetylene moiety adjacent to the C(11)-containing ring and the face of the C(10)-containing ring in the opposite direction of the first interaction. The centroid-to-centroid distance is 3.91 \AA , and the angle between the C(10)-containing ring and the C(18)-containing ring adjacent to the acetylene group is 78° .

Complexes. The development of blue luminescent metal complexes remains as an active research area for various applications. Recently, Zn complexes that contain N-donor

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Scheme 2



fluorescent chromophores, such as 7-azaindole,¹⁹ *N*-(2-pyridyl)-7-azaindole (npa), and tripyridylamine (tpa),²⁰ have emerged as promising candidates for blue emitters in EL devices. In our efforts, we have found that [Ag(tpa)(X)] derivatives display very interesting coordination modes, exhibiting various structures depending on the counterion, and fluorescent chemical sensing potentials,²¹ which prompted us to investigate the interactions of metal ions with ligands **5–8**. Our investigation focused on ligands **7** and **8** because of the presence of two chelating sites. Ligands **7** and **8** show similar behavior toward metal ions. Therefore, only the details of our investigation on complexes of **7** are presented herein.

The dinuclear Zn(II) complex [(ZnX₂)₂(L)] (L = **7**, X = CF₃CO₂[−]), **9**, was prepared conveniently by the reaction of Zn(CF₃CO₂)₂ with a stoichiometric amount of **7** in THF at room temperature. In contrast, a dinuclear Ag(I) macrocycle [AgX(L)]₂ (L = **7**, X = CF₃CO₂[−]), **10**, was obtained from the reaction of either 1 or 2 equiv of Ag(CF₃CO₂) with **7** in the absence of light, as shown in Scheme 2. Despite the addition of Ag(I) to compound **7** in a 2:1 ratio, we did not observe the 2:1 product, an analogue to that of compound

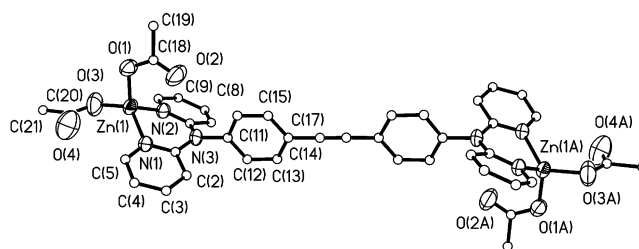


Figure 4. Molecular structure of **9** showing the atom-numbering scheme. For clarity, hydrogen and fluorine atoms are omitted. Carbon atoms are shown as ideal spheres.

9. To understand the difference between the reactions of **7** with Zn(II) and Ag(I), we investigated the structures of **9** and **10** by X-ray diffraction analyses.

As shown in Figure 4, the two Zn(II) ions in compound **9** are related by an inversion center, chelated by the dipyr-dylamino group and coordinated by two terminal trifluoroacetate ligands. The geometry of the Zn(II) ion is a distorted tetrahedron with bond angles ranging from 101.1° to 126.6°. The bond lengths of Zn–N(1) and Zn–N(2) are 1.995(3) and 2.000(3) Å, respectively, within known values of Zn–N in similar complexes.^{9d} Compound **9** exhibits two intramolecular π C–H \cdots O hydrogen-bonding interactions, between H(16) and O(2) (C(16) \cdots O = 3.157 Å), and between H(5) and O(4) (C(5) \cdots O = 3.150 Å). There are also some weak intermolecular π C–H \cdots F interactions between pyridyl rings and fluorine atoms, as evident by the distances of F(2) \cdots C(2') (3.142 Å) and F(3) \cdots C(3') (3.225 Å). The N(1) pyridyl ring is involved in a weak face-to-face π – π stacking interaction with its symmetry-related equivalent, with a centroid-to-centroid distance of 4.21 Å and an interplane angle of 0°. The interaction is not quite optimal, as the rings are slipped slightly more than half their width. The solvent benzene molecule does not appear to have any significant interaction with the complex, but is present only to fill the void space in the lattice. The benzene molecules do not escape from the crystal lattice at ambient temperature as evident by the stability of the crystals over a period of several months at ambient temperature. The stability of the benzene molecule in the lattice is attributable to its complete encapsulation by molecules of **9**.

As shown in Figure 5, the structure of compound **10** also possesses a crystallographically imposed inversion center. In contrast to **9**, where both pyridyl groups of the dipyr-dylamino portion are chelated to the metal ion, only one of the pyridyl groups from each dipyr-dylamino portion in **10** is bound to the Ag(I) center (N(5) and N(1)). The second pyridyl group of each dipyr-dylamino portion remains uncoordinated. Each Ag(I) ion is coordinated by two nitrogen atoms from two ligands. As a consequence, **10** displays a macrocyclic structure. The average bond length between Ag and nitrogen is 2.26 Å. In addition to nitrogen atoms, the Ag(I) center is also bound by an oxygen atom from the trifluoroacetate ligand, resulting in an irregular three-coordinate geometry. Failure to chelate to the 2,2'-dipyr-dylamino group by Ag(I) has been observed frequently previously in complexes containing 2,2'-dipyr-dylamino derivative ligands.²¹ Ag(I) ions appear to consistently favor terminal bonding

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(21) (a) Seward, C.; Chan, J.; Song, D.; Wang, S. *Inorg. Chem.* **2003**, *42*, 1112–1120. (b) Ag(I) ions form various 3D coordination polymers with starburst ligands that contain 2,2'-dipyr-dylamino binding sites. In these complexes, Ag(I) is usually 3-coordinated in the manner similar to that observed in **10**. Seward, C.; Wang, S. Unpublished results.

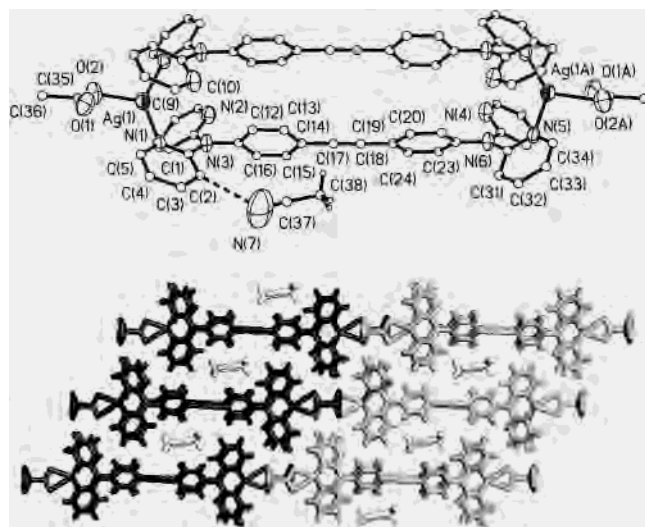


Figure 5. Top: Molecular structure of **10** showing the atom-numbering scheme. Hydrogen (except those of the solvent molecule) and fluorine atoms are omitted for clarity. Carbon atoms are shown as ideal spheres. Bottom: Crystal lattice packing diagram showing the side view and the stacking of **10**, the acetonitrile solvent molecules, and the interaction between two neighboring stacks.

modes by more than one 2,2'-dipyridylamino group in all complexes investigated by our group, leading to the formation of extended coordination polymers. This along with the desire of the Ag(I) ion to achieve 3-coordination may be responsible for the preferential formation of the 1:1 product. Compound **10** displays an interesting extended array in the crystal lattice. The dinuclear units of **10** stack in the lattice and appear to be held together by interlocked rotationally disordered CF₃ groups of adjacent dinuclear units (Figure 5, bottom). There appears to be a face-to-face π - π stacking interaction between the two ligands in the dimer, but while the centroid-to-centroid distance is 4.16 Å and the top and the bottom ligands appear to be parallel, they are slipped by about one benzene width, making any significant interaction unlikely. Acetonitrile solvent molecules are trapped inside the lattice which are bound to the complex through a hydrogen bond between the nitrogen atom of the acetonitrile N(7) and a hydrogen atom on a pyridyl ring H(2) on C(2), as evidenced by the distance of N(7)⋯H(2) (2.59 Å) and N(7)⋯C(2) (3.28 Å). The acetonitrile molecule does not escape from the crystal lattice at ambient temperature. The crystals of **10** are stable under air for a few days at ambient temperature, but become dark gradually, due to light-initiated decomposition.

Given the fact that the Ag complex has both coordinated and noncoordinated pyridyl rings, one would expect to observe two distinct sets of chemical shifts for the pyridyls. However, complexes **9** and **10** display similar chemical shifts in the ¹H NMR spectra with one set of chemical shifts for the pyridyl group at ambient temperature. This is likely caused by dynamic behavior of the complex in solution. In order to confirm the presence of the dynamic exchange process, we carried out a variable-temperature NMR study. Unfortunately, we were unable to obtain the ¹H NMR spectrum at sufficiently low temperature (183 K) due to the low solubility of the Ag complex in CD₂Cl₂. The Ag complex

Table 4. Photoluminescent Data for **5–10**^a

compd	absorption (λ_{\max} , nm) $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	emission (λ_{\max} , nm)	quantum ^c yield (Φ_{em})	conditions
5	324 (83457)	361	0.69	CH ₂ Cl ₂ , 298 K CH ₂ Cl ₂ , 77 K solid, 298 K solid, 298 K
		423, 530 ^b		
		443 450		
6	332 (86438)	382	0.76	CH ₂ Cl ₂ , 298 K CH ₂ Cl ₂ , 77 K solid, 298 K solid, 298 K
		395, 520 ^b		
		397 455		
7	344 (82380)	386	0.79	CH ₂ Cl ₂ , 298 K CH ₂ Cl ₂ , 77 K solid, 298 K solid, 298 K
		405, 514 ^b		
		453 454		
8	356 (84947)	405	0.31	CH ₂ Cl ₂ , 298 K CH ₂ Cl ₂ , 77 K solid, 298 K solid, 298 K
		433, 561 ^b		
		448 454		
9	258 (27472), 316 (45604)	385	0.51	CH ₂ Cl ₂ , 298 K CH ₂ Cl ₂ , 77 K
		388, 517 ^b		
10	310 (sh, 48523), 344 (59493)	384	0.59	CH ₃ CN, 298 K CH ₃ CN, 77 K
		390, 518 ^b		

^a Concentration: [M] $\approx 10^{-5}$ M. ^b Phosphorescent emissions were determined by using time-resolved methods (See the Supporting Information). ^c The quantum yields of all compounds were obtained by comparing to 9,10-diphenylanthracene (0.9).

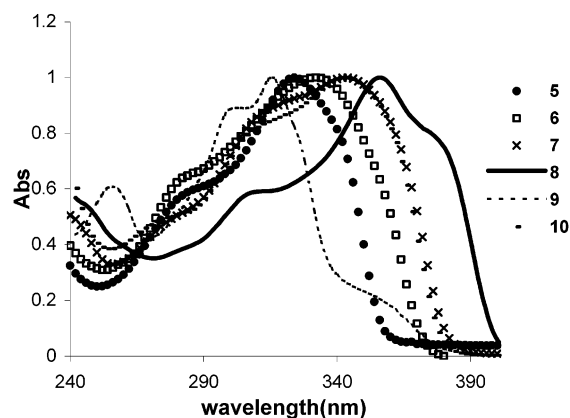


Figure 6. UV/vis absorption spectra of compounds **5–10**.

is only slightly soluble in CH₃CN. The ¹H NMR spectrum of **10** in CD₃CN over a temperature range of 233–333 K does not change significantly (See Supporting Information). However, on the basis of our previous study on zinc and silver tpa complexes,^{9d,21} we believe that **10** is fluxional in solution. The ¹³C NMR spectrum of **9** exhibits quartets at 117.3 and 163.0 ppm, which are due to the chemical shifts and ¹J_{C-F} (299.4 Hz) and ²J_{C-F} (38.5 Hz) coupling of CF₃ and C(O) groups in the trifluoroacetate group, respectively. The ¹⁹F NMR spectra of both complexes show only one peak at -77.76 and -78.12 ppm, respectively, leading to the conclusion that the environments of the trifluoroacetate groups in both complexes are very similar.

Luminescent Properties. Luminescent data are listed in Table 4. The UV/vis spectra of compounds **5–8** display intense absorption bands ranging from 284 to 380 nm, indicating that electronic transitions are mostly $\pi \rightarrow \pi^*$, originating from the phenyl and pyridyl groups (Figure 6). Compounds **5–8** have broad fluorescent emission bands in solution at room temperature, with $\lambda_{\max} = 361, 382, 386,$ and 405 nm, for **5–8**, respectively (Figure 7). The observed

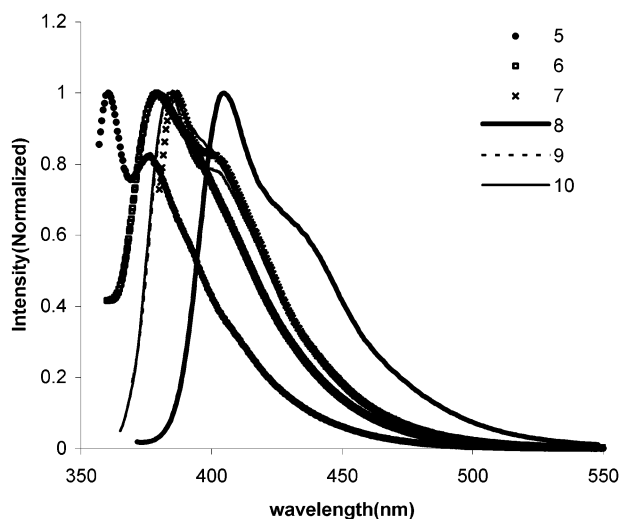


Figure 7. Emission spectra of **5–10** in solution at room temperature.

broad emission bands at room temperature are predominantly fluorescence, as supported by their small Stokes shifts and short decay lifetimes. The red shift of the emission energy of these compounds, compared to those of 2,2'-dipyridylamine ($\lambda_{\text{max}} = 343$ nm) or 7-azaindole ($\lambda_{\text{max}} = 357$ nm), is due to the extended conjugation through the phenylene and ethynyl units and the replacement of the protons on the amino groups in the 2,2'-dipyridylamine and 7-azaindole units. Similar emission energy red shifts have been recently reported by our group in systems with star-shaped 2,2'-dipyridylamine derivatives.^{9b} Interestingly, although phosphorescent emissions of **5–8** are very weak or negligible at room temperature, we have observed both intense fluorescent and weak phosphorescent emission bands at 77 K using steady-state and time-resolved methods (See the Supporting Information). The fluorescent lifetimes of the organic ligands at ambient temperature appear to be in the range of 3.6–5.1 μs , but they cannot be determined accurately due to the limitation of our instrument. The fluorescent emission lifetimes in simple 2,2'-dipyridylamino or 7-azaindoly coordinated Al(III) complexes were found to be in the nanosecond regime,^{9e,f} much shorter than the acetylide functionalized ligands **5–8**. The phosphorescent lifetime of **5–8** at 77 K is in the range of 480–550 μs . Complexes **9** and **10** display two intense absorptions, which are assigned to intraligand $\pi-\pi^*$ transitions. At room temperature the emission spectra of complexes **9** and **10** show emission peaks similar to those of the free ligand **7**, at 388 and 390 nm, respectively, and a decrease in quantum efficiency as compared to **7**, indicating that Zn(II) and Ag(I) partially quench the luminescence without changing the emission energy. In a frozen solution of CH_2Cl_2 or CH_3CN , phosphorescent emissions with long lifetimes (>500 μs) for **9** and **10** at 517 and 518 nm, respectively, were observed (Figure 8). Supramolecular systems containing two components, a fluorescent chromophore and a metal ion complexing site, have been shown previously to be efficient detecting agents for Zn(II), an important biological cation.²² To

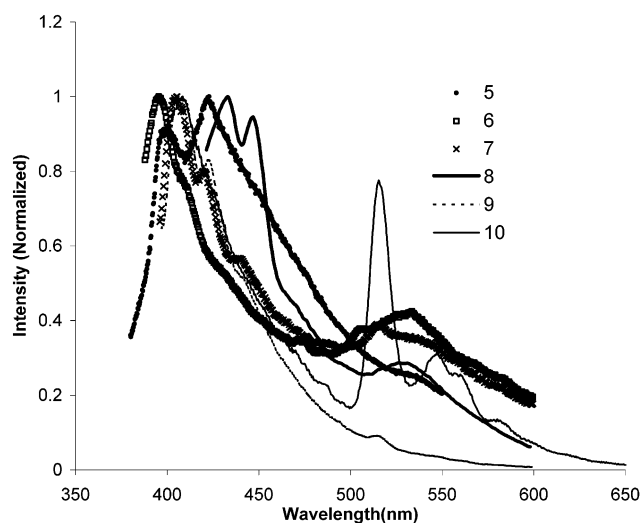


Figure 8. Emission spectra of **5–10** in frozen solution (CH_2Cl_2 or CH_3CN) at 77 K.

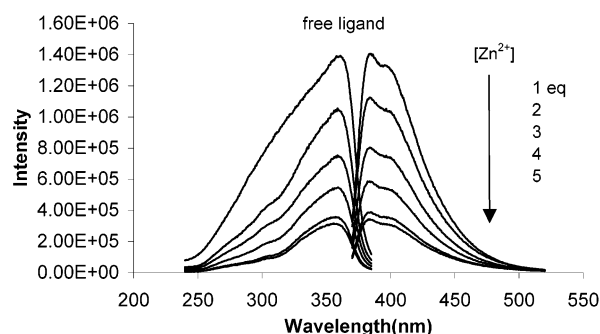


Figure 9. Excitation and emission spectra of **7** ($[\text{M}] = 9.0 \times 10^{-5}$) at room temperature in THF with increasing concentration of ZnCl_2 .

investigate the possible use of our new ligands as Zn(II) sensors, a fluorescent emission study using ligand **7** as a representative example with varying concentrations of Zn(II) was conducted. For comparison, the fluorescent response of **7** toward H^+ was also investigated. As shown in Figure 9, the titration of compound **7** with ZnCl_2 in THF shows a steady fluorescent quenching with increasing concentration of Zn(II). (The titration of **7** in CH_3CN by CF_3COOH (H^+) shows a similar fluorescent quenching with increasing concentration of H^+ . See Supporting Information.) These observations are consistent with recent reports related to Zn^{2+} and protonation-induced fluorescent quenching,²³ and support that compound **7** has the potential as a fluorescent sensor for Zn^{2+} or pH. The behavior of **8** toward metal ions and protons is similar to that of **7**. The selectivity of ligands **7** and **8** as a fluorescent sensor toward Zn(II) ions is being investigated.

In summary, new types of 7-azaindoly and 2,2'-dipyridylamino derivatives with π -conjugated rigid structures have been synthesized. The new organic molecules and their complexes all exhibit a blue or purple luminescence at room temperature when irradiated by UV light. Compound **7** has

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a high glass transition temperature and is promising for applications in organic light emitting devices, which will be evaluated. We have shown that **7** and **8** are useful complexing reagents for metal ions and have the potential as fluorescent sensors for metal ions or protons. Ligands **5** and **6** contain 7-azaindolyl groups which are expected to interact with metal ions in a different manner than **8** and **9**. To date we have not been able to isolate any coordination compounds where the Zn(II) or Ag(I) ion is bound to the 7-azaindolyl nitrogen site in ligands **5** and **6**. The 7-azaindolyl groups in ligands **5** and **6** may be able to bind to metal ions such as Pt(II) and Pd(II) via *cyclometalation* involving an *ortho* C–H bond activation, which is being investigated in our laboratory.

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Supporting Information Available: Enhanced phosphorescent emission spectra for compounds **5–10**, diagram showing the intermolecular stacking of **6**, figure depicting the herringbone-type packing of **8**, variable-temperature ¹H NMR spectra for **10**, excitation and emission spectra of **7**, and tables of crystallographic data for **6** and **8–10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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