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A novel class of Zn(II) Schiff base complexes with aggregation-induced emission enhancement (AIEE) properties: Synthesis, characterization and photophysical/ electrochemical properties

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1. Introduction

ABSTRACT

A series of novel Zn(II) Schiff base complexes with diphenylamino and carbazole groups that exhibited aggregation-induced emission enhancement were designed and synthesized. The properties of four complexes were investigated by UV–Vis absorption and fluorescence emission spectroscopy, cyclic voltammetry and density functional theory calculations. The fluorescence intensities of the four dyes are weak in tetrahydrofuran, but become strong in a mixture of water/tetrahydrofuran ($\nu/\nu = 9/1$). This work constitutes the first observation of this phenomenon for Zn(II) Schiff base complexes. A simple model complex, without the possibility of intramolecular rotational motion, was prepared in order to determine the mechanism of the AIEE. The present aggregation-induced emission enhancement was attributed to restricted intramolecular rotational motions in the solid by carefully analyzing the difference in molecular structure and photophysical properties amongst the new complexes.

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Solid-state organic luminescent dyes have gained a great deal of attention in recent years because of their potential applications in chemosensors [1,2], field-effect transistors [3–6], live-cell imaging [7–9], and organic light-emitting diodes (OLEDs) [10–13]. However, a majority of organic dyes exhibit strong luminescence in their dilute solutions. These dyes become weak luminophores in the solid state or in high concentration in solution because of the strong interactions between closely packed molecules, leading to emission quenching [14–16]. This phenomenon may render the dyes less suitable for some optical devices. A variety of approaches such as attaching enhanced steric hindrance or bulky side groups into the complexes to separate chromophoric units have been recently investigated in an effort to overcome this problem [17–20]. However, limited success has been achieved using these approaches. Some organic compounds exhibiting unusual aggregation-induced

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emission enhancement (AIEE) properties have been recently found [21–27]. These compounds exhibit weak luminescence or have almost no emission in solution, but are highly emissive in the solid state. This characteristic of materials with AIEE properties can provide an efficient way to resolve the problem related to emission quenching in the condensed phase.

A number of studies on Zn(II) Schiff base complexes as potential OLED materials have been conducted since Hamada et al. first reported on this research field in 1993 [28-31]. Recently, Chi et al. have also developed a series of phosphorescent Pt(II) transition metal Schiff base complexes and demonstrated that these complexes are suitable candidates in electroluminescent applications [32,33]. In addition, the Schiff base ligands can be easily prepared and structurally modified. Thus, various Schiff base complexes with desired photophysical properties can be obtained [34-41]. However, these complexes intrinsically suffer from emission quenching in films, decreasing the device performance, especially for non-doped devices. It is speculated that if the Schiff base compounds with the AIEE properties can be explored, the tendency of emission quenching for them would no longer exist. Although the Ir(III) Schiff base complexes exhibiting AIEE properties have been reported by Park recently [42], the Zn(II) Schiff base

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complexes exhibiting AIEE have never been investigated until this present study.

In this contribution, we successfully designed and synthesized four Zn(II) Schiff base complexes, namely, Zn(L1)₂ (1), Zn(L2)₂ (2), Zn $(L3)_2$ (3) and Zn $(L4)_2$ (4), in which the ligands L1-L4 represent 2-(((4-(diphenylamino)phenyl)imino)methyl)phe nol. 1-(((4-(diphenvlamino)phenvl)imino)methyl)naphthalen-2-ol. 2-(((4-(9H-carbazol-9-vl)phenvl)imino)methvl)phenol, 1-(((4-(9Hcarbazol-9-yl)phenyl)imino)methyl)naphthalen-2-ol, respectively (See Scheme 1). Herein, the diphenylamino and carbazole groups were introduced into complexes through single bonds because the incorporation of these aromatic moieties with rotational motions into complexes can be expected to give rise to AIEE [25,26]. The photophysical properties of the designed complexes have been investigated in detail. The results demonstrate that the complexes have AIEE properties and emitted in the yellow-green region, indicating that they may be good candidates for OLEDs. A controlled experiment using compound 5 (Scheme 1) without any aromatic rotational motions was performed to understand the possible mechanism of the present AIEE property. Based on our data, the most probable reasons were claimed to be restricted intramolecular motion in the solid state, which was also considered as the main cause of AIEE properties for reported organic smallmolecules. To the best of our knowledge, this is a first example of Zn(II) Schiff base being shown to AIEE active. To gain insight into the nature of their emissive excited state, guantum chemical calculations were performed.

2. Experimental section

2.1. Materials and physical measurements

All reagents and solvents employed were commercially available and used as received without further purification. The solvents for syntheses were freshly distilled over appropriate drying reagents. All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 240C elemental analyzer. Thermogravimetric analyses (TGA) were performed on a Perkin–Elmer TG-7 analyzer heated from 30 °C to 800 °C under flowing nitrogen. ¹H NMR spectra were measured on a Bruker Avance 500 MHz with tetramethylsilane as the internal standard. The complexes were also verified using matrix-assisted laser desorption-ionization time-offlight mass spectrometry (MS MALDI-TOF). UV-Vis absorption spectra were obtained using a Shimadzu UV-Vis spectrometer. The PL quantum yields of the complexes in the solutions and solid-state were measured using steady-state and time-resolved fluorescence spectrometers (FLSP920) with an integrating-sphere photometer. Fourier transform infrared spectra were obtained using KBr pellets in the 4000–400 cm⁻¹ range on an Irprestige-21 spectrometer. The emission spectra were obtained from a Cary Eclipse spectrofluorometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature. Cyclic voltammetry was performed on a BAS 100 W electrochemical workstation. Tetrabutylammonium perchlorate was used as supporting electrolyte (0.1 M) in dry dichloromethane with a scan rate of 100 mV/s at room temperature under argon. The glassy carbon rod electrode was used as the working electrode, a Pt wire as the counter electrode, with a calomel electrode as a reference. The oxidative potentials were calibrated by using ferrocene as an internal standard.

2.2. Synthesis of ligand and complex

2.2.1. Synthesis of ligand L1

A solution of N',N'-diphenylbenzene-1,4-diamine (0.26 g, 1.0 mmol) and salicylaldehyde (0.12 g, 0.10 mmol) in ethanol (10 mL) was heated under reflux for 4 h. After cooling to room temperature, the precipitate was filtered and washed with ethanol. The precipitate was a light yellow needles (85%). M.P.: 159–160 °C, ¹H NMR (500 MHz, CDCl₃) δ 13.44 (s, 1H), 8.62 (s, 1H), 7.36 (dd, *J* = 13.1, 7.2 Hz, 2H), 27 (t, *J* = 9.1 Hz, 4H), 7.23–7.18 (m, 2H), 7.15–7.07 (m, 6H), 7.07–6.98 (m, 3H), 6.93 (t, *J* = 7.5 Hz, 1H). IR (KBr), *v*/cm⁻¹: 3444, 3032, 1614, 1587, 1489, 1454, 1328, 1278, 1190, 1149, 1112, 831, 754, 696, 533, 507. Anal. calcd. for C₂₅H₂₀N₂O: C, 82.39; H, 5.53; N, 7.69. Found: C, 81.78; H, 5.61; N, 7.60.

2.2.2. Synthesis of ligand L2

The synthesis of ligand **L2** was similar to that of ligand **L1** from N',N'-diphenylbenzene-1,4-diamine and 2-hydroxy-1-naphthalde hyde. The precipitate was a golden yellow powder (82%). M.P.: 158.5–160.1 °C, ¹H NMR (500 MHz, CDCl₃) δ 15.67 (s, 1H), 9.32 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 8.0 Hz,



Scheme 1. The structures of zinc(II) Schiff base complexes 1, 2, 3, 4, and 5. (For interpretation of the references to color in this legend, the reader is referred to the web version of this article.)

1H), 7.51 (t, J = 7.7 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.31–7.27 (m, 6H), 7.19–7.12 (m, 6H), 7.10 (d, J = 9.1 Hz, 1H), 7.06 (t, J = 7.4 Hz, 3H). IR (KBr), ν/cm^{-1} : 3415, 3053, 1622, 1587, 1489, 1421, 1327, 1278, 1244, 1174, 1074, 815, 750, 700, 545, 503. Anal. calcd. for $C_{29}H_{22}N_2O$: C, 84.03; H, 5.35; N, 6.76. Found: C, 84.11; H, 5.29; N, 6.70.

2.2.3. Synthesis of ligand L3

The synthesis of ligand **L3** was similar to that of ligand **L1** from 4-(9*H*-carbazol-9-yl)aniline and salicylaldehyde. The precipitate was a light yellow powder (92%). M.P.: 181.4–182.8 °C, ¹H NMR (500 MHz, CDCl₃) δ 13.20 (s, 1H), 8.77 (s, 1H), 8.18 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.51–7.42 (m, 6H), 7.38–7.29 (m, 2H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H). IR (KBr), *v*/cm⁻¹: 3416, 3024, 1614, 1593, 1566, 1510, 1491, 1450, 1364, 1333, 1314, 1279, 1229, 1180, 1148, 1150, 841, 819, 744, 721, 655, 621, 530, 428. Anal. calcd. for C₂₅H₁₈N₂O: C, 82.85; H, 5.01; N, 7.73. Found: C, 81.92; H, 5.10; N, 7.68.

2.2.4. Synthesis of ligand L4

The synthesis of ligand **L4** was similar to that of ligand **L1** from 4-(9*H*-carbazol-9-yl)aniline and 2-hydroxy-1-naphthaldehyde. The precipitate was an orange powder (90%). M.P.: 189.0–190.3 °C, ¹H NMR (500 MHz, CDCl₃) δ 15.43 (s, 1H), 9.48 (d, *J* = 3.4 Hz, 1H), 8.17 (t, *J* = 8.2 Hz, 3H), 7.85 (d, *J* = 9.1 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.62–7.52 (m, 3H), 7.50–7.41 (m, 4H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.35–7.27 (m, 2H), 7.16 (d, *J* = 9.1 Hz, 1H). IR (KBr), *v*/cm⁻¹: 3418, 3042, 1602, 1534, 1512, 1477, 1450, 1358, 1335, 1315, 1229, 1165, 1134, 1115, 1001, 954, 912, 821, 750, 723, 648, 621, 501, 430. Anal. calcd. for C₂₉H₂₀N₂O: C, 84.44; H, 4.89; N, 6.79. Found: C, 84.35; H, 4.79; N, 6.83.

2.2.5. Synthesis of ligand L5

The synthesis of ligand **L5** was patterned after a published procedure [43,44]. The precipitate was a white powder solid (80%).

2.2.6. Synthesis of complex 1

A solution of ligand **L1** (0.36 g, 1.0 mmol) and zinc acetate (0.1 g, 0.50 mmol) in ethanol (10 mL) was heated under reflux for 4 h.

After cooling to room temperature, the precipitate was filtered and washed with ethanol. A yellow flocculent solid was obtained (75%). ¹H NMR (500 MHz, CDCl₃): δ 8.39 (s, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.21 (dd, *J* = 14.5, 6.9 Hz, 10H), 7.05–6.97 (m, 16H), 6.93 (dd, *J* = 17.4, 8.7 Hz, 6H), 6.65 (t, *J* = 7.3 Hz, 2H). IR (KBr), ν/cm^{-1} : 1607, 1587, 1531, 1498, 1460, 1438, 1384, 1325, 1276, 1180, 1147, 756, 696, 501. Anal. calcd. for C₅₀H₃₈N₄O₂Zn: C, 75.80; H, 4.83; N, 7.07. Found: C, 75.92; H, 4.71; N, 7.11. MS (MALDI-TOF): *m/z* 791.2[M⁺].

2.2.7. Synthesis of complex 2

The synthesis of complex **2** from ligand **L2** and zinc acetate was similar to that of complex **1**. The orange solid was obtained (72%). ¹H NMR (500 MHz, CDCl₃): δ 9.32 (s, 2H), 8.01 (d, *J* = 8.5 Hz, 2H), 7.8 (d, *J* = 9.2 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.9 Hz, 8H), 7.09 (d, *J* = 9.2 Hz, 2H), 7.02–7.00 (m, 12H), 7.00–6.94 (m, 8H). IR (KBr), *v*/cm⁻¹: 1614, 1593, 1535, 1490, 1456, 1427, 1394, 1363, 1328, 1278, 1180, 829, 748, 696, 493. Anal. calcd. for C₅₈H₄₂N₄O₂Zn: C, 78.07; H, 4.74; N, 6.28. Found: C, 78.10; H, 4.70; N, 6.31. MS (MALDI-TOF): *m/z* 891.2[M⁺].

2.2.8. Synthesis of complex 3

The synthesis of complex **3** from ligand **L3** and zinc acetate was similar to that of complex **1**. The yellow solid was obtained (76%). ¹H NMR (500 MHz, CDCl₃): δ 9.50 (s, 2H), 8.15–8.07 (m, 4H), 7.89 (d, *J* = 9.3 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 4H), 7.42 (d, *J* = 8.4 Hz, 4H), 7.38–7.26 (m, 14H), 7.19 (d, *J* = 9.2 Hz, 2H). IR (KBr), *v*/cm⁻¹: 1610, 1585, 1529, 1510, 1446, 1390, 1357, 1332, 1226, 1176, 1145, 842, 748, 723, 626, 567. Anal. calcd. for C₅₀H₃₄N₄O₂Zn: C, 76.19; H, 4.35; N, 7.11. Found: C, 76.02; H, 4.45; N, 7.23. MS (MALDI-TOF): *m/z* 787.2[M⁺].

2.2.9. Synthesis of complex 4

The synthesis of complex **4** from ligand **L4** and zinc acetate was similar to that of complex **1**. The orange solid was obtained (73%). ¹H NMR (500 MHz, CDCl₃): δ 8.58 (s, 2H), 8.14 (d, *J* = 7.7 Hz, 4H), 7.54 (d, *J* = 8.6 Hz, 4H), 7.46 (t, *J* = 7.0 Hz, 4H), 7.42 (d, *J* = 8.6 Hz, 4H), 7.36 (d, *J* = 3.3 Hz, 8H), 7.33–7.23 (m, 8H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 2H). IR (KBr), *v*/cm⁻¹: 1612, 1575, 1535, 1510, 1452,



Scheme 2. Synthetic routes of ligands L1–L5.



Fig. 1. Photophysical properties of L1–L4 in THF solution (10^{-5} M). (a) Absorption spectra; (b) emission spectra.



Fig. 2. Photophysical properties of **1**, **2**, **3**, and **4**. (a) Absorption spectra. (b) Emission spectra in THF solution (10^{-5} M) (The excited wavelength is 329, 366, 305 and 302 nm, respectively). (c) Emission spectra in solid state (The excited wavelength is 277, 274, 276 and 274 nm, respectively).

1427, 1392, 1363, 1336, 1228, 1182, 1165, 833, 748, 503. Anal. calcd. for $C_{58}H_{38}N_4O_2Zn$: C, 78.42; H, 4.31; N, 6.31. Found: C, 78.51; H, 4.20; N, 6.40. MS (MALDI-TOF): m/z 887.2[M⁺].

2.2.10. Synthesis of complex 5

The synthesis of complex **5** from ligand **L5** and zinc acetate was similar to that of complex **1**. The white powder was obtained (78%). ¹H NMR (300 MHz, CDCl3): δ 8.23 (s, 2H), 7.32 (t, *J* = 6.9 Hz, 2H), 7.13 (d, *J* = 9.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.61 (t, *J* = 7.0 Hz, 2H), 3.63 (q, *J* = 7.2 Hz, 4H), 1.27 (t, *J* = 7.3 Hz, 6H). Anal. calcd. for C₁₈H₂₀N₂O₂Zn: C, 59.76; H, 5.57; N, 7.74. Found: C, 59.51; H, 5.20; N, 7.40.

2.3. Theoretical calculations

The electronic structures of the singlet ground state (S_0) for complexes **1–4** were investigated by performing density functional theory (DFT) calculations at the B3LYP level [45,46]. The 6-31G* basis sets were employed to optimize the C, H, N, and Zn atoms. The excitation energies were then studied by time-dependent DFT (TD-DFT). All calculations were performed with the C.02 version of the Gaussian 03 program package [47].

3. Results and discussion

3.1. Synthesis

Ligands **L1–L5** were synthesized according to the procedures described in the literature [43] (Scheme 2). Compounds **1–5** can be readily achieved from the reaction of ligands **L1–L5**, respectively, with zinc acetate in ethanol and then heated under reflux for 4 h. The molecular structures of these complexes were characterized by ¹H NMR, MS, and elemental analysis.

3.2. IR and ¹H NMR spectra

IR spectra of ligands L1–L4 show a very strong absorption band due to the imine C=N stretching at 1614, 1622, 1614 and 1602 cm⁻¹, respectively. It is shifted by about 10 cm⁻¹ in the complex 1–4, shows at 1607, 1614, 1610 and 1612 cm⁻¹, respectively, suggesting that coordination of the Schiff base groups through nitrogen atoms with the zinc ion occurred. ¹H NMR spectra of L1–L4 show the important proton signals at 8.62, 8.10, 8.77 and 9.48 ppm, respectively, which are assigned to the imine CH=N proton. The CH=N protons of complexes 1–4 appear as singlet at 8.39, 9.32, 9.50 and 8.58 ppm, respectively.

3.3. Photophysical properties

3.3.1. Photophysical properties of ligands

The absorption and photoluminescent (PL) spectra of free ligands **L1–L4** recorded in THF solution are presented in Fig. 1. The bands around 300 nm are assigned to the π – π * transition of the aromatic rings. The low-energy absorption peaks are situated at 389 nm for **L1**, 416 nm for **L2**, 342 nm for **L3** and 387 nm for **L4**,

Characters of the absorption and fluorescence spectra of ligands and complexes.									
	^a Ligands	Complexes							
	$\lambda_{abs}/\lambda_{em}$ (nm)	$a\lambda_{abs}(nm)$	λ_{em} (nm)	$^{c}\Phi_{\rm solution}$	$\Phi_{\rm powder}$				
1	389/537	422	^a 518/ ^b 527	3.0%	16.7%				
2	416/544	441	^a 544/ ^b 554	16.0%	20.9%				
3	342/418(526)	409	^a 496/ ^b 504	3.0%	21.4%				
4	387/503	430	^a 503/ ^b 521	2.0%	4.5%				

^a THF solution (10^{-5} M).

^b Powder.

Table 1

^c CH₂Cl₂ solution.



Fig. 3. Emission spectra of 3 (a) and 5 (b) in water/THF mixtures with different water fractions.

respectively, which can be attributed to the π - π * transition resulting from the conjugation between the aromatic rings and nitrogen atoms. The ligands display relatively weak emission at room temperature, with peaks at 537, 544, 418/526 and 503 nm for **L1**, **L2**, **L3** and **L4** in the solution, respectively.

3.3.2. Photophysical properties Zn(II) Schiff base complexes

The UV–Vis and photoluminescent spectra of complexes 1–4 in tetrahydrofuran (THF) solutions (10^{-5} M) and in the solid state at room temperature were measured to investigate their optical properties. As shown in Fig. 2, all of the absorption spectra exhibit two major absorption bands. The absorption bands in the UV region ranging from 250 nm to 350 nm correspond to C=N π - π * transitions. The low-energy absorption band approximately 400 nm extending to the visible region is tentatively attributed to the intramolecular charge transfer of ligands. After coordination with Zn(II), the absorption maxima are significantly red-shifted in comparison with their corresponding free ligands. The red-shift may be due to more efficient conjugation in the Zn(II) complex compared with that in the free ligands. The complexes display relatively weak emission in the solution at room temperature, with peaks at 518, 544, 496, and 503 nm for 1, 2, 3 and 4, respectively (The excited wavelength is 329, 366, 305 and 302 nm, respectively. Excitation spectra see Fig. S1). It is noted that the maximum emission of complexes 2 and 4 in solution are same as their corresponding ligands L2 and L4, respectively. However, complexes 1 and 3 exhibits blue-shifted emission compared with ligands L1 and L3, respectively. It is noted that the maximum emission of complexes in the solid state are red-shift as compared to those in solution (See Table 1.), which may be attributed to the different molecular conformations in solid state and solution [48,49]. The emission of 1 is obviously red-shifted compared with that of 3 because the diphenylamino group is a much stronger electrondonor than the carbazole group, resulting in an increase in the HOMO energy [50,51]. A similar result was also observed when the emission spectrum of 2 was compared with that of 4. Replacing phenol (1 and 3) with naphthalene (2 and 4) also resulted in remarkable bathochromic shifts in the emission because a more extended conjugation of the naphthalene destabilizes the LUMO energy level, leading to a decrease in the energy gap. The experimental results have been confirmed by quantum chemical calculations.

In the emission spectra, the four dyes show weak fluorescence when dissolved in organic solvents, the fluorescence quantum yields (Φ) of the four dyes, are only 3.0%, 16.0%, 3.0% and 2.0% in the dilute CH₂Cl₂ solutions, respectively (Table 1). However, the fluorescence quantum efficiencies of four powdered dyes are 16.7%, 20.9%, 21.4% and 4.5%, respectively, which clearly indicates the AIEE characteristics of **1**–**4**.

3.4. Aggregation-induced emission enhancement (AIEE) properties

The obtained compounds (1-4) readily dissolve in common organic solvents, such as chloroform, THF, acetone, acetonitrile, and dichloromethane, but are insoluble in water. Thus, the aggregated particles should be precipitated as the fraction of water is increased. The emission spectra of 1-4 in water/THF mixtures with different water content (0-90%) were obtained to verify if the compounds displayed AIEE properties [7,52]. For instance, **3** exhibits a blue emission at 496 nm in THF solvent. The emission intensity is very weak and almost does not change when the water fraction (f_w) is below 50% (Fig. 3(a)). However, a significant enhancement in emission is observed in the water/THF mixture with a water fraction above 50%. The emission intensity of the mixture with a water fraction of 90% was about 25 times higher than that in pure THF solvent, indicating that **3** has a strong AIEE property. Complexes **1**, **2**, and **4** also exhibit AIEE properties (Figs. S2–S4).

Previous studies have shown that AIE and/or AIEE might be related to the restriction of intermolecular rotation, formation of specific aggregates, and effects of intramolecular planarization. However, one of the most probable reasons accounting for AIE and/or AIEE is restriction of intramolecular motion, which is usually considered as the main cause of AIE in small organic molecules [21,53]. Herein, we also suppose that the present AIEE phenomenon was caused by the restricted intermolecular rotation. Complex **5** was synthesized with no intermolecular rotation to investigate the possible reason for the present AIEE (Scheme 1). The emission spectra of **5** in water/THF mixtures with different water content (0–90%) were also performed. Complex **5** is highly emissive when dissolved in the solvent, but the emission intensity sharply decreases upon



Fig. 4. TGA curves of complexes 1-4. Inset: DSC curves of 1-4.



Fig. 5. Cyclic voltammetry curves of complexes 1-4 in 0.1 M Bu₄NClO₄/CH₂Cl₂ solution at scan rate of 100 mV/s.

Table 2

HOMO and LUMO energy level of dyes 1-4.

	$E_{\text{onset}}^{\text{ox}}\left(V\right)$	^a HOMO (eV)	^b Eg (eV)	^c LUMO (eV)	^d HOMO (eV)	^d LUMO (eV)	^d Eg (eV)
1	0.33	-5.13	2.67	-2.46	-5.02	-1.80	3.22
2	0.31	-5.11	2.53	-2.58	-4.98	-1.88	3.10
3	0.63	-5.43	3.00	-2.43	-5.41	-1.93	3.48
4	0.34	-5.14	2.73	-2.41	-5.36	-1.98	3.38

^a Determined from the onset of the oxidation voltages.

^b Calculated from the edges of the absorption spectra.

^c obtained by the HOMO values and the energy gaps ($E_{\rm g}$).

^d Calculated from the theoretical simulations.

increasing the water fractions due to the aggregation quenching emission (Fig. 3(b)). Careful analysis of the structures of 1-5 reveals the presence of aromatic rotors (marked in red color, Scheme 1) in 1-4, but not in **5**. The excited intramolecular motions in 1-4 may be considered as one of the possible reasons for AIEE. In

Table 3

Selected frontier orbitals of complexes 1-4.

diluted solutions, the aromatic rotors in **1–4** can rotate freely, resulting in weak emission. The intramolecular rotational motions should be suppressed effectively during aggregation. Thus, radiation decay is enhanced by promoting a relatively small structural relaxation, leading to enhanced emission.

3.5. Thermal analysis

The thermal properties of the four complexes under a nitrogen gas flow were also evaluated by TGA and differential scanning calorimetry (DSC). The decomposition temperatures (T_d) were 364, 389, 370, and 395 °C with a weight loss of 5% for **1**, **2**, **3**, and **4**, respectively, indicating that they also exhibit good thermal stability (Fig. 4). Noticeably, replacement of phenyl group by a naphthalene moiety results in complexes **2** and **4** with much higher T_d values than **1** and **3**. The four complexes have better thermal properties than **5** and other imines compounds [44,54,55]. All complexes, except **1** with high glass-transition temperature (T_g) of 156 °C, show no phase transition during the heating scan period (Fig. 4, inset: DSC curves). The excellent thermal stability and amorphism of the complexes improve the operating lifetime as well as efficiency of an electroluminescent device.

3.6. Electrochemical properties

The anodic scanning cyclic voltammetry was employed to investigate the electrochemical behavior, and to estimate the HOMO energy levels of **1**–**4**. Fig. 5 shows the cyclic voltammetry curves of **1**–**4**, which exhibit reversible processes in the oxidation scan that correspond to the oxidations of the triphenylamine or carbazole units in the molecule [50,56]. The corresponding LUMO levels were obtained by the HOMO values and the energy gaps (E_g), which were deduced from the edges of the absorption spectra. The values obtained are listed in Table 2. Through the cyclic voltammograms, the oxidation potentials of **1**–**4** were measured to be 0.33, 0.31, 0.63 and 0.34 V, and the energy band gaps of about 2.67, 2.53, 3.00 and 2.73 eV can be obtained from extrapolated UV–Vis absorption edge, respectively. The HOMO energy levels of all



complexes were calculated by $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8)$ eV. As result, the HOMO energy of these materials was calculated to be in the range of -5.11 to -5.43 eV which might be beneficial for the hole transport capacity. The LUMO levels (-2.41 to -2.58 eV) of **1–4** represent a small barrier for the electron injection from a commonly used cathode such as barium which has a work function of -2.7 eV. Therefore, these compounds might be very useful as hole-transporting and electron-transporting materials in OLED applications.

3.7. Quantum chemical calculations

Quantum chemical calculations were performed (see Experimental section) to understand the nature of the emissive excited state involved in the emission process of 1-4. The excitation energies and molecular orbitals involved in the excitations of the complexes are summarized in Table S1. The HOMO for all complexes is either on the diphenylamino or carbazole groups of the ligand, whereas the LUMO is mainly delocalized over the phenolic ring group and the nitrogen atom of the ligand (Table 3); results that support the experimental data. Replacing the carbazole and phenyl groups with a diphenylamino and a naphthalene group, respectively, causes the corresponding emission spectra to be redshifted. In addition, the TD-DFT results reveal that S₁ for **1** originates from the excitation of HOMO-1 \rightarrow LUMO (82%) and HOMO \rightarrow LUMO+1 (17%). The TD-DFT calculation shows that the S₁ state of **2** originates from the excitation of HOMO $-1 \rightarrow$ LUMO (54%) and HOMO \rightarrow LUMO+1 (44%). The S₁ state of **3** originates from the excitation of HOMO \rightarrow LUMO+1 (64%) and HOMO-1 \rightarrow LUMO (32%). The S₁ state of **4** originates from the excitation of HOMO \rightarrow LUMO+1 (65%) and HOMO-1 \rightarrow LUMO (33%). Analysis of the orbital diagrams reveals that the excited state of the complexes should have charge transfer characteristics, in agreement with their broad and structure-less emission spectra.

4. Conclusions

In summary, four Zn(II) Schiff base complexes (1–4) with diphenylamino groups for 1 and 2, and carbazole groups for 3 and 4, respectively that can undergo rotation and the model complex **5** without rotational motion were prepared. Their photophysical and electrochemical properties have been investigated in detail. Interestingly, the complexes 1–4 exhibited AIEE property, which has been observed for the first time in Zn(II) Schiff base complexes. In contrast, complex **5** shows that aggregation quenches the emission. According to the results, the mechanism of AIEE in complexes **1–4** was shown to be related to intramolecular rotational motions. This study presents a Zn(II) Schiff base system expressly showing the effect of substitution on the AIEE activity and will be helpful in designing much more AIEE-active Zn(II) Schiff base complexes as well as developing their potential applications in the future.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2012.09.020.

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