Synthesis, structure, optoelectronic properties of novel zinc Schiff-base complexes

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Two novel zinc Schiff-base complexes, bis-(*N*-(2-hydroxybenzidene)-*p*-aminodimethylaniline)zinc(II) (**2**) and bis-(*N*-(2-hydroxy-1-naphthidene)-*p*-aminodimethylaniline)zinc(II) (**4**) were designed and synthesized. Both the complexes exhibit good solubility in organic solvents and excellent thermal stabilities. A single crystal of **2** was grown and its crystalline structure was determined from X-ray diffraction data. Analysis of the electronic structures of both the zinc complexes calculated by density functional theory reveals a localization of orbital. The UV-Vis absorption and photoluminescence profiles of **4** in thin film are similar to those of **2**, but the emission for **4** is red-shifted compared to **2**. Three-layered devices with a configuration of ITO/NPB/**2**/Alq₃/LiF/Al and ITO/NPB/**4**/Alq₃/LiF/Al show a yellow and red emission, respectively.

zinc complexes, Schiff-base ligands, electroluminescence

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A series of metal complexes have attracted much attention due to their wide application in the fields of synthesis, catalysis, and opto-electronic devices [1–4]. Some of the Schiff-base complexes possess interesting nonlinear optical [5,6] and magnetic properties [7,8]. On the other hand, fluorescent complexes have been extensively studied mainly because they may be good candidates for fluorescent sensors and electroluminescent (EL) devices [9,10]. Zinc Schiff-base complexes exhibited strong electroluminescence as well as photoluminescence [11–13] which are strongly coupled to molecular structures and bulk molecular packing characteristics [14,15]. Most of the zinc Schiff-base complexes may exist as either five or six-coordinated ones in their crystals. Hall and Moore [16] reported the first structure of a zinc Schiff-base complex, which is a five-coordinate one and contains one water molecule. The reaction of either 1,2-bis(salicylideneaminoxy)ethane (H₂salamo) or 1,2-bis(3-methoxysalicylideneaminoxy)ethane with zinc acetate

resulted in the formation trinuclear complexes [Zn₃L₂(OAc)₂] (L=Salamo, 3-MeOsalamo) [17]. It is difficult to obtain nuclear four-coordinated zinc Schiff-base complexes due to the tendency for water and solvent molecules to coordinate to metal ions and the ability of oxygen atoms of the ligand to coordinate to another metal ion even after chelation [1,16,17]. Chemical modifications of the ligand, e.g., introduction of some functional groups or substitution of some parts with appropriate ones often changes molecular structures and properties drastically. For example, introduction of butyl group into the positions adjacent to the hydroxyl groups of Schiff-base leads to a formation of four-coordinated complex [18,19]. However, there have been few reports about the crystal structure of zinc Schiff-base complexes used as electroluminescent materials. In the present study, we report the synthesis, structure determination, and optoelectronic properties of novel zinc Schiff-base complexes [20]. The aim of these experiments is to show the possible use of some of the Schiff-base complexes in the construction of organic light-emitting diodes (OLEDs).

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1 Experimental

1.1 Synthesis

N-(2-hydroxybenzidene)-*p*-aminodimethylaniline (**1**): 2-hydroxybenzaldehyde (8 mmol) was added to a solution of *p*-aminodimethylaniline (8 mmol) in ethanol (20 mL). The mixture was heated to reflux. After completion of the reaction, the precipitate was filtered through a glass filter, washed with pure ethanol for several times to remove the starting reagent and impurities, and purified by recrystallization from ethanol to give a pure yellow crystal. ^1H NMR (400 MHz CDCl_3 , δ): 3.01 (s, 6H; CH_3), 6.79 (s, 2H), 6.92 (t, 1H), 7.01 (d, 1H), 7.29 (d, 2H), 7.35 (t, 2H), 8.63 (s, 1H), 13.72 (s, 1H, OH); ^{13}C NMR (100 MHz, CDCl_3 , δ): 160.9, 157.7, 149.8, 132.1, 131.6, 122.3, 122.2, 119.8, 118.9, 117.1, 112.8, 40.7; IR (KBr): ν = 3466w, 2891m, 1617s [ν (C=N)], 1519s, 1453s, 1364s, 1285s, 1225m, 1197m, 1167sm, 1062s, 956s, 907m, 875m, 814s, 749s cm^{-1} ; Elemental analysis calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}$ (%): C 74.91, H 6.71, N 11.66; found: C 74.77, H 6.70, N 11.64; MS (EI) m/z 240 (M^+).

Bis-(*N*-(2-hydroxybenzidene)-*p*-aminodimethylaniline) zinc (II) (**2**): A solution of zinc acetate (30 mmol) in 30 mL of methanol was added dropwise at room temperature to a solution of **1** (60 mmol) in methanol (20 mL), which was stirred. After refluxing the mixture for 2 h, a crude product, which simultaneously precipitated from the solution, was collected by filtration and purified with twice sublimation to afford the pure complex with yellow fluorescence. ^1H NMR (400 MHz CDCl_3 , δ): 2.90 (s, 6H; CH_3), 6.56 (d, 2H), 6.64 (t, 1H), 6.92 (d, 1H), 7.06 (d, 2H), 7.20 (d, 1H), 7.33 (m, 1H), 8.36 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 170.6, 166.2, 149.4, 138.1, 136.1, 134.9, 123.4, 121.9, 118.9, 114.7, 112.9, 40.5; IR (KBr): ν = 3438w, 2921m, 1617s [ν (C=N)], 1519s, 1437s, 1356s, 1285m, 1188m, 1167m, 969m, 814s, 749s cm^{-1} ; Elemental analysis calcd. for $\text{Zn}(\text{C}_{30}\text{H}_{30}\text{N}_4\text{O}_2)$ (%): C 66.24, H 5.56, N 10.30; found: C 66.03, H 5.58, N 10.27; MS (EI) m/z 544 (M^+).

N-(2-hydroxy-1-naphthidene)-*p*-aminodimethylaniline (**3**): 2-hydroxy-1-naphthaldehyde (8 mmol) and *p*-aminodimethylaniline (8 mmol) were mixed in ethanol (50 mL). The product was obtained as a red powder. ^1H NMR (400 MHz CDCl_3 , δ): 3.02 (s, 6H; CH_3), 6.79 (d 2H), 7.09 (d 1H), 7.32 (m, 3H), 7.50 (t, 1H), 7.72 (m, 2H), 8.09 (d, 1H), 9.28 (s, 1H); NMR (100 MHz, CDCl_3 , δ): 169.7, 151.1, 149.4, 135.4, 133.8, 133.1, 129.2, 127.6, 127.0, 122.9, 122.2, 121.1, 118.7, 112.8, 108.7, 40.4; IR (KBr): ν = 2854m, 1612m [ν (C=N)], 1518s, 1464m, 1443m, 1350w, 1227s, 1184m, 1149m, 1063s, 1031s, 944m, 860s, 819s, 757s cm^{-1} ; Elemental analysis calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}$ (%): C 78.59, H 6.25, N 9.65; found: C 78.59, H 6.33, N 9.61; MS (EI) m/z 290 (M^+).

Bis-(*N*-(2-hydroxy-1-naphthidene)-*p*-aminodimethylaniline)zinc (II) (**4**): **4** was prepared by reacting zinc acetate

and **3** under the same conditions used for synthesizing **2**. After purification with twice sublimation, **4** was obtained as a red solid. ^1H NMR (400 MHz CDCl_3): δ = 2.89 (s, 6H; CH_3), 6.58 (d 2H), 7.10 (m, 3H), 7.31 (t, 1H), 7.47 (m, 1H), 7.68 (t, 1H), 7.75 (t, 1H), 8.03 (d, 1H), 9.35 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 170.9, 158.8, 147.5, 137.8, 134.7, 133.9, 127.5, 125.8, 125.1, 125.0, 120.4, 120.3, 117.1, 111.5, 107.3, 38.9; IR (KBr): ν = 2896m, 1616s [ν (C=N)], 1515s, 1458m, 1429m, 1393m, 1360m, 1226w, 1180s, 973m, 949m 818s, 745s cm^{-1} ; Elemental analysis calcd. for $\text{Zn}(\text{C}_{38}\text{H}_{34}\text{N}_4\text{O}_2)$ (%): C 70.86, H 5.32, N 8.70; found: C 70.74, H 5.39, N 8.68; MS (EI) m/z 644 (M^+).

1.2 Instruments and measurements

The ^1H NMR spectra were obtained on a Bruker DMX 400 NMR spectrometer. Chemical shift data for each signal were reported in ppm units with tetramethylsilane (TMS) as internal reference, where δ (TMS) = 0. Mass spectra were recorded on an AEI-MS50-MS spectrometer (EI-MS). ^{13}C NMR spectra were recorded using a Bruker-400 NMR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analysis (TGA) was measured on a Perkin-Elmer thermogravimeter (Model TGA7) under a dry nitrogen gas flow at a heating rate of 20°C/min. Glass transition temperatures (T_g) and melting temperatures (T_m) of the Zn-complexes were carried out using differential scanning calorimetry (DSC) at a heating rate of 20°C/min using a Perkin-Elmer differential scanning calorimeter (DSC7). Cyclovoltammetry measurements were determined by a 283 potentiostat/galvanostat system equipped with a conventional three-electrodes system (i.e., platinum wire, platinum wire, and AgCl/Ag as working, counter, and reference electrodes, respectively). Degassed tetrahydrofuran solution with 0.1 mol/L tetrabutylammonium perchlorate was used as electrolyte.

1.3 X-ray crystallography

Crystal data were obtained with graphine-monochromated Cu K α radiation (λ = 0.71073 Å) on a Rigaku RAPID IP imaging plate system. The structure was solved by direct method with SHELXL97 program, and refined with full-matrix least-squares methods. The crystal structure of **2** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 262722.

1.4 Computational method

The quantum chemical calculations for the zinc-complexes were carried out with LDA-DFT as implemented in the DMol3 package [21,22]. The basic set in chosen was the double numerical plus d-functions (DND). The local function for the exchange-correlation potential was the Perdew-

Wang LDA functional (PWC) [23]. The core electrons for metals were treated by effective core potentials (ECP).

1.5 Photoluminescence

The organic thin films for solid-state photoluminescent (PL) measurement were prepared by vacuum deposition on quartz substrates. The thickness of the films was controlled so that their absorbance at 450 nm was between 0.09–0.12. The relative PL quantum yields of films were estimated by using $\phi_s/\phi_r = (A_r/A_s)(F_s/F_r)(n_s^2/n_r^2) \approx (A_r/A_s)(F_s/F_r)$, assuming the same refractive index for organic films. Where ϕ , A_r , and F_r are quantum yield, absorbance at excitation wavelength, and emission integration area for the reference, while ϕ_s , A_s , and F_s are quantum yield, absorbance at excitation wavelength, and emission integration area for the sample film, respectively. The PL spectra were carried out on a Hitachi F-4500 fluorescence spectrophotometer. The ultra-violet-visible absorption spectra were recorded with a TU-1201 UV-Vis recording spectrophotometer.

1.6 Preparation and characterization of LED devices

N,N'-diphenyl-*N,N'*-bis(1-naphenyl)-1,1'-biphenyl-4,4'-diamine (NPB) and Alq₃ were used as hole and electron transport materials, respectively. The organic layers were evaporated on a glass substrate covered with indium-tin oxide (ITO) at a vacuum of 2×10^{-4} Pa. Finally, aluminum electrode was deposited. The thickness of the NPB, zinc complexes, Alq₃, and LiF was 50, 40, 10, and 1 nm, respectively. The emitting area of the OLED devices was 4 mm². The EL spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer. Brightness was recorded with a

photo research 650 spectrascan colorimeter. Current-voltage characteristics were measured with a Hewlett Packard 4140B semiconductor parameter analyzer. All the measurements were performed in air at room temperature.

2 Results and discussion

2.1 Synthesis and thermal analysis

Zinc(II) schiff-base chelates are well-known for their high photoluminescence efficiencies, and had been used as blue electroluminescent materials as early as in 1993 [24]. From then on, many efforts have been devoted to the development of novel electroluminescent zinc (II) Schiff-base complexes [25–27]. Photoluminescence of the zinc Schiff-base complexes is caused by the light emission of the ligands. Molecular structures, degree of conjugation, and substitutes of the ligands have a large effect on the PL and EL characteristics of the zinc Schiff-base complexes. We designed two novel zinc complexes in order to control their optoelectronic properties using structure modification of the ligands and introduction of the strong donor dimethylamino group. We report a general and direct synthesis of zinc Schiff-base complexes from Schiff-base ligands and zinc acetate. The zinc metalation procedure was tested on easily obtainable Schiff-base ligands **1** and **3** prepared from a variety of aldehyde backbones. The ligands **1** and **3** were synthesized by *p*-aminodimethylaniline with 2-hydrobenzaldehyde and 2-hydroxy-1-naphthaldehyde, respectively, in ethanol (Figure 1). The zinc Schiff-base complexes **2** and **4** were then obtained by the reaction of zinc (II) acetate with the free ligands **1** and **3**.

Most of metal complexes have poor solubility, which

Figure 1 Synthesis of complex **2** and **4**: (i) methanol; (ii) Zn(CH₃CO₂)₂·2H₂O, methanol.

results in difficult purification by recrystallization, in organic solvents. We find that **2** and **4** are soluble in common organic solvents, such as chloroform, acetonitrile, and 1,4-dioxane without an evidence of gel formation. Both the complexes **2** and **4** were easily purified by recrystallization as well as train vacuum-vapor sublimation. The complexes are thermally robust. Figure 2 shows the TGA scans for **2** and **4**. The thermal decomposition temperature for **2** and **4** is about 377 and 387°C, respectively. DSC curves of the complexes exhibit clear glass transition temperatures at 112°C for **2** and 128°C for **4**, and melting points at 276°C for **2** and 344°C for **4**. These results indicate that the thermal stability, glass transition temperature, and melting point of **4** are significantly higher than those of **2**. This is probably due to higher degree of conjugation of the ligands in the complex **4**.

2.2 X-ray crystal structure of **2**

Single crystal of **2** was grown from methanol. The specimen for data collection was mounted in air on a glass fiber and the X-ray diffraction intensity data were collected on a diffractometer. The crystal structure of **2** is shown in Figure 3 and its selected bond lengths and angles are summarized in Table 1. The complex **2** crystallized in two crystallographically independent forms in the triclinic system space group *P*-1. The zinc ion is four-coordinate to *N*-(2-hydroxybenzidine)-*p*-aminodimethylaniline ligands and has a distorted tetrahedral geometry. Similar distortion was also observed for [N,N'-bis(salicylidene)-1,4-diaminobutane] copper (II) [28]. The Zn–O and Zn–N bond lengths are from 1.861(3)

to 1.982(3) Å and from 1.998(3) to 2.104(3) Å, respectively, while the O–Zn–N chelate bite angles are from 93.40(12) to 125.599(12)°. The Zn–N bond length is longer than the Zn–O bond length. This is similar to that were observed for a bis(salicylidimine)zinc complexes with Zn–N and Zn–O distances of 2.088 and 1.958 Å, respectively [1]. Akine and coworkers [29] have recently reported the structure of copper (II) salen-type complex, revealing that the tetracoordinate copper atom lies in the N₂O₂ coordination sphere. Attempts to grow single crystals of **4** suitable for X-ray crystallographic analysis have not been successful.

2.3 Quantum chemical calculations

A number of theoretical studies of the electronic structure of Alq₃ and (Znq₂)_n have been reported, which complement the

Figure 2 The TGA scans for **2** and **4**.

Figure 3 The crystal structure of **2**.

Table 1 Selected bond lengths and angles for **2**

Bond lengths (Å)		Bond angles (°)	
ZnA–O(1A)	1.942(3)	O(1A)–ZnA–O(2A)	114.86(12)
ZnA–O(2A)	1.837(3)	O(1A)–ZnA–N(2A)	96.81(12)
ZnA–N(2A)	2.016(3)	O(2A)–ZnA–N(4A)	96.61(12)
ZnA–N(4A)	2.104(3)	O(1A)–ZnA–N(4A)	116.21(12)
ZnB–O(1B)	1.861(3)	O(2A)–ZnA–N(2A)	112.15(12)
ZnB–O(2B)	1.982(3)	N(2A)–ZnA–N(4A)	121.38(13)
ZnB–N(2B)	2.058(3)	O(1B)–ZnB–O(2B)	110.73(12)
ZnB–N(4B)	1.998(3)	O(1B)–ZnB–N(2B)	93.40(12)
		O(2B)–ZnB–N(4B)	95.18(12)
		O(1B)–ZnB–N(4B)	117.90(12)
		O(2B)–ZnB–N(2B)	125.59(12)
		N(2B)–ZnB–N(4B)	115.86(12)

extensive experimental investigations [30,31]. Interpretation of the observed spectral features is greatly assisted by molecular orbital calculations. To better provide the electronic structure of **2**, the geometric parameters employed in the quantum chemical calculation are from the crystal structure data. For the sake of comparison, molecular orbital calculations were also carried out for **4**. Because crystallographic coordinates are not available for **4**, the structure was obtained by adding a phenyl ring in **1**. Figure 4 shows the highest occupied molecular orbitals (HOMO's) and the lowest unoccupied molecular orbitals (LUMO's) of **2** and **4**.

The filled π orbitals (or HOMO's) and the unfilled orbitals (or LUMO's) are mainly dominated by orbitals originating from the ligands in all cases. The contribution of Zn^{2+} ions of all these orbitals is vanishing small. The distribution of the orbitals in **2** shows that the HOMO's are mainly localized on a ligand, whereas the LUMO's are localized predominantly on another ligand and the phenoxido ring and the C=N bond of this ligand. A similar result is observed for the HOMO's and LUMO's of **4**. Previous works for Alq_3 , $(\text{Znq}_2)_n$ oligomers, and $[\text{Zn}(\text{BTZ})_2]_2$ have shown that the electron density of the HOMO is localized mainly on the phenoxido ring, and the LUMO is inversely localized on the heterocyclic ring [30–32]. Therefore, the electronic π – π^* transition in the **2** or **4** molecule is localized on the ligands, in which π – π^* transitions give rise to absorption and PL spectra. To our best knowledge, **2** and **4** are the first characterized zinc Schiff-base complexes by the theoretical calculation.

2.4 Optical and photoluminescent properties

Either in 1,4-dioxane solution or in the solid state, **2** and **4** emit strong fluorescence under ultraviolet irradiation. Figure 5 shows the absorption and PL spectra obtained from the thin films of **2** and **4** deposited onto fused quartz plates.

Figure 4 Molecular orbital amplitude plots of the (a) HOMO of the compound **2**, (b) LUMO of the compound **2**, (c) HOMO of the compound **4**, and (d) LUMO of the compound **4**.

Figure 5 Absorption and PL spectra of the **2** and **4** films.

The thin film of **2** has a broad absorption with maxima at 228, 260, 327, and 423 nm, which are caused by the π - π^* transition of the ligand. In comparison with **2**, the absorption maximum of **4** shows a 29 nm red shift. The optical band gaps of the complexes **2** and **4** were determined from the absorption onset, and they are evaluated to be about 2.50 and 2.33 eV, respectively. In the case of **4**, reduction of optical band gap in comparison with that of **2** might be due to higher degree of conjugation.

The emission spectrum of the **2** films exhibits a maximum at 557 nm, whose full width at half-maximum (FWHM) is about 110 nm, and its color is yellow. Zn^{2+} ion is the only oxidation state of zinc atom, and has no unoccupied valence electron orbits. Therefore, Zn^{2+} ion does not show fluorescent characteristics. The ligand **1** under the influence of Zn^{2+} ion forms a rigid chelate ring. When illuminated under an ultraviolet-light, the ligand absorbs a light energy and occurs the π - π^* transition, and then the ligand causes PL during radiative decay. The PL emission spectrum of the **4** is obviously red-shifted from that of the **2** thin films and exhibits a red emission at about 600 nm. The locations of the emission maxima of all complexes are independent of the excitation wavelength.

It is important for achievement of high efficiency and luminance in a LED device to obtain an emitting material with high quantum efficiencies in the solid state. To compare their EL performance, the relative PL quantum yield (ϕ) of the **2** thin films was estimated relative to the **4** thin films. We obtain a higher PL quantum yield for the **2** thin film with $\phi_2 \approx 2.65\phi_4$, exciting the film at 450 nm.

2.5 Electroluminescent devices

To evaluate the possibility and performance of using the zinc-complexes as emitting layers, two devices with configurations of ITO/NPB/zinc-complex/ Alq_3 /LiF/Al were fabricated. NPB and Alq_3 are used as hole and electron-transporting layers, respectively. The EL spectra of the devices are shown in Figure 6. The EL spectra of the zinc-complexes are similar to the PL spectra of the

Figure 6 EL spectra of the ITO/NPB/**2**/ Alq_3 /LiF/Al and ITO/NPB/**4**/ Alq_3 /LiF/Al devices.

corresponding films, while no emission from either the Alq_3 or the NPB was observed. The EL spectra do not change significantly in a wide bias ranging from 6 to 14 V. This indicates that in both the devices the emission originates from the corresponding zinc-complex, Alq_3 and NPB only play a role of a carrier transporting material. Figure 7 shows the current-voltage-brightness characteristics of the LEDs. In the device constructed from the **4**, the forward current increases with increasing forward bias voltage, and the curve has a shape that is typical of a diode. Red light emission from this device is observable greater than 8.3 V (@ 1 cd/m^2). The maximum brightness of the device is 520 cd/m^2 with a maximum current efficiency of 0.28 cd/A , which almost is a constant value for current density of 26–250 mA/cm^2 . Interestingly, the EL device constructed from **2** exhibits significantly device performances better than the device constructed from **4**. The maximum brightness of the OLED device based on the compound **2** is 1389 cd/m^2 with a maximum current efficiency of 0.7 cd/A . To explain the difference in the EL device performance, Figure 8 shows the energetic position of the HOMO and LUMO of the organic layers, and the work function of the ITO and Al electrodes. As stated above, the HOMO energy level of **2** and **4** as determined from cyclic voltammetry is -5.0 and -4.9 eV, respectively, while the optical band gap estimated from absorption onset of those are 2.5 and 2.3 eV, respectively. Therefore, we conclude that the LUMO energy level of the **2** and **4** is -2.5 and -2.6 eV, respectively. Thus, electron injection from Alq_3 to **4** is expected to be easier than that to **2**, and as a consequence the charge-carrier injection balance is better in the devices constructed from the **4**. In general, a high barrier to carrier injection between electrode and charge-carrier transporting layer or between carrier transporting and emissive layer results in poor electroluminescent performances. Therefore, one explanation for better EL performance achieved by using **2** is that the complex **2** exhibits higher PL quantum efficiency compared to **4**.

Figure 7 The current density-voltage (a) and brightness-voltage (b) characteristics of the ITO/NPB/2/Alq₃/LiF/Al and ITO/NPB/4/Alq₃/LiF/Al devices.

Figure 8 Energetic position of the HOMO and LUMO of the organic layers, and the work function of the ITO and Al electrodes.

3 Conclusions

Novel soluble zinc Schiff base complexes **2** and **4** have been prepared and tested in OLEDs. Using either **2** or **4** as the emitter, Alq₃ as the electron-transporting layer, and NPB as the hole-transporting layer, highly efficient organic LEDs are realized. While **4** gave red organic LEDs with a luminescence efficiency of 0.28 cd/A, the **2**-based devices provide a yellow emission.

The single crystal of **2** was grown from methanol. **2** crystallized in two crystallographically independent forms in the triclinic system space group *P*-1. The electronic

structures of the **2** and **4** were investigated by using quantum chemical calculations. The HOMO's and LUMO's are mainly dominated by orbitals originated from the ligands. The contribution of Zn²⁺ ions of all these orbitals is vanishing small. Molecules **2** and **4** exhibit similar orbital amplitude plots of the HOMO or LUMO. The HOMO's are mainly localized on one ligand, whereas the LUMO's are localized predominantly on another ligand and the phenoxido ring and C=N bond of this ligand.

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