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Syntheses, Characterization, and Luminescent Properties of Monoethylzinc Complexes with Anilido–Imine Ligands

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The syntheses of three anilido–imine ligands of the general formula *ortho*-C_6H_4(NHAr′)(CH=NAr′′ [Ar′ = 7-(2,4-Me_2)-C_9H_4N, Ar′′ = 2,6-$Me_2C_6H_3$ (**2a**); Ar′ = 7-(2,4-Me_2)C_9H_4N, Ar′′= 2,6-$Et_2C_6H_3$ (**2b**); Ar′ = 7-(2,4-Me_2)C_9H_4N, Ar′′= 2,6-*i*$Pr_2C_6H_3$ (**2c**)] and four zinc(II) complexes of the general formula [*ortho*-C_6H_4(NHAr′)(CH=NAr′′)]ZnEt [Ar′ = 7-(2,4-Me_2)C_9H_4N, Ar′′= 2,6-$Me_2C_6H_3$ (**3a**); Ar′ = 7-(2,4-Me_2)-C_9H_4N, Ar′′= 2,6-$Et_2C_6H_3$ (**3b**); Ar′ = 7-(2,4-Me_2)C_9H_4N, Ar′′ = 2,6-*i*$Pr_2C_6H_3$ (**3c**); Ar′′ = 2,6-$Me_2C_6H_3$, Ar′′ = 2,6-*i*$Pr_2C_6H_3$ (**3d**)] are described. The complexes were synthesized from the reaction of $ZnEt_2$ with corresponding ligands **2** by alkane elimination. All compounds were characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy. The molecular structures of compounds **2a**, **2b**, **3b**, and **3c** were determined by single-crystal X-ray crystallography. The X-ray analysis reveals that complexes **3b** and **3c** exist in the dimeric form with the N atom in the quinolyl ring coordinating to the other Zn atom to make the Zn atoms four coordinate. Luminescent properties of ligands **2a**–**2d** and complexes **3a**–**3d** in both solution and the solid state were studied.

Introduction

Zinc(II) complexes as luminescent materials have been extensively studied in recent years.[1–9] Among these known luminescent Zn complexes, the ligands are mainly benzothiazolates,[1] quinolinolates,[2] salicylideneaminates,[3] dipyrrin,[6c] N-7-azaindolyl,[8] and 2,2′-dipyridylamino.[9] As Zn^{II} with a closed shell is spectroscopically silent in essence, the luminescent properties of Zn^{II} complexes can be easily tuned by the modification of the ligands. Meanwhile, Zn^{II} complexes can have relatively flexible coordination numbers ranging from three-coordinate to six-coordinate depending on the structure of their ligands. Bis(8-hydroxyquinoline)-zinc(II) (Znq_2) was reported to be a good electroluminescent (EL) material that exists in the form of $(Znq_2)_4$.[2] Bis[2-(2-hydroxyphenyl)benzothiazolate]zinc $[Zn(BTZ)_2]_2$ was found to be an excellent white EL material.[1] Some polynuclear Zn^{II} complexes[7,8] were also reported to have intriguing structural and photoluminescent properties. We reported a number of aluminum[10a,10b] and boron[10c] complexes with chelating anilido–imine ligands showing good luminescent properties. Similarly, zinc complexes with the anilido–imine ligands might also be efficient luminescent materials considering that the anilido–imine ligands and the salicylaldiminate ligands have similar structures. Recently, Lee et al. reported some dinuclear Zn^{II} complexes with anilido–imine ligands.[11] As we are interested in tuning the luminescent properties of Zn^{II} complexes by modification of the ligands and the coordination geometries of Zn^{II} complexes, we synthesized three new anilido–imine ligands with a 7-amino-2,4-dimethylquinolyl chromophore, in which the nitrogen atom in the quinolyl ring might coordinate to the Zn^{II} in another molecule to form dinuclear or polynuclear Zn^{II} complexes. The results indicate that all three Zn^{II} complexes with quinolyl exist in a novel dimeric form. Herein we report the syntheses, characterizations, and fluorescent properties of four new zinc complexes with anilido–imine ligands, *ortho*-C_6H_4(NHAr′)(CH=NAr′′)ZnEt [Ar′ = 7-(2,4-Me_2)C_9H_4N, Ar′′ = 2,6-$Me_2C_6H_3$ (**3a**); Ar′ = 7-(2,4-Me_2)C_9H_4N, Ar′′ = 2,6-$Et_2C_6H_3$ (**3b**); Ar′ = 7-(2,4-Me_2)-C_9H_4N, Ar′′ = 2,6-*i*$Pr_2C_6H_3$ (**3c**); Ar′ = 2,6-$Me_2C_6H_3$, Ar′′ = 2,6-*i*$Pr_2C_6H_3$ (**3d**)].

Results and Discussion

Syntheses of the Ligands

Preligands **1a**–**1c** *ortho*-C_6H_4F(CH=NAr′′) [Ar′′ = 2,6-$Me_2C_6H_3$ (**1a**), 2,6-$Et_2C_6H_3$ (**1b**), 2,6-*i*$Pr_2C_6H_3$ (**1c**)] were synthesized by a condensation reaction of *ortho*-fluorobenzaldehyde with 1 equiv. of the relevant amine in *n*-hexane in the presence of anhydrous $MgSO_4$ according to a modified literature method.[12] Among them, **1b** is a new compound and characterized by NMR spectroscopy along with ele-

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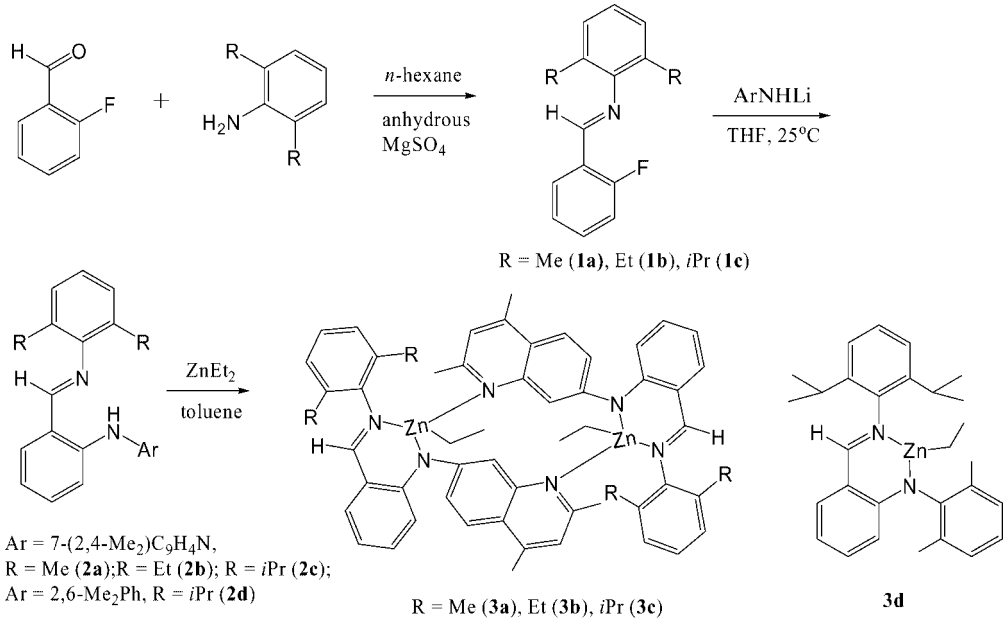
mental analysis. The imino CH proton of compound **1b** exhibits resonance at δ = 8.55 ppm and the corresponding imino CH carbon exhibits resonance at δ = 156.1 ppm. At room temperature, **1b** exists in the form of a yellow oil but as a yellow solid at lower temperatures. It can be purified by reduced-pressure distillation. Three new ligands, *ortho*-$C_6H_4(NHAr')(CH{=}NAr'')$ [Ar′ = 7-(2,4-Me_2)C_9H_4N, Ar″ = 2,6-$Me_2C_6H_3$ (**2a**); Ar′ = 7-(2,4-Me_2)C_9H_4N, Ar″ = 2,6-$Et_2C_6H_3$ (**2b**); Ar′ = 7-(2,4-Me_2)C_9H_4N, Ar″ = 2,6-*i*$Pr_2C_6H_3$ (**2c**)], were synthesized by nucleophilic aromatic substitution of fluoride in **1a**–**1c** by 7-amino-2,4-dimethylquinoline lithium salt according to a modified literature procedure[12] (Scheme 1) and characterized by ^{1}H and ^{13}C NMR spectroscopy along with elemental analysis. Ligands **2a** and **2b** were purified by chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to give pure products as yellow crystals, whereas compound **2c** was purified by crystallization from methanol. For comparison, ligand **2d**[13] was synthesized according to a literature method and characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of **2a**–**2c** exhibit resonances in the range of δ = 8.35–8.37 ppm for the imino CH proton, whereas the corresponding ^{13}C NMR resonances are in the range of δ = 165.6–165.8 ppm. The NH proton resonance in **2a**–**2c** appears at relatively low field (δ = 11.64, 11.62, and 11.59 ppm, respectively) relative to those in compound **2d**[13] (δ =10.50 ppm) and other reported compounds of this type [δ =10.53 ppm for *ortho*-C_6H_4{$NH(C_6H_3$*i*Pr_2-2,6)}-[$CH{=}NC_6H_3Me_2$-2,6],[10b] 10.60 ppm for *ortho*-C_6H_4-{$NH(C_6H_3Me_2$-2,6)}($CH{=}NC_6H_3Me_2$-2,6),[10a] 11.16 ppm for *ortho*-C_6H_4{$NH(C_6H_4$Me-*p*)}($CH{=}NC_6H_3$*i*Pr_2-2,6),[10a] 11.24 ppm for *ortho*-C_6H_4{$NH(C_6H_4$Me-*p*)}($CH{=}NC_6H_4$-Me-*p*)[10a]] as a result of the electron-withdrawing properties of the quinolyl group.

Syntheses of the Complexes

Treatment of **2a**–**2d** with 1 equiv. of $ZnEt_2$ in toluene caused the elimination of ethane and afforded the corresponding monoethylzinc complexes **3a**–**3d** in good yields (78–85%). All complexes have good solubility in common solvents, such as toluene, dichloromethane, diethyl ether, THF, and *n*-hexane. All complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as elemental analysis, and satisfactory analytic results were obtained. The N–H proton signals of the free ligands disappear, and the new Zn–CH_2 proton signals appear at a higher field (0.55–0.02 ppm) in the ^{1}H NMR spectra of complexes **3a**–**3d**, which is indicative of the formation of Zn–N bond in these compounds. The Zn–CH_2 carbon signals in the ^{13}C NMR spectra are observed at –1.2 (for **3a**), –1.8 (for **3b**), –1.3 (for **3c**), and –2.9 (for **3d**) ppm. The two methyl groups of the isopropyl units in complex **3c** are inequivalent, for the coordination of the anilido–imine ligands to the zinc center causes the rotation about the N–aryl bond to become slow on the NMR timescale.[10a] All complexes have pretty good thermal stability and can be heated in boiling toluene for several hours without obvious decomposition. All complexes are air- and/or moisture-sensitive in solution and the solid state.

Crystal Structures

The molecular structures of ligands **2a** and **2b** as well as complexes **3b** and **3c** were determined by X-ray crystallographic analysis. Crystals of ligands **2a** and **2b** suitable for X-ray crystal structure determination were grown from ethyl acetate/petroleum ether at room temp. Crystals of complexes **3b** and **3c** suitable for X-ray crystal structure de-



Scheme 1. Synthetic route for ligands **2a**–**2d** and complexes **3a**–**3d**.

termination were grown from *n*-hexane at room temp. The ORTEP drawings of the molecular structures of **2a**, **2b**, **3b**, and **3c** are shown in Figures 1 (top), 2, 3, and 4, respectively. Selected bond lengths and angles for **3b** and **3c** are given in Table 1. The crystal packing [Figure 1 (bottom)] of **2a** is consolidated by intramolecular N–H···N hydrogen bonds and weak intermolecular C–H···N interactions [3.496(2) Å, 170.2°, (x, 1.5 – y, 0.5 + z)] arising from the interactions between the nitrogen atom in the quinolyl ring and the hydrogen atom of the imino CH=N to form an infinite one-dimensional chain. There are no interactions between each adjacent chain. X-ray analysis revealed that the unit cell of **2b** contains two independent molecules, one of which is shown in Figure 2. There are intramolecular N–H···N hydrogen bonds but no intermolecular C–H···N interactions in the packing of **2b**. The C=N bond lengths in **2a** and **2b** [1.271(2) Å for **2a**, 1.267(4) and 1.275(4) Å for **2b**] are in the normal range.[11a] Complexes **3b** and **3c** belong to the monoclinic space group $C2/c$ and the triclinic space group $P\bar{1}$, respectively. There is an *n*-hexane solvent molecule in the unit cell of **3c**. Both **3b** and **3c** exist in the dimeric form with the nitrogen atom in the quinolyl ring coordinating to the zinc atom in another molecule. As seen in Figures 3 and 4, the zinc ions in both **3b** and **3c** adopt a distorted tetrahedral geometry with the metal center coordinated by an ethyl group, a quinolyl group, and the bidentate anilido–imine ligand. The anilido–imine ligand chelates to the zinc center to form a six-membered chelating ring that is nearly planar with the zinc atom lying 0.0371 Å (**3b**), 0.0327 Å, and 0.0926 Å (**3c**) out of the plane. The imino C=N bond [1.277(7) Å for **3b**] is slightly longer than that in the free ligand after coordination to Zn^{II}. The imino C=N bond in **3c** [1.290(5) Å] is longer than that in **3b** as a result of the increased steric hindrance of the isopropyl group rel-

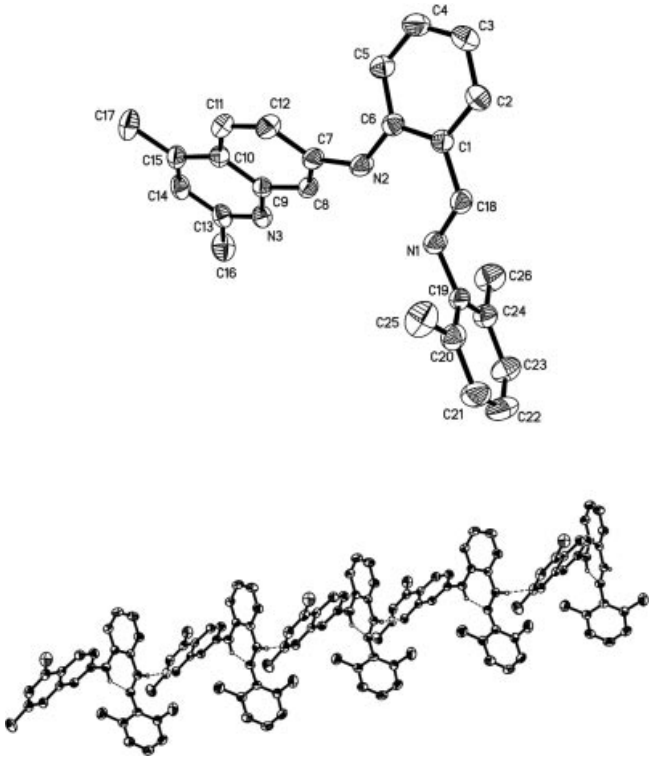


Figure 1. Top: Molecular structure of compound **2a**. Bottom: The packing of compound **2a** (hydrogen bonds are indicated by dashed lines and hydrogen atoms not involved in these interactions have been omitted for clarity, and the thermal ellipsoids are drawn at 30% probability levels).

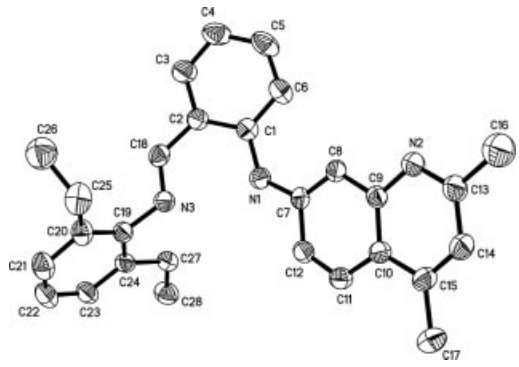


Figure 2. Molecular structure of compound **2b** (all hydrogen atoms and the other molecule have been omitted for clarity, and the thermal ellipsoids are drawn at 30% probability levels).

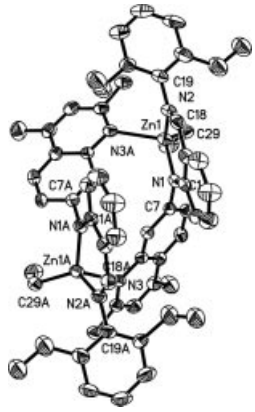


Figure 3. Molecular structure of complex **3b** (all hydrogen atoms have been omitted for clarity, and the thermal ellipsoids are drawn at 30% probability levels).

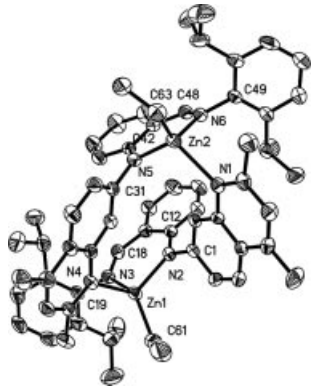


Figure 4. Molecular structure of complex **3c** (all hydrogen atoms and the *n*-hexane solvent molecule have been omitted for clarity, and the thermal ellipsoids are drawn at 30% probability levels).

ative to that of the ethyl group. The Zn–$N_{anilido}$ distances [2.014(4) Å in **3b**, 2.028(3) Å and 2.025(3) Å in **3c**] are shorter than the Zn–N_{imine} distances [2.040(4) Å in **3b**, 2.055(4) Å and 2.063(3) Å in **3c**] owing to the formation of a polar (partially ionic) single bond from an electron-rich anilido nitrogen atom to the Zn^{II} center as opposed to a coordination bond in the latter case. The Zn–$N_{quinolyl}$ distances [2.313(4) Å in **3b**, 2.290(4) Å and 2.266(3) Å in **3c**] are much longer than the Zn–N_{imine} distances, indicating the weak coordination interaction between the zinc atom and the nitrogen atom in the quinolyl ring. The Zn–C lengths for complexes **3b** [2.012(6) Å] and **3c** [1.985(5) Å and 1.998(5) Å] are typical for such a bond[14] although slightly longer than that of similar [($C_6H_3iPr_2$)N=C(Me)CH=C(Me)N($C_6H_3iPr_2$)]ZnEt (1.96 Å).[15] The Zn–Zn separation distances are 6.625 Å in **3b** and 6.707 Å in **3c**, which is indicative of no metal–metal interaction. The N_{imine}–Zn–$N_{anilido}$ bite angles are 92.63(16)° (in **3b**), 92.33(14)° and 93.38(14)° (in **3c**), respectively. The dihedral angles between the six-membered chelating ring and the phenyl ring at the imine nitrogen are 80.7° (in **3b**), 77.7° and 85.6° (in **3c**), respectively. The dihedral angles between the six-membered chelating ring and the quinolyl ring are 58.7° (in **3b**), 59.9° and 122.3° (in **3c**), respectively.

Table 1. Selected bond lengths [Å] and angles [°] for **3b** and **3c**.[a]

Complex **3b**			
Zn1–N1	2.014(4)	N1–Zn1–N2	92.63(16)
Zn1–N2	2.040(4)	C29–Zn1–N3#1	107.1(2)
Zn1–C29	2.012(6)	N1–Zn1–N3#1	112.90(16)
Zn1–N3#1	2.313(4)	N2–Zn1–N3#1	95.14(16)
N1–C1	1.366(6)	C7–N1–Zn1	114.0(3)
N2–C18	1.277(7)	C1–N1–Zn1	127.2(3)
C29–Zn1–N1	119.5(2)	C18–N2–Zn1	123.0(4)
C29–Zn1–N2	127.1(2)	C19–N2–Zn1	119.8(3)
Complex **3c**			
Zn1–N2	2.028(3)	Zn2–N5	2.025(3)
Zn1–N3	2.055(4)	Zn2–N6	2.063(3)
Zn1–N4	2.290(4)	Zn2–N1	2.266(3)
Zn1–C61	1.985(5)	Zn2–C63	1.998(5)
N2–C12	1.353(5)	N5–C42	1.361(5)
N3–C18	1.290(5)	N6–C48	1.290(5)
N2–Zn1–N3	92.33(14)	N5–Zn2–N6	93.38(14)
N2–Zn1–N4	112.36(13)	N5–Zn2–N1	110.00(13)
N2–Zn1–C61	118.2(2)	N5–Zn2–C63	117.21(19)
N3–Zn1–N4	96.08(14)	N6–Zn2–N1	95.95(13)
N3–Zn1–C61	127.9(2)	N6–Zn2–C63	121.79(18)
N4–Zn1–C61	107.7(2)	N1–Zn2–C63	114.99(18)
C1–N2–Zn1	113.3(2)	C31–N5–Zn2	114.7(3)
C12–N2–Zn1	127.5(3)	C42–N5–Zn2	125.6(3)
C18–N3–Zn1	122.6(3)	C48–N6–Zn2	121.5(3)
C19–N3–Zn1	119.7(3)	C49–N6–Zn2	121.7(3)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x$, y, $-z + 0.5$.

Fluorescent Properties

Table 2 summarizes the UV/Vis and fluorescent properties of compounds **2a**–**2d** and **3a**–**3d** determined in both solution and the solid state. In solution, free ligands **2a**–**2d** all have a weak emission band at λ = 437, 437, 436, and 423 nm, respectively, whereas complexes **3a**–**3d** in solution show a stronger emission band (bandwidth at half-height = 77–79 nm) with λ = 573, 565, 555, and 515 nm, respectively (Figure 5). The quantum yields of these complexes are relatively low in solution. According to the literature,[6a,6b,10] the observed luminescence of these complexes could be attributed to π*–π transitions of their conjugated ligands. The emission energies of these complexes are significantly red-shifted relative to those of the free ligands, which could be attributed to the fact that the coordination of the ligand to the metal center lowers the energy gap between π* and π of the ligand.[16] The emission energies of complexes **3a**–**3c** change in the order **3a** < **3b** < **3c**, depending on the size of the *ortho*-substituents of the rotatable aromatic ring attached to the imine N atom that might affect the dihedral angles between the aromatic ring and the six-membered chelating ring and thus the extent of conjugation in these complexes.[10a] The emission maxima of complexes **3a**–**3c**

Table 2. Optical properties of ligands **2a**–**2d** and complexes **3a**–**3d** in *n*-hexane and the solid state.

Compound	Absorption [nm] (ε [$dm^3 mol^{-1} cm^{-1}$])	Emission λ [nm]	Quantum yields[a] ϕ	Conditions (at T = 298 K)
2a	386 (14713)	437	0.002	*n*-hexane
		468		solid
2b	383 (20480)	437	0.002	*n*-hexane
		468		solid
2c	384 (23431)	436	0.003	*n*-hexane
		467		solid
2d	372 (14253)	423	0.015	*n*-hexane
		436		solid
3a	476 (11319)	573	0.042	*n*-hexane
		583		solid
3b	472 (24198)	565	0.048	*n*-hexane
		561		solid
3c	466 (22475)	555	0.087	*n*-hexane
		553		solid
3d	454 (12176)	515	0.070	*n*-hexane
		523		solid

[a] Determined by using quinine sulfate in 0.1 M sulfuric acid as a standard.

are redshifted by about 40–58 nm relative to the emission maximum of complex **3d** because of the larger conjugated quinolyl ring in **3a**–**3c**. All complexes **3a**–**3d** emit bright fluorescence in the solid state upon irradiation with an adequate excitation wavelength. The emission spectra of complexes **3a**–**3d** in the solid state are shown in Figure 6. Complexes **3a**–**3d** have a relatively narrow band (bandwidth at half-height = 72, 64, 55, and 60 nm) in the solid state with λ = 583, 561, 553, and 523 nm, respectively. It seemed that the coordination number of zinc does not play a role in the fluorescence. The emission maxima of complexes **3b** and **3c** in the solid state are slightly blueshifted relative to their corresponding emission maxima in solution; this may be due to the reduced conjugation of the two complexes, as the free rotation of the aryl rings in these complexes is blocked in the solid state. The emission maxima of complexes **3a** and **3d** in the solid state show a redshift relative to their corresponding emission maximum in solution, which is normally observed for most fluorescent compounds in the solid state probably owing to π–π stacking of aromatic rings in the molecules.[6b]

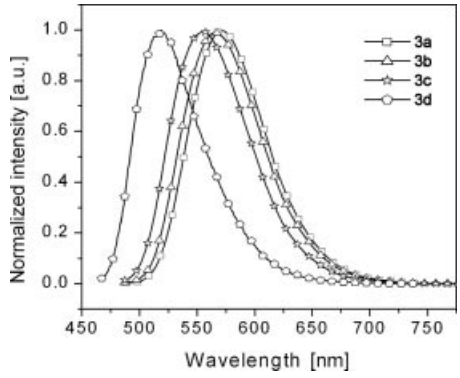


Figure 5. Emission spectra of complexes **3a**–**3d** in *n*-hexane.

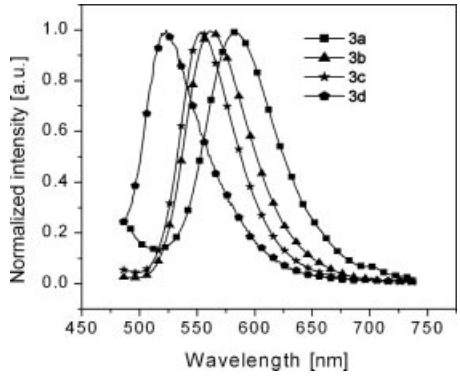


Figure 6. Emission spectra of complexes **3a**–**3d** in the solid state.

Experimental Section

General: All organometallic reactions were performed by using standard Schlenk techniques under an atmosphere of high-purity argon or by using glove box techniques. Toluene, *n*-hexane, and THF were dried by refluxing over sodium and benzophenone and distilled under an atmosphere of argon prior to use. C_6D_6 was dried with activated 4 Å molecular sieves and vacuum-transferred to a sodium-mirrored air-free flask. $CDCl_3$ was dried with CaH_2 for 48 h and vacuum-transferred to an air-free flask. $ZnEt_2$ and *n*BuLi were purchased from Aldrich and used as received. *ortho*-$C_6H_4F(CH{=}NC_6H_3Me_2$-2,6) (**1a**) and *ortho*-$C_6H_4F(CH{=}NC_6H_3$-*i*Pr_2-2,6) (**1c**) were synthesized according to literature procedures.[11] 7-Amino-2,4-dimethylquinoline was synthesized according to a literature procedure.[17] The ligand *ortho*-C_6H_4-$(NHC_6H_3Me_2$-2,6)$(CH{=}NC_6H_3i Pr_2$-2,6) (**2d**) was synthesized according to a literature method.[12] ^{1}H and ^{13}C NMR spectra were measured with a Varian Mercury-300 or Bruker AVANCE-500 NMR spectrometer. Elemental analyses were performed with a Perkin–Elmer 2400 analyzer. UV/Vis absorption spectra were recorded with an UV-3100 spectrophotometer. Fluorescent measurements were carried out with an RF-5301PC.

***ortho*-$C_6H_4F(CH{=}NC_6H_3Et_2$-2,6) (1b):** A mixture of *ortho*-fluorobenzaldehyde (4.00 mL, 37.7 mmol), 2,6-diethylaniline (6.20 mL, 37.7 mmol), and anhydrous $MgSO_4$ (1 g) in *n*-hexane (40 mL) was stirred at room temp. for 2 h. The mixture was filtered, and the solvents were evaporated to dryness to give the product as salmon pink oil. The crude product was purified by reduced-pressure distillation. Yield: 6.0 g, 62%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 1.16 (t, J = 7.5 Hz, 2×3 H, CH_2CH_3), 2.51 (q, J = 7.5 Hz, 2×2 H, CH_2CH_3), 7.06 (d, J = 6.5 Hz, 1 H), 7.11 (d, J = 7.5 Hz, 2 H), 7.16 (t, J = 9.5 Hz, 1 H), 7.29 (t, J = 7.5 Hz, 1 H), 7.50 (q, J = 7.5 Hz, 1 H), 8.25 (t, J = 7.5 Hz, 1 H), 8.55 (s, 1 H, C*H*=N) ppm. ^{13}C{^{1}H} NMR (125.1 MHz, $CDCl_3$, 298 K): δ = 15.1 (CH_2CH_3), 25.1 (CH_2CH_3), 116.3 (d, $^2J_{C,F}$ = 21 Hz), 124.2 (quaternary aromatic), 124.6, 124.9 (d, $^3J_{C,F}$ = 3.5 Hz), 126.7, 128.1 (d, $^4J_{C,F}$ = 2.6 Hz), 133.4 (d, $^3J_{C,F}$ = 8.5 Hz), 133.5 (quaternary aromatic), 150.8 (quaternary aromatic), 156.1 (d, $^3J_{C,F}$ = 4.8 Hz, *C*H=N), 163.2 (d, $^1J_{C,F}$ = 253.5 Hz, *C*F) ppm. $C_{17}H_{18}FN$ (255.33): calcd. C 79.97, H 7.11, N 5.49; found C 79.89, H 7.20, N 5.56.

***ortho*-C_6H_4{7-NH(2,4-Me_2)C_9H_4N}$(CH{=}NC_6H_3Me_2$-2,6) (2a):** A solution of *n*BuLi (1.60 M, 22.5 mmol) in *n*-hexane was added to a solution of 7-amino-2,4-dimethylquinoline (3.89 g, 22.5 mmol) in THF (30 mL) at –78 °C. The mixture was warmed to room temp. and stirred overnight. The resulting solution was transferred into a solution of *ortho*-$C_6H_4F(CH{=}NC_6H_3Me_2$-2,6) (5.09 g, 22.5 mmol) in THF (30 mL) at 25 °C. After stirring for 2 d, the reaction was quenched with H_2O (20 mL). The organic phase was evaporated to dryness to give the crude product as a brown oil that was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) to give the pure product as yellowish crystals (3.5 g, 41%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 2.21 (s, 2×3 H, CH_3), 2.65 (s, 3 H, quinolyl-CH_3), 2.72 (s, 3 H, quinolyl-CH_3), 6.93 (t, J = 7.5 Hz, 1 H, Ph-*H*), 6.98–7.03 (m, 2 H, Ph-*H* and quinolyl-*H*), 7.11–7.13 (d, 2 H, Ph-*H*), 7.33–7.42 (m, 3 H, Ph-*H* and quinolyl-*H*), 7.81 (d, J = 8.4 Hz, 1 H, Ph-*H*), 7.86 (d, J = 9.3 Hz, 1 H, Ph-*H*), 8.03 (s, 1 H, quinolyl-*H*), 8.36 (s, 1 H, C*H*=NAr), 11.64 (s, 1 H, quinolyl-N*H*) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ = 18.5 (CH_3), 18.6 (CH_3), 24.9 (quinolyl-CH_3), 114.3, 114.9, 118.3, 119.0, 121.0, 121.2, 122.4, 124.1, 124.7, 127.8, 128.2, 132.1, 134.8, 142.4, 144.3, 144.8, 148.7, 150.1, 158.9, 165.8 (*C*H=N) ppm. $C_{26}H_{25}N_3$ (379.50): calcd. C 82.29, H 6.64, N 11.07; found C 82.21, H 6.70, N 11.02.

***ortho*-C_6H_4{7-NH(2,4-Me_2)C_9H_4N}$(CH{=}NC_6H_3Et_2$-2,6) (2b):** A solution of *n*BuLi (1.60 M, 12.8 mmol) in *n*-hexane was added to a solution of 7-amino-2,4-dimethylquinoline (2.20 g, 12.8 mmol) in THF (20 mL) at –78 °C. The mixture was warmed to room temp. and stirred overnight. The resulting solution was transferred into a

solution of *ortho*-$C_6H_4F(CH{=}NC_6H_3Et_2$-2,6) (3.29 g, 12.8 mmol) in THF (30 mL) at 25 °C. After stirring for 2 d, the reaction was quenched with H_2O (20 mL). The organic phase was evaporated to dryness to give the crude product as a dark brown oil that was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) to give the pure product as yellowish crystals (2.20 g, 43%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.16 (t, J = 7.8 Hz, 2×3 H, CH_3CH_2), 2.57 (q, J = 7.8 Hz, 2×2 H, CH_3CH_2), 2.64 (s, 3 H, quinolyl-CH_3), 2.70 (s, 3 H, quinolyl-CH_3), 6.92 (t, J = 7.5 Hz, 1 H, Ph-*H*), 7.01 (s, 1 H, quinolyl-*H*), 7.06–7.16 (m, 3 H, Ph-*H*), 7.32 (dd, J = 8.7, 2.4 Hz, 1 H, quinolyl-*H*), 7.38–7.43 (m, 2 H, Ph-*H* and quinolyl-*H*), 7.82 (d, J = 9.0 Hz, 1 H, Ph-*H*), 7.87 (d, J = 9.0 Hz, 1 H, Ph-*H*), 8.07 (s, 1 H, quinolyl-*H*), 8.37 (s, 1 H, C*H*=NAr), 11.62 (s, 1 H, quinolyl-N*H*) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ = 14.8 (CH_2CH_3), 18.4 (quinolyl-CH_3), 24.9 (CH_3CH_2), 25.0 (quinolyl-CH_3), 114.2, 115.0, 118.3, 118.9, 121.0, 121.3, 122.4, 124.4, 124.7, 126.4, 132.1, 133.7, 134.9, 142.3, 144.2, 144.8, 148.5, 149.4, 158.9, 165.6 (*C*H=N) ppm. $C_{28}H_{29}N_3$ (407.55): calcd. C 82.52, H 7.17, N 10.31; found C 82.59, H 7.21, N 10.20.

***ortho*-C_6H_4{7-NH(2,4-Me_2)C_9H_4N}(CH=$NC_6H_3i Pr_2$-2,6) (2c):** A solution of *n*BuLi (1.60 M, 14.4 mmol) in *n*-hexane was added to a solution of 7-amino-2,4-dimethylquinoline (2.50 g, 14.4 mmol) in THF (30 mL) at –78 °C. The mixture was warmed to room temp. and stirred overnight. The resulting solution of LiNHAr [Ar = 7-(2,4-Me_2)C_9H_4N] was transferred into a solution of *ortho*-$C_6H_4F(CH{=}NC_6H_3iPr_2$-2,6) (4.10 g, 14.4 mmol) in THF (30 mL) at 25 °C. After stirring for 2 d, the reaction was quenched with H_2O (20 mL). The organic phase was evaporated to dryness to give the crude product as a dark brown oil that was recrystallized from methanol to give the pure product as yellow solid (3.01 g, 48%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.19 [d, J = 6.5 Hz, 12 H, $CH(CH_3)_2$], 2.63 (s, 3 H, quinolyl-CH_3), 2.68 (s, 3 H, quinolyl-CH_3), 3.05 [sept, J = 6.5 Hz, 2 H, $CH(CH_3)_2$], 6.97 (t, J = 7.5 Hz, 1 H, Ph-*H*), 7.01 (s, 1 H, quinolyl-*H*), 7.17–7.22 (m, 3 H, Ph-*H* and quinolyl-*H*), 7.31–7.43 (m, 3 H, Ph-*H* and quinolyl-*H*), 7.81–7.88 (m, 2 H, Ph-*H*), 8.04 (s, 1 H, quinolyl-*H*), 8.35 (s, 1 H, C*H*=NAr), 11.59 (s, 1 H, quinolyl-N*H*) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ = 18.5 (quinolyl-CH_3), 23.5 [$CH(CH_3)_2$], 25.0 (quinolyl-CH_3), 28.1 [$CH(CH_3)_2$], 114.3, 115.1, 118.3, 118.9, 121.0, 121.3, 122.5, 123.1, 124.6, 124.7, 132.2, 135.0, 138.1, 142.3, 144.2, 144.9, 148.3, 149.0, 159.0, 165.7 (*C*H=N) ppm. $C_{30}H_{33}N_3$ (435.60): calcd. C 82.72, H 7.64, N 9.65; found C 82.82, H 7.70, N 9.51.

***ortho*-C_6H_4{7-N(2,4-Me_2)C_9H_4N}(CH=$NC_6H_3Me_2$-2,6)ZnEt (3a):** A solution of *ortho*-C_6H_4{7-NH(2,4-Me_2)C_9H_4N}(CH=$NC_6H_3Me_2$-2,6) (0.19 g, 0.50 mmol) in toluene (20 mL) was slowly added to a solution of $ZnEt_2$ (0.50 mmol) in toluene (10 mL) at room temp. with stirring. The mixture was stirred at room temp. for 1 h and at 90 °C for an additional 3 h. The solvent was removed in vacuo, and the obtained orange-red residue was recrystallized from *n*-hexane (10 mL) to give an orange-red solid (0.18 g, 78%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.55 (q, J = 7.8 Hz, 2 H, $ZnCH_2CH_3$), 1.16 (t, J = 7.8 Hz, 3 H, $ZnCH_2CH_3$), 1.95 (s, 2×3 H, CH_3), 2.23 (s, 3 H, quinolyl-CH_3), 2.60 (s, 3 H, quinolyl-CH_3), 6.51 (t, J = 7.8 Hz, 1 H, Ph-*H*), 6.63 (s, 1 H), 6.94–7.05 (m, 6 H), 7.49 (d, J = 8.4 Hz, 1 H), 7.70 (s, 2 H), 8.40 (s, 1 H, C*H*=N) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 298 K): δ = –1.2 ($ZnCH_2CH_3$), 12.2 ($ZnCH_2CH_3$), 18.2 (quinolyl-CH_3), 18.5 (CH_3), 25.2 (quinolyl-CH_3), 114.4, 116.3, 117.5, 121.5, 124.6, 124.9, 125.7, 126.0, 128.7, 130.1, 134.7, 138.0, 143.2, 149.3, 150.6, 152.1, 157.5, 159.0, 170.2 (*C*H=N) ppm.$C_{56}H_{58}N_6Zn_2$ (945.88): calcd. C 71.11, H 6.18, N 8.88; found C 71.22, H 6.14, N 8.75.

***ortho*-C_6H_4[7-N(2,4-Me_2)C_9H_4N](CH=$NC_6H_3Et_2$-2,6)ZnEt (3b):** A solution of *ortho*-C_6H_4{7-NH(2,4-Me_2)C_9H_4N}(CH=$NC_6H_3Et_2$-2,6) (0.19 g, 0.47 mmol) in toluene (20 mL) was slowly added to a solution of $ZnEt_2$ (0.47 mmol) in toluene (10 mL) at room temp. with stirring. The mixture was stirred at room temp. for 1 h and at 90 °C for an additional 3 h. The solvent was removed in vacuo, and the obtained orange-red residue was recrystallized from *n*-hexane (10 mL) to give orange-red crystals (0.19 g, 82%). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 0.63 (q, J = 8.0 Hz, 2 H, $ZnCH_2CH_3$), 1.09 (t, J = 7.5 Hz, 2×3 H, CH_2CH_3), 1.22 (t, J = 8.0 Hz, 3 H, $ZnCH_2CH_3$), 2.30 (s, 3 H, quinolyl-CH_3), 2.43–2.52 (m, 2×2 H, CH_2CH_3), 2.63 (s, 3 H, quinolyl-CH_3), 6.57 (t, J = 7.5 Hz, 1 H, Ph-*H*), 6.70 (s, 1 H), 7.04–7.10 (m, 4 H), 7.15 (t, J = 8.0 Hz, 1 H), 7.29 (t, J = 9.0 Hz, 1 H), 7.57 (d, J = 9.0 Hz, 1 H), 7.76 (d, J = 9.0 Hz, 1 H), 7.92 (s, 1 H), 8.47 (s, 1 H, C*H*=N) ppm. ^{13}C{^{1}H} NMR (125.1 MHz, C_6D_6, 298 K): δ = –1.8 ($ZnCH_2CH_3$), 12.0 ($ZnCH_2CH_3$), 14.5 (CH_2CH_3), 17.9 (quinolyl-CH_3), 25.0 (quinolyl-CH_3 and CH_2CH_3), 114.3, 115.9, 117.3, 121.3, 123.7, 124.5, 124.6, 125.5, 126.3, 126.6, 134.6, 135.9, 137.6, 142.9, 148.1, 150.5, 151.8, 157.4, 158.7, 170.0 (*C*H=N) ppm. $C_{60}H_{66}N_6Zn_2$ (1001.98): calcd. C 71.92, H 6.64, N 8.39; found C 71.85, H 6.58, N 8.50.

***ortho*-C_6H_4{7-N(2,4-Me_2)C_9H_4N}(CH=$NC_6H_3iPr_2$-2,6)ZnEt (3c):** A solution of *ortho*-C_6H_4{7-NH(2,4-Me_2)C_9H_4N}(CH=$NC_6H_3iPr_2$-2,6) (0.20 g, 0.55 mmol) in toluene (20 mL) was slowly added to a solution of $ZnEt_2$ (0.55 mmol) in toluene (10 mL) at room temp. with stirring. The mixture was stirred at room temp. for 1 h and at 90 °C for an additional 3 h. The solvent was removed in vacuo, and the obtained orange-red residue was recrystallized from *n*-hexane (10 mL) to give orange-red crystals (0.25 g, 84%). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.56 (q, J = 8.1 Hz, 2 H, $ZnCH_2CH_3$), 0.99 [d, J = 6.6 Hz, 6 H, $CH(CH_3)_2$], 1.05 [dd, J = 18.3, 6.9 Hz, 6 H, $CH(CH_3)_2$], 1.16 (t, J = 8.1 Hz, 3 H, $ZnCH_2CH_3$), 2.15 (s, 3 H, quinolyl-CH_3), 2.49 (s, 3 H, quinolyl-CH_3), 2.97 [sept, J = 6.9 Hz, 2×1 H, $CH(CH_3)_2$], 6.44 (t, J = 8.1 Hz, 1 H, Ph-*H*), 6.55 (s, 1 H, quinolyl-*H*), 6.94–6.99 (m, 2×1 H, Ph-*H*), 7.03–7.10 (m, 3×1 H, Ph-*H*), 7.49 (dd, J = 8.7, 2.1 Hz, 1 H, quinolyl-*H*), 7.62 (d, J = 8.7 Hz, 1 H, quinolyl-*H*), 7.97 (s, 1 H, quinolyl-*H*), 8.41 (s, 1 H, C*H*=N) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 298 K): δ = –1.3 ($ZnCH_2CH_3$), 12.4 ($ZnCH_2CH_3$), 18.2 (quinolyl-CH_3), 24.4 [$CH(CH_3)_2$], 25.2 (quinolyl-CH_3), 28.8 [$CH(CH_3)_2$], 114.6, 116.1, 117.4, 121.6, 123.8, 123.9, 124.6, 124.9, 125.7, 127.0, 134.9, 138.0, 140.9, 143.3, 146.9, 150.6, 152.1, 157.6, 159.0, 170.2 (*C*H=N) ppm. $C_{64}H_{74}N_6Zn_2{\cdot}C_6H_{14}$ (1144.20): calcd. C 73.47, H 7.75, N 7.34; found C 73.36, H 7.81, N 7.16.

***ortho*-C_6H_4($NC_6H_3Me_2$-2,6)(CH=$NC_6H_3iPr_2$-2,6)ZnEt (3d):** A solution of *ortho*-C_6H_4($NHC_6H_3Me_2$-2,6)(CH=$NC_6H_3iPr_2$-2,6) (0.28 g, 0.72 mmol) in toluene (20 mL)was slowly added to a solution of $ZnEt_2$ (0.72 mmol) in toluene (10 mL) at room temp. with stirring. The mixture was stirred at room temp. for 1 h and at 90 °C for an additional 3 h. The solvent was removed in vacuo, and the obtained yellow-green residue was recrystallized from *n*-hexane (10 mL) to give a yellow solid (0.25 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.02 (q, J = 8.1 Hz, 2 H, $ZnCH_2CH_3$), 0.70 (t, J = 8.1 Hz, 3 H, $ZnCH_2CH_3$), 1.27 [d, J = 6.6 Hz, 4×3 H, $CH(CH_3)_2$], 2.23 (s, 2×3 H, CH_3), 3.10 [sept, J = 6.6 Hz, 2×1 H, $CH(CH_3)_2$], 6.38 (d, J = 9.0 Hz, 1 H), 6.56 (t, J = 6.9 Hz, 1 H), 7.15–7.32 (m, 8 H), 8.29 (s, 1 H, C*H*=N) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 298 K): δ = –2.9 ($ZnCH_2CH_3$), 11.3 ($ZnCH_2CH_3$), 18.3 (CH_3), 24.1 [$CH(CH_3)_2$], 28.5 [$CH(CH_3)_2$], 113.0, 114.2, 115.1, 123.5, 124.2, 126.5, 128.5, 133.1, 134.7, 137.6, 140.5, 146.6, 147.3, 156.4, 169.5 (*C*H=N) ppm. $C_{29}H_{36}N_2Zn$ (478.00): calcd. C 72.87, H 7.59, N 5.86; found C 72.71, H 7.68, N 5.75.

X-ray Structure Determinations of 2a, 2b, 3b, and 3c: Single crystals of **2a** and **2b** suitable for X-ray structural analysis were obtained from ethyl acetate/petroleum ether at room temp. Single crystals of **3b** and **3c** suitable for X-ray structural analysis were obtained from *n*-hexane at room temp. Diffraction data were collected at 293 K with a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) for all compounds. The structures were solved by direct methods[18] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealized position. All calculations were performed by using the SHELXTL[19] crystallographic software packages. Details of the crystal data, data collections, and structure refinements are summarized in Tables 3 (**2a** and **2b**) and 4 (**3b** and **3c**). CCDC-636086 (for **2a**), -636087 (for **2b**), -636088 (for **3b**), and -636089 (for **3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystal data and structural refinement details for **2a** and **2b**.

	2a	**2b**
Empirical formula	$C_{26}H_{25}N_3$	$C_{28}H_{29}N_3$
Formula mass	379.49	407.54
Temperature [K]	293(2)	293(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a [Å]	17.371(4)	9.989(2)
b [Å]	8.4558(17)	13.204(3)
c [Å]	15.347(3)	18.038(4)
α [°]	90	75.85(3)
β [°]	107.62(3)	87.79(3)
γ [°]	90	88.84(3)
Volume [Å^3]	2148.5(7)	2305.1(8)
Z	4	4[a]
$D_{calcd.}$ [Mg m^{-3}]	1.173	1.174
$F(000)$	808	872
θ range for data collection [°]	3.11–27.48	3.01–27.48
Limiting indices	$-22 \le h \le 20$	$-12 \le h \le 12$
	$-10 \le k \le 10$	$-17 \le k \le 17$
	$-19 \le l \le 19$	$-23 \le l \le 23$
Data/restraints/parameters	4864/0/271	10002/30/568
Goodness-of-fit on F^2	1.026	1.029
Final R indices [$I > 2\sigma(I)$]	R_1[b] = 0.0546	R_1[b] = 0.0816
	wR_2[c] = 0.1200	wR_2[c] = 0.2028
R indices (all data)	R_1[b] = 0.1054	R_1[b] = 0.1636
	wR_2[c] = 0.1393	wR_2[c] = 0.2450
Largest diff. peak/hole [e Å^{-3}]	0.152/–0.138	0.374/–0.315

[a] There are two crystallographically independent molecules in the asymmetric unit. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w\,(F_o^2 - F_c^2)^2]/\Sigma[w\,(F_o^2)^2]\}^{1/2}$.

Table 4. Crystal data and structural refinement details for **3b** and **3c**.

	3b	**3c**
Empirical formula	$C_{60}H_{66}N_6Zn_2$	$C_{70}H_{88}N_6Zn_2$
Formula mass	1001.93	1144.20
Temperature [K]	293(2)	293(2)
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a [Å]	25.656(5)	13.538(3)
b [Å]	17.437(4)	15.539(3)
c [Å]	17.348(4)	16.885(3)
α [°]	90	105.85(3)
β [°]	129.37(3)	108.94(3)
γ [°]	90	96.33(3)
Volume [Å^3]	5999(2)	3153.8(11)
Z	4	2
$D_{calcd.}$ [Mg m^{-3}]	1.109	1.205
$F(000)$	2112	1220
θ range for data collection [°]	3.04–27.48	3.03–27.48
Limiting indices	$-33 \le h \le 33$	$-17 \le h \le 16$
	$-22 \le k \le 22$	$-20 \le k \le 20$
	$-18 \le l \le 22$	$-21 \le l \le 21$
Data/restraints/parameters	6726/0/289	13686/5/719
Goodness-of-fit on F^2	1.021	0.996
Final R indices [$I > 2\sigma(I)$]	R_1[a] = 0.0811	R_1[a] = 0.0621
	wR_2[b] = 0.1988	wR_2[b] = 0.1668
R indices (all data)	R_1[a] = 0.1565	R_1[a] = 0.1243
	wR_2[b] = 0.2430	wR_2[b] = 0.2109
Largest diff. peak/hole [e Å^{-3}]	0.981/–1.248	0.576/–0.436

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w\,(F_o^2 - F_c^2)^2]/\Sigma[w\,(F_o^2)^2]\}^{1/2}$.

Acknowledgments

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