Synthesis and Characterization of Luminescent Zinc(II) and Cadmium(II) Complexes with N,S-Chelating Schiff Base Ligands

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The reactions of zinc(II) acetate with a variety of 2-substituted benzothiazolines afforded tetrahedral mononuclear complexes with a N_2S_2 donor set, $[Zn(R-Ph-C(H)=N-C_6H_4-S)_2]$. The obtained zinc(II) complexes can be divided into three groups based on the characteristics of the absorption spectra; Group 1 (R = 2,4,6-triMe (**1**), 2,6-diCl (**2**)) showing an intense band at 250–300 nm and a weak band at 400–450 nm, Group 2 (R = 4-Cl (**3**), H (**4**), 4-Et (**5**), 4-OMe (**6**)) showing two intense bands at 250–300 nm and a weak band at 400–450 nm, and Group 3 (R = 4-NMe$_2$ (**7**), 4-NEt$_2$ (**8**)) showing an intense band at 250–300 nm and two very intense bands at 350–450 nm. The Group 2 and Group 3 complexes exhibited a strong emission on irradiating with ultraviolet light while the Group 1 complexes were not emissive at room temperature. However, all the zinc(II) complexes were luminescent in CH$_2$Cl$_2$/toluene glass at 77 K, and their emission peak energies were found to correlate with the Hammett constant of the substituent at *para* position of a pendent phenyl ring in each complex. Similar reactions of cadmium(II) acetate with 2-substituted benzothiazolines were also carried out to synthesize corresponding cadmium(II) complexes. While $[Cd(R-Ph-C(H)=N-C_6H_4-S)_2]$ (R = 2,4,6-triMe (**9**)) with bulky substituents at *ortho* positions of a pendent phenyl ring had a tetrahedral mononuclear structure, other cadmium(II) complexes $[Cd_2(R-Ph-C(H)=N-C_6H_4-S)_4]$ (R = 4-Et (**10**), 4-OMe (**11**), 4-NMe$_2$ (**12**)) possessed S-bridged dinuclear structures. These cadmium(II) complexes, which are assumed to have a mononuclear structure in solution, showed photophysical properties similar to those of the corresponding zinc(II) complexes.

Introduction

Since the success of the application of tris(8-hydroxyquinolinato)aluminum(III) (Alq$_3$) as an organic light-emitting diode,[1] photoluminescent metal complexes with appropriate organic ligands have received considerable attention as emitting materials.[2,3] Previously, it has been reported that zinc(II) complexes with Schiff bases type chelating ligands can be used as an effective emitting layer.[4] Motivated by

this report, some Schiff base zinc(II) complexes with N$_2$O$_2$ donor sets have been prepared to elucidate their photophysi-

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Scheme 1
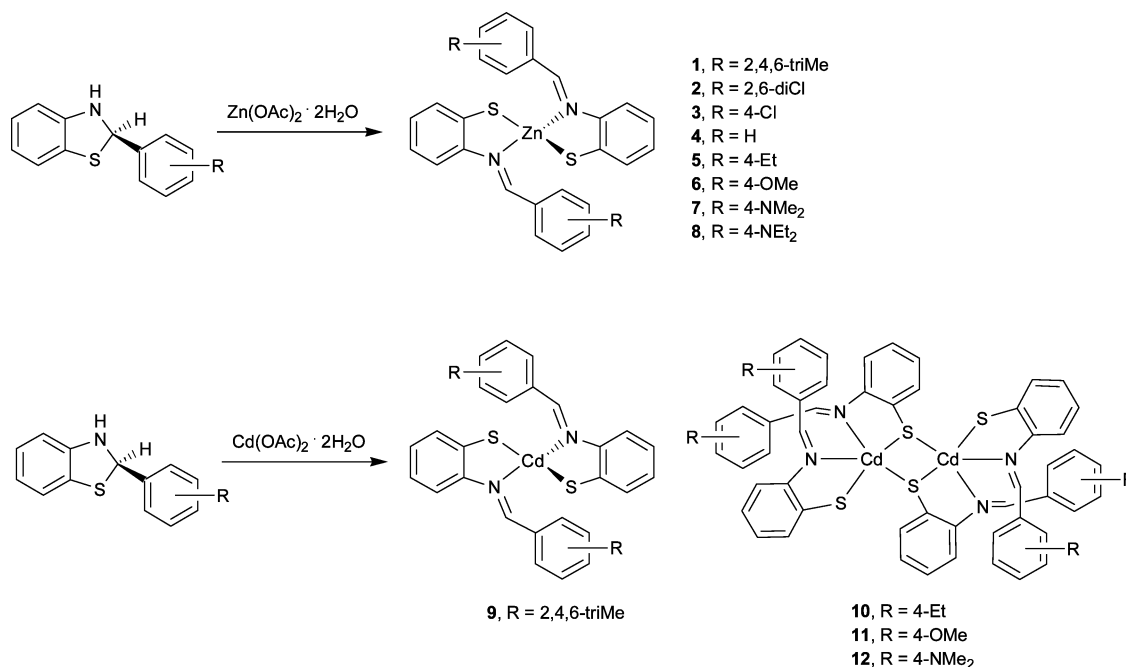
cal properties.[5] In addition, it has also been shown that zinc(II) complexes with benzothiazoles, which are oxidized forms of benzothiazolines, are luminescent.[6] On the other hand, the luminescent properties of zinc(II) complexes containing N,S-chelating Schiff base ligands derived from benzothiazolines have not been investigated so far; nevertheless, several molecular structures of analogous zinc(II) complexes have been reported.[7] As part of our work on transition metal complexes derived from 2-substituted benzothiazolines,[8] we now investigated the reactions of zinc(II) ion or cadmium(II) ion with a variety of 2-substituted benzothiazolines. The present paper reports the synthesis, characterization, and photophysical properties of Schiff base zinc(II) and cadmium(II) complexes with a N_2S_2 donor set obtained by these reactions.

Results and Discussion

Synthesis. Benzothiazolines were prepared from 2-aminobenzenethiol and appropriate aldehydes according to the general procedures[9] and characterized by IR and ^{1}H NMR spectroscopies and elemental analyses. The zinc(II) complexes **1**−**8** and cadmium(II) complexes **9**−**12** were obtained by treating the corresponding benzothiazolines with zinc(II) acetate dihydrate or cadmium(II) acetate dihydrate (Scheme 1). These complexes were also characterized by IR and ^{1}H NMR spectroscopies, along with X-ray crystallography for **1**, **5**, **6**, **7**, **9**, and **12**, and the purity of these complexes was confirmed by elemental analyses.

It was shown by single-crystal X-ray analyses (vide infra) that the zinc(II) complexes **1** (R = 2,4,6-triMe), **5** (R = 4-Et), **6** (R = 4-OMe), and **7** (R = 4-NMe$_2$) have a mononuclear structure. As anticipated from the structures, these zinc(II) complexes, together with the other zinc(II) complexes **2** (R = 2,6-diCl), **3** (R = 4-Cl), **4** (R = H), and **8** (R = 4-NEt$_2$), exhibited a well-defined single set of signals in the ^{1}H NMR spectra. On the other hand, the cadmium(II) complexes **9** (R = 2,4,6-triMe) and **12** (R = 4-NMe$_2$) were determined to have mononuclear and dinuclear structures, respectively, based on X-ray analyses. In addition, it was assumed that the other cadmium(II) complexes **10** (R = 4-Et) and **11** (R = 4-OMe), which have a substituent at the *para* position of a pendent phenyl ring, as does **12** (R = 4-NMe$_2$), also adopt a dinuclear structure (vide infra). The ^{1}H NMR spectra of **10**, **11**, and **12**, as well as the spectrum of **9**, showed only a single set of signals, indicative of the equivalence of each

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Table 1. Crystallographic Data For **1**, **5**, **6**, **7**, **9**, and **12**

	1	5	6	7	9	12
empirical formula	$C_{32}H_{32}N_2S_2Zn$	$C_{30}H_{28}N_2S_2Zn$	$C_{28}H_{24}N_2O_2S_4Zn$	$C_{30}H_{30}N_4S_2Zn$	$C_{32}H_{32}CdN_2S_2$	$C_{60}H_{60}Cd_2N_8S_4$
M_r	574.09	546.03	549.98	576.07	621.12	1246.20
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	orthorhombic
space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$	$Pbca$
a, Å	9.568(3)	14.080(6)	12.908(4)	14.198(6)	8.370(6)	16.531(4)
b, Å	13.364(6)	13.612(6)	13.639(3)	15.037(8)	11.298(6)	11.279(3)
c, Å	22.457(8)	14.469(6)	14.250(5)	13.609(10)	16.018(11)	29.569(8)
α, °					90.462(19)	
β, °	97.787(14)	108.554(14)	98.004(13)		101.04(2)	
γ, °					109.05(2)	
V, Å^3	2845.0(18)	2629.1(19)	2484.2(12)	2905(3)	1401.1(16)	5513(3)
Z	4	4	4	4	2	4
$F(000)$	1200	1136	1136	1200	636	2544
D_c, g cm^{-3}	1.340	1.380	1.471	1.317	1.472	1.501
μ/mm^{-1}	1.034	1.115	1.186	1.014	0.952	0.970
reflections collected	13820	22811	23338	3727	13726	46009
indep. reflns (R_{int})	3258 (0.0547)	5870 (0.0901)	5654 (0.0410)	3727 (0.0000)	6312 (0.0206)	6274 (0.1021)
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.0382, 0.0808	0.0555, 0.0905	0.0304, 0.0697	0.0425, 0.0882	0.0259, 0.0765	0.0503, 0.0908
$R1$, $wR2$ (all data)	0.0597, 0.0888	0.1128, 0.1073	0.0441, 0.0755	0.1824, 0.1211	0.0290, 0.0779	0.0905, 0.1027
goodness-of-fit on F^2	1.030	1.027	1.041	0.934	1.099	1.028

Table 2. Selected Bond Distances (Å) and Angles (°) of **1**, **5**, **6**, and **7**

	1	5	6	7
Zn1−S1	2.2564(8)	2.2636(14)	2.2629(8)	2.263(2)
Zn1−S2		2.2755(12)	2.2771(8)	2.271(2)
Zn1−N1	2.0976(17)	2.092(3)	2.1013(15)	2.100(6)
Zn1−N2		2.100(3)	2.1046(16)	2.114(7)
S1−Zn1−S2	125.93(4)	120.81(5)	117.80(3)	122.11(10)
S1−Zn1−N1	87.73(5)	89.02(8)	89.00(4)	89.26(18)
S1−Zn1−N2	128.76(5)	118.88(8)	125.90(4)	121.1(2)
S2−Zn1−N1		125.07(8)	126.71(4)	123.60(19)
S2−Zn1−N2		88.03(8)	87.92(5)	87.86(19)
N1−Zn1−N2	99.66(9)	118.43(10)	113.65(6)	116.4(2)

**Table 3.** Selected Bond Distances (Å) and Angles (°) of **9** and **12**[a]

	9	12
Cd1−S1	2.4376(12)	2.4721(12)
Cd1−S2	2.4232(12)	2.5231(11)
Cd1−S2*		2.7496(11)
Cd1−N1	2.346(2)	2.345(3)
Cd1−N2	2.347(2)	2.766(3)
S1−Cd1−S2	144.29(3)	122.52(4)
S1−Cd1−S2*		110.97(4)
S1−Cd1−N1	79.38(5)	81.57(8)
S1−Cd1−N2	124.92(6)	115.86(7)
S2−Cd1−S2*		87.30(4)
S2−Cd1−N1	119.09(6)	154.18(8)
S2−Cd1−N2	81.89(6)	70.66(7)
S2*−Cd1−N1		92.45(8)
S2*−Cd1−N2		133.06(7)
N1−Cd1−N2	105.46(7)	91.26(10)
Cd1−S2−Cd1*		92.70(4)

[a] An asterisk refers to the following equivalence positions relative to the x, y, z set: $-x, -y, -z$.

ligand. Thus, it is considered that these dicadmium(II) complexes also have a mononuclear structure in solution.

Molecular Structures of Zinc(II) Complexes. The crystal structures of the zinc(II) complexes, **1**, **5**, **6**, and **7**, along with the cadmium(II) complexes **9** and **12** (vide infra), were determined by X-ray crystallography. Table 1 gives crystallographic data, and Tables 2 and 3 summarize selected bond distances and angles of these complexes. Oak Ridge thermal ellipsoid plot (ORTEP) diagrams for **1** (R = 2,4,6-triMe), **5** (R = 4-Et), **6** (R = 4-OMe), and **7** (R = 4-NMe$_2$) are illustrated in Figures 1, Supporting Information Figure S1,

2, and 3, respectively. The gross structural features of **1**, **5**, **6**, and **7** show a ZnN$_2$S$_2$ coordination sphere with distorted tetrahedral geometry, constituted by two thiolato sulfur and two imino nitrogen atoms from two Schiff base ligands. The
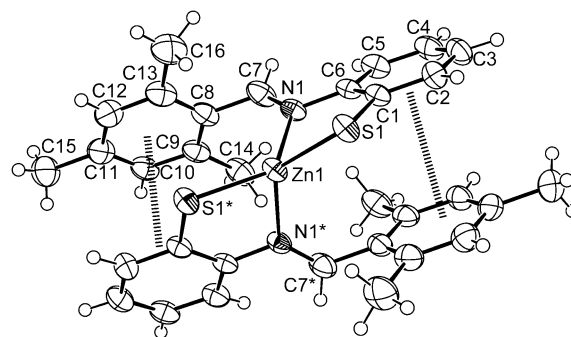
Figure 1. Molecular structure of **1** with 50% probability ellipsoids.
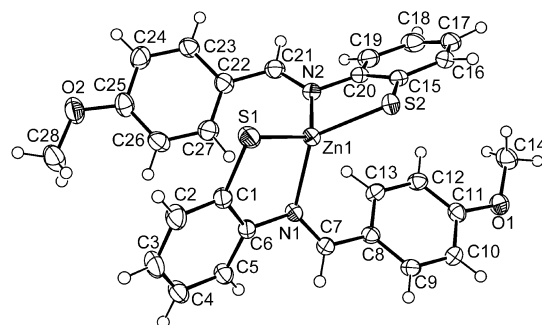
Figure 2. Molecular structure of **6** with 50% probability ellipsoids.
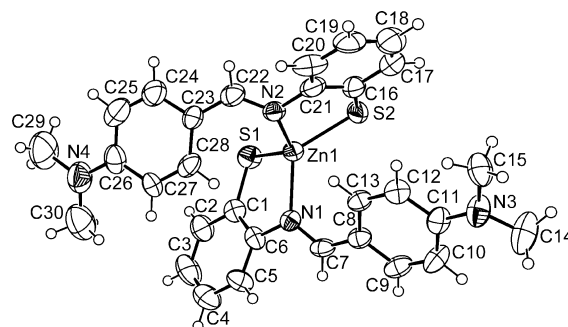
Figure 3. Molecular structure of **7** with 50% probability ellipsoids.

Scheme 2
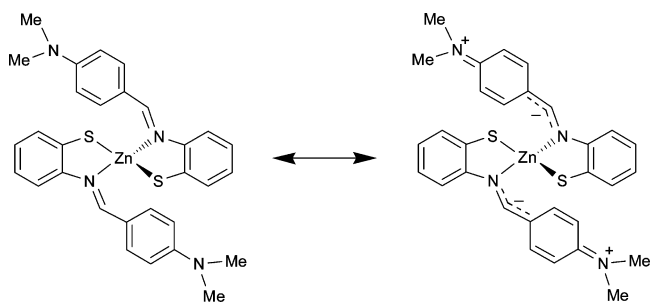
Zn−S and Zn−N bond lengths in **1**, **5**, **6**, and **7** are very similar to one another (2.2564(8) Å and 2.0976(17) Å in **1**, 2.2636(14) and 2.2755(12) Å and 2.092(3) and 2.100(3) Å in **5**, 2.2629(8) and 2.2771(8) Å and 2.1013(15) and 2.1046(16) Å in **6**, and 2.263(2) and 2.271(2) Å and 2.100(6) and 2.114(7) Å in **7**) and lie within the range observed for the analogues.[7] A comparison of the dihedral angles between pendent phenyl rings and azomethine moieties, which refer to the twisting around the azomethine carbon atom in each complex, is informative. The mean values of the dihedral angles in **1**, **5**, **6**, and **7** decrease in the order **1** (78.1(2)°; the dihedral angle between the mean planes of C7−C8−C9−C10−C11−C12−C13 and N1−C7−C8), **5** (av. 27.9°; the dihedral angles between the mean planes of C7−C8−C9−C10−C11−C12−C13 and N1−C7−C8, between the mean planes of C22−C23−C24−C25−C26−C27−C28 and N2−C22−C23, and between the mean planes of C22−C23−C24−C25′−C26′−C27′−C28′ and N2−C22−C23 are 22.3(4)°, 27.9(8)°, and 33.5(8)°), **6** (av. 23.8°; the dihedral angles between the mean planes of C7−C8−C9−C10−C11−C12−C13 and N1−C7−C8 and between the mean planes of C21−C22−C23−C24−C25−C26-C27 and N2−C21−C22 are 25.9(2)° and 21.6(2)°), and **7** (av. 20.2°; the dihedral angles between the mean planes of C7−C8−C9−C10−C11−C12−C13 and N1−C7−C8 and between the mean planes of C22−C23−C24−C25−C26−C27−C28 and N2−C22−C23 are 15.1(6)° and 25.3(8)°). The extremely large angle for **1** induces a highly distorted tetrahedral structure; the dihedral angle between the ZnNS trigonal planes in **1** (72.90(5)°) is much smaller than the corresponding angles in **5** (88.07(8)°), **6** (80.59(4)°), and **7** (87.2(2)°). In complex **7** (R = 4-NMe₂) with the smallest angle (20.2°), the quinoid type distortion is observed for two pendent phenyl rings. That is, two shorter aromatic C−C bonds (av. 1.370(10) Å for C9−C10 and C12−C13, av. 1.344(12) Å for C24−C25 and C27−C28) and four longer aromatic C−C bonds (av. 1.407(12) Å for C8−C9, C8−C13, C10−C11, and C11−C12, av. 1.412(13) Å for C23−C24, C23−C28, C25−C26, and C26−C27) are found in the six C−C distances of the pendent phenyl part. The azomethine C=N bond distances (av. 1.298(9) Å) in **7** are relatively long as a C=N double bond. On the other hand, the bond distances (av. 1.358(11) Å) between the nitrogen atom of the dimethylamino group and the aromatic carbon atom are relatively short as a C−N single bond, and the sum of the angles around each nitrogen atom is close to 360° (358.8° for N3 and 359.2° for N4). Therefore, the resonance contribution is considered to the ligand structure in **7**
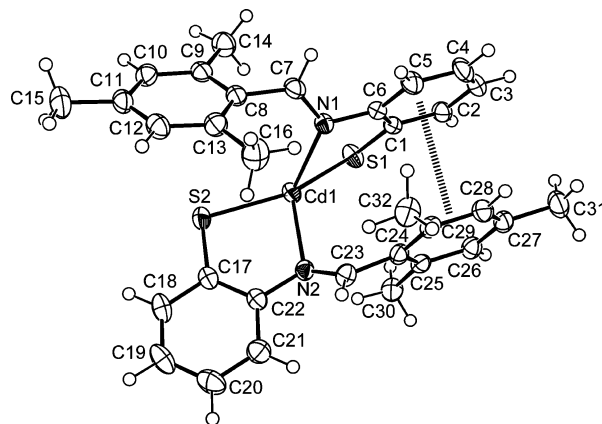

Figure 4. Molecular structure of **9** with 50% probability ellipsoids.

(Scheme 2). In addition, **7** crystallizes in the orthorhombic space group $P2_12_12_1$, indicating that **7** is subject to spontaneous resolution. The Δ and Λ absolute configurations are possible for this structure with respect to the substantial C_2 axis of the molecule.[10] Refinement of the Flack enantiopole parameter [0.00(3)] implies that the crystal used for the X-ray analysis contains only the Δ enantiomer of the molecule. The lack of optical activity of this crystal in CH_2Cl_2 is suggestive of the racemization in solution.

In **1** (R = 2,4,6-triMe), there exist two intramolecular face-to-face interactions between the chelating aromatic and the pendent aromatic rings; the centroid···centroid distance is 3.789 Å (Figure 1). On the other hand, in **5** (R = 4-Et), **6** (R = 4-OMe), and **7** (R = 4-NMe₂), there are no noteworthy intra and intermolecular interactions or short contacts.

Molecular Structures of Cadmium(II) Complexes. ORTEP diagram of complex **9** (R = 2,4,6-triMe) is shown in Figure 4. The cadmium(II) ion adopts a distorted tetrahedral coordination geometry bonded by two five-membered N,S chelate rings. The dihedral angle between the CdN1S1 and the CdN2S2 trigonal planes is 86.35(6)°. The Cd−S bond distances (2.4376(12) and 2.4232(12) Å) are shorter and the Cd−N bond distances (2.346(2) and 2.347(2) Å) are longer than those of the related four-coordinate cadmium(II) complexes.[11] In addition, this complex has unsymmetrical structure in the chelate ligands as observed in the twisting around the azomethine carbon atoms (the dihedral angles between C7−C8−C9−C10−C11−C12−C13 and N1−C7−C8 and C23−C24−C25−C26−C27−C28−C29 and N2−C23−C24 are 79.3(2)° and 46.7(2)°, respectively). This structural feature is different from that of the corresponding zinc(II) complex **1**, in which metal center is located on a crystallographic 2-fold axis. An intramolecular face-to-face interaction between the chelated aromatic ring and the pendent aromatic ring is observed; the centroid···centroid distance is 3.707 Å.

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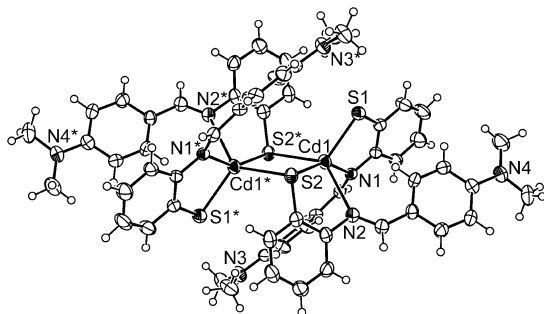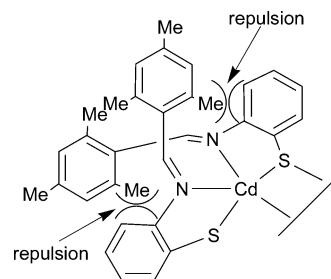
Figure 5. Molecular structure of **12** with 50% probability ellipsoids.

Complex **12** (R = 4-NMe$_2$) crystallizes in the orthorhombic space group *Pbca* with four formula units in the unit cell, and the asymmetric unit consists of one-half of the complex molecule. The ORTEP diagram of **12** is shown in Figure 5. There is a crystallographic inversion center at the midpoint of the Cd1···Cd1* vector. Two cadmium(II) ions are bridged by two thiolato sulfur atoms from two Schiff base ligands, and each cadmium(II) center has a five-coordinate geometry formed by two nitrogen and two sulfur atoms from two N,S-chelate ligands and one sulfur atom from one bridging ligand. A long Cd1···Cd1* separation of 3.8185(9) Å is indicative of the absence of a Cd···Cd interaction. To estimate the relative geometry about each cadmium atom in the five-coordinated environment, the angular parameter χ was calculated.[12] The χ value (0.53) suggests that each cadmium(II) center resides in a coordination geometry just between trigonal bipyramid and square-pyramid. While the Cd–S2* bond distance (2.7496(11) Å) is longer than the Cd–S1 (2.4721(12) Å) and Cd–S2 (2.5231(11) Å) distances, these values fall in the range found for dimeric five-coordinate cadmium(II) complexes.[13] The Cd–N1 bond distance (2.345(3) Å) agrees with those found in cadmium(II) complexes with a five-coordinated environment,[14] but the Cd–N2 bond (2.766(3) Å) is considerably longer than the sum of the covalent radii of cadmium and nitrogen atoms (2.15 Å).[15]

Molecular model examination revealed that a serious steric repulsion arises between the N,S-chelating benzene moiety and a substituent at the *ortho* position of a pendent phenyl ring in the S-bridged dinuclear structure (Scheme 3). In fact, the related cadmium(II) complex **9** that has methyl groups at *ortho* positions adopts a mononuclear structure. Because the other cadmium(II) complexes **10** (R = 4-Et) and **11** (R = 4-OMe) have no substituent at *ortho* positions, as does **12** (R = 4-NMe$_2$), it is likely that these complexes also adopt a dinuclear structure.

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Scheme 3

UV/vis Absorption Spectra. The present zinc(II) complexes [Zn(R—Ph—C(H)=N—C$_6$H$_4$—S)$_2$] are classified into three groups on the basis of the position and intensity of the absorption bands. That is, the Group 1 complexes (R = 2,4,6-triMe (**1**), 2,6-diCl (**2**)) show an intense band at 250−300 nm and a weak band at 400−450 nm, the Group 2 complexes (R = 4-Cl (**3**), H (**4**), 4-Et (**5**), 4-OMe (**6**)) show two intense bands at 250−300 nm and a weak band at 400−450 nm, and the Group 3 complexes (R = 4-NMe$_2$ (**7**), 4-NEt$_2$ (**8**)) show an intense band at 250−300 nm and two very intense bands at 350−450 nm (Table 4, Supporting Information Figure S2); the representative absorption spectra of each group are shown in Figure 6. Similarly, the cadmium(II) complexes [Cd(R—Ph—C(H)=N—C$_6$H$_4$—S)$_2$] can also be classified into three groups; Group 1 (R = 2,4,6-triMe (**9**)), Group 2 (R = 4-Et (**10**), 4-OMe (**11**)), and Group 3 (R = 4-NMe$_2$ (**12**)) (Table 5, Supporting Information Figure S3).

To elucidate the origin of the very intense absorption bands observed for the Group 3 complexes, DFT calculations were carried out using the X-ray structural data of **7**. Frontier molecular orbitals obtained at the B3LYP/LAN2DZ level are shown in Figure 7. The highest occupied molecular orbital (HOMO), HOMO−1, and HOMO−4 possess a large contribution from the 3p orbitals on the thiolato sulfur atoms and π orbitals on N,S-benzene moieties. The HOMO−2 and HOMO−3 are dominated by the π orbitals delocalized over the conjugated R—Ph—C(H)=N (R = 4-NMe$_2$) moiety, while the lowest unoccupied molecular orbital (LUMO) and the LUMO+1 are dominated by the π* orbitals on the conjugated R—Ph—C(H)=N moiety. Time-dependent DFT calculation indicates that the lowest-energy excitation occurs from HOMO → LUMO which is characterized by a charge transfer transition from the thiolato sulfur atoms to the conjugated R—Ph—C(H)=N moiety. The strongly allowed transitions corresponding to the intense band at 384 nm involve several one-electron transitions: HOMO−2 → LUMO+1, HOMO−4 → LUMO, and HOMO−4 → LUMO+1. Because the LUMO (or LUMO+1) has no contribution from the sulfur 3p orbitals, the transition dipole moment for HOMO−4 → LUMO (or LUMO+1) is considered to be small. Thus, the origin of the intense 384 nm band is ascribable to HOMO−2 → LUMO+1, π−π* transition within the R—Ph—C(H)=N moiety. Such very large bathochromic shifts of π−π* absorption bands in Group 3 complexes can be explained on the basis of the valence-

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Table 4. Photophysical Properties of Zinc(II) Complexes

complex	$\lambda_{max,abs}$, nm (ε, M^{-1} cm^{-1}) (CH$_2$Cl$_2$, r.t., 1×10^{-5} to 3×10^{-4} M)	$\lambda_{max,em}$, nm[a] (CH$_2$Cl$_2$/ toluene, 77 K)	$\lambda_{max,em}$, nm[a] (solid, r.t.)	lifetime, ns[c] (solid, r.t.)	quantum yield, Φ^e (solid, r.t.)
1	265 (3.15×10^4), 308^{sh} (1.34×10^4), 405 (4.46×10^3)	615	b	d	f
2	265 (2.88×10^4), 423 (3.42×10^3)	649	b	<0.2	f
3	260 (3.54×10^4), 281 (3.29×10^4), 309^{sh} (2.31×10^4), 447 (5.62×10^3)	632	633	0.37 ± 0.05	0.009
4	259 (3.48×10^4), 279 (3.32×10^4), 307^{sh} (1.87×10^4), 441 (5.34×10^3)	620	627	<0.2	f
5	261 (3.20×10^4), 283 (3.28×10^4), 309^{sh} (2.48×10^4), 438 (6.20×10^3)	613	606	0.42 ± 0.05	0.014
6	260 (2.48×10^4), 282 (2.33×10^4), 325 (3.09×10^4), 432 (6.93×10^3)	605	600	0.56 ± 0.05	0.021
7	255 (3.20×10^4), 280^{sh} (2.08×10^4), 317 (7.25×10^3), 384 (5.33×10^4), 424 (3.52×10^4)	578	584	0.38 ± 0.1(80%) 1.1 ± 0.1(20%)	0.062
8	256 (2.79×10^4), 282^{sh} (1.98×10^4), 318 (6.53×10^3), 389 (5.34×10^4), 429 (4.01×10^4)	572	591	0.23 ± 0.1(80%) 0.78 ± 0.1(20%)	0.088

[a] The excitation wavelength was set to 355 nm. [b] Not observed. [c] Determined for solid-state sample with excitation at 473nm. A value in parenthesis denotes the fraction of each component in dual exponential decay. [d] The emission was too weak for lifetime measurements. [e] Error ± 10%. [f] Less than 0.001.
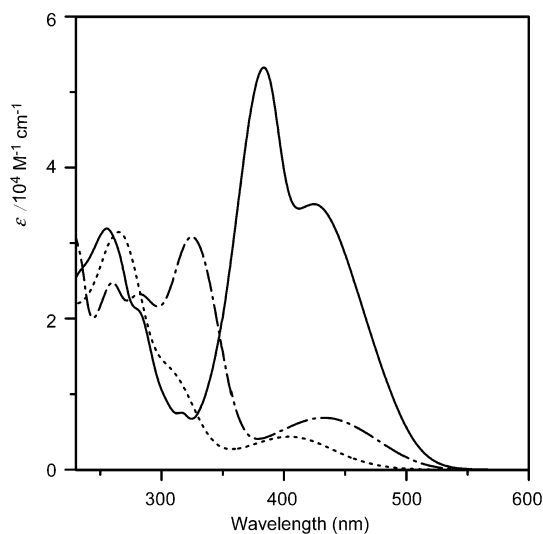

Figure 6. Absorption spectra of **1** (dotted line), **6** (dashed-dotted line), and **7** (solid line) in CH$_2$Cl$_2$. (concentrations: 1×10^{-5} to 2×10^{-4} M).

bond (resonance) approach as shown in the X-ray analysis of **7** (Scheme 2).[16]

Photoluminescence Properties. The emission spectral data in the solid state for all the zinc(II) complexes were recorded with excitation at 355 nm. As summarized in Table 4, **1** (R = 2,4,6-triMe) and **2** (R = 2,6-diCl), which belong to Group 1, did not show emission while a moderately strong emission and a considerably strong orange emission were observed for the Group 2 complexes (R = 4-Cl (**3**), H (**4**), 4-Et (**5**), 4-OMe (**6**)) and the Group 3 complexes (R = 4-NMe$_2$ (**7**), 4-NEt$_2$ (**8**)), respectively, in the region of 584−633 nm at room temperature. Typical examples of emission spectra for each group are shown in Figure 8, and the quantum yields for the Zn(II) and Cd(II) complexes in the solid state are summarized in Tables 4 and 5. The quantum yields of the new emissive compounds are not high compared with those of the zinc(II) complexes with N,O-chelating Schiff base ligands.[5] However, the Group 3 complexes show a quantum efficiency higher than those of the other complexes. Thus, the substituent positions on the pendent phenyl rings substantially affect the emission in the solid state. This behavior can be mainly correlated to the twisting around the azomethine carbon atom; the highly twisted structure observed in the Group 1 complexes, compared with the other Group 2 and 3 complexes, results in the obvious decrease of emission intensity. The emission lifetimes of the Group 2 complexes were very short, less than 0.6 ns. The Group 3 complexes showed dual exponential decays with a long lifetime component of about 1 ns. Such multiple exponential decays are often observed for emissive crystalline samples, probably because of quenching of migrating excitons by defects inside or at the surface of crystals. All the zinc(II) complexes were luminescent in CH$_2$Cl$_2$/toluene glass at 77 K though they are almost nonemissive in the fluid solution probably because of the rapid nonradiative transition induced by solvent interactions. Among the various substituted complexes, **7** and **8**, having the strongest electron-donating groups, exhibit emissions at much shorter wavelengths ($\lambda_{em, max}$) than those of the other complexes (Table 4, Figure 9). In addition, **3**, having a chloro group, exhibits an emission at a slightly longer wavelength than does **4**, which has an unsubstituted phenyl group. Thus, the emission peaks for the monosubstituted zinc(II) complexes, including **4**, show the hypsochromic shift as the substituent becomes more electron-donating, and the emission maxima for the zinc(II) complexes are linearly related to the Hammett constants (Figure 10).[17] A similar relation holds for the cadmium(II) complexes (Table 5, Supporting Information Figure S4). This tendency is in contrast to the fact that Alq$_3$ derivatives with electron-donating substituents show the bathochromic shifts.[18] The relationship between the emission wavelength and the properties of substituents for the present complexes is rationalized on the basis of the distribution of the frontier orbitals (HOMO and LUMO) involved in the emission. That is, the HOMO is localized on the thiolato sulfur atoms with a high nucleophilic property, whereas the LUMO is delocalized over the ligands (Figure 7). Thus, the LUMO energy rises to give a wide HOMO−LUMO gap as the electron-donating ability of the substituents
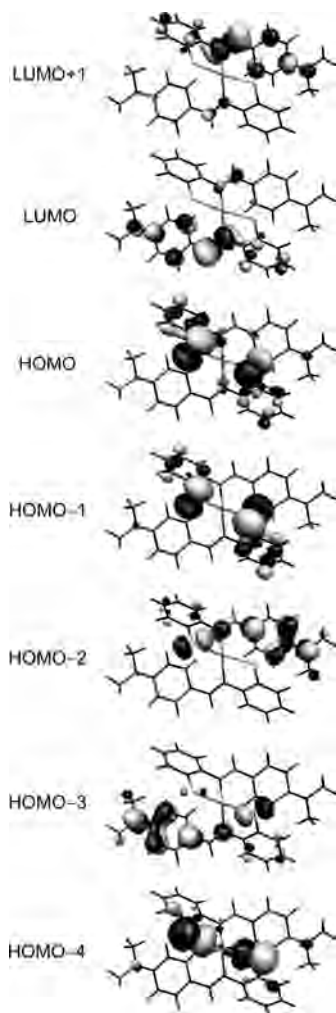
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Table 5. Photophysical Properties of Cadmium(II) Complexes

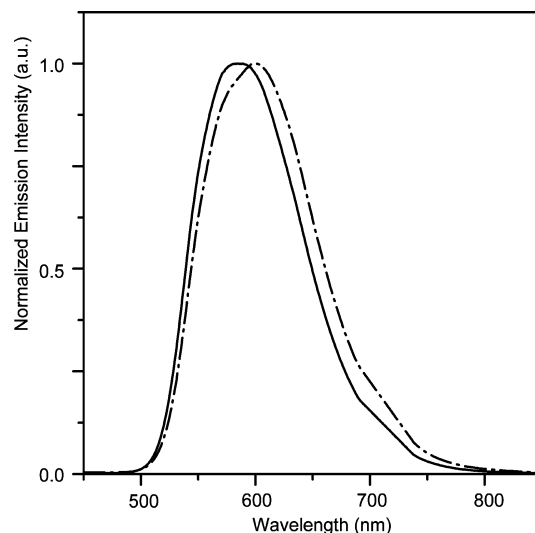| complex	$\lambda_{max,abs}$, nm (ε, M^{-1} cm^{-1}) (CH$_2$Cl$_2$, r.t., 4×10^{-5} to 2×10^{-4} M)	$\lambda_{max,em}$, nm[a] (CH$_2$Cl$_2$/toluene, 77 K)	$\lambda_{max,em}$, nm[a] (solid, r.t.)	lifetime, ns[c] (solid, r.t.)	quantum yield, Φ[e] (solid, r.t.)
9	273 (3.50×10^4), 394 (4.29×10^3)	601	b	d	f
10	285 (3.97×10^4), 422 (5.84×10^3)	610	574	0.33 ± 0.05	0.012
11	287 (3.19×10^4), 322 (3.40×10^4), 415 (7.38×10^3)	594	566	0.38 ± 0.05	0.015
12	262 (3.36×10^4), 379 (4.66×10^4), 419^{sh} (3.22×10^4)	561	548	$0.36 \pm 0.1(80\%)$ $1.1 \pm 0.1(20\%)$	0.049

[a] The excitation wavelength was set to 355 nm. [b] Not observed. [c] Determined for solid-state sample with excitation at 473nm. A value in parenthesis denotes the fraction of each component in dual exponential decay. [d] The emission was too weak for lifetime measurements. [e] Error $\pm 10\%$. [f] Less than 0.001.

Figure 7. Molecular orbitals of **7** based on the DFT calculations.

Figure 8. Emission spectra of **6** (dashed-dotted line) and **7** (solid line) in the solid state at room temperature.
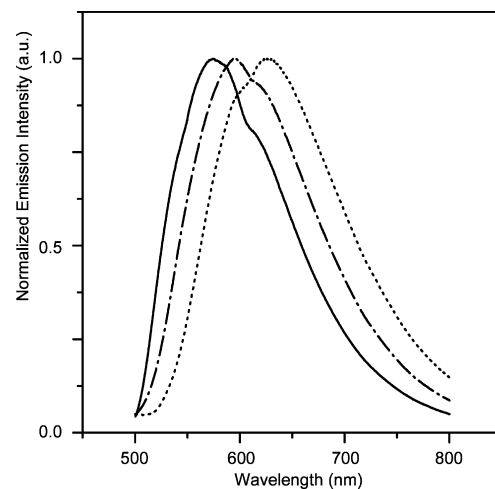
Figure 9. Emission spectra of **4** (dotted line), **6** (dashed-dotted line), and **7** (solid line) in CH$_2$Cl$_2$/toluene glass at 77 K.

increases, which results in the emission shift to the shorter wavelength side.

It has been well-known that the oxidation species of benzothiazolines are luminescent.[19] However, the benzothiazolines themselves, which are the starting material in this study, virtually do not possess the luminescent property. Therefore, the origin of the present luminescence observed for the zinc(II) and cadmium(II) complexes is based on the Schiff base ligands newly formed via the ring opening of benzothiazolines; that is, the formation of N$_2$S$_2$−Schiff base ligands in zinc(II) and cadmium(II) complexes results in the obvious luminescent property.

Conclusion

A series of Schiff base zinc(II) complexes with various substituents on the pendent phenyl rings ([Zn(R−Ph−C(H)=N−C$_6$H$_4$−S)$_2$], R = 2,4,6-triMe (**1**), 2,6-diCl (**2**), 4-Cl (**3**), H (**4**), 4-Et (**5**), 4-OMe (**6**), 4-NMe$_2$ (**7**), 4-NEt$_2$ (**8**)) have been newly synthesized and characterized. X-ray analyses revealed that they have a mononuclear structure with

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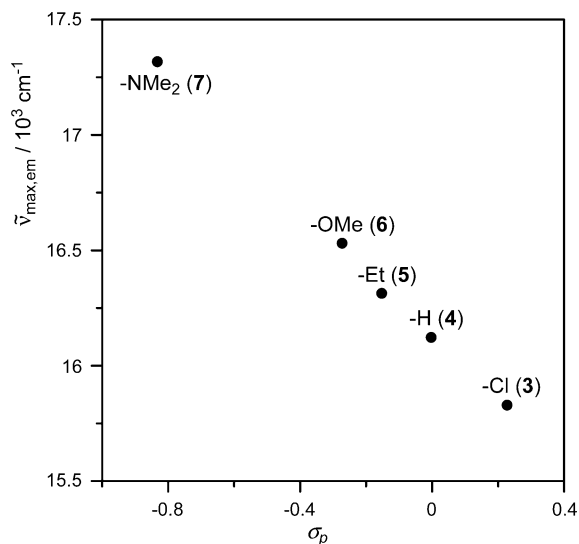
Figure 10. Relationship between the emission maxima and the Hammett substituent constants in zinc(II) complexes.

a distorted tetrahedral geometry. It has been found that the electronic property of the substituents, as well as their positions on the pendent phenyl rings of the Schiff base ligands, affects the electronic absorption spectra of the complexes. All the complexes were luminescent in CH_2Cl_2/toluene glass at 77 K, and the emission wavelengths were correlated with the Hammett constant of the substituents on the pendent phenyl rings. The analogous cadmium(II) complexes ([Cd(R—Ph—C(H)=N—C_6H_4—S)$_2$], R = 2,4,6-triMe (**9**) and [Cd$_2$(R—Ph—C(H)=N—C_6H_4—S)$_4$], R = 4-Et (**10**), 4-OMe (**11**), 4-NMe$_2$ (**12**)) were synthesized, but they have a dinuclear structure in the solid state, except **9**. The cadmium(II) complexes also gave emission spectra in the CH_2Cl_2/toluene glass at 77 K. These zinc(II) and cadmium(II) complexes with N_2S_2—Schiff base ligands are a new class of luminescent compounds, and the careful derivatization of the substituents on the pendent phenyl rings permits a fine-tuning of the emission wavelength.

Experimental Section

General Procedures. All of the synthetic reactions were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques. Workup procedures were performed in air. The reagents were commercial samples and not purified further. The 2-(2,4-dichlorophenyl)benzothiazoline,[9a] 2-(4-chlorophenyl)-benzothiazoline,[9c] 2-phenylbenzothiazoline,[8b] 2-(4-methoxyphenyl)-benzothiazoline,[8c] and 2-(4-dimethylaminophenyl)benzothiazoline[9d]were prepared as described previously. The absorption spectra were recorded with a JASCO V-570 spectrophotometer at room temperature. The emission spectra in the solid state were obtained using a JASCO FP-6600 luminescent spectrometer with the slits of 5 nm at room temperature. Measurements of low-temperature emission spectra were carried out using a grating monochromator with the entrance slit of 4 nm (Triax 1900, Jobin Yvon) equipped with a CCD image sensor (S7031, Hamamatsu) of which the spectral sensitivity was corrected using a bromine lamp (IPD 100V 500WCS, Ushio). A sample in a 1-mm quartz cell was excited using an LD-excited solid-state Nd: YAG laser (355 nm, 440 ps, 13 kHz, 6 mW, JDS Uniphase). The measurements at 77 K were performed using a cylindrical quartz

cell (1 mm inner diameter) and a liquid-nitrogen Dewar flask. Emission quantum yields of the complexes in the solid state were determined in a similar way to that described by Islam et al.[20] Dilute samples of 5% Zn(II) or Cd(II) complexes in MgO were prepared by homogeneously mixing sample powder and commercial grade MgO powder and were packed into a 1 mm quartz cell. A powder of pure MgO packed in another 1 mm quartz cell was used as a reference. A monochromated light of a 150 W xenon lamp was irradiated onto the surface of the sample or the reference, and a part of the scattered light or emission was measured by the grating monochromator with the CCD image sensor. The difference in reflectance between the sample and reference was less than 1.5% when irradiated with the light at 600 nm where the complexes have no absorption. The quantum yield of emission (Φ) was calculated by eq 1.

$$\Phi = \frac{D_s}{(D_r - D_s{'})/F} \tag{1}$$

where D_s is integrated intensity of the emission spectrum. $D_s{'}$ and D_r are the integrated intensity of the reflected excitation light for the sample and the reference, respectively. F is the absolute reflectance of MgO (0.9). For the determination of emission lifetimes, the sample was photoexcited using a Q-switched DPSS laser (μFLARE, 473 nm, 1 ns, 3 kHz, 3 mW, Lumanova GmbH). The emission from the sample was focused into a grating monochromator (H-10, Jobin Yvon) with a Si avalanche photodiode (Si-APD, S5139, Hamamatsu). The photocurrent from the Si-APD was amplified through a wide-band amplifier (DC-500 MHz, CLC110) and accumulated on a digitizing oscilloscope (HP 54520 Hewlett-Packard) to get the decay-profile of the emission intensity, which was fitted to single or double exponential function with convolution of the instrumental response function of the measuring system. The time resolution of the system was 0.2 ns. The ^{1}H NMR spectra were recorded with a JEOL GSX 500 spectrometer. The IR spectra in the region of 4000−400 cm^{-1} were recorded as KBr pellets on a JASCO FT/IR-550 spectrometer. Elemental analyses were performed at Osaka University. Calculations using density functional theory (DFT) were performed by with the GAUSSIAN 03 software.[21] The basis functions used in the computations were the Dunning−Hay split valence double-ζ for the C, H, and N atoms (D95) and the Hay−Wadt double-ζ with the Los Alamos relativistic effective core potential for heavy atoms (LANL2DZ).[22,23] Becke's style three-parameter hybrid functional of B3LYP was employed.[24]

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The drawing of molecular orbitals was performed using MOLEKEL.[25,26]

Synthesis of 2-(Mesit)benzothiazoline. To a solution of 2-aminobenzenethiol (4.09 g, 32.7 mmol) in ethanol (40 mL) was added mesitbenzaldehyde (4.84 g, 32.7 mmol). The mixture was refluxed for 30 min and then cooled to room temperature. The resulting yellow solution was evaporated to dryness. The pale yellow solid was dissolved in CH_2Cl_2 (2 mL), and *n*-hexane (20 mL) was added to the pale yellow solution. The precipitated white powder was collected by filtration and dried in vacuo. Yield: 3.85 g, 46.2%. Anal. Calcd for $C_{16}H_{17}NS$: C, 75.25; H, 6.71; N, 5.48. Found. C, 75.13; H, 6.69; N, 5.48. IR (KBr; cm^{-1}): 3356 (ν_{N-H}). ^1H NMR (500 MHz, CDCl$_3$): δ 7.09 (1H, s, 2-CH), 7.03 (1H, d, $J = 7.9$, benzene), 6.91 (1H, t, $J = 7.6$, benzene), 6.86 (2H, s, benzene), 6.71 (1H, t, $J = 7.6$, benzene), 6.57 (1H, d, $J = 7.9$, benzene), 4.05 (1H, s, NH), 2.49 (6H, s, CH$_3$), 2.27 (3H, s, CH$_3$).

Synthesis of 2-(4-Ethylphenyl)benzothiazoline. To a solution of 2-aminobenzenethiol (1.43 g, 11.4 mmol) in ethanol (20 mL) was added 4-ethylbenzaldehyde (1.53 g, 11.4 mmol). The mixture was heated under reflux for 30 min. The resulting solution was evaporated to approximately one-half of the initial volume and then allowed to cool in a freezer overnight. White powder was collected by filtration and dried in vacuo. Yield: 1.49 g, 54.1%. Anal. Calcd for $C_{15}H_{15}NS$: C, 74.65; H, 6.26; N, 5.80. Found. C, 74.39; H, 6.15; N, 5.88. IR (KBr; cm^{-1}): 3314 (ν_{N-H}). ^1H NMR (500 MHz, CDCl$_3$): δ 7.46 (2H, d, $J = 8.0$, benzene), 7.19 (2H, d, $J = 7.5$, benzene), 7.04 (1H, d, $J = 7.5$, benzene), 6.94 (1H, t, $J = 7.7$, benzene), 6.76 (1H, t, $J = 7.5$, benzene), 6.65 (1H, d, $J = 8.0$, benzene), 6.36 (1H, s, 2-CH), 4.33 (1H, s, NH), 2.65 (2H, q, $J = 7.5$, CH$_2$), 1.23 (3H, t, $J = 7.5$, CH$_3$).

Synthesis of 2-(4-Diethylaminophenyl)benzothiazoline. To a solution of 2-aminobenzenethiol (1.44 g, 11.5 mmol) in ethanol (20 mL) was added 4-diethylaminobenzaldehyde (1.36 g, 7.67 mmol). The mixture was heated under reflux for 1 h. The resulting solution was evaporated to approximately one-half of the initial volume and then allowed to cool in a freezer for 4 days. Dark yellow powder was collected by filtration and dried in vacuo. Yield: 1.64 g, 75.1%. Anal. Calcd for $C_{17}H_{20}N_2S$: C, 71.79; H, 7.09; N, 9.85. Found. C, 72.24; H, 7.37; N, 9.41. IR (KBr; cm^{-1}): 3334 (ν_{N-H}). ^1H NMR (500 MHz, CDCl$_3$): δ 7.39 (2H, d, $J = 8.6$, benzene), 7.03 (1H, d, $J = 7.5$, benzene), 6.92 (1H, t, $J = 7.7$, benzene), 6.73 (1H, t, $J = 7.7$, benzene), 6.62 (3H, m, benzene), 6.33 (1H, s, 2-CH), 4.23 (1H, s, NH), 3.34 (4H, q, $J = 6.9$, CH$_2$), 1.15 (6H, t, $J = 6.9$, CH$_3$).

Synthesis of 1. To a light yellow suspension of 2-(mesit)benzothiazoline (0.83 g, 3.3 mmol) in ethanol (20 mL) was added zinc(II) acetate dihydrate (0.36 g, 1.6 mmol). The reaction mixture was refluxed for 30 min and then cooled to room temperature. The resulting yellow powder was collected by filtration. Yield: 0.78 g, 84%. Crystals of **1** suitable for a structure determination were grown by slow evaporation of a CH_2Cl_2-ethanol mixed solution of **1**. Anal. Calcd for $C_{32}H_{32}N_2S_2Zn$: C, 66.94; H, 5.62; N, 4.88. Found. C, 66.64; H, 5.49; N, 4.91. IR (KBr; cm^{-1}): 1615 ($\nu_{C=N}$). ^1H NMR (500 MHz, CDCl$_3$): δ 8.84 (2H, s, CH=N), 7.13 (2H, d, $J = 7.9$, benzene), 7.03 (2H, d, $J = 7.9$, benzene), 7.01 (2H, t, $J = 7.9$, benzene), 6.93 (2H, t, $J = 7.3$, benzene), 6.58 (4H, s, benzene), 2.23 (6H, s, CH$_3$), 2.08 (12H, s, CH$_3$).

Synthesis of 2. To a light yellow suspension of 2-(2,6-dichlorophenyl)benzothiazoline (0.87 g, 3.1 mmol) in ethanol (20

mL) was added zinc(II) acetate dihydrate (0.34 g, 1.5 mmol). The reaction mixture was refluxed for 30 min and then cooled to room temperature. The resulting orange powder was collected by filtration. Yield: 0.33 g, 34%. Anal. Calcd for $C_{26}H_{16}Cl_4N_2S_2Zn$: C, 49.75; H, 2.57; N, 4.46. Found. C, 49.91; H, 2.55; N, 4.48. IR (KBr; cm^{-1}): 1611 ($\nu_{C=N}$). ^1H NMR (500 MHz, CDCl$_3$): δ 8.69 (2H, s, CH=N), 7.20 (2H, d, $J = 7.3$, benzene), 7.15 (2H, d, $J = 7.6$, benzene), 7.13 (2H, t, $J = 7.9$, benzene), 7.00 (2H, d, $J = 7.9$, benzene), 6.97 (2H, d, $J = 7.3$, benzene).

Synthesis of 3. To a light yellow suspension of 2-(4-chlorophenyl)benzothiazoline (0.61 g, 2.5 mmol) in ethanol (20 mL) was added zinc(II) acetate dihydrate (0.27 g, 1.2 mmol). The reaction mixture was refluxed for 30 min and then cooled to room temperature. The resulting reddish orange powder was collected by filtration. Yield: 0.47 g, 68%. Anal. Calcd for $C_{26}H_{18}Cl_2N_2S_2Zn$: C, 55.88; H, 3.25; N, 5.01. Found. C, 55.78; H, 3.24; N, 5.00. IR (KBr; cm^{-1}): 1599 ($\nu_{C=N}$). ^1H NMR (500 MHz, CDCl$_3$): δ 8.57 (2H, s, CH=N), 7.64 (4H, d, $J = 7.9$, benzene), 7.55 (2H, d, $J = 7.3$, benzene), 7.20 (2H, t, $J = 6.9$, benzene), 7.02 (8H, m, benzene).

Synthesis of 4. To a light yellow suspension of 2-phenylbenzothiazoline (0.60 g, 2.8 mmol) in ethanol (20 mL) was added zinc(II) acetate dihydrate (0.31 g, 1.4 mmol). The reaction mixture was refluxed for 30 min and then cooled to room temperature. The resulting orange powder was collected by filtration. Yield: 0.38 g, 56%. Anal. Calcd for $C_{26}H_{20}N_2S_2Zn$: C, 63.73; H, 4.11; N, 5.72. Found. C, 63.42; H, 4.10; N, 5.74. IR (KBr; cm^{-1}): 1593 ($\nu_{C=N}$). ^1H NMR (500 MHz, CDCl$_3$): δ 8.46 (2H, s, CH=N), 7.76 (4H, d, $J = 7.3$, benzene), 7.58 (2H, d, $J = 7.9$, benzene), 7.36 (2H, t, $J = 7.6$, benzene), 7.15 (2H, d, $J = 7.3$, benzene), 7.09 (4H, d, $J = 7.6$, benzene), 7.00 (2H, t, $J = 7.6$, benzene), 6.97 (2H, t, $J = 7.6$, benzene).

Synthesis of 5. To a light yellow suspension of 2-(4-ethylphenyl)benzothiazoline (0.72 g, 3.0 mmol) in ethanol (20 mL) was added zinc(II) acetate dihydrate (0.33 g, 1.5 mmol). The reaction mixture was refluxed for 30 min and then cooled to room temperature. The resulting orange powder **5** was collected by filtration. Yield: 0.69 g, 85%. Anal. Calcd for $C_{30}H_{28}N_2S_2Zn$: C, 65.98; H, 5.17; N, 5.13. Found. C, 65.54; H, 5.18; N, 5.10. IR (KBr; cm^{-1}): 1597 ($\nu_{C=N}$). ^1H NMR (500 MHz, CDCl$_3$): δ 8.44 (2H, s, CH=N), 7.67 (4H, d, $J = 7.6$, benzene), 7.57 (2H, d, $J = 7.9$, benzene), 7.14 (2H, t, $J = 7.3$, benzene), 7.00 (2H, d, $J = 7.6$, benzene), 6.96 (2H, t, $J = 7.5$, benzene), 6.88 (2H, d, $J = 7.3$, benzene), 2.56 (4H, q, $J = 7.6$, CH$_2$), 1.14 (6H, t, $J = 7.6$, CH$_3$).

Synthesis of 6. To a light yellow suspension of 2-(4-methoxyphenyl)benzothiazoline (1.37 g, 5.63 mmol) in ethanol (20 mL) was added zinc(II) acetate dihydrate (0.61 g, 2.8 mmol). The reaction mixture was refluxed for 30 min and then cooled to room temperature. The resulting orange powder was collected by filtration. Yield: 1.03 g, 66%. Crystals of complex **6** suitable for a structure determination were grown by the slow diffusion of diethyl ether into a CH_2Cl_2 solution of **6**. Anal. Calcd for $C_{28.1}H_{24.2}Cl_{0.2}N_2O_2S_2Zn$: C, 60.43; H, 4.37; N, 5.02. Found. C, 60.44; H, 4.32; N, 5.11. IR (KBr; cm^{-1}): 1593 ($\nu_{C=N}$). ^1H NMR (500 MHz, DMSO-d_6): δ 8.78 (2H, s, CH=N), 7.81 (4H, d, $J = 8.5$, benzene), 7.40 (2H, d, $J = 7.9$, benzene), 7.32 (2H, d, $J = 7.9$, benzene), 7.14 (2H, t, $J = 7.6$, benzene), 7.02 (2H, t, $J = 7.6$, benzene), 6.57 (4H, d, $J = 8.5$, benzene), 3.71 (6H, s, CH$_3$).

Synthesis of 7. To a light yellow suspension of 2-(4-dimethylaminophenyl)benzothiazoline (1.24 g, 4.86 mmol) in ethanol (20 mL) was added zinc(II) acetate dihydrate (0.53 g, 2.4 mmol). The reaction mixture was refluxed for 30 min and then cooled to room temperature. The resulting orange powder was collected by filtration. Yield: 1.12 g, 79%. Crystals of complex **7** suitable for a structure

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determination were grown by the slow diffusion of diethyl ether into a CHCl$_3$ solution of **7**. Anal. Calcd for C$_{30.1}$H$_{30.2}$Cl$_{0.2}$N$_4$S$_2$Zn: C, 61.84; H, 5.21; N, 9.58. Found. C, 62.09; H, 5.22; N, 9.65. IR (KBr; cm^{-1}): 1609 ($\nu_{C=N}$). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.19 (2H, s, CH=N), 7.65 (4H, d, $J = 8.5$, benzene), 7.60 (2H, d, $J = 7.3$, benzene), 7.05 (2H, t, $J = 7.3$, benzene), 6.95 (2H, d, $J = 7.6$, benzene), 6.93 (2H, t, $J = 7.3$, benzene), 6.18 (4H, d, $J = 8.5$, benzene), 2.92 (12H, s, CH$_3$).

Synthesis of 8. To a light yellow suspension of 2-(4-diethyl-aminophenyl)benzothiazoline (1.27 g, 4.47 mmol) in ethanol (20 mL) was added zinc(II) acetate dihydrate (0.47 g, 2.1 mmol). The reaction mixture was refluxed for 30 min and then cooled to room temperature. The resulting orange powder was collected by filtration. Yield: 1.09 g, 80%. Anal. Calcd for C$_{34}$H$_{38}$N$_4$S$_2$Zn: C, 64.59; H, 6.06; N, 8.86. Found. C, 64.28; H, 6.02; N, 8.84. IR (KBr; cm^{-1}): 1607 ($\nu_{C=N}$). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.11 (2H, s, CH=N), 7.66 (4H, d, $J = 8.5$, benzene), 7.62 (2H, d, $J = 7.9$, benzene), 7.03 (2H, t, $J = 7.3$, benzene), 6.95 (2H, d, $J = 7.6$, benzene), 6.91 (2H, t, $J = 7.3$, benzene), 6.19 (4H, d, $J = 9.1$, benzene), 3.26 (8H, q, $J = 7.3$, CH$_2$), 1.08 (12H, d, $J = 7.0$, CH$_3$).

Synthesis of 9. To a light yellow suspension of 2-(mesit)benzothiazoline (0.55 g, 2.2 mmol) in ethanol (20 mL) was added cadmium(II) acetate dihydrate (0.29 g, 1.1 mmol). The reaction mixture was stirred at room temperature for 2 h. The resulting yellow powder was collected by filtration. Crystals suitable for a structure determination were grown by the slow evaporation of CHCl$_3$-ethanol-n-hexane mixed solution of **9**. Yield: 0.57 g, 84%. Anal. Calcd for C$_{32}$H$_{32}$CdN$_2$S$_2$: C, 61.88; H, 5.19; N, 4.51. Found. C, 61.67; H, 5.25; N, 4.60. IR (KBr; cm^{-1}): 1613 ($\nu_{C=N}$). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.73 (2H, s, CH=N), 7.39 (2H, d, $J = 7.9$, benzene), 7.08 (2H, t, $J = 7.6$, benzene), 6.98 (2H, d, $J = 7.9$, benzene), 6.93 (2H, t, $J = 8.0$, benzene), 6.62 (4H, s, benzene), 2.24 (6H, s, CH$_3$), 2.14 (12H, s, CH$_3$).

Synthesis of 10. To a light yellow suspension of 2-(4-ethylphenyl)benzothiazoline (0.51 g, 2.1 mmol) in ethanol (20 mL) was added cadmium(II) acetate dihydrate (0.28 g, 1.1 mmol). The reaction mixture was stirred at room temperature for 1 h. The resulting orange powder was collected by filtration. Yield: 0.52 g, 83%. Anal. Calcd for C$_{60}$H$_{56}$Cd$_2$N$_4$S$_4$: C, 60.75; H, 4.76; N, 4.72. Found. C, 60.76; H, 4.73; N, 4.78. IR (KBr; cm^{-1}): 1603 ($\nu_{C=N}$). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.40 (2H, s, CH=N), 7.65 (2H, d, $J = 7.9$, benzene), 7.61 (4H, d, $J = 7.9$, benzene), 7.15 (2H, t, $J = 7.6$, benzene), 7.00 (2H, t, $J = 7.6$, benzene), 6.90 (2H, d, $J = 7.9$, benzene), 6.88 (4H, d, $J = 7.9$, benzene), 2.56 (4H, q, $J = 7.5$, CH$_2$), 1.15 (6H, t, $J = 7.6$, CH$_3$).

Synthesis of 11. To a light yellow suspension of 2-(4-methoxyphenyl)benzothiazoline (0.40 g, 1.7 mmol) in ethanol (20 mL) was added cadmium(II) acetate dihydrate (0.22 g, 0.83 mmol). The reaction mixture was stirred at room temperature for 1 h. The resulting yellow powder was collected by filtration. Yield: 0.44 g,

89%. Anal. Calcd for C$_{56}$H$_{48}$Cd$_2$N$_4$O$_4$S$_4$: C, 56.33; H, 4.05; N, 4.69. Found. C, 56.08; H, 4.14; N, 4.70. IR (KBr; cm^{-1}): 1593 ($\nu_{C=N}$). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.35 (2H, s, CH=N), 7.66 (6H, d, $J = 9.1$, benzene), 7.14 (2H, t, $J = 7.6$, benzene), 7.01 (2H, t, $J = 7.6$, benzene), 6.92 (2H, d, $J = 6.7$, benzene), 6.52 (4H, d, $J = 8.5$, benzene), 3.71 (6H, s, CH$_3$).

Synthesis of 12. To a light yellow suspension of 2-(4-dimethyl-aminophenyl)benzothiazoline (0.59 g, 2.3 mmol) in ethanol (20 mL) was added cadmium(II) acetate dihydrate (0.31 g, 1.2 mmol). The reaction mixture was refluxed for 30 min and then cooled to room temperature. The resulting yellow powder was collected by filtration. Crystals of suitable for a structure determination were grown by the slow diffusion of diethyl ether into a CH$_2$ClCH$_2$Cl solution of **12**. Yield: 0.55 g, 76%. Anal. Calcd for C$_{60}$H$_{60}$Cd$_2$N$_8$S$_4$: C, 57.83; H, 4.85; N, 8.99. Found. C, 57.34; H, 4.81; N, 8.92. IR (KBr; cm^{-1}): 1609 ($\nu_{C=N}$). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.25 (2H, s, CH=N), 7.66 (2H, d, $J = 7.9$, benzene), 7.57 (4H, d, $J = 9.1$, benzene), 7.08 (2H, t, $J = 7.6$, benzene), 6.99 (2H, t, $J = 7.3$, benzene), 6.93 (2H, d, $J = 7.9$, benzene), 6.16 (4H, d, $J = 8.5$, benzene), 2.92 (12H, s, CH$_3$).

X-ray Crystallography. X-ray crystallographic data for complexes **1**, **5**, **6**, **9**, and **12** were collected with the ω scan technique on a Rigaku RAXIS-RAPID image plate diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at 200 K. Empirical absorption corrections were applied. Complex **7** was measured on a Rigaku AFC5R diffractometer with Mo Kα radiation at room temperature. θ-2θ scans were employed; no significant decomposition of the crystal occurred during the data collection. The solution and refinement procedures were made with the CrystalStructure software package. The structures of complexes **1**, **5**, **6**, **7**, **9**, and **12** were solved by direct methods using SIR 92 and refined anisotropically for all nonhydrogen atoms with full-matrix least-squares calculations. Hydrogen atoms were placed at calculated positions and refined isotropically. A part of one pendent phenyl group (C25−C30) in **5** was found to be disordered and was split on two positions in a ratio of 50:50.

Supporting Information Available: X-ray crystallographic files in CIF format for the structures in this work, molecular structure of **5** (Figure S1), absorption spectra of zinc(II) and cadmium(II) complexes (Figures S2 and S3), and relationship between the emission maxima and the Hammett substituent constants in cadmium(II) complexes (Figure S4, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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