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One-Pot Synthesis and Unpredicted Hydrogen Bonds of the Guanidinium Triflates from Readily Available Amines, Carbodiimides, and Zn(OTf)$_2$

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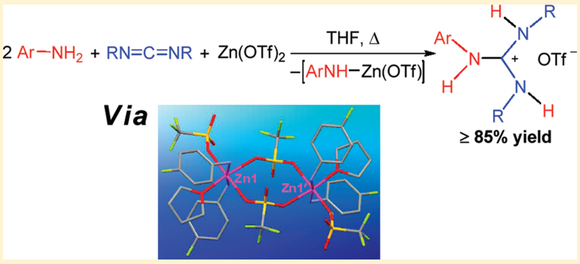
S *Supporting Information*

ABSTRACT: The first synthesis of trisubstituted guanidinium triflates has been achieved by a simple one-step procedure from readily available amines, carbodiimides, and Zn(OTf)$_2$. X-ray analysis revealed they adopt 1-D chain-like or novel 3-D hydrogen-bonded networks, which have not been reported previously in the solid structure of guanidinium salts. Isolation of a binuclear zinc complex and its subsequent carbodiimide insertion provide the insight into the mechanism for the formation of guanidinium triflates.

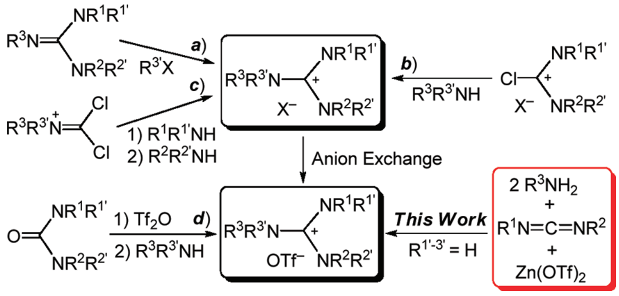


INTRODUCTION

Multisubstituted guanidinium salts, $[C(NR^1R^{1'})(NR^2R^{2'})(NR^3R^{3'})][X]$ (X = Cl, OTf, PF$_6$, BF$_4$, etc.), are an important class of "CN$_3$"-core-containing ion-pair compounds.[1,2] These guanidinium salts can serve as building blocks of many biologically active compounds[3] and of ionic liquids,[4] and also as base catalysts in many organic transformations.[5] The classical methods for their preparation employ protonation or alkylation of a pre-existing guanidine core (Scheme 1, ***a***).[6,4b] Guanidinium salts are also obtained by reaction of amines with guanidine precursors, such as chloroformamidinium salts (Scheme 1, ***b***).[7] Mioskowski et al. reported the synthesis of guanidinium chlorides using nonguanidine precursors, such as phosgeniminium chlorides (Scheme 1, ***c***).[8] These three types of methods generally involve the preparation of guanidinium halides. Guanidinium salts having other anionic species, such as OTf, PF$_6$, and BF$_4$, have to employ the halide exchange between guanidinium halides and the corresponding metal salts MX (M = Li, Na, K or Ag, X = OTf, PF$_6$, BF$_4$, etc.). In 1981, Stang et al. reported the two-step synthesis of guanidinium triflates from the starting ureas in the presence of triflic anhydride (Scheme 1, ***d***).[9] Generally, the triflate ion in guanidinium triflates is introduced by anion exchange. All reported methods for the preparation of guanidinium salts involve the synthesis of guanidine or non-guanidine precursors. Two or more synthetic steps are required for guanidinium triflates.

We have been interested in the reaction chemistry of carbodiimide.[10−14] Herein we report the one-pot synthesis of the guanidinium triflates from readily available amines, carbodiimides, and Zn(OTf)$_2$. X-ray analysis of two different substituted guanidinium triflates revealed they adopt 1-D chain-like or novel 3-D hydrogen-bonded networks. The active binuclear zinc complex was isolated from the reaction system and confirmed the true intermediate for the formation of guanidinium triflates.

Scheme 1. Methodology for the Preparation of Guanidinium Salts



RESULTS AND DISCUSSION

Synthesis. The neat aniline could not react with *N*,*N*′-diisopropylcarbodiimide (^{i}PrN═C═N^{i}Pr) at room temperature or higher temperatures. Very recently we have found that Zn(OTf)$_2$ could serve as a good catalyst for addition of amine N−H bonds to carbodiimides, yielding efficiently guanidines.[13c] In this initial step, the active catalyst species containing a Zn−N bond is produced by release of a guanidinium triflate. So we pondered that a guanidinium triflate could be prepared from the reaction system of aniline, ^{i}PrN═C═N^{i}Pr, and Zn(OTf)$_2$.

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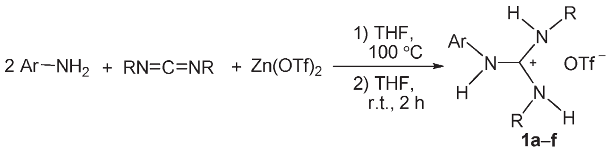
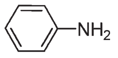
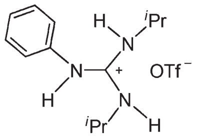
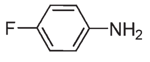
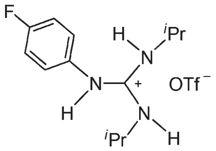
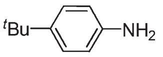
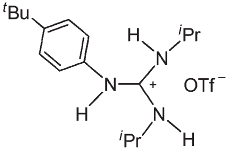
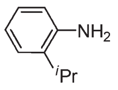
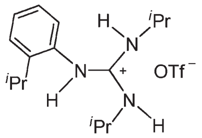
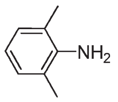
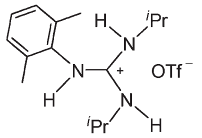
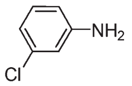
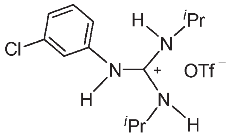
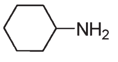
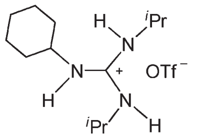
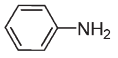
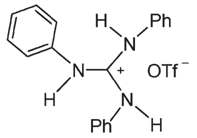
Table 1. Formation of Guanidinium Triflates from Two Amines, Carbodiimides, and $Zn(OTf)_2$[a,b]



Entry	Ar−NH$_2$	R	Guanidinium Triflates	Yield/%[b]
1		^{i}Pr		**1a**, 91
2		^{i}Pr		**1b**, 85
3		^{i}Pr		**1c**, 96
4		^{i}Pr		**1d**, 95
5		^{i}Pr		**1e**, 94
6		^{i}Pr		**1f**, 94
7		^{i}Pr		**1g**, 95
8		Ph		**1h**, 82

[a] Conditions: amines, 2.25 mmol; carbodiimides, 1 mmol; Zn(OTf)2, 1 mmol; THF, 5 mL. [b] Isolated yield.

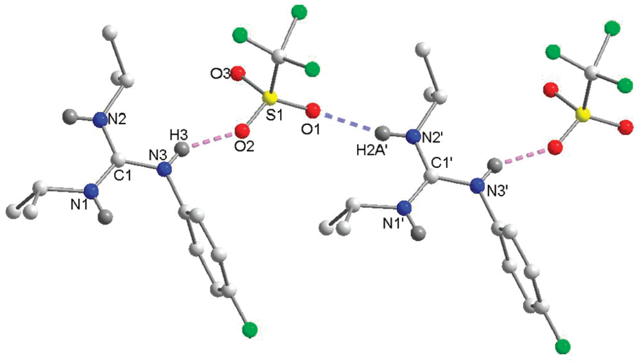


Figure 1. Hydrogen bond pattern between the guanidinium cation and triflate anion in **1b**. Hydrogen atoms except those on the nitrogen atoms are omitted for clarity. Selected bond length (Å) and angles (deg): N1−C1 1.362(6), N2−C1 1.327(6), N3−C1 1.338(6), N1−C1−N2 120.0(4), N1−C1−N3 119.0(4), N2−C1−N3 120.9(4). Hydrogen bonds: $d_{H3\cdots O2}$ = 2.02 Å, $d_{N3\cdots O2}$ = 2.825 Å, ∠N3−H3···O2 151.6°; $d_{H2A'\cdots O1}$ = 2.16 Å, $d_{N2'\cdots O1}$ = 2.997 Å, ∠N2′−H2A′···O1 159.2°. ′ = $x + 1, y, z$. C gray, H light gray, O red, N blue, F green, S orange.

At the beginning, we tried to heat a 1:1:1 mixture of aniline, ^{i}PrN═C═N^{i}Pr, and $Zn(OTf)_2$ in different solvents such as THF, benzene, and toluene. The guanidine was obtained almost quantitatively, suggesting that the catalytic addition of aniline to ^{i}PrN═C═N^{i}Pr occurred once the Zn−N active species was produced by release of a guanidinium triflate. This result also suggested the guanidine remained inert to $Zn(OTf)_2$. To avoid the formation of guanidine, after many screening experiments, a new protocol was established. Thus, after $Zn(OTf)_2$ was first treated with a THF solution of 2 equiv of aniline in a closed Schlenk tube at 100 °C for 3 h, then reacted with ^{i}PrN═C═N^{i}Pr at room temperature for 2 h, guanidinium triflate **1a** was obtained in 91% isolated yield (Table 1, entry 1).

Under the optimized conditions the scope of this protocol was further explored by using different substituted anilines. As shown in Table 1, almost all of the substrates produced the guanidinium triflates **1b**−**h** in excellent yields (entries 2−6). The presence of an electron-donating *tert*-butyl group (entry 3) and weakly electron-withdrawing fluoro (entry 2) or chloro (entry 6) groups at *para* or *meta* position of this phenyl ring produced the expected guanidinium triflates. Sterically hindered *ortho*-substituted anilines also smoothly provided the corresponding guanidinium triflates **1d** and **1e** in excellent yields (entries 4 and 5). These results demonstrated that the present reaction was insensitive to the steric nature of the substituents on the phenyl ring. In addition to anilines, aliphatic amine is suitable for this reaction (entry 7). Furthermore, *N,N*′-diaryl-substituted carbodiimides were also applicable (entry 8).

All guanidinium triflates **1a**−**h** were fully characterized by their ^{1}H and ^{13}C NMR spectroscopy as well as FTMS. The ^{1}H NMR spectrum of **1c** in THF-d_8 revealed two broad singlets at δ 7.09 (2H) and 8.77 ppm (1H), which were assigned to the N−H protons of ^{t}BuC$_6$H$_4$N*H* and ^{i}PrN*H*, respectively. In the ^{13}C NMR spectroscopy, the singlet at δ 154.0 ppm corresponded to the central carbon atom of the "CN_3" core. The quartet at 121.7 ppm with a $^1J_{C,F}$ = 318 Hz was unambiguously assigned to the CF_3 carbon atom of the triflate.

Crystallography and Hydrogen Bonds. The structures of guanidinium triflates **1b** and **1d** were characterized by X-ray diffraction analysis. **1b** crystallized in the triclinic $P\bar{1}$ space group; however, **1d** crystallized in the non-centrosymmetric orthorhombic space group *Pna*2(1).[15] **1b** and **1d** have one crystallographically independent cation−anion pair in the asymmetric unit. The sum of the angles at the central carbon equals 359.9° (**1b**) and 359.98° (**1d**), indicating complete planarity within the range of errors. The C−N bond lengths are in the range 1.32−1.36 Å within the "CN_3" core of both structures, which

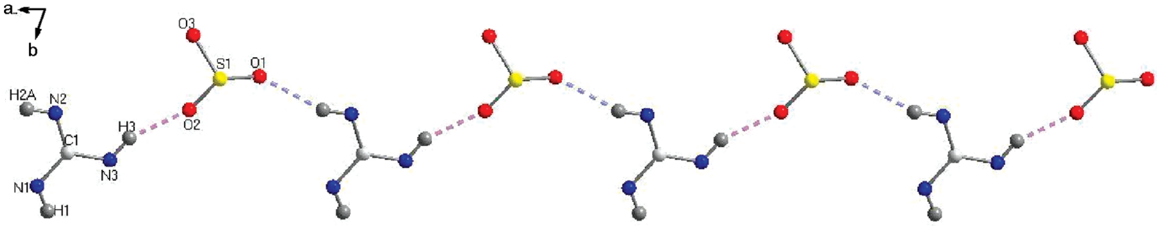


Figure 2. 1-D chain-like packing motif in crystalline **1b** via hydrogen bonds viewed along the *c* axis. Only "SO_3" and "CN_3H_3" units are shown, and other atoms are omitted for clarity. C gray, H light gray, O red, N blue, S orange.

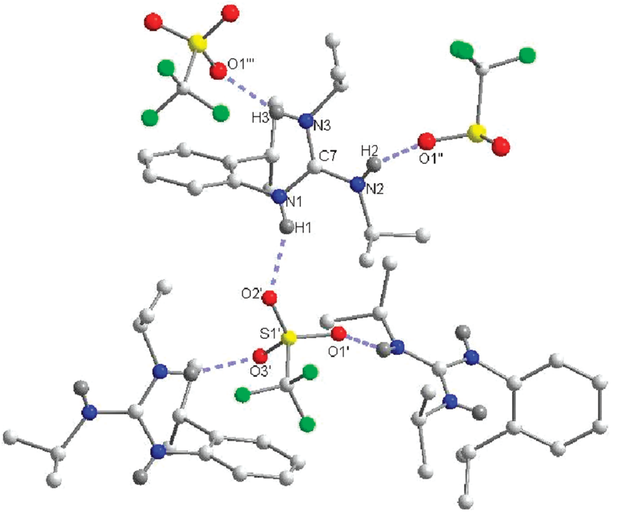


Figure 3. Hydrogen bond pattern between the guanidinium cation and triflate anion in **1d**. Hydrogen atoms except those on the nitrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N(1)−C(7) 1.357(3), N(2)−C(7) 1.332(3), N(3)−C(7) 1.325(3), N(1)−C(7)−N(2) 119.94(19), N(1)−C(7)−N(3) 118.93(19), N(2)−C(7)−N(3) 121.11(19). Hydrogen bonds: $d_{H1\cdots O2'}$ = 2.08 Å, $d_{N1\cdots O2'}$ = 2.882 Å, ∠N1−H1···O2′ 151.9°; $d_{H2\cdots O1''}$ = 2.07 Å, $d_{N2\cdots O1''}$ = 2.907 Å, ∠N2−H2···O1″ 158.1°, $d_{H3\cdots O1'''}$ = 2.11 Å, $d_{N3\cdots O1'''}$ = 2.899 Å, ∠N3−H3···O3‴ 149.5°. $'$ = $x, y + 1, z$, $''$ = $-x, -y + 1, z - 1/2$, $'''$ = $-x + 1/2, y + 1/2, z - 1/2$. C gray, H light gray, O red, N blue, F green, S orange.

are shorter than a pure C−N single bond (1.41 Å) and longer than a pure C═N double bond (1.27 Å).[16] This suggested the delocalization within the π-system of the "CN_3" core of the guanidinium cation.

Owing to the good ability of the triflate anion acting as a weak hydrogen-bond acceptor, the different N−H···O hydrogen bonds and networks were observed in the solid structures of **1b** and **1d** and provided the major driving force for their crystal packing.

Figure 1 showed the interaction of hydrogen bonds among the cation−anion pair in **1b**. There are only two hydrogen bonds between each guanidinium cation and each triflate anion in **1b**. One hydrogen bond, such as N3−H3···O2, comes from the interaction in the same unit of the guanidinium cation and triflate anion, the other N2′−H2A′···O1 hydrogen bond from a different unit of the guanidinium cation and triflate anion. One N−H bond of the guanidinium cation and one oxygen atom of the triflate anion do not involve a hydrogen-bond interaction. The guanidinium cation and triflate anion are linked in a 1-D chain by two N−H···O hydrogen bonds (Figure 2).

Figure 3 showed the interaction of hydrogen bonds among the cation−anion pair in **1d**. Being different from **1b**, each guanidinium cation in **1d** forms three hydrogen bonds to oxygen lone electron pairs on each of three neighboring triflate anions. There is no hydrogen-bond interaction between the guanidinium cation and triflate anion in the same independent unit. A brick-like unit was composed of five alternate cation−anion pairs. Three guanidinium cations and three triflate anions are positioned on the corners of the bricks and extend to form a two-dimensional brick wall monolayer viewed along the *c* axis in crystalline **1d** via hydrogen bonds (Figure 4a). The brick wall monolayers are linked by N−H···O hydrogen bonds to form the 3-D network (Figure 4b).

Several guanidinium sulfonates, especially for the guanidinium cation $C(NH_2)_3^+$, have been reported, and their X-ray analyses reveal that they adopt dimers, ribbons, or 2-D sheets.[17] As far as we are aware, this is the first example of efficient preparation of well-defined trisubstituted guanidinium triflates, and also the 3-D hydrogen-bonded network in **1d** has not been reported previously in the solid structure of guanidinium salts.

Mechanism. A possible mechanism for the formation of guanidinium triflates was proposed in Scheme 2. Initially, the reaction of $Zn(OTf)_2$ with 2 equiv of anilines in THF yielded the amine-coordinated binuclear zinc intermediate **2**. **2** might undergo coordination of a carbodiimide to the Zn center, yielding intermediate **A**. **A** would undergo 2-fold protonation toward the nitrogen atoms of a carbodiimide, affording the final guanidinium triflates by the release of the Zn−N amido species.

The proposed mechanism is further confirmed by isolation and reaction of the amine-coordinated binuclear zinc complex **2-F**. We successfully isolated the zinc complex **2-F** (Scheme 2, Ar = 4-F-C_6H_4) from the reaction mixture of $Zn(OTf)_2$ and 2 equiv of 4-fluoroaniline in THF at refluxing temperature. An X-ray structure analysis of **2-F** revealed that it adopts a dimeric structure, in which two Zn atoms are bridged by the oxygen atoms of two triflates (Figure 5). The isolated **2-F** was allowed to react with ^{i}PrN═C═N^{i}Pr at room temperature for 3 h to yield quantitatively the guanidinium triflate **1b** (Ar = 4-F-C_6H_4).

CONCLUSION

We have reported a simple and convenient one-step procedure from readily available amines, carbodiimides, and $Zn(OTf)_2$, providing efficiently for the first time the trisubstituted guanidinium triflates. Two different substituted guanidinium triflates were characterized by X-ray diffraction analysis. The 4-fluoroaniline-substituted guanidinium triflate **1b** adopts 1-D chain-like packing motif; however, 2-isopropylaniline-substituted guanidinium triflate **1d** adopts a 3-D hydrogen-bonded network in the solid structure. The reason for the different hydrogen-bonded

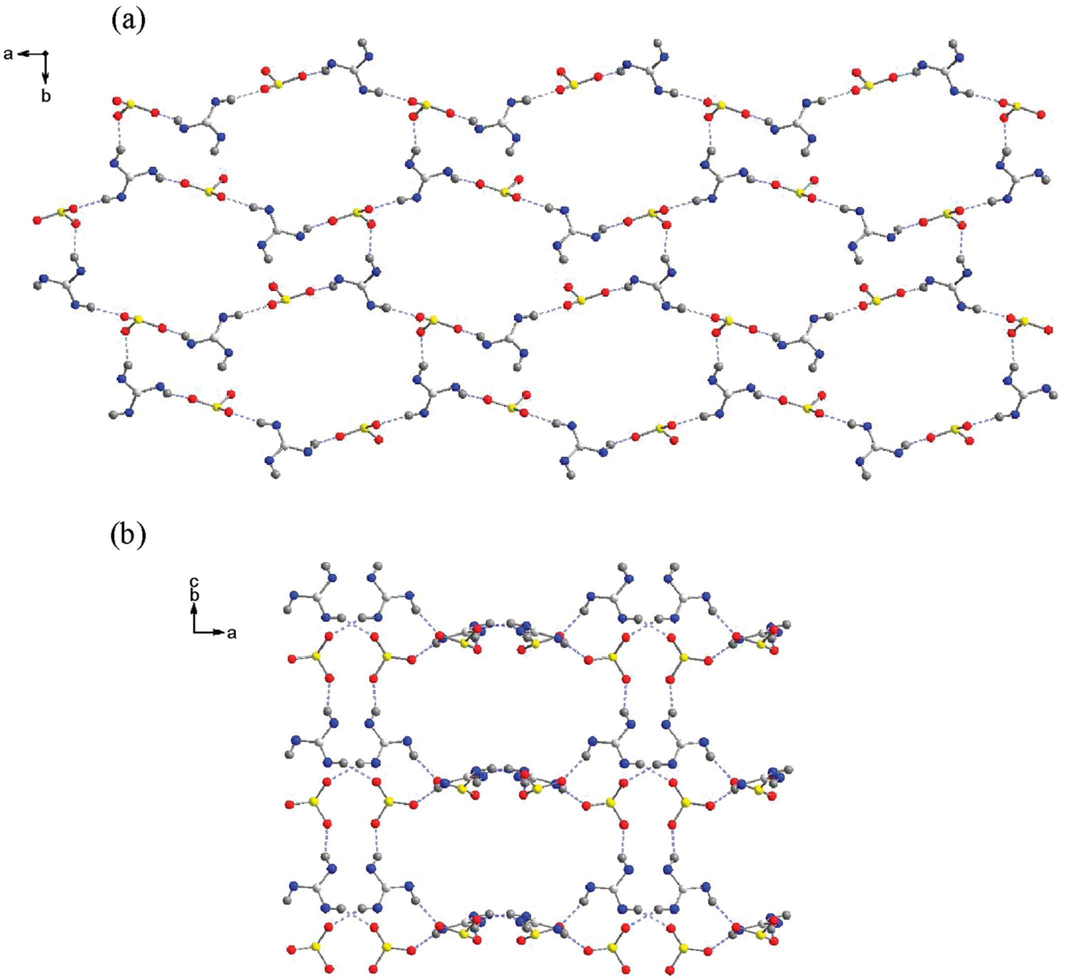
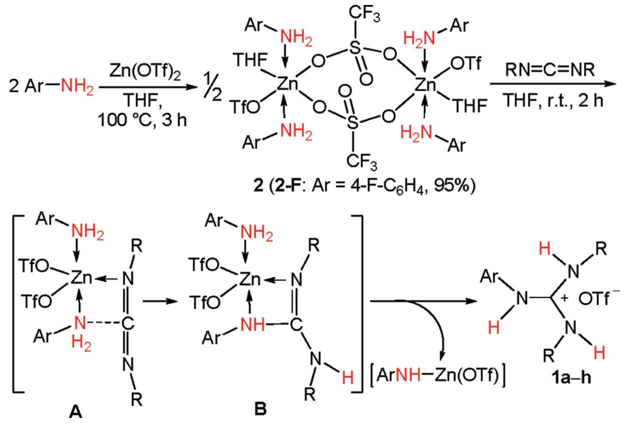


Figure 4. (a) Two-dimensional brick wall motif in crystalline **1d** via hydrogen bonds viewed along the *c* axis. (b) Three-dimensional network in crystalline **1d** via hydrogen bonds. Only "SO_3" and "CN_3H_3" units are shown, and other atoms are omitted for clarity. C gray, H light gray, O red, N blue, S orange.

Scheme 2. Possible Mechanism for the Formation of Guanidinium Triflates



networks is not clear, but are probably due to the steric and substituent effects on the aromatic ring. A binuclear zinc complex was characterized by X-ray diffraction analysis and confirmed to be an active intermediate in the formation of guanidinium triflates.

■ EXPERIMENTAL SECTION

General Method. Unless otherwise noted, all starting materials and solvents were commercially available and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C) at room temperature, unless otherwise noted. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using electrospray ionization.

Typical Procedure for the Preparation of Guanidinium Triflates 1a–f. In a Schlenk tube, Zn(OTf)$_2$ (363 mg, 1 mmol) was added to a solution of aniline (2.25 mmol) in THF (5 mL). The Schlenk tube was sealed, and the mixture was stirred at 100 °C for 3 h. *N,N'*-Diisopropylcarbodiimide (1 mmol) was then allowed to react with the above reaction mixture at room temperature for 2 h. The reaction mixture was quenched by water at room temperature and extracted with ether. The combined organic layer was dried over anhydrous MgSO$_4$. Solvent was removed under reduced pressure, and the residue was recrystallized to provide colorless solid **1**.

[C(PhNH)(^{i}PrNH)$_2$][OTf] (***1a***). Colorless solid, isolated yield 91% (336 mg); mp 102.9–103.6 °C; ^{1}H NMR (300 MHz, THF-d_8) 1.22 (d, *J* = 6.0 Hz, 12H, CH$_3$), 3.91–4.00 (m, 2H, CH), 7.17–7.40 (m, 7H, 5CH, 2NH), 8.73 (br, 1H, NH); ^{13}C NMR (75 MHz, THF-d_8) 22.5, 46.2, 121.7 (q, *J* = 318 Hz), 124.1, 126.7, 130.4, 137.9, 154.2; HRMS calcd for $C_{13}H_{22}N_3$ [M − HOTf]$^+$ 220.1803, found 220.1808.

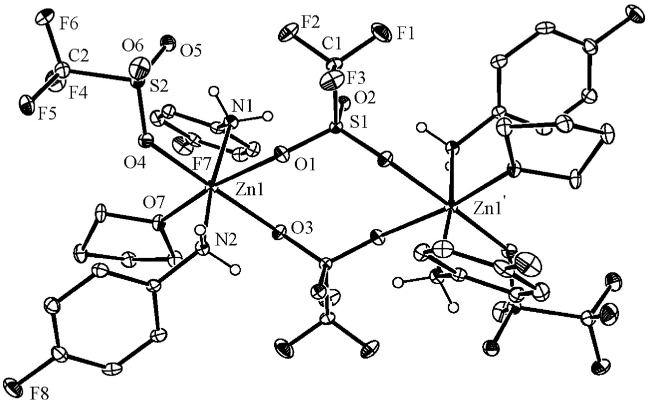


Figure 5. ORTEP drawing of **2-F** with 30% thermal ellipsoids. Hydrogen atoms except those on the nitrogen atoms are omitted for clarity. Selected bond lengths (Å): Zn(1)−N(1) 2.096(3), Zn(1)−N(2) 2.079(3), Zn(1)−O(1) 2.284(3), Zn(1)−O(3) 2.235(3), Zn(1)−O(4) 2.118(3), Zn(1)−O(7) 2.088(3), S(1)−O(1) 1.450(3), S(1)−O(2) 1.444(2), S(2)−O(4) 1.460(3), S(2)−O(5) 1.445(3), S(2)−O(6) 1.422(3). ′ = −x + 2, −y + 2, −z.

*[C(4-F-C_6H_4NH)(^{i}PrNH)$_2$][OTf] (**1b**).* Single crystals suitable for X-ray analysis were grown in THF/hexane at room temperature for 12 h. Colorless solid, isolated yield 85% (329 mg); mp 158.1−159.0 °C; ^{1}H NMR (300 MHz, THF-d_8) 1.23 (d, J = 6.0 Hz, 12H, CH_3), 3.89−3.98 (m, 2H, CH), 7.10−7.33 (m, 7H, 5CH, 2NH); ^{13}C NMR (75 MHz, THF-d_8) 22.5, 46.2, 117.2 (d, J = 23 Hz), 121.8 (q, J = 319 Hz), 126.9 (d, J = 8.0 Hz), 134.0 (d, J = 2.5 Hz), 154.3, 161.7 (d, J = 243 Hz); HRMS calcd for $C_{13}H_{21}FN_3$ [M − HOTf]$^+$ 238.1714, found 238.1714.

*[C(4-^{t}Bu-C_6H_4NH)(^{i}PrNH)$_2$][OTf] (**1c**).* Colorless solid, isolated yield 96% (408 mg); mp 176.5−176.8 °C; ^{1}H NMR (300 MHz, THF-d_8) 1.23 (d, J = 6.6 Hz, 12H, CH_3), 1.30 (s, 9H, CH_3), 3.95−4.02 (m, 2H, CH), 7.09 (br, 2H, NH), 7.19−7.44 (m, 4H, CH), 8.77 (br, 1H, NH); ^{13}C NMR (75 MHz, THF-d_8) 22.5, 31.6, 35.0, 46.0, 121.7 (q, J = 318 Hz), 123.7, 127.2, 135.2, 149.4, 154.0; HRMS calcd for $C_{17}H_{30}N_3$ [M − HOTf]$^+$ 276.2435, found 276.2434.

*[C(2-^{i}Pr-C_6H_4NH)(^{i}PrNH)$_2$][OTf] (**1d**) (ref 13c).* Colorless solid, isolated yield 95% (390 mg); mp 122.8−123.7 °C; ^{1}H NMR (300 MHz, THF-d_8) 1.20−1.24 (m, 18H, CH_3), 3.09−3.18 (m, 1H, CH), 3.91−4.00 (m, 2H, CH), 6.74 (br, 2H, NH), 7.23−7.44 (m, 4H, CH), 8.52 (br, 1H, NH); ^{13}C NMR (75 MHz, THF-d_8) 22.5, 23.6, 28.7, 45.9, 121.4 (q, J = 317 Hz), 128.1, 128.5, 129.6, 133.5, 146.4, 154.7; HRMS calcd for $C_{16}H_{28}N_3$ [M − HOTf]$^+$ 262.2278, found 262.2278.

*[C(2,6-Me$_2$-C_6H_3NH)(^{i}PrNH)$_2$][OTf] (**1e**).* Colorless solid, isolated yield 94% (373 mg); mp 157.5−158.3 °C; ^{1}H NMR (300 MHz, THF-d_8) 1.20 (d, J = 5.4 Hz, 12H, CH_3), 2.24 (s, 6H, CH_3), 3.96−4.05 (m, 2H, CH), 6.52 (br, 2H, NH), 7.11−7.16 (m, 3H, CH), 8.37 (br, 1H, NH); ^{13}C NMR (75 MHz, THF-d_8) 18.1, 22.6, 45.5, 121.7 (q, J = 318 Hz), 129.4, 129.7, 132.8, 137.6, 153.4; HRMS calcd for $C_{15}H_{26}N_3$ [M − HOTf]$^+$ 248.2116, found 248.2121.

*[C(3-Cl-C_6H_4NH)(^{i}PrNH)$_2$][OTf] (**1f**).* Colorless solid, isolated yield 94% (379 mg); mp 129.0−129.8 °C; ^{1}H NMR (300 MHz, THF-d_8) 1.25 (d, J = 6.6 Hz, 12H, CH_3), 3.92−4.01 (m, 2H, CH), 7.19−7.40 (m, 6H, 4CH, 2NH), 8.91 (br, 1H, NH); ^{13}C NMR (75 MHz, THF-d_8) 22.5, 46.4, 121.4 (q, J = 318 Hz), 122.1, 123.7, 126.3, 131.8, 135.5, 139.7, 153.8; HRMS calcd for $C_{13}H_{21}ClN_3$ [M − HOTf]$^+$ 254.1418, found 254.1419.

*[C(CyNH)(^{i}PrNH)$_2$][OTf] (**1g**).* Colorless solid, isolated yield 95% (308 mg); mp 164.4−165.2 °C; ^{1}H NMR (300 MHz, THF-d_8) 1.15−1.26 (m, 6H, CH_3), 1.30−1.43 (m, 6H, CH_3), 1.60−1.64 (m, 2H, CH_2), 1.76−1.79 (m, 4H, CH_2), 2.01−2.05 (m, 4H, CH_2), 3.09−3.19 (m, 3H, CH), 6.71 (br, 3H, NH); ^{13}C NMR (75 MHz, THF-d_8) 22.5, 25.1, 25.6, 45.2, 51.7, 121.6 (q, J = 318 Hz), 153.4; HRMS calcd for $C_{13}H_{28}N_3$ [M − HOTf]$^+$ 226.2279, found 226.2278.

*[C(C_6H_5NH)(C_6H_4NH)$_2$][OTf] (**1h**).* Colorless solid, isolated yield 82% (358 mg); mp 107.7−108.3 °C; ^{1}H NMR (300 MHz, THF-d_8) 6.53 (br, 3H, NH), 6.90−7.42 (m, 15H, CH); ^{13}C NMR (75 MHz, THF-d_8) 121.4 (q, J = 316 Hz), 124.3, 127.2, 130.2, 136.7, 153.3; HRMS calcd for $C_{19}H_{18}N_3$ [M − HOTf]$^+$ 288.1500, found 288.1495.

Isolation of 2-F. In a Schlenk tube, Zn(OTf)$_2$ (726 mg, 2 mmol) was added to a solution of 4-fluoroaniline (500 mg, 4.5 mmol) in THF (5 mL), and the mixture was stirred at 100 °C for 3 h. The solvent of the reaction mixture was evaporated under vacuum, and the residue was washed by THF (5 mL) three times. The thus obtained colorless powder as amine-coordinated binuclear zinc complex **2-F** was pure enough for NMR analysis. Single crystals suitable for X-ray analysis were grown in THF/hexane at room temperature for 2 days. Colorless solid, isolated yield 95% (1246 mg); ^{1}H NMR (300 MHz, THF-d_8) 2.17−2.26 (m, 4H, CH_2), 4.03−4.10 (m, 4H, CH_2), 6.04 (br, 8H, NH), 7.32−7.53 (m, 16H, CH); ^{13}C NMR (75 MHz, THF-d_8) 26.2, 68.2, 116.2 (d, J = 22.4 Hz), 120.9 (q, J = 316 Hz, 2CF_3), 121.6 (d, J = 8.0 Hz), 138.7 (d, J = 2.5 Hz), 159.8 (d, J = 239 Hz).

Reaction of 2-F with *N*,*N*′-Diisopropylcarbodiimide. *N*,*N*′-Diisopropylcarbodiimide (126 mg, 1.0 mmol) was added to a solution of complex **2-F** (658 mg, 0.5 mmol) in THF (5 mL). The reaction was carried out at room temperature for 2 h. After the normal workup, the reaction provided quantitatively a colorless solid, **1b**.

■ ASSOCIATED CONTENT

S Supporting Information. Copies of ^{1}H and ^{13}C NMR spectra for all isolated compounds and crystallographic data for **1a**, **1d**, and **2-F**. This material is available free of charge via the Internet at http://pubs.acs.org.

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