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Alkali Metal and Zinc Complexes of a Bridging 2,5-Diamino-1,4-Benzoquinonediimine Ligand

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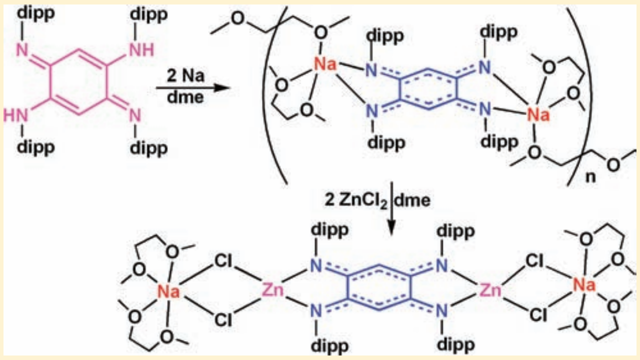
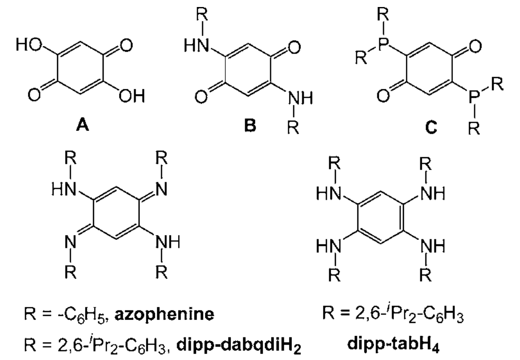
Supporting Information

ABSTRACT: Two alkali metal complexes of a bridging 2,5-diamino-1,4-benzoquinonediimine ligand (dipp-dabqdiH$_2$), [(thf)$_2$Li(μ-dipp-dabqdi)Li(thf)$_2$] (**1**) and [(dme)$_{1.5}$Na(μ-dipp-dabqdi)Na(dme)$_{1.5}$]$_n$ (**2**, dme = 1,2-dimethoxyethane), have been synthesized by the reaction of dipp-dabqdiH$_2$ with Li^{n}Bu or sodium metal. In addition, treatment of 1,2,4,5-tetrakis(2,6-diisopropylamino)benzene (dipp-tabH$_4$) with potassium metal in dme afforded the complex [(dme)$_2$K(μ-dipp-tabH$_2$)K(dme)$_2$] (**3**). X-ray crystal diffraction analyses revealed that complexes **1** and **3** have dinuclear structures, while the sodium complex **2** aggregates to a one-dimensional polymer through bridging dme ligands. With increasing ion radius, the coordination number of the alkali metal (Li, Na, and K) increases from four to five to six, while the coordination geometry changes from distorted tetrahedral to square pyramidal and further to octahedral in **1**, **2**, and **3**, respectively. The salt metathesis reactions of **1** and **2** with anhydrous ZnCl$_2$ yielded the ion-contacted zinc complexes [(thf)$_3$Li(μ-Cl)ClZn(μ-dipp-dabqdi)ZnCl(μ-Cl)Li(thf)$_3$] (**4**), [(dme)$_2$Li(μ-Cl)ClZn(μ-dippdabqdi)-ZnCl(μ-Cl)Li(dme)$_2$] (**5**), and [(dme)$_2$Na(μ-Cl)$_2$Zn(μ-dipp-dabqdi)Zn(μ-Cl)$_2$Na(dme)$_2$] (**6**), respectively. The ligand exists as the dianionic form in compounds **1**−**6** upon double deprotonation, and a complete electronic delocalization (except for **3**) of the quinonoid π-system is observed between the metal centers over the two N=C—C=C—N halves of the ligand. The electronic structures of the complexes were studied by density functional theory (DFT) computations.



Quinonoid molecules have attracted much attention for decades because they have shown many applications in organic and physical chemistry and can potentially serve as bridging ligands in coordination and supramolecular chemistry.[1] Particularly, the deprotonated, enolate form of the bis-chelating 2,5-dihydroxy-1,4-benzoquinone ligand (**A**, Scheme 1) has been widely used to prepare numerous dinuclear metal complexes possessing specific electronic properties induced by the extended conjugated π-system of the ligands.[2] Moreover, the amine analogues 2,5-diamino-1,4-benzoquinones (**B**, Scheme 1) have been popular structural linkers in the investigation of metal—metal electronic coupling and communication,[3] and the bis(phosphine)-substituted benzoquinone (**C**, Scheme 1) has also been reported to display dramatic changes in the ligand redox potentials upon coordination to two electronically "inactive" palladium ions.[4] In contrast, the coordination chemistry of their nitrogen-based analogues, 2,5-diamino-1,4-benzoquinonediimines (dabqdiH$_2$), remains relatively underdeveloped. Initial explorations of the coordination chemistry of these ligands revealed specific electronic delocalization. Therefore, extending the derivatives of 1,4-benzoquinone to dabqdiH$_2$ is a nice approach to new bridging ligands for multimetallic complexes with tunable metal—metal electronic interactions.

Scheme 1. Selected Examples of Bridging Bis-Chelating Ligands



The azophenine compound[5] (Scheme 1) was synthesized in as early as 1875. However, introduction of the closely related

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ligand dabqdiH_2 to the synthesis of metal complexes has not been described until 1998,[6] and by now, only some twenty complexes have been prepared.[6,7] Most of the known examples are transition metal complexes, including mononuclear Cu, Re, W, dinuclear Ni, Pd, Pt, Cu, and tetranuclear Pd complexes. These complexes not only added to the coordination chemistry of amino/imino-type donor groups, but also showed catalytic ability in the oligomerization of olefins.[7d,f] Very recently, Hahn and co-workers[7g] reported the first main group complexes of bridging dabqdiH_2 ligands, {[$(Me_3Si)_2N$]Sn(μ-N-CH_2^{t}Bu-N′-^{i}Bu-dabqdi)Sn[$N(SiMe_3)_2$]} and {[$(Me_3Si)_2N$]Sn(μ-^{i}Bu-dabqdi)Sn[$N(SiMe_3)_2$]}, by direct metalation of the corresponding dabqdiH_2 ligand with Sn[$N(SiMe_3)_2$]$_2$.

In our previous work, we have used alkali metal complexes of α-diimine ligands for the synthesis of a series of metal−metal-bonded or mononuclear metal compounds.[8] The α-diimine ligands can be reduced to the monoanion or dianion, which can effectively stabilize many low-valent transition and main group metals. As an extension of our studies on electronically tunable ligands in the construction of novel metal complexes, we turned to the dabqdiH_2 ligands, which can be viewed as hybrids of the diimine and diamine-type ligands. Herein, we report the synthesis and structures of the first *s*-block complexes with dipp-dabqdiH_2, [$(thf)_2$Li(μ-dipp-dabqdi)Li$(thf)_2$] (**1**) and [$(dme)_{1.5}$Na(μ-dipp-dabqdi)-Na$(dme)_{1.5}$]$_n$ (**2**), and with the tetramine ligand dipp-tabH_4, [$(dme)_2$K(μ-dipp-tabH_2)K-$(dme)_2$] (**3**). Moreover, the zinc complexes [$(thf)_3$Li(μ-Cl)ClZn(μ-dipp-dabqdi)ZnCl(μ-Cl)Li$(thf)_3$] (**4**), [$(dme)_2$Li-(μ-Cl)ClZn(μ-dipp-dabqdi)-ZnCl(μ-Cl)Li$(dme)_2$] (**5**), and [$(dme)_2$Na$(\mu\text{-Cl})_2$Zn-(μ-dipp-dabqdi)Zn$(\mu\text{-Cl})_2$Na$(dme)_2$] (**6**) have also been synthesized from the salt metathesis of **1** and **2** with $ZnCl_2$.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of the Ligand dipp-dabqdiH_2. The ligand dipp-dabqdiH_2 was synthesized by a slightly modified literature procedure of Buchwald−Hartwig Pd-catalyzed cross-coupling amination of 1,2,4,5-tetrabromobenzene with aromatic amines under basic conditions.[9] The reaction was conducted with excess 2,6-diisopropylphenylamine (6 equiv) in refluxing toluene for three days (instead of with 4 equiv of 2,6-diisopropylphenylamine in *o*-xylene at 143 °C for 24 h). The crude azophenine dipp-dabqdiH_2 was obtained as a mixture that contained the unoxidized 1,2,4,5-tetrakis-(2,6-diisopropylamino)benzene derivative, dipp-tabH_4. The mixture was then dissolved in CH_2Cl_2 and stirred under an atmosphere of oxygen at room temperature for 2 h, giving the ligand dipp-dabqdiH_2 as the sole isolated product in 35% yield.

Prior to oxidation of the crude product, we isolated colorless crystals of the unoxidized tetramine (dipp-tabH_4) from the benzene solution of the mixture (see Scheme 1). This confirmed that the azophenine dipp-dabqdiH_2 is derived from oxidation of the initially formed dipp-tabH_4. At 25 °C, ^{1}H NMR spectrum of the latter compound exhibits a single, diagnostic signal at δ = 5.23 ppm (C_6D_6) for the four NH protons, indicative of a high-symmetry structure in solution. The IR shift is in the expected region ($\nu_{\text{N−H}}$ 3339 cm^{-1}). Single-crystal X-ray diffraction of the tetramine dipp-tabH_4 (Figure 1, left) revealed that the four N atoms are coplanar with nearly equivalent N−C (1.422(3) and 1.423(3) Å) and aryl C−C (1.38−1.40 Å) bond distances. The aryl rings of dipp on the nitrogen atoms are almost perpendicular to the plane formed by the four N atoms with dihedral angles of 78.2° and 81.7°.

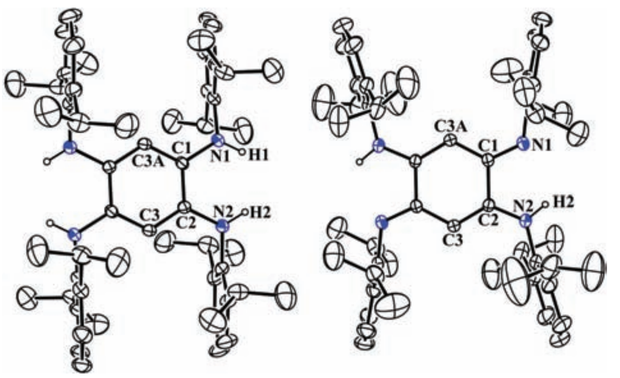


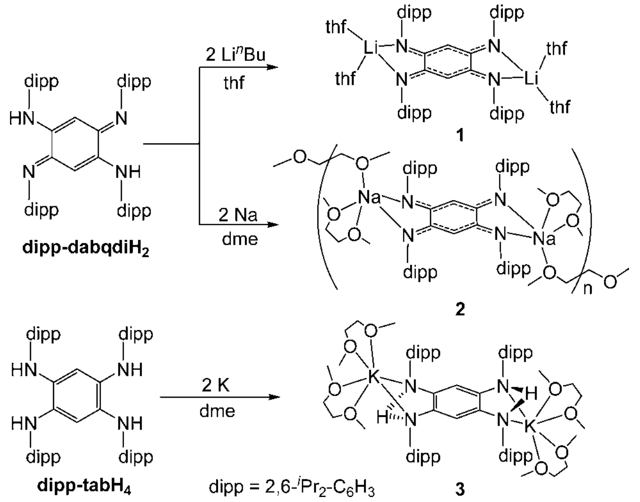
Figure 1. Molecular structures of dipp-tabH_4 (left) and **dipp-dabqdiH_2** (right) (thermal ellipsoids at the 30% probability level with hydrogen atoms on all carbon atoms omitted for clarity). Symmetry codes: (A) 0.5 − *x*, 0.5 − *y*, −*z* (dipp-tabH_4); 1 − *x*, 1 − *y*, −*z* (dipp-dabqdiH_2).

For the ligand dipp-dabqdiH_2, the proton resonances in the ^{1}H NMR (δ_{NH} 8.10 ppm, 2H; δ_{CH} 5.14 ppm, 2H, C_6D_6, 25 °C) and IR shift ($\nu_{\text{N−H}}$ 3276 cm^{-1}) are also in the expected region for azophenine. Orange crystals of dipp-dabqdiH_2 were obtained by slow evaporation of an acetone solution. In the centro-symmetric structure, the four N atoms and the central ring are also coplanar, but with varied N−C (1.296(3) and 1.340(3) Å) and quinone C−C (C1−C2 = 1.496(3), C2−C3 = 1.371(3), and C1−C3A = 1.425(3) Å) lengths (Figure 1, right). Thus the molecule may be described as composed of two equivalent, delocalized, six-electron π-systems (the N1−C1−C3A−C2A−N2A unit and the N2−C2−C3−C1A−N1A unit), which are not conjugated but linked by C−C single bonds. The dihedral angles of the plane formed by the four N atoms and the phenyl rings are 75.1° and 84.0°, respectively. Furthermore, the dihedral angle of the phenyl planes on each side of the dipp-dabqdiH_2 ligand is 28.1°, which is significantly larger than that (3.5°) in the corresponding dipp-tabH_4. These results enable a direct comparison of 1,2,4,5-tetrakis(arylamino)-benzene with its oxidized derivative.

Synthesis and Structures of the Dinuclear Alkali Metal Complexes 1−3. The alkali metal complexes were synthesized from the ligands dipp-dabqdiH_2 and dipp-tabH_4. Reaction of Li^{n}Bu with the neutral ligand dipp-dabqdiH_2 in thf yielded the lithium complex [$(thf)_2$Li(μ-dipp-dabqdi)Li$(thf)_2$] (**1**), while the sodium complex [$(dme)_{1.5}$Na(μ-dipp-dabqdi)Na$(dme)_{1.5}$]$_n$ (**2**) was obtained by reaction of dipp-dabqdiH_2 with sodium metal in dme, which possesses chelating effect on the larger alkali metal ions. Meanwhile, the potassium complex [$(dme)_2$K-(μ-dipp-tabH_2)K$(dme)_2$] (**3**) was obtained by reaction of dipp-tabH_4 with potassium metal in dme (Scheme 2).

Complexes **1**−**3** are thermally stable as solids under nitrogen or argon atmosphere and can be stored for several weeks at room temperature without decomposition. All of them can be prepared in bulk and are quite soluble in thf and dme. These properties make them good precursors for further reactions. The ^{1}H NMR spectra (C_6D_6, 25 °C) of complexes **1** and **2** revealed the absence of NH resonances, consistent with a bischelating, tetradentate coordination for the deprotonated dianionic ligand derived from dipp-dabqdiH_2, which is further proved by the absence of the N−H stretch in the IR spectra. In the ^{1}H NMR spectrum of complex **3**, the broad singlet at δ =

Scheme 2. Synthesis of the Dinuclear Alkali Metal Complexes 1−3



5.29 ppm (2H, N*H*) indicates that the amine functions are not completely deprotonated, as also confirmed by the presence of the N−H stretch ($\nu_{\mathrm{N-H}}$ 3340 cm^{-1}) in the IR spectrum.

The molecular structure of **1** (Figure 2) consists of a dinuclear centrosymmetric unit in which the 4N ligand behaves as a bischelating species and bridges two $[\mathrm{Li(thf)_2}]^+$ fragments. Compared with the corresponding bond parameters of the neutral dipp-dabqdiH$_2$ ligand, the bond lengths of N1−C1 (1.323(2) Å) and C2−C3 (1.394(2) Å) become longer and those of N2−C2 (1.328(2) Å) and C1−C3A (1.401(2) Å) are shortened. This is consistent with the extensive electron delocalization of N1−C1−C3A−C2A−N2A and N2−C2−C3−C1A−N1A moieties.[7] Notably, there is no conjugation between these two 6π-systems because the C1−C2 (and C1A−C2A) distance (1.524(2) Å) corresponds to a typical single bond. The coordination geometry around each lithium center is distorted tetrahedral, with an acute bite angle of the bridging ligand (N1−Li−N2 = 84.3(1)°). The Li atom is located slightly out of the plane defined by the four N atoms, with a vertical distance of 0.802 Å. The almost equivalent Li−N bond lengths (1.994(3) and 1.989(3) Å) are different from the presentation of a shorter Li−N$_{\mathrm{amido}}$ bond and a longer Li−N$_{\mathrm{imino}}$ bond in analogous lithium compounds bearing a monoanionic chelating amido/imino ligand,[10] which further confirms the complete electron delocalization of the two 6π-systems. The Li−O bond lengths (1.973(3) and 1.929(3) Å) are in the expected range for thf coordination.[11]

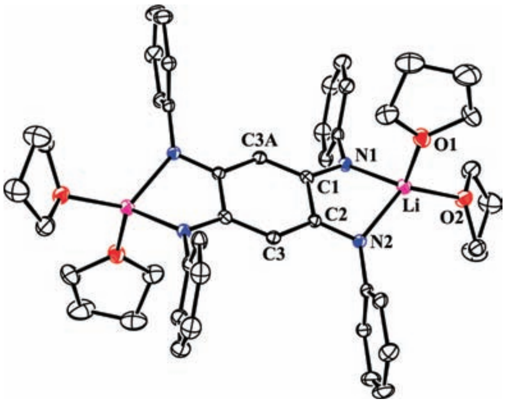


Figure 2. Molecular structure of **1** (thermal ellipsoids are set at the 30% probability level with hydrogen atoms and ^{i}Pr groups omitted for clarity). Symmetry code: (A) 2 − *x*, −*y*, 1 − *z*.

The reaction of the ligand dipp-dabqdiH$_2$ with Na metal resulted in a polymeric structure, $[\mathrm{(dme)_{1.5}Na}(\mu\text{-dipp-dabqdi})\mathrm{Na(dme)_{1.5}}]_n$ (**2**). The repeating dinuclear unit is similar to the lithium analogue **1**. The elongation of C1−N1 (1.323(3) Å) and C2−C3 (1.400(3) Å) bonds, shortening of the C2−N2 (1.313(3) Å) and C1−C3A (1.393(2) Å) bonds, and maintenance of the typical single bond of C1−C2 (1.518(3) Å) in the bridging ligand are also observed (Figure 3a), indicating the existence of two equivalent, delocalized 6π NCCCN moieties, which are chemically connected but electronically nonconjugated.[7] The most significant structural feature of **2**, however, is the aggregation of the $[\mathrm{(dme)Na}(\mu\text{-dipp-dabqdi})\mathrm{Na(dme)}]$ units. In contrast to the four-coordinate Li atom with two chelating N atoms and two thf molecules in **1**, the Na atom is five-coordinated with two N atoms from the ligand, two O atoms from a chelating dme molecule, and one O atom from another dme molecule, which serves as a bridge and links two $[\mathrm{(dme)Na}(\mu\text{-dipp-dabqdi})\mathrm{Na(dme)}]$ units, forming a one-dimensional chain (Figure 3b).

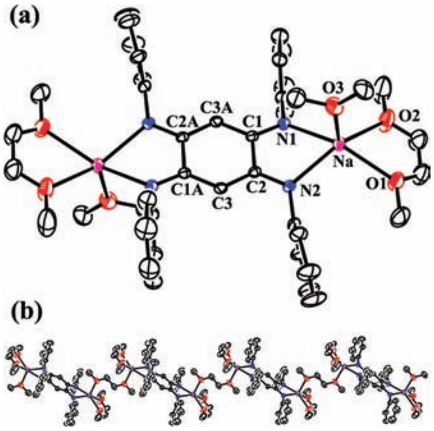


Figure 3. Crystal structure of **2**. (a) Dimeric repeating unit $[\mathrm{(dme)_{1.5}Na}(\mu\text{-dipp-dabqdi})\mathrm{Na(dme)_{1.5}}]$. (b) 1D chain linked by bridging dme molecules (thermal ellipsoids are set at the 30% probability level with hydrogen atoms and ^{i}Pr groups omitted for clarity). Symmetry code: (A) 2 − *x*, −*y*, 1 − *z*.

The coordination geometry around each Na$^+$ ion is square pyramidal (τ_5 = 0.06),[12] with the O3 atom of the bridging dme molecule occupying the apical position and two almost equivalent Na−N and Na−O bonds defining the basal plane. The apical Na−O3 bond (2.498(3) Å) is longer than the basal Na−O bonds (2.414(3) and 2.414(3) Å), but they are all in the expected range for the coordinated dme molecules. In addition, the bite angle of the bridging ligand (N1−Na−N2 = 69.74(8)°) is more acute than that of the lithium analogue **1**.

By reaction of the unoxidized tetramine ligand dipp-tabH$_4$ with K metal in dme, the potassium complex $[\mathrm{(dme)_2K}(\mu\text{-dipp-tabH_2})\mathrm{K(dme)_2}]$ (**3**) was obtained. The molecular structure of **3** (Figure 4) also consists of a dinuclear centrosymmetric unit, with two $[\mathrm{K(dme)_2}]^+$ fragments bridged by one ligand. The C2−C3 (1.404(4) Å), C1−C3A (1.400(4) Å), and C1−C2 (1.426(4) Å) bonds in **3** are typical aryl C−C bond distances, while the N1−C1 and N2−C2 are single N−C bonds, which are comparable to the neutral dipp-tabH$_4$ ligand. The tetramine

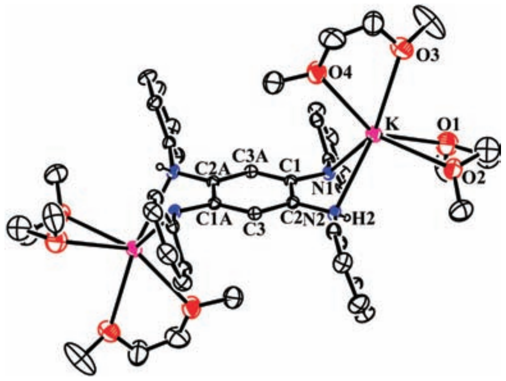


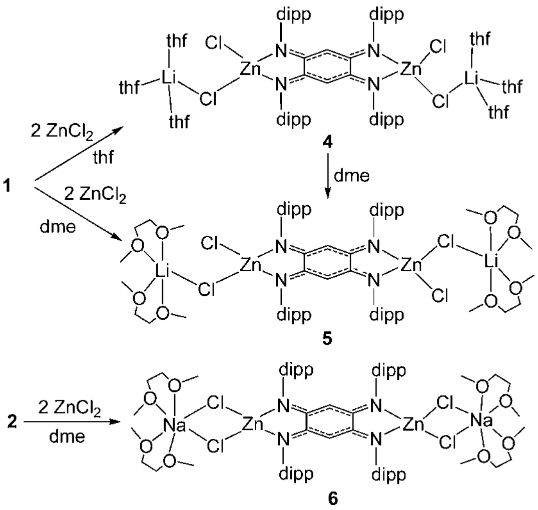
Figure 4. Molecular structure of **3** (thermal ellipsoids are set at the 30% probability level with hydrogen atoms and ^{i}Pr groups omitted for clarity). Symmetry code: (A) −*x*, 1 − *y*, 1 − *z*.

is doubly deprotonated to form the $[\text{dipp-tabH}_2]^{2-}$ ion that coordinates to two K^+ ions. There is one proton remaining at each side of the $[\text{dipp-tabH}_2]^{2-}$ ligand, which is distributed to two N atoms with 50% occupancy each as indicated by the structural analysis. As mentioned above, the presence of the amine protons was also proved by NMR and IR studies.

The coordination geometry around each potassium atom is distorted octahedral completed by two N atoms of the ligand and two bidentate dme molecules. The bridging ligand shows the most acute bite angle (N1−K−N2 = 57.43(8)°) among the three alkali metal complexes. Notably, the K atom deviates dramatically from the plane defined by the four N atoms, with a much larger vertical distance of 2.124 Å than that of the lithium and sodium analogues with the ligand $[\text{dipp-dabqdi}]^{2-}$. This is caused by the nature of the amido ligand $[\text{dipp-tabH}_2]^{2-}$ in **3**, which possesses tetrahedral N atoms. In contrast, the imido/amido N atoms in ligand $[\text{dipp-dabqdi}]^{2-}$ show trigonal planar geometries in complexes **1** and **2**. The average K−N distance (2.803(3) Å) is significantly longer than that (2.557(3) Å) of the dipotassium salt of *N*,*N*′-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene.[13] The K−O(dme) bond lengths range from 2.769(5) to 2.930(4) Å.

Reactions of the Dinuclear Alkali Metal Complexes with ZnCl$_2$. It is known that the alkali metal salts of some ligands, such as *α*-diimines, *β*-diketiminates, amidinates, and guanidines, can be used as precursors for the synthesis of organometallic compounds through salt metathesis with other metal halides. Here the use of the alkali metal salts (**1**−**3**) in the synthesis of novel metal complexes was examined. In the literature most of the metal complexes of dabqdiH$_2$ ligands were prepared by direct metalation. The attempt of metalation of dabqdiH$_2$ ligands with $[\text{Zn(acac)}_2]$ to synthesize the analogue of [(acac)M(*μ*-dabqdi)M(acac)] (M = Ni or Pd) was carried out by Braunstein et al., but the product appeared to be unstable in solution.[7d] This instability of the zinc complexes may result in part from the repulsion of the bulky acac$^-$ ligand and/or the chelating effect of acac$^-$. However, the same group reported that the reaction of $[\text{Zn(acac)}_2]$ with a less bulky N_2O_2 ligand, N-substituted benzoquinonemonoimine, which is isoelectronic to the N_4 ligand dabqdiH$_2$, afforded the mononuclear zinc complex $\{\text{Zn}[\text{C}_6\text{H}_2(\text{NHCH}_2\text{CH}_2\text{NMe}_2)(=\text{NCH}_2\text{CH}_2\text{NMe}_2)(=\text{O})(\text{O})]_2\}$ in dichloromethane at room temperature.[3c] To this end, metal halides may be suitable precursors to react with the alkali metal complexes **1**−**3**. Three dinuclear zinc complexes (Scheme 3) were obtained.

Scheme 3. Synthesis of the Dinuclear Zinc Complexes 4−6 from 1 or 2



Reaction of the lithium complex **1** with anhydrous ZnCl$_2$ in thf or dme afforded the dinuclear ion-contacted zinc complexes, $[(\text{thf})_3\text{Li}(\mu\text{-Cl})\text{ClZn}(\mu\text{-dipp-dabqdi})\text{ZnCl}(\mu\text{-Cl})\text{Li}(\text{thf})_3]$ (**4**) and $[(\text{dme})_2\text{Li}(\mu\text{-Cl})\text{ClZn}(\mu\text{-dipp-dabqdi})\text{ZnCl}(\mu\text{-Cl})\text{Li}(\text{dme})_2]$ (**5**), respectively. Given the chelating character of the dme ligand, complex **5** (with two chelating dme molecules) should be more stable than **4** (with the $[\text{Li(thf)}_3]^+$ fragments). This was confirmed by the conversion of **4** to **5** when the former was dissolved in dme. Furthermore, we conducted the reaction of the disodium complex **2** with ZnCl$_2$ in dme and obtained the complex $[(\text{dme})_2\text{Na}(\mu\text{-Cl})_2\text{Zn}(\mu\text{-dipp-dabqdi})\text{Zn}(\mu\text{-Cl})_2\text{Na}(\text{dme})_2]$ (**6**). Treatment of complexes **1** or **2** with ZnCl$_2$ in refluxing toluene led to insoluble precipitates, which may be inferred as chloride-bridging oligomers or polymers.

Purple crystals of complex **4** were grown from a thf/hexane (10:1) solution at −20 °C. The molecular structure of **4** (Figure 5) consists of a dinuclear unit in which the 4N bischelating ligand bridges two $[\text{ZnCl}]^+$ fragments contacting with solvated alkali metal ions $[\text{Li(thf)}_3]^+$. The Zn and Li atoms are linked by one bridging chloride ligand on each side. The bonding parameters of the dianionic dipp-dabqdi^{2-} ligand indicate a delocalized *π* system along each NCCCN unit, which is significantly different from the localized 6*π* + 6*π* systems

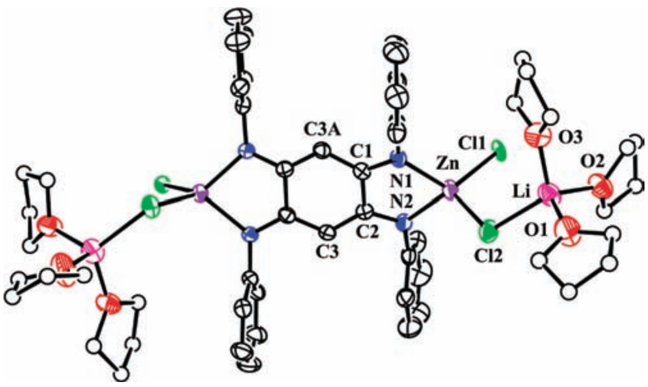


Figure 5. Molecular structure of **4** (thermal ellipsoids are set at the 30% probability level; hydrogen atoms and ^{i}Pr groups are omitted; and C atoms of thf molecule are drawn as smaller spheres for clarity). Symmetry code: (A) −*x*, *y*, 1.5 − *z*.

within the quinoneimine core with an alternation of single and double bonds in the mononuclear zinc complex {Zn-$[C_6H_2(NHCH_2CH_2NMe_2)(=NCH_2CH_2NMe_2)(=O)(O)]_2$}.[3c] As in the lithium precursor **1**, no conjugation occurs along the connecting C1−C2 bond, as indicated by its length of 1.498(7) Å for a single bond. Unlike the precursor **1** and complexes **5** and **6** (vide infra), this complex is not centrosymmetric but shows a C_2 symmetry, wherein the two terminal $(thf)_3LiCl$ ion pairs are located at the same side of the molecule. The two 6*π*-systems are not coplanar but have a dihedral angle of 15.2°.

The coordination geometry around the zinc center (d^{10}) is distorted tetrahedral, which is different from the square planar arrangement for group 10 metal centers (d^8) in analogous complexes.[7d−f] The Zn···Zn distance of 7.86 Å is slightly longer than the Cu···Cu separation (7.69 Å) in the dinuclear copper complex [(acac)Cu(*μ*-R-dabqdi)Cu(acac)] (R = $-2,6-Me_2C_6H_3$)[7f] and the Ni···Ni separation in dinuclear nickel complexes [(acac)Ni(*μ*-R-dabqdi)Ni(acac)] (R = $-CH_2{}^tBu$, 7.62 Å; R = $-2,6-Me_2C_6H_3$, 7.65 Å; R = $-4-MeC_6H_4$, 7.70 Å),[7f] which may be attributed to the steric repulsion of the bulky dipp groups in the zinc compound **4**. In each five-membered metallacycle, the metal atom is slightly out of the N_2C_2 plane, with a vertical distance of 0.420 Å and an acute chelating angle (82.05(15)°). The two Zn−N bond lengths (2.028(4) and 2.023(4) Å) are close, and the Zn−Cl(terminal) distance is also almost identical to the Zn−Cl(bridging) distance (2.3038(13) vs 2.2999(17) Å). Each Li atom is coordinated by one bridging chloride ion and three thf molecules in a distorted tetrahedral geometry. The Li−Cl contact (2.361(11) Å) is at the lower end of those in the reported compounds containing chloride-bridged Li atoms (ca. 2.30−2.78 Å). The Li−O(thf) bond lengths range from 1.907(12) to 1.953(12) Å and are comparable to those in complex **1**.

Reaction of the same reactants in dme resulted in purple crystals of $[(dme)_2Li(\mu\text{-}Cl)ClZn(\mu\text{-dipp-dabqdi})ZnCl(\mu\text{-}Cl)Li(dme)_2]$ (**5**). Unfortunately, the crystal data is poor and one coordinated dme molecule on the Li atom is disordered, resulting in high *R* values. Moreover, there is one disordered toluene molecule, which is treated by SQUEEZE/PLATON. Several attempts to obtain more precise structural parameters were unsuccessful. The structural features of the centrosymmetric complex **5** (Figure 6) are very similar to **4**, such as the extensive electronic delocalization but no conjugation between two 6*π*-systems, the tetrahedral geometry around Zn atoms, and incorporation of solvated lithium ions bridged by one chloride ion to Zn. However, there are some minor differences between **4** and **5**. The most apparent point is that the Li^+ ion in **5** is five-coordinated by one bridging chloride ion and four O atoms of two chelating dme molecules in a distorted trigonal bipyramidal geometry (O1−Li−O4 = 169.4(10)°), while in **4** it is four-coordinated with one bridging Cl atom and three thf molecules. The two 6*π* systems in complex **5** are coplanar, but there is a large dihedral angle between the two moieties in complex **4** as mentioned above. In addition, the Zn···Zn separation of 7.84 Å in **5** is marginally shorter than that (7.86 Å) in complex **4**. In both cases, only one of the two chloride ions acts as a bridge between the Zn^{2+} and Li^+ ions, while the other one is a terminal ligand to the Zn^{2+} ion.

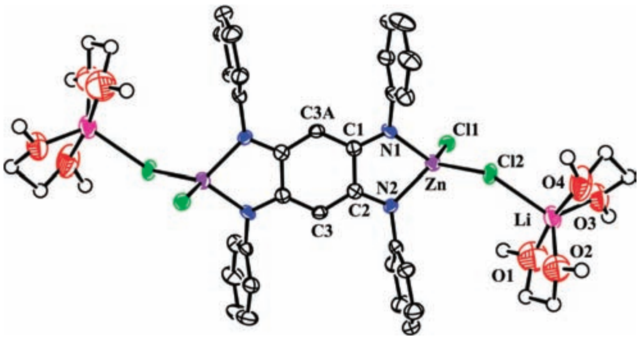


Figure 6. Molecular structure of **5** (thermal ellipsoids are set at the 30% probability level; hydrogen atoms and ^{i}Pr groups are omitted; and C atoms of dme are drawn as smaller spheres for clarity). Symmetry code: (A) 1 − *x*, −*y*, 2 − *z*.

Complex **6** was obtained also as purple crystals by treatment of the sodium salt **2** with $ZnCl_2$ and crystallization from dme solution at −20 °C. There are two independent molecules in the asymmetric unit and the metrical parameters of them are very close. The central core of **6** (Figure 7) is similar to the lithium-containing analogue **5**, with electronic delocalization but no conjugation between the two coplanar 6*π*-systems, tetrahedral geometry around Zn atoms, and dme-solvated alkali metal ions. Differences between the lithium species (**4** and **5**) and the sodium compound **6** lie in the coordination sphere of the terminal alkali metal. Instead of four- or five-coordinate Li atom with only one bridging chloride ion in **4** and **5**, the Na atom in **6** assumes the octahedral geometry where both of the Cl^- ions serve as bridges linking the Zn and Na atoms. The increase of the coordination number of the alkali metals can be attributed to the larger radius of sodium ion than Li^+.

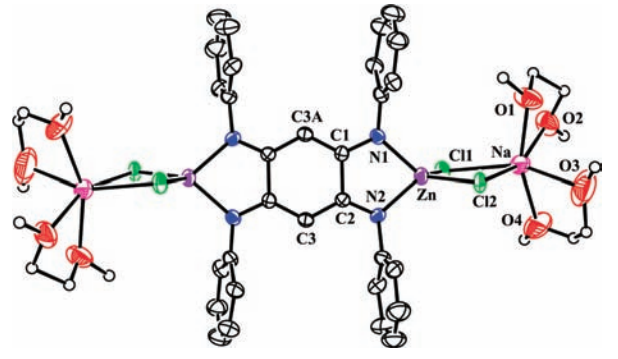


Figure 7. Molecular structure of **6** (thermal ellipsoids are set at the 30% probability level; hydrogen atoms and ^{i}Pr groups are omitted, and C atoms of dme are drawn as small spheres for clarity). Symmetry code: (A) 2 − *x*, 1 − *y*, 1 − *z*.

DFT Calculations. To gain more insight into the electronic structures of the ligands and complexes, DFT computations were carried out at the B3LYP/6-31G* level. Since the basic structure is essentially the same for complexes **1** and **2** and for **4**−**6**, while differences have been observed for the two forms of the ligand and complex **3**, we used the models ph-dabqdiH_2, ph-tabH_4, $[(H_2O)_3Na(\mu\text{-ph-dabqdi})Na(H_2O)_3]$ (**2a**), $[(H_2O)_4K(\mu\text{-ph-tabH}_2)K(H_2O)_4]$ (**3a**), and the dianionic $[Cl_2Zn(\mu\text{-ph-dabqdi})ZnCl_2]^{2-}$ ($[\mathbf{6a}]^{2-}$) for the evaluation of compounds dipp-dabqdiH_2, dipp-tabH_4, and complexes **2**, **3**, and **6**. In these model molecules, the dipp substituents on the nitrogen atoms of the parent compounds were replaced by phenyl groups, and the coordinated dme molecules in **2** and **3** were simplified to H_2O in **2a** and **3a**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Ligands dipp-dabqdiH$_2$, dipp-tabH$_2$, and Complexes 1−6

	dipp-dabqdiH$_2$	dipp-tabH$_2$	1	2	3	4	5	6
C1−N1	1.296(3)	1.422(3)	1.323(2)	1.323(3)	1.408(4)	1.325(6)	1.330(9)	1.331(4)
C2−N2	1.340(3)	1.423(3)	1.328(2)	1.313(3)	1.413(4)	1.323(6)	1.329(9)	1.327(4)
C1−C2	1.496(3)	1.399(3)	1.524(2)	1.518(3)	1.426(4)	1.498(7)	1.508(10)	1.515(5)
C2−C3	1.371(3)	1.386(3)	1.394(2)	1.400(3)	1.404(4)	1.405(7)	1.397(9)	1.394(4)
C1−C3A	1.425(3)	1.387(3)	1.401(2)	1.393(3)	1.400(4)	1.397(7)	1.411(10)	1.392(5)
M^a−N1			1.994(3)	2.348(3)	2.829(3)	2.025(4)	2.033(6)	2.017(3)
M−N2			1.989(3)	2.352(2)	2.777(3)	2.025(4)	2.023(6)	2.017(3)
N1−C1−C2	114.7(2)	118.6(2)	115.83(14)	116.1(2)	116.8(3)	115.5(4)	115.6(6)	115.5(3)
N2−C2−C1	114.0(2)	118.2(2)	115.57(13)	116.5(2)	116.7(3)	115.4(4)	115.4(6)	115.2(3)
C1−C2−C3	120.4(2)	119.4(2)	117.98(14)	117.3(2)	119.0(3)	118.0(4)	120.2(6)	119.1(3)
N1−M−N2			84.30(12)	69.74(8)	57.43(8)	82.04(16)	81.8(2)	82.25(11)

^{a}**1**: M = Li. **2**: M = Na. **3**: M = K. **4**−**6**: M = Zn.

The optimized structures of ph-dabqdiH$_2$ and ph-tabH$_4$ are very close to those from the X-ray diffraction. The theoretical bond distances of C1−N1, C2−N2, C1−C2, C2−C3, and C1−C3A (Table 2) agree well with the experimental data (Table 1) for dipp-dabqdiH$_2$, with the corresponding bond order (Wiberg bond index) of 1.60, 1.19, 1.02, 1.53, and 1.18, respectively. This is consistent with the description of two chemically connected but electronically unconjugated 6π systems in the ligand dipp-dabqdiH$_2$. For the model compound ph-tabH$_4$, the calculated C1−N1 (1.420 Å) and C2−N2 (1.422 Å) distances are comparable to the X-ray structural data (1.422(3) and 1.423(2) Å). These values fall in the range of C−N single bond, which, together with the theoretical aryl C−C bonds (1.387−1.401 Å), confirm the tetramine nature of ligand tabH$_4$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Model Compounds ph-dabqdiH$_2$, ph-tabH$_4$, 2a, 3a, and the Anionic [6a]$^{2-}$ from DFT Computations

	ph-dabqdiH$_2$	ph-tabH$_4$	2a	3a	[6a]$^{2-}$
C1−N1	1.302	1.420	1.320	1.422	1.333
C2−N2	1.363	1.422	1.319	1.413	1.333
C1−C2	1.503	1.401	1.511	1.446	1.513
C2−C3	1.370	1.387	1.401	1.402	1.401
C1−C3A	1.437	1.391	1.399	1.397	1.401
M^a−N1			2.354	2.822	2.042
M−N2			2.351	2.777	2.042
N1−C1−C2	114.9	119.0	116.7	115.2	115.4
N2−C2−C1	113.0	118.6	116.6	115.6	115.4
C1−C2−C3	120.2	119.5	117.8	118.3	118.3
N1−M−N2			69.9	57.1	81.0

^{a}**2a**: M = Na. **3a**: M = K. [**6a**]$^{2-}$: M = Zn.

The calculated structure of the model compound **2a** is in good agreement with the experimental values. The optimized geometry revealed that a double deprotonation resulted in elongation of the C1−N1 (1.320 Å) and C2−C3 (1.401 Å) bonds, shortening of the C2−N2 (1.319 Å) and C1−C3A (1.399 Å) bonds, and maintenance of C1−C2 (1.511 Å) single bond in the dabqdiH$_2$ unit, confirming the complete electronic delocalization of the π-system through the two NCCCN fragments of the bridging ligand. The charge distribution of **2a** was obtained by the natural bonding orbital (NBO) analysis, which showed that each Na atom has +1 charge (0.74) and the ligand bears a total of −2.19 electrons. From the theoretical results, the bond order of C1−N1 and C2−C3 decreased from 1.60 and 1.53 to 1.47 and 1.32, respectively, while the connecting C1−C2 bond was still a single one (bond order 0.99) and the bond order of C2−N2 and C1−C3A increased to 1.47 and 1.32 (from 1.19 and 1.18), respectively. The bonding between the Na atom and the N atoms of the [dabqdi]$^{2-}$ ligand in complex **2a** is largely ionic, with a bond order of 0.10.

The bond distances and angles of the model compound **3a** [(H$_2$O)$_4$K(μ-ph-tabH$_2$)K(H$_2$O)$_4$] are also very similar to the results of X-ray diffraction for **3**, except that the two benzene rings in the ligand are not coplanar but are curved. For instance, the central aryl C−C bonds are nearly identical to the experimental data. The theoretical distances of C1−N1 and C2−N2 (1.422 and 1.413 Å) in **3a** are very close to those observed (1.417(4) and 1.418(4) Å) in **3** but are much longer than those calculated for **2a**, indicating single C−N bonds. This was further confirmed by the NBO analysis. Compared with **2a**, bond orders of both C1−N1 and C2−N2 were decreased to 1.08 and 1.10, respectively, and that of C1−C2 was increased to 1.25. The K atom shows a formal +1 valence (natural charge: +0.81), while the ligand has a total negative charge of −1.81. In addition, there is no obvious covalent bonding between the K atoms and the ligands, as is confirmed by the bond orders of 0.035 and 0.020, respectively.

The optimized structure of the model [**6a**]$^{2-}$ also compares well to the zinc complexes **4**−**6** obtained from X-ray diffraction. The Zn−N (2.042 Å) distance and N1−Zn−N2 (81.0°) angle are close to the experimental values (2.017 Å and 82.25(11)°). The geometric parameters within the NCCCN fragments were found to be very similar to the experimental data of **4**−**6** and those calculated for **2a**, confirming the double deprotonation of the ligand in [**6a**]$^{2-}$. The NBO analysis showed that the Zn atom has nearly +2 valence (+1.57), and the charge of the whole ligand is −2.25. NBO results also revealed that no considerable covalent bonding is available between Zn and N atoms of the ligand, with a bond order of 0.13.

■ CONCLUSION

We report the reactions of the neutral azophenine ligand dipp-dabqdiH$_2$ with Li^{n}Bu or Na metal which yielded the first alkali metal complexes (**1** and **2**) with the bridging [dipp-dabqdi]$^{2-}$ ligand. Reaction of the lithium and sodium complexes with anhydrous ZnCl$_2$ afforded three ion-contacted zinc complexes. In these complexes, a complete electronic delocalization of the quinonoid π-system occurs between the metal centers over the two N=C—C=C—N halves of the [dipp-dabqdi]$^{2-}$ ligand. In addition, the unoxidized tetramine ligand 1,2,4,5-tetrakis-(2,6-diisopropylamino)benzene (dipp-tabH$_4$) was also isolated, which reacted with K metal to give the potassium complex (**3**) of the doubly deprotonated ligand [dipp-tabH$_2$]$^{2-}$. The electronic structures of the complexes were confirmed by DFT calculations. These alkali metal complexes with the bridging [dipp-dabqdi]$^{2-}$ ligand may be suitable starting materials for the preparation of new dinuclear metal complexes possessing electronic communications mediated by the bridging ligand.

■ EXPERIMENTAL SECTION

General Procedures. All reactions were performed under an inert atmosphere of argon or nitrogen gas using standard Schlenk vacuum-line and glovebox techniques. Solvents were dried prior to use by refluxing over and distillation from sodium/benzophenone (hexane, toluene, thf, and dme) or calcium hydride (dichloromethane). NMR spectra were recorded on a Bruker DPX-200 spectrometer at 298 K in C_6D_6. FT-IR spectra were recorded on a Niclolet FT-IR spectrometer.

Synthesis of dipp-dabqdiH$_2$. The ligand [dipp-dabqdiH$_2$] was synthesized by the literature procedure of Buchwald–Hartwig Pd-catalyzed cross-coupling amination of 1,2,4,5-tetrabromobenzene with aromatic amine under basic conditions, except that excess 2,6-diisopropylaniline (6 equiv) were used and the reaction time was prolonged to 3 days. Yield: 35%. Orange crystals were obtained by slow evaporation of an acetone solution. ^{1}H NMR (400 MHz, C_6D_6, 298 K, TMS): δ 1.08 (d, J = 6.8 Hz, 24H, C*H*$_3$), 1.14 (d, J = 6.8 Hz, 24H, C*H*$_3$), 3.15 (br, 8H, C*H*(CH$_3$)$_2$), 5.14 (s, 2H, N···C···C*H*), 7.02 (s, 12H, C*H*-aryl), 8.10 (s, 2H, N*H*). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 23.02 (CH(CH$_3$)$_2$), 28.81 (CH(CH$_3$)$_2$), 91.02 (C_{sp2}H), 123.46 (p-C_6H_3), 125.66 (m-C_6H_3), 129.29 (o-C_6H_3), 131.18 (i-C_6H_3), 145.28 (C_{sp2}-NH). IR (KBr): ν (cm^{-1}) 3276, 3060, 2956, 2923, 2864, 1607, 1565, 1490, 1463, 1431, 1382, 1358, 1331, 1303, 1259, 1210, 1140, 1094, 1045, 930, 845, 791, 770, 741, 671, 526. Anal. Calc. for $C_{54}H_{72}N_4$ (777.16): C, 83.45; H, 9.34; N, 7.21. Found: C, 83.67; H, 9.45; N, 7.00.

[dipp-tabH$_4$]. ^{1}H NMR (400 MHz, C_6D_6, 298 K, TMS): δ 1.05 (br, 24H, C*H*$_3$), 1.19 (br, 24H, C*H*$_3$), 3.32 (m, 8H, C*H*(CH$_3$)$_2$), 5.23 (s, 4H, N*H*), 5.79 (s, 2H, N···C···C*H*), 7.13–7.23 (m, 12H, C*H*-aryl). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 23.34, 25.78 (CH(CH$_3$)$_2$), 28.30 (CH(CH$_3$)$_2$), 105.38 (C_{sp2}H), 123.80 (p-C_6H_3), 126.15 (m-C_6H_3), 131.17 (o-C_6H_3), 138.17 (i-C_6H_3), 145.29 (C_{sp2}-NH). IR (KBr): ν (cm^{-1}) 3339, 3061, 3028, 2960, 2867, 1604, 1496, 1460, 1382, 1327, 1255, 1200, 1179, 1112, 1078, 1033, 897, 850, 795, 730, 695, 558. Anal. Calc. for $C_{54}H_{74}N_4 \cdot C_6H_6$: C, 84.06; H, 9.41; N, 6.54. Found: C, 84.47; H, 9.62; N, 6.12.

*Synthesis of [(thf)$_2$Li(μ-dipp-dabqdi)Li(thf)$_2$] (**1**).* To a solution of dipp-dabqdiH$_2$ (0.16 g, 0.20 mmol) in thf (50 mL) at −78 °C was added a solution of Li^{n}Bu (26 mg, 0.40 mmol) in hexane (0.17 mL). The mixture was warmed to room temperature and stirred for two hours to give a bluish green solution, which was filtered and the filtrate concentrated to about 5 mL. Slow evaporation at −20 °C for several days afforded the product as dark red crystals (crystal yield: 0.13 g, 61%). ^{1}H NMR (400 MHz, C_6D_6, 298 K, TMS): δ 1.20 (16H, thf), 1.25 (d, J = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.33 (d, J = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 3.34 (16H, thf), 3.42 (m, 8H, C*H*(CH$_3$)$_2$), 4.42 (s, 2H, N···C···C–*H*), 7.02–7.17 (m, 12H, C*H*-aryl). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 23.49, 24.67, 25.45 (CH(CH$_3$)$_2$), 28.58 (CH(CH$_3$)$_2$), 28.82 (thf), 67.98 (thf), 87.52 (C···CH), 122.88 (p-C_6H_3), 123.00 (m-C_6H_3), 140.68 (o-C_6H_3), 148.63 (i-C_6H_3), 164.14 (C···N). IR (KBr): ν (cm^{-1}) 3059, 3026, 2955, 2923, 2863, 1606, 1567, 1490, 1464, 1430, 1383, 1360, 1332, 1258, 1209, 1106, 934, 846, 792, 771, 743, 670. Anal. Calc. for $C_{70}H_{102}N_4O_4Li_2 \cdot C_4H_8O$ (1149.57): C, 77.32; H, 9.64; N, 4.87. Found: C, 77.74; H, 9.79; N, 4.49.

*Synthesis of [(dme)$_{1.5}$Na(μ-dipp-dabqdi)Na(dme)$_{1.5}$]$_n$ (**2**).* Freshly cut sodium metal (10 mg, 0.40 mmol) was added to a solution of dipp-dabqdiH$_2$ (0.16 g, 0.20 mmol) in dme (30 mL) and the reaction mixture was stirred at ambient temperature for one day. The resulting mixture was filtered and the filtrate concentrated to about 5 mL. Slow evaporation at ambient temperature for several days afforded the product as dark red crystals (crystal yield: 0.17 g, 74%). ^{1}H NMR (400 MHz, C_6D_6, 298 K, TMS): δ 1.26 (d, J = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.37 (d, J = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 2.76 (18H, dme), 2.89 (12H, dme), 3.49 (m, 8H, C*H*(CH$_3$)$_2$), 4.40 (s, 2H, N···C···C–*H*), 6.91–7.17 (m, 12H, C*H*-aryl). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 23.3, 25.1 (CH(CH$_3$)$_2$), 28.3 (CH(CH$_3$)$_2$), 58.7 (dme), 65.9 (dme), 72.2 (C···CH), 123.8 (p-C_6H_3), 126.1 (m-C_6H_3), 131.2(o-C_6H_3), 138.2 (i-C_6H_3), 160.3 (*C*–N). IR (KBr): ν (cm^{-1}) 3053, 3026, 2958, 2924, 2870, 2819, 1604, 1562, 1485, 1464, 1456, 1383, 1362, 1320, 1304, 1253, 1193, 1109, 1080, 1028, 980, 935, 855, 793, 730, 694, 541. Anal. Calc. for $C_{33}H_{50}N_2O_3Na$ (545.74): C, 72.63; H, 9.23; N, 5.13. Found: C, 73.04; H, 9.38; N, 4.89.

*Synthesis of [(dme)$_2$K(μ-dipp-tabH$_2$)K(dme)$_2$] (**3**).* Complex **3** was prepared by a similar procedure to that employed for **2**, from dipp-tabH$_4$ (0.16 g, 0.20 mmol) and K (16 mg, 0.40 mmol). Dark red crystals (0.19 g, 78%) were isolated. ^{1}H NMR (400 MHz, C_6D_6, 298 K, TMS): δ 1.16 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.22 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.26 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.39 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 3.01 (s, 24H, dme), 3.19 (s, 16H, dme), 3.49 (m, 8H, C*H*(CH$_3$)$_2$), 5.29 (br s, 2H, N*H*), 5.52 (s, 2H, N–C···C–*H*), 7.01–7.22 (m, 12H, C*H*-aryl). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): $\delta\delta$ 24.3, 24.9 (CH(CH$_3$)$_2$), 28.3 (CH(CH$_3$)$_2$), 58.6 (dme), 71.9 (dme), 120.7 ($C_{sp}{}^{2}$H), 122.8 (p-C_6H_3), 123.8 (m-C_6H_3), 140.0 (o-C_6H_3), 145.3 (i-C_6H_3), 152.5 (*C*–N). IR (KBr): ν (cm^{-1}) 3340, 3049, 2958, 2897, 2926, 2865, 2824, 1608, 1564, 1535, 1489, 1429, 1385, 1363, 1320, 1303, 1262, 1202, 1129, 1091, 1036, 936, 857, 791, 748, 732, 660,532. Anal. Calc. for $C_{70}H_{112}N_4O_8K_2$ (1215.86): C, 69.15; H, 9.28; N, 4.61. Found: C, 69.57; H, 8.95; N, 4.91.

*Synthesis of [(thf)$_3$Li(μ-Cl)ClZn(μ-dipp-dabqdi)ZnCl(μ-Cl)Li(thf)$_3$] (**4**).* Anhydrous $ZnCl_2$ (0.055 g, 0.40 mmol) was added to a vigorously stirred solution of **1** [generated in situ from dipp-dabqdiH$_2$ (0.16 g, 0.20 mmol) and 2 equiv of Li^{n}Bu (26 mg, 0.40 mmol)] in thf (30 mL) at −78 °C. The resulting solution was warmed to room temperature and stirred for 3 days. It was then filtered and the filtrate was concentrated to ca. 5 mL. Slow evaporation at −20 °C for several days gave the product **4** as purple crystals (crystal yield: 0.27 g, 86%). ^{1}H NMR (400 MHz, C_6D_6, 298 K, TMS): δ 1.23 (d, J = 7.2 Hz, 24H, CH(C*H*$_3$)$_2$), 1.28 (24H, thf), 1.53 (d, J = 6.4 Hz, 24H, CH(C*H*$_3$)$_2$), 3.42 (24H, thf), 3.68 (m, 8H, C*H*(CH$_3$)$_2$), 4.86 (s, 2H, N···C···C–*H*), 7.02–7.12 (m, 12H, C*H*-aryl). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 25.2, 25.4 (CH(CH$_3$)$_2$), 25.5 (thf), 28.5 (CH(CH$_3$)$_2$), 67.9 (thf), 88.8 (C···C–H), 123.8 (p-C_6H_3), 125.5 (m-C_6H_3), 143.1 (o-C_6H_3), 143.5 (i-C_6H_3), 162.4 (C···N). IR (KBr): ν (cm^{-1}) 3060, 3023, 2980, 2925, 2882, 2819, 2721, 1601, 1556, 1495, 1455, 1366, 1290, 1247, 1194, 1110, 1030, 984, 940, 854, 797, 751, 734, 695, 673, 540. Anal. Calc. for $C_{84}H_{132}N_4O_6Cl_4Li_2Zn_2$ (1494.27): C, 62.70; H, 7.96; N, 3.75. Found: C, 63.14; H, 8.18; N, 3.39.

*Synthesis of [(dme)$_2$Li(μ-Cl)ClZn(μ-dipp-dabqdi)ZnCl(μ-Cl)Li(dme)$_2$] (**5**).* Complex **5** was prepared by a similar procedure to that employed for **4**, except for in dme (30 mL). Purple crystals (0.23 g, 80%) were isolated. ^{1}H NMR (400 MHz, C_6D_6, 298 K, TMS): δ 1.24 (d, J = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.55 (d, J = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 3.09 (16H, dme), 3.28 (24H, dme), 3.70 (m, 8H, C*H*(CH$_3$)$_2$), 4.89 (s, 2H, N···C···C–*H*), 6.95–7.12 (m, 12H, C*H*-aryl). IR (KBr): ν (cm^{-1}) 3061, 3027, 2978, 2920, 2875, 2816, 1605, 1574, 1523, 1496, 1459, 1379, 1366, 1287, 1245, 1192, 1110, 1081, 1030, 983, 939, 897, 853, 799, 786, 728, 695, 541. Anal. Calc. for $C_{70}H_{110}N_4O_8Cl_4Li_2Zn_2$ (1422.04): C, 59.12; H, 7.80; N, 3.94. Found: C, 59.53; H, 7.96; N, 3.68.

*Synthesis of [(dme)$_2$Na(μ-Cl)$_2$Zn(μ-dipp-dabqdi)Zn(μ-Cl)$_2$Na(dme)$_2$] (**6**).* Anhydrous $ZnCl_2$ (0.055 g; 0.40 mmol) was added to a vigorously stirred solution of **2** in dme [generated in situ from dipp-dabqdiH$_2$ (0.16 g, 0.20 mmol) and 2 equiv of sodium (0.020 g; 0.40 mmol)]. The mixture was stirred for 3 days at room temperature. It was then filtered and the filtrate was concentrated to ca. 5 mL. Slow evaporation at −20 °C for several days gave the product **6** as purple crystals (crystal yield: 0.26 g, 87%). ^{1}H NMR (400 MHz, C_6D_6, 298 K, TMS): δ 1.26 (d, J = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.37 (d, J = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 3.11 (24H, dme), 3.28 (16H, dme), 3.58 (m, 8H, C*H*(CH$_3$)$_2$), 5.15 (s, 2H, N···C···C–*H*), 6.99–7.12 (m, 12H, C*H*-aryl). IR (KBr): ν (cm^{-1}) 3058, 2982, 2924, 2880, 2819, 2721, 1604, 1560, 1498, 1455, 1400, 1365, 1328, 1293, 1247, 1194, 1109, 1029, 983, 937, 852, 801, 753, 734, 696, 539. Anal. Calc. for $C_{70}H_{110}N_4O_8Cl_4Na_2Zn_2$ (1454.22): C, 57.81; H, 7.62; N, 3.85. Found: C, 58.04; H, 7.74; N, 3.63.

X-ray Crystal Structure Determination. Diffraction data for the ligand dipp-dabqdiaH_2, tetramine dipp-tabH_4, and complexes **1**−**6** were collected on a Bruker SMART APEX II diffractometer at room temperature (293 K) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS[14] was applied for all data. The structures were solved by direct methods using the SHELXS[15] program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the SHELXL program.[15] Hydrogen atoms bonded to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. SQUEEZE/PLATON was employed to treat one highly disordered toluene molecule in **5**. CCDC numbers 867873−867880.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

DFT computations and detailed information of the X-ray crystal structure analysis of the ligand dipp-dabqdiaH_2, tetramine dipp-tabH_4, and complexes **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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