Electronic Structures Hot Paper

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Tuning Ground States of Bis(triarylamine) Dications: From a Closed-Shell Singlet to a Diradicaloid with an Excited Triplet State**

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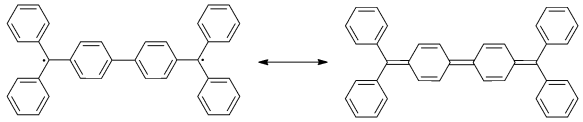
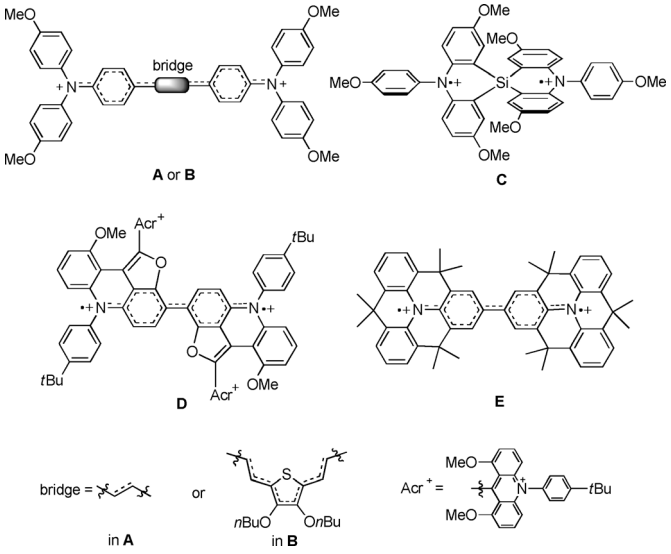
Abstract: *Three bis(triarylamine) dications were isolated by using weakly coordinating anions. Their electronic structures in the ground state were investigated by various experiments in conjunction with theoretical calculations. The ground-state electronic structures of these species were tunable by substituent effects, with two of them as closed-shell singlets and one of them as an open-shell singlet in the solid state. The excited state of the latter is thermally accessible, indicated by EPR and SQUID measurements. The work provides a new and stable diradicaloid structure motif with an excited triplet sate.*

Molecules with partial singlet diradical nature in their ground state, that is, singlet diradicaloids, are not only important for understanding the nature of chemical bonds, but also expected to have interesting physical properties (optical, electronic, magnetic, etc.) and promising applications as functional materials in electronic devices, quantum information processing systems, lithium ion batteries, and organic spintronics.[1,2] Stable and isolable diradicaloids delocalized over π-conjugated systems have attracted much attention, and their synthesis, structure, and electronic properties have been extensively studied in conjunction with theoretical calculations.[1d,2] Among them, Chichibabin's hydrocarbon,[3] which was synthesized shortly after Gomberg discovered the triphenylmethyl radical,[4] has been the subject of interest over 100 years. Structural analysis and various spectroscopic studies indicate that Chichibabin's hydrocarbon possesses a characteristic resonance structure between an open-shell diradical and a closed-shell quinonoid form (Scheme 1).[3] However, Chichibabin's hydrocarbon and its derivatives readily undergo oxidation, dimerization, polymerization, and decomposition, which has prevented their further investigation and practical application.[2a] It is therefore essential to explore novel and stable structural motifs with diradical character.



Scheme 1. Chichibabin's hydrocarbon.

On the other hand, bipolarons, conjugated molecules or polymers with two positive charges located in the center of the chain or at their termini, play significant roles in conducting polymers and some of them are reported to have enhanced nonlinear optical properties.[5,6] Bis(triarylamine)-based materials have a wide range of applications in electrical conductivity, electroluminescence, organic light-emitting devices, polymer batteries, and photorefractive materials.[7] While monoradical cations of bis(triarylamine) systems have been extensively studied as mixed-valence (MV) compounds for the investigation of basic electron-transfer phenomena,[8] two-electron oxidation of bis(triarylamine) derivatives have only been randomly studied[1d,9] and their stable dications in the solid state are rare.[10,11] Bis(triarylamine) dications with arylene/vinylene conjugated bridges (**A** and **B**, Scheme 2) were reported to be closed-shell singlets,[10] while bis(triarylamine) dications, spiro-fused by a silicon atom (**C**) or linked by *meta*-phenylenediamine pillars, were shown to be a triplet or an open-shell singlet.[11a,b]



Scheme 2. Bridged bis(triarylamine) dications and tetracations.

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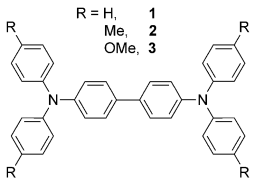
A bis(acridine) tetracation (**D**) was serendipitously obtained and characterized as a singlet diradicaloid with excellent two-photon absorptions.[12] We recently also unexpectedly isolated a methylene-bridged dication (**E**) with diradical character during the one-electron oxidation of a methylene-bridged triarylamine.[13a] It appears that bridging plays an important role in the stabilization of these reactive species. The excited triplet states of both **D** and **E**, however, are not thermally accessible. Other related dicationic species with diradical character include *para*-phenylenedihydrazine- and dianisylamine-substituted squaraine dications.[11c,d]

Recently, we have demonstrated that the weakly coordinating anion $[Al(OR_F)_4]^-$ ($OR_F = OC(CF_3)_3$) is an efficient tool to stabilize reactive organic radical cations and dications.[13,14] Herein, we present our investigation of the double-oxidation of parent bis(triphenylamine) and its derivatives (Scheme 3). The resulting tetraphenylbenzidine dications are



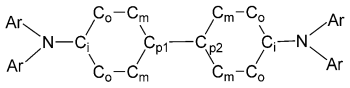
Scheme 3. Bis(triphenylamine) and derivatives.

isoelectronic to Chichibabin's hydrocarbons and expected to have similar resonance structures, and furthermore electron-donating groups may help to delocalize the spin density and possibly increase the diradical character of the dications. The ground-state geometries and electronic structures of these dications were consequently investigated by UV/Vis, EPR, single-crystal X-ray diffraction, and superconducting quantum interference device (SQUID) measurements, in conjunction with DFT calculations.

Neutral compounds **1** and **2** are commercially available. Compound **3** was synthesized under standard Buchwald–Hartwig Pd-catalyzed cross-coupling amination conditions following a reported procedure.[15] Upon oxidation with two equivalents of $Ag[Al(OR_F)_4]$[16] in CH_2Cl_2, the neutral precursors **1**–**3** were converted to dications $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$ in high yields, respectively. These dications are thermally stable as crystals under nitrogen or argon atmosphere and can be stored for several weeks at room temperature.

Crystals suitable for X-ray crystallographic studies were obtained by cooling solutions of salts $\mathbf{1}^{2+}\cdot 2[Al(OR_F)_4]^-$–$\mathbf{3}^{2+}\cdot 2[Al(OR_F)_4]^-$ in CH_2Cl_2.[17] The structures of dications $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$ are illustrated as stereoviews in Figure 1. Their important structural parameters are given in Table 1 and Figures S1–S4 in the Supporting Information. The biphenyl backbone of $\mathbf{1}^{2+}$ is bent and twisted, that of $\mathbf{2}^{2+}$ is planar, while that of $\mathbf{3}^{2+}$ is slightly twisted (Figure 1). Three dications show planar geometries around the nitrogen centers and the average N–C_i bond lengths to the biphenyl moieties are shorter than those to the peripheral aryl ring systems (N–Ar). Table 1 shows clear substituent effects of ground-state electronic structures from $\mathbf{1}^{2+}$ to $\mathbf{3}^{2+}$. The lengths of N–C_i bonds increase while those of N–Ar bonds decrease. The bond (C_{p1}–C_{p2}) between the two triarylamine moieties of $\mathbf{3}^{2+}$ (1.457(7) Å) is slightly shorter than that of a typical biphenyl single bond (1.48 Å), but longer than those of $\mathbf{1}^{2+}$ (1.414(4) Å) and $\mathbf{2}^{2+}$ (1.422(9) Å), thus indicating that $\mathbf{3}^{2+}$ may have a diradical nature. Reduced bond-length alteration (BLA) of a bridged benzene ring has been considered as a signature feature of diradical character in Chichibabin's hydrocarbon and related systems.[3b,10,12] BLA is the difference between C_o–C_m versus C_i–C_o and C_m–C_p in this work (Table 1), which is greatly reduced from $\mathbf{1}^{2+}$ (0.074) to $\mathbf{2}^{2+}$ (0.063) to $\mathbf{3}^{2+}$ (0.037), and that of $\mathbf{3}^{2+}$ is less than that of Chichibabin's hydrocarbon

Table 1: Selected experimental and calculated bond lengths (Å), relative energy (kcal mol^{-1}), maximum absorptions (nm), and diradical character (*y*) for $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$.



	λ_{max}		$\Delta E_{X\text{-}OS}$[a]	avg. N–Ar	avg. N–C_i	C_{p1}–C_{p2}	avg. C_i–C_o and C_m–C_p	avg. C_o-C_m	BLA[b]	*y*
$\mathbf{1}^{2+}$	742	X-ray		1.439(4)	1.339(4)	1.414(4)	1.431(4)	1.357(4)	0.074	0.47
		CS[c,d]	4.0	1.430	1.368	1.434	1.432	1.369	0.063	
		OS[c,e]	0	1.418	1.403	1.470	1.414	1.383	0.031	0.81
		T[c,e]	1.5	1.413	1.418	1.482	1.409	1.387	0.022	
$\mathbf{2}^{2+}$	800	X-ray		1.436(6)	1.365(6)	1.422(9)	1.426(7)	1.363(6)	0.063	0.61
		CS	4.9	1.425	1.374	1.439	1.428	1.371	0.057	
		OS	0	1.413	1.411	1.474	1.411	1.385	0.026	0.85
		T	1.0	1.410	1.421	1.482	1.408	1.388	0.020	
$\mathbf{3}^{2+}$	878	X-ray		1.417(7)	1.383(7)	1.457(7)	1.407(7)	1.370(7)	0.037	0.79
		CS	5.8	1.418	1.386	1.448	1.423	1.375	0.048	
		OS	0	1.409	1.419	1.477	1.408	1.387	0.021	0.88
		T	0.7	1.408	1.425	1.483	1.406	1.389	0.017	

[a] Energy relative to the OS state. X = CS, OS, or T. [b] BLA = bond length alteration, that is, difference between the average of all C_i–C_o and C_m–C_p bond lengths and the average of C_o–C_m bond lengths. [c] CS = closed-shell singlet, OS = open-shell singlet, T = triplet. [d] Calculated at the B3LYP/6-31G(d) level. [e] Optimized at the UB3LYP/6-31G(d) level, and *y* values were calculated at the UBHandHLYP/6-31G(d) level.

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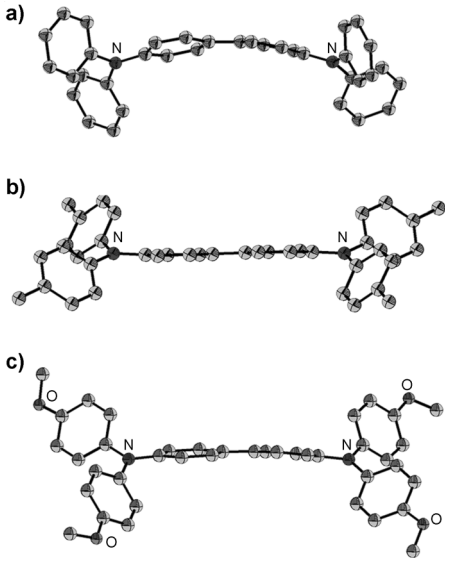
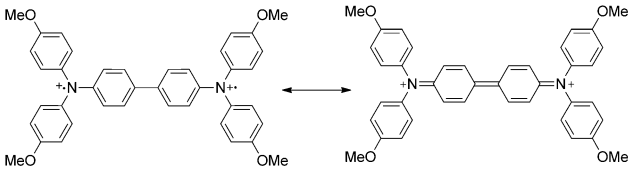


Figure 1. X-ray crystal structures of a) $\mathbf{1}^{2+}$, b) $\mathbf{2}^{2+}$ and c) $\mathbf{3}^{2+}$. Thermal ellipsoid at 50% probability, hydrogen atoms omitted for clarity.

(0.052),[3b,10] thus further supporting the diradical character of $\mathbf{3}^{2+}$.

To further understand the ground-state electronic structures, we carried out calculations for species $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$.[18] Full geometry optimizations were performed at the (U)B3LYP/6–31G(d) level and the obtained stationary points were characterized by frequency calculations. Relative energy, bond lengths, and their alterations (BLAs) in the averages of bonds C_o–C_m, C_i–C_o, and C_m–C_p of the optimized closed-shell singlets, open-shell singlets, and pure diradical triplets, as well as the diradical character *y*, are listed in Table 1. For dications $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$, the calculated energy differences $\Delta E_{CS\text{-}OS}$ between the open-shell singlet diradicals and closed-shell singlet states increase, while singlet–triplet energy gaps $\Delta E_{OS\text{-}T}$ decrease, thus showing clear substituent dependence.[19] The biphenyl moieties of optimized geometries of all closed-shell singlets are almost planar, but those of open-shell states are slightly twisted with dihedral angles increasing from open-shell singlets to triplets. The bent geometry of $\mathbf{1}^{2+}$ in the solid state is probably due to crystal packing.[20] Similar to tetracation bis(acridine) dimer diradicaloid (Table S2 in the Supporting Information),[12] the N–Ar and N–C_i bond lengths of the X-ray crystal structure of $\mathbf{3}^{2+}$ are close to those of their closed-shell singlets, which may decrease its diradical character to some extent. The comparison of BLAs of the X-ray structures, optimized closed-shell singlet, open-shell singlet, and pure diradical triplet structures (Table 1) clearly shows closed-shell singlet configurations for $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$, but a singlet ground state with an intermediate diradical character for $\mathbf{3}^{2+}$, as the BLAs of the X-ray crystal structure and the optimized open-shell singlet of $\mathbf{3}^{2+}$ are found to lie between those for the optimized closed-shell singlet and diradical triplet. Dication $\mathbf{3}^{2+}$ is thus best described as a resonance hybrid of a diradical structure and quinoidal structure (Scheme 4), similar to Chichibabin's hydrocarbon (Scheme 1).

The diradical character *y*, which is estimated by the occupancy of the lowest unoccupied natural orbital (LUNO),



Scheme 4. Resonance structures of $\mathbf{3}^{2+}$.

represents the "degree" of the singlet diradical character.[12] The *y* value of the X-ray structure of $\mathbf{3}^{2+}$ (0.79) at the UBHandHLYP/6-31G(d) level is consistent with that of $\mathbf{3}^{2+}$-OS (0.88; optimized at the UB3LYP/6-31G(d) level) and comparable to that of Chichibabin's hydrocarbon (0.70; Table S2 in the Supporting Information),[21] but higher than that of the recently reported tetracation bis(acridine) dimer (0.615).[12] Mulliken charge and spin density distributions on peripheral aryl rings, nitrogen atoms, and biphenyl rings in $\mathbf{1}^{2+}$-OS to $\mathbf{3}^{2+}$-OS dications clearly show substituent dependence (Table S3 in the Supporting Information). The spin densities are distributed throughout the whole molecules (Figure 2c for $\mathbf{3}^{2+}$-OS), and in $\mathbf{3}^{2+}$-OS the spin density is further delocalized to the oxygen atoms. The stability of $\mathbf{3}^{2+}$-OS is probably ascribed to its lower spin density on nitrogen atoms. The HOMO and LUMO orbitals of $\mathbf{3}^{2+}$-OS are delocalized over one triarylamine unit, and the peripheral aryl rings possess larger coefficients than the aryl ring of the biphenyl moiety (Figure 2a and b).

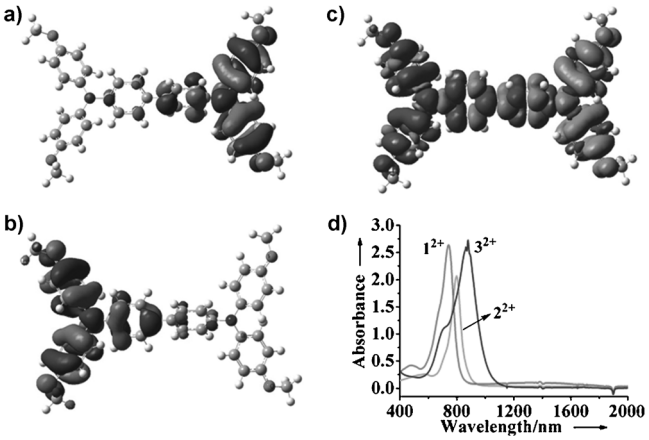


Figure 2. a) LUMO (α) of $\mathbf{3}^{2+}$-OS, b) HOMO (α) of $\mathbf{3}^{2+}$-OS, c) spin densities of $\mathbf{3}^{2+}$-OS, calculated at the UB3LYP/6-31G(d) level, and d) absorption spectra of $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$ (1×10^{-4} M in CH_2Cl_2) at 25 °C.

The diradical character of $\mathbf{3}^{2+}$ is consistent with its maximum absorption in the near-infrared region (878 nm, Figure 2d), which is higher than those of $\mathbf{1}^{2+}$ (742 nm) and $\mathbf{2}^{2+}$ (800 nm). TD-DFT calculation at the UPBE0/6-31G(d) level on the open-shell singlet geometry of $\mathbf{3}^{2+}$ indicates that the maximum absorption is due to HOMO→LUMO transition, and in good agreement with the experimental absorption (Figure S11 in the Supporting Information). The small HOMO–LUMO gap is a typical feature for a high singlet

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diradical character in the ground state. The absorptions of dications are distinct from those of monocations $\mathbf{1}^{\bullet+}$–$\mathbf{3}^{\bullet+}$ purposely prepared upon one-electron oxidations of **1**–**3** (Figures S6–S8 in the Supporting Information), which are broad and in the region of 1400-1600 nm, and are assigned to the SOMO→LUMO and HOMO→SOMO excitations.[22]

Variable temperature (VT) NMR measurements are used for the detection of open-shell singlet ground states, as the broad resonances of singlet diradical species in ^{1}H NMR spectra become sharper at lower temperatures.[12] However, in the cases of $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$, such sharpening could not be observed because of the presence of monoradical cation residues. To gain information on whether $\mathbf{3}^{2+}$ has an open-shell electronic structure, we recorded an EPR spectrum of the solid and conducted SQUID measurements.

Solution- and solid-state EPR spectra of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ exhibited no signals, apart from the signal of monoradical cation residues, even at elevated temperatures (up to 350 K), which is ascribed to their closed-shell singlet ground states. The solution of $\mathbf{3}^{2+}$ was also EPR silent, which may be due to the low spin concentration in its dilute solution. The powder EPR spectrum of $\mathbf{3}^{2+}\cdot 2[Al(OR_F)_4]^-$, however, is typical of a triplet state with a zero-field parameter of $D = 9.45$ mT (8.84×10^{-3} cm^{-1}) and $E = 0.92$ mT (8.60×10^{-4} cm^{-1}) determined by spectral simulation (Figure 3a and b). The g factor is anisotropic with $g_x = 2.0051$, $g_y = 2.0036$, and $g_z = 2.0043$. The hyperfine coupling constant with N atoms is $A_{xx}(N) = 0$, $A_{yy}(N) = 1.11$, and $A_{zz}(N) = 0$ mT, respectively. The average spin–spin distance was estimated from D to be 6.6 Å, which is smaller than the distance (9.8 Å) between the two N atoms in the X-ray structure. This suggests that an unpaired electron is not only localized on one triarylamine unit, but delocalized on the other triarylamine unit, similar to reported bisphenalenyl diradicaloids.[23] The forbidden $\Delta m_s = \pm 2$ half-field absorption was also observed. The distinct fine structure attributed to spin-triplet species, together with the forbidden resonance resulting from $\Delta m_s = \pm 2$, unambiguously indicates that $\mathbf{3}^{2+}$ is a di(cation radical).

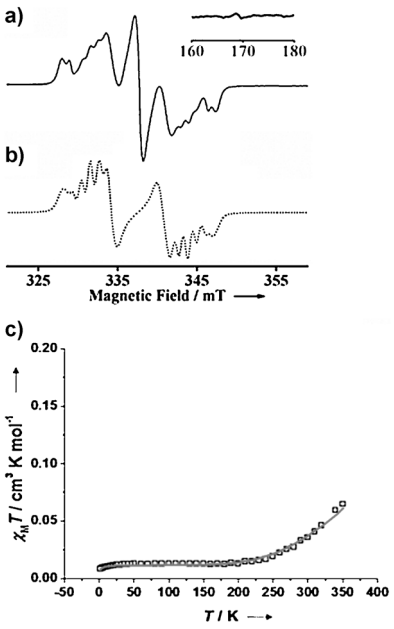

Figure 3. a) Powder EPR spectrum of $\mathbf{3}^{2+}$ at 320 K. The central peak shows the signal derived from a monoradical impurity. b) Simulated EPR spectrum, and c) χT versus T curve for the powder of $\mathbf{3}^{2+}$ in SQUID measurements, and the fitting plots obtained with the Bleaney–Bowers equation.

SQUID measurements for $\mathbf{3}^{2+}$ in the powder form at 5–350 K show an increasing susceptibility above 200 K (Figure 3c) that can be well fitted with the Bleaney–Bowers equation.[24] The singlet–triplet energy gap was estimated to be $2J = -2.8$ kcal mol^{-1},[25] indicating that $\mathbf{3}^{2+}$ has a singlet open-shell ground state, which can be thermally excited to its triplet excited state at room temperature as a result of the small singlet–triplet energy gap. In contrast, SQUID measurements on $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ only showed diamagnetism (Figures S9 and S10 in the Supporting Information), consistent with their closed-shell singlet ground states.

In conclusion, a class of bis(triarylamine) dications, analogues of Chichibabin's hydrocarbons, were stabilized and isolated by using weakly coordinating anions, and their structures in the ground state were investigated by various experiments in conjunction with theoretical calculations. The work demonstrated an interesting substituent dependence of the structures, energy gaps, diradical character, and spectroscopic as well as magnetic properties. The ground-state electronic structures of these species were tunable with $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ as closed-shell singlets, and $\mathbf{3}^{2+}$ as an open-shell singlet diradicaloid in the solid state. Such a tuning was achieved by modification of triarylamines with donor substituents at the *para* positions and the recovery of aromaticity, that is, reduced BLAs, of the quinoidal benzene rings in the forms of diradicaloids. EPR and SQUID measurements indicated that the excited state of $\mathbf{3}^{2+}$ is readily thermally accessible as a result of its smaller singlet–triplet energy gap. The work provides a new and stable structural motif with diradical character. It is expected that more dications based on OMe-substituted systems featuring diradical character may be accessible by using weakly coordinating anions. Investigation of the application of these unique dication systems to functional materials is under way, and the results will be reported in due course.

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Keywords: bis(triarylamine) · cations · radicals · substituent effects · triplet state

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[17] X-ray data for $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$ are listed in Table S1 in the Supporting Information. CCDC 957061 ($\mathbf{1}\cdot 2[Al(OR_F)_4]$), 957062 ($\mathbf{3}\cdot 2[Al(OR_F)_4]$), and 957063 ($\mathbf{2}\cdot 2[Al(OR_F)_4]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[18] All calculations were performed using the Gaussian 09 program suite. Gaussian 09, Revision B.01, M. J. Frisch, et al. Gaussian, Inc.: Wallingford, CT, **2010**. See the Supporting Information for coordinates and full citation.

[19] It is worth noting that the most stable electronic states for $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ are the open-shell singlets in the gas phase (Table 1). Such a difference between the calculation and experimental observation may be ascribed to a counterion effect. For example,[10] bis(triarylamine) dications with arylene/vinylene conjugated bridges were reported to be closed-shell singlets in the solid state, but their open-shell singlets have the lowest energy in the gas phase (see Table S6 in Ref. [10]).

[20] A planar structure of $\mathbf{1}^{2+}$ with anion $[Al(OR_H)_4]^-$ ($OR_H = OC(CF_3)_2H$) was observed from the reaction of **1** with two equivalents of $Ag[Al(OR_H)_4]$, thus indicating that the geometry of $\mathbf{1}^{2+}$ is dependent on the anion and the crystal packing. For the synthesis, characterization, and X-ray structure of $\mathbf{1}^{2+}$ (in $\mathbf{1}\cdot 2[Al(OR_H)_4]$), see the Supporting Information.

[21] Calculated at the UBHandHLYP/6-31G(d) level on the reported X-ray crystal structure.[3b]

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