

Hydrogen Bonds

Redox-Controlled Hydrogen Bonding: Turning a Superbase into a Strong Hydrogen-Bond Donor

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Abstract: Herein the synthesis, structures and properties of hydrogen-bonded aggregates involving redox-active guanidine superbases are reported. Reversible hydrogen bonding is switched on by oxidation of the hydrogen-donor unit, and leads to formation of aggregates in which the hydrogenbond donor unit is sandwiched by two hydrogen-bond acceptor units. Further oxidation (of the acceptor units) leads again to deaggregation. Aggregate formation is associated with a distinct color change, and the electronic situation could be described as a frozen stage on the way to hydrogen transfer. A further increase in the basicity of the hydrogen-bond acceptor leads to deprotonation reactions.

Introduction

Hydrogen-bonding^[1-3] is considered as the master key of molecular recognition and is of extreme importance for supramolecular and biological assemblies.^[4,5] Especially cooperativity, meaning the combination of several hydrogen-bonding interactions, could lead to a strong total stabilization,^[6] and consequently much effort has been spent into synthesizing receptor-type molecules with several sites suitable for hydrogenbonding.^[7-11] Multiple hydrogen bonding can be used, for example, to self-assemble guanine derivatives into macrocycles or ribbon-like aggregates.^[12,13] For a strong bonding in a hydrogen-bonded dimer it is obviously advantageous that the hydrogen-bond donor (D) and acceptor (A) sites are preorganized.^[14,15] With relevance to this work, a guanidinium salt was recently synthesized which contains four donor atoms for hydrogen bonding arranged in a linear array, and was combined with a suitable molecule with four acceptor atoms, building a AAAA-DDDD quadruple hydrogen-bond array (Scheme 1).^[14] A hydrogen bond is composed of electrostatic, induction, charge-transfer and dispersion contributions, but electrostatic interactions generally dominate.^[16] Therefore, it is not surpris-



Scheme 1. Linear array of hydrogen bonding interactions involving guanidinium salts.

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ing that oxidation of the hydrogen-bond donor or reduction of the hydrogen-bond acceptor component strengthens the bond. A variety of redox-active molecules were studied in which hydrogen bonding is greatly enhanced upon electron transfer, leading in some cases to "redox-controlled switches".^[17-19] Redox-active metallocenes were used in some reported receptors, in which hydrogen bonding is strengthened by oxidation. Two examples are shown in Scheme 2.^[17]



Scheme 2. Two literature examples for strengthening of hydrogen bonding upon oxidation of the hydrogen-bond donor unit.

One-electron oxidation of the ferrocenyl unit, but also oneelectron reduction of the flavine derivative sketched in Scheme 2a strengthen the hydrogen bond by one order of magnitude. Examples for receptors in which hydrogen bonding is strengthened by reduction of the hydrogen-bond acceptor component include *o*-quinones, naphthalimide and also nitrobenzene.^[18] Using the same concepts it was also possible to build electrochemically switchable hydrogen-bonded molecular shuttles.^[20] In a very recent publication, a molecular shuttle was reported in which photolysis causes, in the presence of an

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electron donor, reduction of a hydrogen acceptor unit initiating movement of a hydrogen-bond donor unit to this now preferred site, and the authors show the influence of added water on the rate of this process.^[21]

Guanidines are known as strong bases, and have been intensively used in the past,^[22] especially for the synthesis of proton sponges^[23] and in coordination chemistry.^[24,25] In the last years we have developed guanidinyl-functionalized aromatic compounds, such as 1,2,4,5-tetrakis(tetramethylguanidinyl)benzene (1),^[26,27] and 1,2,4,5-tetrakis(*N*,*N'*-dimethylethylene-guanidinyl)benzene (2),^[28] as strong organic electron donors (Scheme 3). We denoted this class of molecule GFA-*n* (GFA = guanidinyl-functionalized aromatic compound, *n* being the number of guanidinyl groups).^[29] Compounds 1 and 2, which will both be applied in this work, simultaneously lose two electrons at $E_{1/2}$ (CH₂Cl₂) = -0.76 V versus Fc/Fc⁺ for 1 and -0.79 V for 2.^[29-31] In the oxidized form, the aromaticity is lost and the dication is



Scheme 3. The two known GFA-4 compounds 1 (ttmgb) and 2 (tdmegb) and preparation of the new compound 3, which is oxidized to the dication and hydrogen-bond donor 3^{2+} .

best described as a pair of bisguanidinyl allyl cations connected by two C–C single bonds. The positive charge is delocalized into the guanidinyl groups. Moreover, GFAs are strong Brønsted bases, and **2** was even shown to deprotonate CH₃CN in the presence of PhAuCl, resulting in formation of a gold–cyanomethyl complex.^[28] Herein we now report the construction of a first redox-controlled switch with GFAs as hydrogen-bond donor units. For this purpose, the dimethylamino groups (NMe₂) of the guanidinyl functions had to be replaced by NHR groups (R = alkyl or aryl). We, therefore, prepared the new redox-active GFA-4 compound 1,2,4,5-tetrakis(diisopropylguanidinyl)benzene (**3**; Scheme 3), which features in total eight N–H groups for hydrogen bonding.

Results and Discussion

The new compound 1,2,4,5-tetrakis(N,N'-diisopropylguanidinyl)-benzene (**3**) was prepared by reaction between 1,2,4,5-tetraamino-benzene and diisopropylcarbodiimide with 2 mol% of Full Paper

Figure 1. Molecular structure of **3**. Vibrational ellipsoids are drawn at the 50% probability level. Hydrogen atoms attached to C atoms omitted for clarity. Selected structural parameters (bond lengths in Å, angles in deg): N1–C2 1.423(5), N1–C4 1.283(5), N2–C4 1.374(5), N3–C4 1.369(5), N4–C3 1.405(5), N4–C11 1.310(5), N5–C11 1.350(5), N6–C11 1.375(5), C1–C2 1.400(5), C2–C3 1.409(5), C3–C1' 1.392(5), C2-N1-C4 119.9(3), C3-N4-C11 118.8(3).

Zn(OTf)₂ as catalyst. Pale yellow crystals of 3 precipitated from CH₃CN solutions, and its molecular structure is illustrated in Figure 1. The molecules display crystallographic inversion symmetry with two half-molecules in the asymmetric unit. The N=C bond lengths measure in average 1.299(5) Å, and the N···N separation (N1...N4) between the imino N atoms of adjacent guanidinyl groups measures 2.979(5) Å. The crystal structure data showed no sign of a significant intermolecular interaction in the solid state. The UV/Vis spectra recorded for 3 in solution are similar to those of 1 and 2, for which aggregation via hy-

drogen-bridges is not possible. Hence the molecules do not aggregate in the solid state or in solution. Compound 3 was subsequently oxidized with the two ferrocenium (Fc) salts $Fc[B(C_6F_5)_4]$ and $Fc[B(Ar^F)_4]$ (where $B(Ar^F)_4^$ denotes $B[(3,5-(CF_3)_2C_6H_3]_4^-)$. We crystallized the two salts $[(3)(thf)_2 (dioxane)][B(C_6F_5)_4]_2$ and $[3(Et_2O)_4][B(Ar^F)_4]_2$. In both structures, solvent ether molecules are coordinated via hydrogen bonds to the dications 3^{2+} , demonstrating already the hydrogendonor capacity of the oxidized GFA. The two structures are shown in Figure 2a and b. Upon oxidation, two C-C lengths within the C₆ ring (the C atoms which are directly bonded to guanidinyl) increase from 1.409(5) Å in neutral 3 to 1.503(3) Å in $[(3)(thf)_2(dioxane)]^{2+}$ and 1.506(3) Å in $[3(Et_2O)_4]^{2+}$. The other C-C lengths in the C₆ ring shrink, in line with the description of the dication as a pair of bis-guanidinyl-allyl cations connected by two C-C single bonds (see the Lewis structure in Scheme 3). Structural changes are also registered for the guanidinyl units. Hence, the shortest bond, the imino CN bond, is elongated and the other CN bonds shrink, signaling delocaliza-

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Figure 2. Crystal structures of: a) [(3)(thf)₂(dioxane)][B(C₆F₅)₄]₂ (only the cationic portion is shown), b) $[(3)(Et_2O)_4][B(Ar^F)_4]_2$ (only one of the two independent dications is shown), and c) 3(dca)₂. Vibrational ellipsoids are drawn at the 50% probability level. Hydrogen atoms attached to C atoms omitted for clarity. Selected bond lengths (Å) for [(3)(thf)₂(dioxane)][B(C₆F₅)₄]₂: N1-C1 1.306(3), N1-C4 1.361(3), N2-C4 1.338(3), N3-C4 1.330(3), N4-C2 1.342(3), N4-C11 1.344(3), N5-C11 1.340(3), N6-C11 1.336(3), C1-C2 1.503(3), C1-C3 1.418(3), C2-C3 1.378(3), N3H···O1 2.337(6), N5H···O3 1.883(4). Selected bond lengths (Å) for [(3)(Et₂O)₄][B(Ar^F)₄]₂: N1···N4 2.623(2), N1-C1 1.318(3), N1-C4 1.350(3), N2-C4 1.340(3), N3-C4 1.322(3), N4-C2 1.312(3), N5-C11 1.336(3), N6-C11 1.346(3), C1-C2' 1.506(3), C1-C3 1.397(3), C2-C3 1.395(3), N2H-O2 2.073(3), N3H-O2 2.28(1), N5H-O2 2.333(7), N6H-O2 2.16(2). Selected structural parameters (bond lengths in Å, angles in deg) for 3(dca)₂: N1-C1' 1.362(2), N1-C4 1.330(2), N2-C4 1.344(2), N3-C4 1.352(2), N4-C2 1.300(2), N4-C11 1.367(2), N5-C11 1.329(2), N6-C11 1.322(2), N7-C18 1.310(2), N7-C19 1.311(3), N8-C18 1.154(2), N9-C19 1.167(2), C1-C2 1.503(2), C1-C3' 1.364(2), C2-C3 1.432(2), N5H···N8' 2.156(3), N6H···N9 2.161(2), C18-N7-C19 121.23(16).

tion of the positive charge equally into all guanidinyl units. In the olive-green colored salt $[(3)(thf)_2(dioxane)][B(C_6F_5)_4]_2$, two of the four guanidinyl groups are connected to a thf molecule, leading to short NH--O distances of 1.83(4) Å, and the other two guanidinyl groups are connected to dioxane molecules, which interconnect the $\mathbf{3}^{2+}$ dications. In the case of $[\mathbf{3}(Et_2O)_4]$ $[B(Ar^{F})_{4}]_{2}$, each guanidinyl group of $\mathbf{3}^{2+}$ establishes two NH···O hydrogen bonds of 2.16(2) and 2.333(7) Å length to a co-crystallized Et₂O molecule. In the ¹H NMR spectrum (in CH₃CN), the N–H protons give rise for a signal at $\delta = 5.95$ ppm for both [(3) $(thf)_2(dioxane)][B(C_6F_5)_4]_2$ and $[3(Et_2O)_4][B(Ar^F)_4]_2$. The crystals of $[(3)(thf)_2(dioxane)][B(C_6F_5)_4]_2$ are green-colored. The green color is typical for oxidized GFA compounds, and was also observed, for example, in the case of 1^{2+} and 2^{2+} . Interestingly, the $[3(Et_2O)_4][B(Ar^F)_4]_2$ crystals are initially orange-colored and change their color over time to green when kept for a week under an Ar atmosphere or for 1 h under vacuum, leading to evaporation of the hydrogen-bonded Et₂O molecules. We have included a photograph of a crystal after partial removal of the Et₂O molecules in the Supporting Information (Figure S1). Hence it appears that hydrogen bonding could change the electronic properties (see Discussion below). In addition we prepared the salt $3(dca)_2$ (dca⁻ = dicyanamide, N(CN)₂⁻) as product of the reaction between 3 and two equivalents of Ag(dca). This salt again immediately gives green-colored crystals. The crystal structure also shows hydrogen bonding, leading to chains (Figure 2 c). The ¹H NMR spectrum (measured again in CH₃CN) is similar to that of $[3(Et_2O)_4][B(Ar^F)_4]_2$, but the N–H protons occur at lower field (δ =6.50 ppm). The compound is a potential precursor to C,N materials (carbon, e.g., graphitic, network in which some C atoms are replaced by N atoms),^[32] and its thermogravimetric (TG) and differential scanning calorimetric (DSC) curves are displayed and discussed in the Supporting Information (Figure S2 and text). Subsequently, the $[B(C_6F_5)_4]^-$ and $[B(Ar^F)_4]^-$ salts of the oxidized GFA 3 were used as starting reagents for the synthesis of hydrogen-bonded aggregates.

First, we tested hydrogen-bond formation between dicationic and neutral **3**. Experiments, in which the salt $3[B(C_6F_5)_4]_2$ was treated with slightly more than two equivalents of neutral **3**, indeed resulted in formation of the salt $[(3)_3][B(C_6F_5)_4]_2$ (orangecolored crystals). Hydrogen bonding, which is switched on by oxidation, leads to an aggregate in which the hydrogen-bond donor 3^{2+} is sandwiched between two units of neutral **3**. Further oxidation leads to deaggregation (Scheme 4). The structure of the hydrogen-bonded cationic assembly as obtained from XRD analysis is shown in Figure 3a. In total eight NH-··N interactions, involving the NH protons of 3^{2+} and the imino



Scheme 4. Reversible formation of the hydrogen-bonded aggregate by electron transfer.

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Figure 3. Structures of the dications: a) $[(3)_3]^{2+}$, b) $[(1)_2(3)]^{2+}$, and c) $[(2)_2(3)]^{2+}$ (the anions $B(C_6F_5)_4^{-}$ are not shown). Vibrational ellipsoids are drawn at the 50% probability level. Hydrogen atoms attached to C atoms omitted for clarity. A list of bond lengths and angles for each structure can be found the Supporting Information.

N atoms of neutral **3** stabilize the structure. Further experiments showed that the dication 3^{2+} could also form hydrogen-bonded aggregates with **1** and **2**. The structures of the two aggregates $[(1)_2(3)][B(C_6F_5)_4]_2$ and $[(2)_2(3)][B(C_6F_5)_4]_2$ (both orange-colored solids), being the products of the reaction between (**3**)[B(C_6F_5)_4]_2 and slightly more than two equivalents of neutral **1** or **2**, are displayed in Figure 3 b and c. Further details of the structures and some bond parameters can be found in Figures S3–S5 in the Supporting Information. The three dications $[(3)_3]^{2+}$, $[(1)_2(3)]^{2+}$ and $[(2)_2(3)]^{2+}$ also formed in experiments in which $3[B(Ar^F)_4]_2$ was treated with two equivalents of the neutral compounds **3**, **1** or **2**, but the crystals were of poorer quality. Nevertheless, the structural parameters of the dicationic aggregate units were very similar indicating that the influence of the anions or crystal packing is small.

In all three aggregates $[(3)_3]^{2+}$, $[(1)_2(3)]^{2+}$ and $[(2)_2(3)]^{2+}$, eight NH-N interactions dominate and strongly connect the central dication $\mathbf{3}^{2+}$ with the two neutral guanidine units. Nevertheless, the structures show some differences. In $[(2)_2(3)]$ $[B(C_6F_5)_4]_2$, all guanidinyl groups are involved in hydrogen bonding, and the NH-N distances cover a relatively narrow range of 2.030-2.282 Å (average value: 2.128 Å). This symmetric structure is in line with the short N-N distances between adjacent imino N atoms in the two neutral units of 2 (2.760(3) and 2.753(3) Å), which match relatively well the separations of 2.229(2) and 2.243(2) Å between the relevant hydrogen atoms of the central 3^{2+} dicationic unit (see Figure 3 c and the visualization of the hydrogen array in Figure S5 in the Supporting Information). In $[(\mathbf{3})_3][B(C_6F_5)_4]_2$, the N···N distances between adjacent imino N atoms in the two neutral units of 3 measure 2.864(5) and 2.803(5) Å. This results in a more asymmetric structure, since the values already do not ideally match the

separations of 2.255(4) and 2.227(5) Å between the relevant hydrogen atoms of the central 3^{2+} dicationic unit. Consequently, only three of the four guanidinyl groups of each neutral 3 unit are engaged in significant hydrogen bonding (Figure 3a). There are still eight NH-N interactions, since one of the imino N atoms of each hydrogen-bond acceptor unit is engaged in two interactions. However, the average value of 2.242 Å is larger, and the bond lengths cover a larger range of 1.988-2.592 Å. Finally, in $[(1)_2(3)][B(C_6F_5)_4]_2$, only two of the four guanidinyl groups in each neutral 1 unit are involved in hydrogen bonding. The N···N distances between adjacent imino N atoms in the two neutral units of 1 adopt values of 2.855(5) and 2.867(4) Å, which do not fit with the separations of 2.155 and 2.210 Å between the relevant hydrogen atoms of the central 3^{2+} dicationic unit. Nevertheless, also in this case eight NH-N interactions could be identified, now with an average value of 2.202 Å, covering the range 2.029-2.363 Å. The difference in hydrogen bonding has consequences on the angle between the C₆ ring plane of the central $\mathbf{3}^{2+}$ donor unit and the C₆ ring plane of the neutral acceptor units. Hence this dihedral angle decreases in the order: $[(2)_2(3)]^{2+}$ $(94.5^{\circ}) > [(3)_3]^{2+}$ $(81.1^{\circ}) >$ $[(1)_2(3)]^{2+}$ (33.7°).

The optical properties of the aggregates clearly differ from those of the components. As example, photographs of crystalline **3**, green-colored **3**[B(Ar^F)₄]₂ and orange-colored [(**3**)₃] [B(Ar^F)₄]₂ are shown in Figure 4a. In addition, the diffuse reflectance spectra, recorded in a BaSO₄ matrix, for the three compounds are compared in Figure 4b. The spectrum of [**3**(Et₂O)_n] [B(Ar^F)₄]₂ (n < 4) is also included. In the case of pale-yellow **3**, the lowest energy band is located at 420 nm. Olive-colored [**3**(Et₂O)_n][B(Ar^F)₄]₂ (n < 4) gives a spectrum with a band at 433 nm, but in addition a band centered at 611 nm and

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Figure 4. a) Photographs of crystals of **3**, **3**[B(Ar^{F)}₁₄]₂ and [(**3**)₃][B(Ar^{F)}₁₄]₂. b) Diffuse reflectance spectra for **3**, [**3**(Et₂0)_n][B(Ar^{F)}₁₄]₂, **3**[B(Ar^{F)}₁₄]₂, and [(**3**)₃] [B(Ar^{F)}₁₄]₂ in a BaSO₄ matrix. To allow for a better comparison, the spectra were plotted on top of each other by adding a constant to the diffuse reflectance values. The original spectra with the diffuse reflectance values given in percentages are displayed in the Supporting Information.

a weaker extremely broad absorption in the region 750-710 nm. If the material is kept for several hours under vacuum to remove all the Et₂O molecules, the color changes to intense green and a very broad absorption in the region 760-710 nm gains in intensity. In the aggregate $[(\mathbf{3})_3][B(Ar^F)_4]_2$, a band around 560 nm is found (in addition to a band at 409 nm). Similar results are obtained for the other aggregate salts. A full list of the absorptions for all relevant compounds is given in Table 1 (the original spectra are displayed in Figure S6 in the Supporting Information). Hydrogen bonding thus clearly significantly influences the energies of the frontier orbitals. We interpret the situation as a frozen stage on the way to deprotonation of 3^{2+} .

Such a deprotonation is indeed possible if stronger bases are applied. Hence, when $3[B(Ar^F)_4]_2$ was treated with the superbase and proton sponge 1,4,5,8-tetrakis(tetramethylguanidinyl)-naphthalene (4)^[33,34] we observed, instead of formation of a hydrogen-bonded aggregate, double proton abstraction leading from the dication 3^{2+} to the neutral compound **5** (Scheme 5). In this case the intramolecular NH···N bridges in the protonated proton sponge **4** replace the NH···N bonds between the donor and acceptor units of the hydrogen-bonded aggregate. Red-colored crystals of **5** were obtained after layering the CH₂Cl₂/Et₂O solutions with petroleum ether 30/75. Its structure is shown in Figure 5. The diffuse reflectance spectrum of **5** displays in the visible region a broad band centered at



Figure 5. Structure of 5. Selected bond lengths [Å]: N1–C1 1.297(4), N1–C4 1.407(4), N2–C4 1.372(4), N3–C4 1.290(4), N4–C2 1.366(3), N4–C11 1.309(3), N5–C11 1.367(4), N6–C11 1.362(3), C1–C2 1.502(4), C1–C3 1.443(4), C2–C3' 1.365(4).

Compound	nd Wavelength for maxima of absorption [nm]						
3			420	340	291		
2			421	340	292	260	
1			431	350 (sh)	320	270	
5		530	416	390 (sh)	280		
$[3(Et_2O)_n][B(Ar^F)_4]_2$	750–710 (broad) ^[a]	611	433		266		
$3[B(Ar^{F})_{4}]_{2}$	760–710 (broad) ^[a]	625	430		277		
$[(3)(thf)_2(dioxane)] [B(C_6F_5)_4]_2$	750–680 (broad) ^[a]	600	433		292	263	
$3[B(C_6F_5)_4]_2$	740–640 (broad) ^[a]	601	434		295	265	
3(dca) ₂	780–740 (broad) ^[a]	605	429		305		
$[(3)_3][B(Ar^F)_4]_2$		560 (broad)	410	389 (sh)	325	280	
$[(3)_3][B(C_6F_5)_4]_2$		560 (broad)	409	388 (sh)	320	280	
$[(1)_2(3)][B(Ar^F)_4]_2$		565 (broad)	412	390 (sh)	335	275	
$[(1)_2(3)][B(C_6F_5)_4]_2$		569 (broad)	413	390 (sh)	335	275	
$[(2)_{2}(3)][B(Ar^{F})_{4}]_{2}$		575 (broad)	419	398 (sh)	338	270	
$[(2)_{2}(3)][B(C_{6}F_{5})_{4}]_{2}$		566 (broad)	411	389 (sh)	330	259	

ed exactly. The band grows over time or when the compound is kept under vacuum (removal of the solvent molecules, see Discussion).

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Scheme 5. Double proton abstraction reaction leading to neutral 5.

530 nm, and another band at 416 nm. The spectrum clearly differs from that of the aggregate, and the lowest energy band of the aggregate $[(3)_3]^{2+}$ is in between those of the dication 3^{2+} and 5. Compound 5 could also be synthesized directly in 68% yield by treatment of 3·4 HCl with an excess of KOtBu and O₂. The O₂ is reduced in a two-proton-two-electron transfer reaction. According to quantum chemical calculations (B3LYP/6-311G*), the gas-phase reaction between 3 and $\frac{1}{2}O_2$ to give 5 and H₂O is exergonic ($\Delta G^0 = -24$ kJ mol⁻¹ at 1 bar).

The aggregates $[(3)_3]^{2+}$, $[(1)_2(3)]^{2+}$ and $[(2)_2(3)]^{2+}$ are also present in solution. Hence, their CH₃CN or CH₂Cl₂ solutions are orange-colored, while solutions of salts of the dication 3^{2+} are green-colored. The UV/Vis spectra in CH₃CN solution are comparable to those measured for the solid material in BaSO₄ matrices (all spectra are displayed in the Supporting Information). The spectrum of $[(3)_3][B(Ar^F)_4]_2$ contained a broad absorption centered roughly at 389 nm with a tail to lower wavenumbers, which should arise from another band around 565 nm, and sharper features at 389 and 325 nm. The spectrum of $[(1)_2(3)]$ $[B(Ar^F)_4]_2$ displayed a broad absorption at about 400 nm with a shoulder at 585 nm, and sharper and stronger bands in the UV region at 356, 328 and 270 nm. However, massive band overlapping of the broad bands prohibited a more detailed analysis.

The room temperature NMR spectra showed signals at positions which differ from those of the components. For example, ¹H NMR spectra of CD₃CN solutions of $[(1)_2(3)][B(Ar^F)_4]_2$ showed signals at δ = 2.70 (CH₃) and 5.83 ppm (H_{arom.}) assignable to the hydrogen-bond acceptor units 1, and at 1.07 (CH₃) and 3.59 ppm (CH) for the isopropyl groups of the hydrogen-bond donor units $\mathbf{3}^{2+}$ (the aromatic protons and unfortunately also the NH protons could not be detected, even at low temperatures). The chemical shifts for 1 are in between those found for unprotonated 1 (2.63 (CH₃) and 5.54 ppm (H_{arom})) and for the diprotonated form $[1H_2]^{2+}$ (2.78 (CH₃) and 6.11 ppm (H_{arom})). Also, the signals due to the hydrogen-bond donor component 3^{2+} in $[(1)_2(3)][B(Ar^F)_4]_2$ differ from those of 3^{2+} in $3[B(Ar^F)_4]_2$ solutions (1.15 and 3.65 ppm), and are close to those observed for 5. In no case did we observe signals due to protonated 1. Thus, the NMR spectra are in line with the description of the aggregates as frozen-stages on the way to hydrogen transfer. Spectra recorded at various temperatures showed no evidence for an equilibrium between the aggregate and the components, indicating strong hydrogen bonding in the aggregates. All NMR spectroscopy results are summarized in Tables S1 and



S2 as well as Figure S8 in the Supporting Information. In the CV curve of **3**, broad waves are visible, in sharp contrast to the sharp waves observed for **1** or **2**, indicating hydrogen-bond formation (Figure S9 in the Supporting Information). Electrospray ionisation (ESI) mass spectrometric analysis (in CH_2Cl_2) showed evidence for weak signals due to $[(3)_2]^+$, $[(1)(3)-4H]^{2+}$

and $[(\mathbf{2})(\mathbf{3})H_2]^{2+}$ (see the Experimental Section).

However, a detailed analysis of the aggregation process in solution was not possible for the following reasons. The solubility of the aggregates turned out to be poor. More profoundly, the aggregates are not stable in solution, and are converted with time to other species. We assume ring-closing reactions leading to bis-imidazolium salts to slowly proceed (see the Supporting Information and also related ring-closing processes observed during synthesis of 1).^[30] A similar ring-closing reaction was observed when solutions of $\mathbf{3}^{2+}$ were treated with NaOH, and it appears that the presence of strong bases initiates this reaction. Moreover, in the case of $[(2)_2(3)]^{2+}$, redox reactions slowly occur, leading to 2^{2+} and neutral 3. For solutions of $[(1)_2(3)]^{2+}$, we also observed oxidation of the hydrogen-bond acceptor unit and formation of 1^{2+} , although this process was slower. Nevertheless, the NMR and UV/Vis spectra measured in solution point to strong hydrogen bonding in the aggregates. Additional NMR experiments indicated that the aggregation is reversible and that the aggregates can be annihilated both by oxidation with a salt of FeCp₂⁺ or by reduction with CoCp₂ (see Experimental Section).

Conclusions

Strong and reversible hydrogen bonding could be switched on by two-electron oxidation of the new redox-active guanidinylfunctionalized aromatic compound (GFA) 1,2,4,5-tetrakis(diisopropylguanidinyl)benzene, which features eight hydrogenbond donor sites. Hydrogen bonding leads to the formation of aggregates, in which the dication $\mathbf{3}^{2+}$ is sandwiched by two neutral guanidine units. Three aggregates were structurally characterized, which show that 3^{2+} could not only form aggregates with itself, but also with other guanidine bases. Aggregation is accompanied by a distinct change in the optical properties. Whereas crystals of neutral 3 are pale-yellow and crystals of the dication 3^{2+} green colored, the aggregate crystals are orange. Further oxidation leads to deaggregation. If the strength of the guanidine base is further increased, 3^{2+} is deprotonated and the neutral compound 5 formed. The electronic situation in the aggregates could be described as a frozenstage on the way to hydrogen transfer. Ongoing and future work in this area focuses on the synthesis of extended hydrogen-bonded structures with the dication 3^{2+} as hydrogenbond donor component.

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Experimental Section

General

All reactions were carried out under inert gas atmosphere using standard Schlenk techniques. The solvents were rigorously dried prior to their use. Compounds 1, 2 and 4 were synthesized as described previously.^[26, 28, 32] Elemental analyses were carried out at the Microanalytical Laboratory of the University of Heidelberg. UV/ Vis (in solution) and diffuse reflectance (of BaSO₄ matrices) measurements were carried out on a Cary 5000 spectrophotometer. Infrared spectra were recorded using a BIORAD Excalibur FTS 3000. NMR spectra were taken on a BRUKER Avance III 600, a BRUKER Avance II 400 or on a BRUKER Avance DPX AC200 spectrometer. A Bruker ApexQe FT-ICR (ESI) machine was used for mass spectrometry (MS). 1,2,4,5-Tetraaminobenzene-tetrahydrochloride and N,N'diisopropylcarbodiimide were purchased from Aldrich and used as delivered. Ag(dca) and the two salts $Fc[B(C_6F_5)_4]$ and $Fc[B(Ar^F)_4]$ $(Fc = FeCp_2, [B(Ar^F)_4]^- = [B\{C_6H_3(CF_3)_2\}_4]^-)$ were prepared according to the literature.^[32, 35, 36]

1,2,4,5-Tetrakis(N,N'-diisopropylguanidinyl)benzene (3): 1,2,4,5-Tetraaminobenzene-tetrahydrochloride (0.28 g, 1.00 mmol) was suspended in THF (10 mL) together with 2 mol% of Zn(OTf)₂ (7 mg). Then, N,N'-diisopropylcarbodiimid (0.50 g, 4.00 mmol; 0.62 mL) was added. The reaction mixture was stirred at room temperature for a period of 6 d. Then the precipitate was separated by filtration, washed three times with 5 mL portions of diethylether, and dried under vacuum. Yield of 3.4 HCI: 0.58 g (74%, 0.74 mmol). Crystals of 3.4 HCl were obtained at room temperature from CH₃CN. C₃₄H₇₀Cl₄N₁₂ (788.81 g mol⁻¹) calcd: C 51.77, H 8.94, N 21.31; found: C 48.98, H 8.80, N 19.50. The deviation is most likely caused by traces of the zinc salt, which cannot be removed completely at this stage. ¹H NMR (600.13 MHz, D₂O): δ = 7.30 (s, 2 H, CH_{arom}), 3.77 (br, 8H, CH), 1.14 ppm (d, ³J=6.12 Hz, 48H, CH₃); ¹³C{¹H} NMR (150.92 MHz, D_2O): $\delta = 154.55$ (CN), 135.23 (C_{arom}), 133.43 (CH_{arom}), 47.90 (CH), 24.47 ppm (CH₃); MS (ESI⁺): *m/z* (%): 322.3 (100) $[M-2H]^{2+}$; UV/Vis (H₂O, $c=2.28\times10^{-5}$ mol L⁻¹, d=1 cm): λ_{max} (ε) = 213 (3.263×10^4) , 238 nm $(3.407 \times 10^4 \text{ Lmol}^{-1} \text{ cm}^{-1})$. Then 0.8 mL of a 1 M NaOH solution was added to 0.12 g (0.15 mmol) of 3.4 HCl dissolved in H₂O (6 mL). The reaction mixture was extracted three times with 6 mL portions of CH₂Cl₂. Subsequently the combined organic phases were dried over K2CO3. Then the solvent was removed under vacuum, yielding 0.09 g pale-yellow colored product 3 (93%, 0.14 mmol). Recrystallization from CH₃CN afforded crystals of **3** suitable for an XRD analysis. ¹H NMR (600.13 MHz, CD₂Cl₂): $\delta =$ 6.31 (s, 2H, CH_{arom}), 4.01 (br, 8H, NH), 3.71 (br, 8H, CH), 1.12 ppm (d, ${}^{3}J = 6.23$ Hz, 48 H, CH₃); ${}^{13}C{}^{1}H$ NMR (150.92 MHz, CD₂Cl₂): $\delta =$ 149.77 (CN), 136.56 (C_{arom}), 119.22 (CH_{arom}), 43.69 (CH), 23.60 ppm (CH₃); MS (HR-EI⁺): *m*/*z* (%): [C₃₄H₆₆N₁₂]⁺ calcd 642.5533 [**3**]⁺, exptl 642.5581 (88), $[C_{17}H_{29}N_7]^+$ calcd 331.2579 $[M-C_{17}H_{37}N_5]^+$, exptl 331.2532 (40), $[C_{14}H_{20}N_6]^+$ calcd 272.1750 $[M-C_{20}H_{46}N_6]^+$, exptl 272.1764 (100); IR (CsI): $\tilde{v} = 3454$ (w), 3381 (m), 3333 (m), 2969 (s), 2933 (m), 2870 (w), 1631 (vs), 1601 (vs), 1543 (s), 1486 (s), 1381 (s), 1363 (s), 1330 (m), 1287 (m), 1259 (w), 1179 (s), 1126 (m), 1063 (w), 1031 (w), 896 (m), 874 (w), 803 (w), 709 (w), 574 (w), 492 cm⁻¹ (w); UV/Vis (CH₃CN, $c = 3.92 \times 10^{-5} \text{ mol L}^{-1}$, d = 1 cm): λ_{max} (ϵ) = 370 (0.394×10^{4}) , 324 (0.896×10^{4}) , 241 nm $(2.063 \times 10^{4} \text{ L mol}^{-1} \text{ cm}^{-1})$; diffuse reflectance (BaSO₄ matrix): λ_{max} = 420, 340, 291 nm. Crystal data for $C_{34}H_{66}N_{12}$, $M_r = 642.99$, $0.19 \times 0.11 \times 0.04$ mm³, triclinic, space group $P\bar{1}$, a = 10.8873(8), b = 13.5200(12), c = 14.350(2) Å, a =75.621(10)°, $\beta = 74.886(10)°$, $\gamma = 89.997(7)°$, V = 1970.5(4) Å³, Z = 2, $ho_{
m calcd}$ = 1.084 Mg m⁻³, Cu radiation (graphite monochromated, λ = 0.71073 Å), T = 110 K, θ_{range} 2.108 to 33.398°. Reflections measured: 48608, independent: 11847, $R_{int} = 0.088$. Final *R* indices $[l > 2\sigma(l)]$: $R_1 = 0.1005$, $wR_2 = 0.2308$.

[(3)(thf)₂(dioxane)][B(C₆F₅)₄]₂: Compound 3 (20 mg; 0.031 mmol) and $Fc[B(C_{6}F_{5})_{4}]$ (49 mg; 0.057 mmol) were suspended in a mixture of CH₂Cl₂ (2 mL) and dioxane (2 mL; C₄H₈O₂). Then THF (3 mL) was added until the solid is completely dissolved. The green-colored solution was stirred for a period of 20 min at room temperature. Crystals were obtained at -20 °C after layering the solution with petroleum ether 40/60. Yield: 70 mg olive-green crystals (0.028 mmol, 98%). Elemental analysis (%) for C₈₂H₆₆N₁₂F₄₀B₂ (2001.05)·2CH₂Cl₂·2thf·2dioxane (2491.34): calcd: C 48.21, H 4.13, N 6.75; found: C 47.98, H 4.20, N 6.21; ¹H NMR (399.89 MHz, CD₃CN, 295.5 K): $\delta\!=\!$ 5.95 (bs, 8H, NH), 5.23 (s, 2H, CH $_{arom}$), 3.64 (m, 8H, CH_{isopropyl}), 1.15 ppm (d, J=6.47 Hz, 48 H, CH₃); ¹³C NMR (150.56 MHz, CD₃CN, 297.6 K): $\delta = 98.63$ (CH_{arom}), 45.54 (CH_{isopropyl}), 22.68 ppm (CH₃); ¹¹B NMR (128.30 MHz, CD₃CN, 295.9 K): $\delta =$ -16.71 ppm; ¹⁹F NMR (376.23 MHz, CD₃CN, 295.9 K): $\delta = -133.79$, -163.91, -168.42 ppm; IR (CsI): $\tilde{v} = 3426$ (w), 3305 (w), 2971 (w), 2920 (w), 2863 (w), 1668 (sh), 1626 (m), 1605 (m), 1586 (m), 1565 (m), 1514 (s), 1463 (s), 1379 (m), 1368 (m), 1330 (w), 1319 (m), 1280 (m), 1256 (m), 1216 (w), 1173 (m), 1158 (sh), 1115 (sh), 1091 (s), 980 (vs), 873 (m), 865 (s), 775 (m), 757 (s), 726 (w), 685 (s), 662 (s), 611 (m), 578 (w), 504 (w), 430 cm⁻¹ (w); diffuse reflectance (BaSO₄ matrix): $\lambda_{max} = 750-680$ (broad), 600, 433, 292, 263 nm. UV/Vis (c =2.770·10⁻⁵ mol I⁻¹, d = 1 cm, CH₃CN): λ_{max} (ε) = 597 (0.089×10⁴), 422 (3.218×10^{4}) , 280 (1.99×10^{4}) , 266 nm $(2.049 \times 10^{4} \text{ Lmol}^{-1} \text{ cm}^{-1})$. MS (ESI, CH₂Cl₂): *m/z* (%): 907 (100) [**3**(dioxane)₃]⁺, 935 (42) [**3**H₄(thf)₄]⁺ , 951 (24) [3H₄(thf)₃(dioxane)]⁺, 967 (12) [3H₄(dioxane)₂(thf)₂]⁺, 979 (11) $[3(dioxane)_3(thf)]^+$. Crystal data for $C_{98}H_{98}B_2F_{40}N_{12}O_6$, $M_r =$ 2321.50, $0.40 \times 0.40 \times 0.20$ mm³, triclinic, space group *P*1, *a*= 11.535(2), b = 13.629(3), c = 17.890(4) Å, $a = 112.16(3)^{\circ}$, $\beta = 112.16(3)^{\circ}$ $\gamma = 91.42(3)^{\circ}$, $V = 2515.9(9) \text{ Å}^3$, Z = 1, 103.25(3)°, $ho_{
m calcd} =$ 1.532 Mg m⁻³, Mo_{Ka} radiation (graphite monochromated, $\lambda =$ 0.71073 Å), T = 100 K, θ_{range} 2.29 to 30.06°. Reflections measured: 25414, independent: 14521, $R_{int} = 0.0405$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0553, wR_2 = 0.1315.$

[3(Et₂O)_n][B(Ar^F)₄]₂ (n≤4): Compound 3 (23 mg; 0.036 mmol) and Fc[B(Ar^F)₄] (75 mg; 0.071 mmol) were dissolved in a mixture of Et₂O (2 mL) and CH₂Cl₂ (2 mL). The green-colored solution was stirred at room temperature for a period of 10 min. Then the solution was layered by 10 mL petroleum ether 35/70 and the orange-colored product was crystallized at -20 °C. Yield: 61 mg (0.023 mmol, 65%), upon removal of the solvent in the form of green-colored crystals. Elemental analysis (%) for C₉₈H₉₀N₁₂F₄₈B₂ (2369.40 g mol⁻¹)·2 CH₂Cl₂·Et₂O calcd: C 47.80, H 4.01, N 6.43; found: C 47.91, H 4.19, N 6.89; ¹H NMR (399.89 MHz, CD₃CN, 295.7 K): $\delta =$ 7.69, 7.67 (bs, 24 H, CH_{arom.} B(Ar^F)₄), 5.95 (bs, 8 H, NH), 5.22 (s, 2 H, CH_{arom}), 3.65 (m, 8 H, CH_{isopropyl}), 1.15 ppm (d, J=6.49 Hz, 48 H, CH₃); ¹³C NMR (150.56 MHz, CD₃CN, 296.2 K): δ = 163.44, 163.26, 162.27, 161.77, (CN), 129.98, 129.63, 129.43, 126.73, 124.02 $(\mathsf{C}_{\textit{arom}}), \quad 135.57, \quad 118.61 \quad (\mathsf{C}_{\textit{arom}}, \quad \mathsf{B}(\mathsf{Ar}^{\mathsf{F}})_{4}), \quad 97.88 \quad (\mathsf{CH}_{\textit{arom}}), \quad 45.53$ (CH_{isopropyl}), 22.68 ppm (CH₃); ¹¹B NMR (128.30 MHz, CD₃CN, 295.2 K): $\delta = -6.71 \text{ ppm}$; ¹⁹F (376.24 MHz, CD₃CN, 295 K): $\delta = -63.24 \text{ ppm}$; IR (Csl): $\tilde{v} = 3450$ (w), 3431 (w), 2984 (w), 2946 (w), 2880 (w), 1643 (sh), 1610 (m), 1568 (m), 1520 (s), 1469 (w), 1356 (s), 1279 (vs), 1164 (sh), 1126 (vs), 1096 (sh), 932 (w), 898 (w), 888 (m), 839 (s), 744 (w), 716 (vs), 683 (vs), 669 (vs), 586 (w), 503 (w), 448 cm⁻¹ (w); diffuse reflectance (BaSO₄ matrix): $\lambda_{max} = 750-710$ (broad), 611, 433, 266 nm. UV/Vis ($c = 2.304 \times 10^{-5}$ mol L⁻¹, d = 1 cm, CH₂Cl₂/Et₂O 1:1): λ_{max} (ϵ) = 797 (0.029×10⁴), 606 (0.076×10⁴), 422 (2.705×10⁴), 278 (2.421×10^4) , 270 nm $(2.549 \times 10^4 \text{ Lmol}^{-1} \text{ cm}^{-1})$; MS (ESI, CH₃CN, MeOH): m/z (%): 321 (100) [3]²⁺, 753 (60) {[3][B(Ar^F)₄]}²⁺, 1505 (10) $\{3-H[B(Ar^{F})_{4}]\}^{+}$. Crystal data for $[3(Et_{2}O)_{4}][B(Ar^{F})_{4}]_{2}$, $C_{114}H_{130}B_{2}F_{48}N_{12}O_{4}$,

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 $M_r = 2665.92, 0.40 \times 0.30 \times 0.30 \text{ mm}^3$, monoclinic, space group P21/n, a = 13.050(3), b = 27.005(5), c = 21.075(4) Å, $\beta = 104.51(3)^\circ$, V = 7190(2) Å³, Z = 2, $\rho_{calcd} = 1.231 \text{ Mg m}^{-3}$, $Mo_{K\alpha}$ radiation (graphite monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 1.78 to 27.49°. Reflections measured 32306, independent 16455, $R_{int} = 0.0399$. Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0627, wR_2 = 0.1608$.

[3(Et₂O)_n][B(C₆F₅)₄]₂: Compound 3 (30 mg; 0.047 mmol) was dissolved together with $Fc[B(C_6F_5)_4]$ (77 mg; 0.089 mmol) in CH_2Cl_2 (2 mL) and Et₂O (2 mL). The green-colored solution was stirred at room temperature for a period of 20 min. Then the solvent was removed under vacuum. The green-colored residue was redissolved in a small portion of Et₂O, and then precipitated again upon addition of petroleum ether 40/60. The solution was separated with a cannula, and the green-colored solid was washed several times with petroleum ether 40/60. Yield: 73 mg green-colored powder, 0.034 mmol, 76%. Elemental analysis (%) for C₈₂H₆₆N₁₂F₄₀B₂ (2001.05 $g\,mol^{-1}) {\cdot} 2\,CH_2Cl_2$ calcd: C 46.47, H 3.25, N 7.74; found: C 46.28, H 3.15, N 7.76; ¹H NMR (399.89 MHz, CD₃CN, 295.0 K): $\delta =$ 5.87 (bs, 8H, NH), 5.22 (s, 2H, CHarom), 3.66 (m, 8H, CHisopropyl), 1.15 ppm (d, J=6.48 Hz, 48 H, CH₃); ¹³C NMR (150.56 MHz, CD₃CN, 295.0 K): $\delta = 153.69$ (CN), 98.50 (CH_{arom}), 45.54 (CH_{isopropy}), 22.65 ppm (CH₃); ¹⁹F NMR (376.23 MHz, CD₃CN, 295.0 K): $\delta =$ -133.76, -163.92, -168.43 ppm; ¹¹B NMR (128.30 MHz, CD₃CN, 295.0 K): $\delta = -16.71$ ppm; IR (CsI): $\tilde{v} = 3426$ (w), 3409 (w), 2977 (w), 2928 (w), 2868 (w), 1643 (m), 1607 (m), 1587 (m), 1564 (sh), 1514 (s), 1462 (s), 1379 (w), 1373 (m), 1316 (w), 1273 (m), 1251 (m), 1170 (w), 1156 (m), 1116 (sh), 1084 (s), 980 (vs), 912 (w), 851 (w), 775 (s), 757 (s), 684 (m), 661 (m), 612 (w), 572 (w), 500 cm⁻¹ (w); diffuse reflectance (BaSO₄ matrix): $\lambda_{\rm max}\!=\!740\text{-}640$ (broad), 601, 434, 295, 265 nm. UV/Vis ($c = 3.095 \times 10^{-5} \text{ mol L}^{-1}$, d = 1 cm, CH₃CN): λ_{max} (ε) = 673 (0.045×10^4) , 597 (0.079×10^4) , 422 (2.880×10^4) , 281 (1.777×10^4) 10⁴), 266 nm (1.834×10⁴ Lmol⁻¹ cm⁻¹). MS (ESI, CH₂Cl₂): m/z (%): 322 (100) [**3**H]²⁺, 643 (11) [**3**]⁺

3(dca)₂: Ag(dca) (63 mg; 0.36 mmol) and 3 (116 mg; 0.181 mmol) were dissolved in CH₃CN (10 mL) and stirred for a period of 20 h in the dark. The green-colored solution was filtrated and the solvent was removed under vacuum. The green-colored residue was washed three times with Et₂O. Yield: 101 mg (0.13 mmol, 72%). Single crystals suitable for single-crystal X-ray analysis were obtained from a concentrated CH₃CN solution. For purification a CH_2CI_2 solution was layered with Et_2O and the resulting greencolored needles used for the analytical measurements. $C_{\scriptscriptstyle 38}H_{\scriptscriptstyle 66}N_{\scriptscriptstyle 18}$ (775.05 g mol⁻¹): calcd: C 58.89, H 8.58, N 32.53; found: C 58.13, H 8.26, N 32.49; ¹H NMR (399.89 MHz, CD₃CN, 295.2 K): $\delta = 6.50$ (bs, 8H, NH), 5.31 (s, 2H, CH), 3.72 (m, 8H, CH), 1.17 ppm (d, 48H, J= 6.47, CH₃); ^{13}C NMR (100.56 MHz, CD₃CN, 296.0 K): $\delta\!=\!$ 160.42, 158.32, 154.46 (CN), 123.40, 120.70, 120.35 (CN, dca), 99.50, 97.54 (Carom), 45.47 (CH), 22.69 ppm (CH₃); MS (ESI, CH₃CN): m/z (%): 321 (100) $[\mathbf{3}]^{2+}$ 708 (42) $[\mathbf{3}+\text{dca}]^+$, 641 (13) $[\mathbf{3}-\text{H}]^+$; IR (CsI): $\tilde{v}=3348$ (w), 3248 (w), 3161 (sh), 2977 (m), 2932 (w), 2912 (w), 2872 (w), 2845 (w), 2247 (s), 2202 (s), 2142 (vs), 1620 (sh), 1606 (vs), 1575 (s), 1523 (s), 1467 (m), 1437 (m), 1368 (w), 1344 (w), 1325 (m), 1244 (m), 1169 (m), 1074 (sh), 1068 (m), 1018 (sh), 866 (w), 802 (m), 764 (w), 716 (w), 669 (w), 504 (m), 470 cm⁻¹ (m); diffuse reflectance (BaSO₄ matrix): $\lambda_{max} = 780-740$ (broad), 605, 429, 305 nm. UV/Vis (CH₃CN, $c = 3.59 \times 10^{-5} \text{ mol } \text{L}^{-1}$, d = 1 cm): $\lambda_{\text{max}} (\varepsilon) = 678 (0.037 \times 10^4)$, (0.073×10^4) , 422 $(2.856 \times 10^4),$ 598 279 nm $(1.802 \times$ $10^4 \,\mathrm{Lmol^{-1} cm^{-1}}$). Crystal data for $C_{38}H_{66}N_{18}$, $M_r = 775.09$, $0.40 \times$ 0.20×0.20 mm³, monoclinic, space group C2/c, a = 17.703(4), b =21.007(4), c = 15.555(3) Å, $\beta = 124.39(3)^{\circ}$, V = 4773.6(16) Å³, Z = 4, $\rho_{\text{calcd}}\!=\!$ 1.078 Mg m $^{-3}$, Mo $_{\text{K}\alpha}$ radiation (graphite monochromated, $\lambda\!=$ 0.71073 Å), T = 100 K, θ_{range} 2.51 to 27.08°. Reflections measured: 10266, independent: 5233, $R_{int} = 0.0487$. Final *R* indices $[l > 2\sigma(l)]$: $R_1 = 0.0532$, $wR_2 = 0.1266$.

 $[(3)_3][B(Ar^F)_4]_2$: Compound 3 (30 mg; 0.047 mmol) and $Fc[B(Ar^F)_4]$ (20 mg; 0.019 mmol) were dissolved in a mixture of Et₂O (2 mL) and CH₂Cl₂ (2 mL). The orange-colored solution was stirred at room temperature for a period of 5 min. Then it was layered by 10 mL of petroleum ether 35/70 and the product was crystallized at a temperature of $-20\,^\circ\text{C}$. Yield: 30 mg orange-colored crystals (0.0082 mmol, 86%). Elemental analysis for C₁₆₆H₂₂₂N₃₆F₄₈B₂ $(3655.34 \text{ gmol}^{-1})$ calcd: C 54.54, H 6.12, N 13.79; found: C 54.81, H 6.06, N 14.68; IR (CsI): $\tilde{v} = 3452$ (w), 3400 (w), 2972 (m), 2927 (w), 2872 (w), 1636 (sh), 1609 (s), 1517 (s), 1479 (m), 1464 (m), 1429 (w), 1394 (w), 1387 (sh), 1355 (s), 1278 (vs), 1163 (sh), 1126 (vs), 937 (w), 887 (m), 840 (m), 790 (w), 713 (m), 683 (s), 669 cm⁻¹ (m); diffuse reflectance (BaSO₄ matrix): $\lambda_{max} = 560$ (broad), 410, 389 (sh), 325, 280 nm; UV/Vis (CH₃CN, $c = 3.59 \times 10^{-5}$ molL⁻¹, d = 1 cm): λ_{max} (ε) = (sh, 0.130×10^4), 389 (1.724×10^4), 325 nm ($3.152 \times$ 565 $10^{4} \text{ Lmol}^{-1} \text{ cm}^{-1}$); MS (ESI, CH₂Cl₂): *m/z* (%): 643 (100) [**3**]⁺, 322 $(12)[\mathbf{3}H]^{2+}$, 1507 (3) $\{\mathbf{3}H[B(Ar^{F})_{4}]\}^{+}$, 1285 (1) $[(\mathbf{3})_{2}]^{+}$.

[(3)₃][B(C₆F₅)₄]₂: Compound 3 (19 mg; 0.030 mmol) was suspended in Et_2O (2 mL). Then a solution of $Fc[B(C_6F_5)_4]$ (47 mg; 0.054 mmol) in CH₂Cl₂ (2 mL) was added dropwise. The green-colored solution was stirred at room temperature for a period of 10 min, and then another 42 mg of 3 (0.065 mmol) was added in solid form. The orange-colored solution was layered by 10 mL of petroleum ether 35/70, and the product was crystallized at a temperature of -20°C. Yield: 70 mg orange-colored crystals (0.021 mmol, 79%). Elemental analysis for $C_{150}H_{198}N_{36}F_{40}B_2$ (3286.99 g mol⁻¹)·CH₂Cl₂ calcd: C 53.79, H 5.98, N 14.95; found: C 53.29, H 6.06, N 14.96; IR (Csl): $\tilde{v} = 3450$ (w), 3397 (w), 2970 (m), 2927 (w), 2871 (w), 1627 (sh), 1609 (s), 1514 (s), 1464 (s), 1371 (m), 1368 (m), 1330 (w), 1270 (m), 1171 (m), 1103 (w), 1085 (s), 980 (vs), 902 (w), 780 (w), 775 (m), 757 (m), 707 (w), 690 (w), 684 (m), 662 (m), 602 (w), 573 (w), 473 cm⁻¹ (w); diffuse reflectance (BaSO₄ matrix): $\lambda_{max} = 560$ (broad), 409, 388 (sh), 320, 280 nm; MS (ESI, CH₂Cl₂): m/z (%): 322 (100) [**3**H]²⁺, 643 (6) $[\mathbf{3H}]^+$, 1323 (4) $\{\mathbf{3H}[B(C_6F_5)_4]\}^+$. Crystal data for $[(\mathbf{3})_3]$ $[B(C_6F_5)_4]_2 \cdot 2.6 \text{ CH}_2\text{Cl}_2, \quad C_{152.60}\text{H}_{203.20}\text{B}_2\text{Cl}_{5.20}\text{F}_{40}\text{N}_{36}, \quad M_r = 3507.87, \quad 0.60 \times 10^{-10} \text{ C}_{152.60}\text{C}_{15$ 0.40×0.40 mm³, triclinic, space group *P*1, *a*=15.063(3), *b*= 17.303(4), c = 18.676(4) Å, $\alpha = 86.05(3)^{\circ}$, $\beta = 76.13(3)^{\circ}$, $\gamma = 83.71(3)^{\circ}$, V = 4692.7(16) Å³, Z = 1, $\rho_{calcd} =$ 1.241 Mg m⁻³, Mo_{Ka} radiation (graphite monochromated, $\lambda\!=\!0.71073$ Å), T $\!=\!100$ K, $\theta_{\rm range}$ 2.08 to 27.50°. Reflections measured: 86597, independent: 21514, $R_{int} =$ 0.0829. Final *R* indices $[l > 2\sigma(l)]$: $R_1 = 0.0784$, $wR_2 = 0.2251$.

General procedure for the synthesis of the other hydrogenbonded aggregates

Compound **3** and approximately 1.9 equiv of the ferrocenium salt were dissolved in a mixture of Et_2O (2 mL) and CH_2Cl_2 (2 mL). The green-colored solution was stirred at room temperature for a period of 10 min. Then approximately 2.2 equiv of **1** or **2** were added. The reaction mixture was layered by 10 mL petroleum ether 35/70, and the product was crystallized at a temperature of -20 °C in the form of orange-colored crystals.

$$\begin{split} & [(1)_2(3)][B(Ar^F)_4]_2: \text{ Compound } 3 \ (23 \text{ mg}; \ 0.036 \text{ mmol}), \ Fc[B(Ar^F)_4] \\ & (75 \text{ mg}; \ 0.071 \text{ mmol}), \ 1 \ (48 \text{ mg}; \ 0.09 \text{ mmol}). \ Yield: 50 \text{ mg product} \\ & (0.015 \text{ mmol}, \ 42\%). \ Elemental \ analysis \ for \ C_{150}H_{196}N_{36}F_{48}B_2 \\ & (3436.96 \text{ g mol}^{-1}) \ calcd: C \ 52.42, \ H \ 5.75, \ N \ 14.67; \ found: C \ 52.22, \ H \\ & 5.42, \ N \ 14.69; \ IR \ (Csl): \ \tilde{v} = 2961 \ (w), \ 2928 \ (m), \ 2872 \ (w), \ 1608 \ (s), \\ & 1584 \ (s), \ 1515 \ (m), \ 1457 \ (w), \ 1381 \ (m), \ 1354 \ (s), \ 1278 \ (vs), \ 1154 \ (sh), \\ & 1125 \ (vs), \ 1062 \ (w), \ 1019 \ (w), \ 928 \ (w), \ 886 \ (w), \ 840 \ (w), \ 713 \ (m), \\ & 682 \ (s), \ 670 \ cm^{-1} \ (m); \ diffuse \ reflectance \ (BaSO_4 \ matrix): \ \lambda_{max} = 565 \ (broad), \ 412, \ 390 \ (sh), \ 335, \ 275 \ nm; \ UV/Vis \ (CH_3CN, \ c = 3.67 \times 1000 \ cm^{-1}) \\ \end{aligned}$$

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$$\begin{split} &10^{-5} \mbox{ mol } L^{-1}, \ d = 1 \mbox{ cm}; \ \lambda_{max} \ (\varepsilon) = ca. \ 585 \ (sh, \ 0.069 \times 10^4), \ ca. \ 400 \\ &(1.257 \times 10^4), \ 356 \ (sh, \ 3.308 \times 10^4), \ 328 \ (4.385 \times 10^4), \ 270 \ nm \ (7.603 \times 10^4 \ Lmol^{-1} \ cm^{-1}); \ MS \ (ESI, \ CH_2 Cl_2); \ m/z \ (\%); \ 531 \ (100) \ [1]^+, \ 266 \ (45) \\ &[1H]^{2+}, \ 322 \ (30) \ [3H]^{2+}, \ 641 \ (11) \ [3-H]^+, \ 1395 \ (8) \ \{1H[B(Ar^F)_4]\}^+, \ 584 \\ &(5) \ [(1)(3)-4H]^{2+}, \ 1505 \ (1) \ \{3[B(Ar^F)_4]\}^+. \end{split}$$

[(1)₂(3)][B(C₆F₅)₄]₂: Compound 3 (35 mg; 0.055 mmol), Fc[B(C₆F₅)₄] (86 mg; 0.099 mmol), 1 (64 mg; 0.12 mmol). Yield: 133 mg crystalline product (0.043 mmol, 88%). Elemental analysis for $C_{134}H_{166}N_{36}F_{40}B_2$ (3062.57 g mol⁻¹) calcd: C 52.55, H 5.46, N 16.47; found: C 53.35, H 5.62, N 16.05; IR (CsI): $\tilde{v} = 2953$ (w), 2922 (m), 2864 (w), 2788 (w), 1632 (sh), 1594 (m), 1570 (m), 1510 (s), 1460 (s), 1422 (m), 1393 (w), 1381 (m), 1331 (w), 1273 (m), 1237 (w), 1174 (w),1156 (s), 1137 (s), 1085 (s), 1063 (w), 1017 (m), 980 (vs), 923 (w), 878 (m), 795 (w), 757 (s), 726 (w), 684 (s), 662 (s), 610 (w), 572 (w), 500 cm⁻¹ (w); diffuse reflectance (BaSO₄ matrix): $\lambda_{max} =$ 569 (broad), 413, 390 (sh), 335, 275 nm; MS (ESI, CH₂Cl₂): m/z (%): 266 (100) $[1H]^{2+}$, 531 (87) $[1]^+$, 1211 (9) $\{1H[[B(C_6F_5)_4]\}^+$, 321 (4) $[3]^{2+}$, 641 (1) $[3-H]^+$, 1060 (1) $[(1-H)_2]^+$. Crystal data for $[(1)_2(3)]$ $[B(C_6F_5)_4]_2 \cdot 1.7 CH_2CI_2, C_{135.70}H_{169.40}B_2CI_{3.40}F_{40}N_{36}, M_r = 3207.02, 0.40 \times$ 0.30×0.30 mm³, triclinic, space group $P\bar{1}$, a = 16.946(3), b =17.141(3), c = 18.680(4) Å, $\alpha = 78.76(3)^{\circ}$, $\beta = 66.92(3)^{\circ}$, $\gamma = 60.71(3)^{\circ}$, V = 4353.4(15) Å³, Z = 1, $\rho_{calcd} =$ 1.223 Mg m⁻³, Mo_{Ka} radiation (graphite monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 2.19 to 27.50°. Reflections measured: 83975, independent: 19949, $R_{int} =$ 0.0842. Final *R* indices $[l > 2\sigma(l)]$: $R_1 = 0.0653$, $wR_2 = 0.1559$.

[(2)₂(3)][B(Ar^F)₄]₂: Compound **3** (23 mg; 0.036 mmol), Fc[B(Ar^F)₄] (75 mg; 0.071 mmol), **2** (47 mg; 0.09 mmol). Yield: 80 mg crystalline product (0.023 mmol, 66%). Elemental analysis for C₁₅₀H₁₈₀N₃₆F₄₈B₂ (3420.84 g mol⁻¹) calcd: C 52.67, H 5.30, N 14.74; found: C 52.84, H 5.35, N 16.29; IR (Csl): \vec{v} = 2950 (m), 2914 (m), 2913 (m), 2856 (sh), 2848 (m), 1631 (s), 1624 (s), 1577 (sh), 1513 (m), 1464 (m), 1451 m), 1449 (m), 1391 (w), 1365 (w), 1355 (s), 1277 (vs), 1154 (sh) 1124 (vs), 1035 (m), 971 (w), 884 (m), 885 (m), 840 (m), 799 (m), 744 (w), 711 (m), 682 (s), 669 (m), 634 (w), 500 cm⁻¹ (w); diffuse reflectance (BaSO₄ matrix): λ_{max} = 575 (broad), 419, 398 (sh), 338, 270 nm; MS (ESI, CH₂Cl₂): *m/z* (%): 523 (100) [2]⁺, 322 (53)[3H]²⁺, 643 (12) [3]⁺, 1045 (2) [(2)₂]⁺, 1164 (<1) [(2)(3)-H]⁺, 1388 (<1) {2H₂[B(Ar^F)₄]}⁺, 1507 (<1) {3H[B(Ar^F)₄]}⁺.

 $[(2)_{2}(3)][B(C_{6}F_{5})_{4}]_{2}$: Compound 3 (20 mg; 0.031 mmol), Fc[B(C_{6}F_{5})_{4}] (49 mg; 0.057 mmol), 2 (37 mg; 0.071 mmol). The crystals were washed several times with Et₂O to remove impurities. Yield: 30 mg crystalline product (0.0098 mmol, 35%). Elemental analysis for $C_{134}H_{150}N_{36}F_{40}B_2 \ (3046.44 \ g \ mol^{-1}) \ calcd: \ C \ 52.83, \ H \ 4.96, \ N \ 16.55;$ found: C 52.84, H 5.35, N 16.29; IR (Csl): v=2980 (w), 2941 (w), 2965 (w), 1669 (sh), 1646 (s), 1617 (sh), 1517 (s), 1462 (s), 1401 (m), 1394 (m), 1369 (w), 1336 (w), 1289 (m), 1279 (m), 1246 (w), 1198 (w), 1160 (w), 1093 (s), 1039 (s), 982 (vs), 938 (w), 898 (w), 802 (w), 775 (s), 756 (s), 729 (w), 684 (s), 661 (s), 638 (w), 611 (w), 578 (w), 502 cm⁻¹ (w); diffuse reflectance (BaSO₄ matrix): $\lambda_{max} =$ 566 (broad), 411, 389 (sh), 330, 259 nm; MS (ESI, CH₂Cl₂): *m/z* (%): 523 (100) [**2**]⁺, 262 (62) $[2H]^{2+}$, 322 (11) $[3H]^{2+}$, 584 (4) $[(2)(3)H_2]^{2+}$, 641 (1) $[3-H]^+$, 1201 (1) $\{\mathbf{2}[B(C_6F_5)_4]\}^+$, 1045 (<1) $[(\mathbf{2})_2]^+$, 1324 (<1) $\{\mathbf{3}H_2[B(C_6F_5)_4]\}^+$. Crystal data for $C_{134}H_{150}B_2F_{40}N_{36}$, $M_r = 3046.52$, $0.35 \times 0.30 \times$ 0.25 mm³, monoclinic, space group P21/c, a = 16.415(3), b =18.911(4), c = 24.238(5) Å, $\beta = 90.48(3)^{\circ}$, V = 7524(3) Å³, Z = 2, $\rho_{calcd} =$ 1.345 Mg m $^{-3},~$ Mo $_{K\!\alpha}~$ radiation (graphite monochromated, $~\lambda =$ 0.71073 Å), T = 100 K, θ_{range} 2.00 to 27.43°. Reflections measured: 61666, independent: 17154, $R_{int} = 0.0753$. Final R indices $[l > 2\sigma(l)]$: $R_1 = 0.0634, wR_2 = 0.1480.$

Compound 5: Compound **3** (20 mg; 0.031 mmol) and $Fc[B(Ar^{F})_{4}]$ (57 mg; 0.054 mmol) were dissolved in a mixture of $Et_{2}O$ (2 mL) and $CH_{2}CI_{2}$ (2 mL). The green-colored solution was stirred at room temperature for a period of 20 min. Then 38 mg of **4** (0.066 mmol)

were added. The red-colored reaction mixture was layered by 10 mL petroleum ether 35/70. Red colored crystals were grown at a temperature of -20 °C. Yield: 16 mg, 0.024 mmol, 95%.

Alternative route: KOtBu (94 mg, 0.82 mmol) was added over 5 min in portions to a suspension of 3.4 HCl (109 mg, 0.14 mmol) in THF (15 mL) under an argon gas atmosphere. The dark solution was stirred for an additional 5 min. Then compressed dry air was passed via a glass tube into the solution until a clear, orange-red colored solution was obtained. After partial removal of the solvent (until clouding was observed) the solution was filtrated over Celite under an argon gas atmosphere, and the residue was rinsed with a small amount of THF. The solvent was removed from the filtrate under vacuum, and the remaining orange-colored solid was dissolved in some THF. Unfortunately, it was not possible to free the product completely from KCl. Yield: 61 mg (0.095 mmol, 68%). Elemental analysis (%) for $C_{34}H_{64}N_{12}$ (640.96 g mol⁻¹)·0.75 KCl calcd: C 58.62, H 9.27, N 24.14; found: C 58.38, H 9.21, N 23.92. Red crystals were obtained from THF at -20°C. ¹H NMR (600.13 MHz, $[D_6]$ acetone, 295 K): $\delta = 5.83$ (bs, 1 H, NH or CH), 3.80, 3.58 (m, 8 H, CH), 1.12, 1.05 ppm (br, 48 H, CH_3); ^{13}C NMR (150.92 MHz, CD_3CN, 295.1 K): $\delta = 45.3-44.3$ (CH), 24.67 ppm (CH₃); weak NMR signals due to a low solubility; MS (ESI, CH₃OH): m/z (%): 321 (100) [5H]²⁺, 641 (17) [5]⁺. IR (Csl): $\tilde{v} = 3431$ (w), 3280 (w), 2970 (m), 2931 (w), 2872 (w), 1628 (s), 1595 (s), 1522 (s), 1489 (sh), 1465 (sh), 1385 (w), 1364 (w), 1324 (w), 1240 (m), 1194 (w), 1168 (w), 1127 (w), 1062 (w), 1043 (w), 855 (w), 839 (w), 797 (w), 730 cm⁻¹ (w); diffuse reflectance (BaSO₄ matrix): λ_{max} = 530, 416, 390, 280 nm; UV/Vis (CH₃CN, $c = 5.37 \times 10^{-5} \text{ mol L}^{-1}, d = 1 \text{ cm}$: λ_{max} (ε) = 500 (0.125 × 10⁴), 420 (0.608×10^4) , 358 (1.309×10^4) , 332 (1.376×10^4) , 253 nm (1.584×10^4) $10^4 \text{ Lmol}^{-1} \text{ cm}^{-1}$). Crystal data for **5**·4 CH₂Cl₂, C₃₈H₇₂Cl₈N₁₂, $M_r =$ 980.68, $0.40 \times 0.30 \times 0.25$ mm³, monoclinic, space group P21/n, a = 14.375(3), b = 11.336(2), c = 16.775(3) Å, $\beta = 110.64(3)^{\circ}$, V =2558.2(9) ų, Z=2, $\rho_{\rm calcd}$ =1.273 Mg m⁻³, Mo_{Ka} radiation (graphite monochromated, λ = 0.71073 Å), *T* = 100 K, θ_{range} 2.22 to 27.50°. Reflections measured: 11669, independent: 5874, R_{int} = 0.0465. Final R indices $[l > 2\sigma(l)]$: $R_1 = 0.0611$, $wR_2 = 0.1508$.

Reversibility tests

A) $[(3)_3][B(C_6F_5)_4]_2$ ·CH₂Cl₂ (15 mg; 0.0044 mmol) was dissolved in an NMR tube in $[D_8]$ THF (0.4 mL). Then 0.1 mL of a solution of CoCp₂ (0.009 mmol; 17 mg CoCp₂ in 1 mL $[D_8]$ THF) was added dropwise. The color change and NMR spectrum indicated the reduction to **3**. B) In an NMR tube, $[(3)_3][B(C_6F_5)_4]_2$ ·CH₂Cl₂ (15 mg; 0.0044 mmol) and Fc[B(C_6F_5)_4] (14 mg; 0.016 mmol) were dissolved in $[D_8]$ THF (0.5 mL). The color change and NMR spectrum indicated oxidation to **3**[B(C_6F_5)_4]_2.

X-ray crystallographic study

Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil and fixed on top of a glass capillary. Measurements were made with a Nonius-Kappa CCD diffractometer with low-temperature unit using graphite-monochromated Mo_{Kα} radiation. The temperature was set to 100 K. The data collected were processed using the standard Nonius software.^[37] All calculations were performed using the SHELXT-PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.^[38,39] Graphical handing of the structural data during solution and refinement was performed with XPMA.^[40] Atomic coordinates and anisotropic thermal parameters of nonhydrogen atoms were placed at calculated positions and refined with a riding model. In the case

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of 3, full shells of intensity data were collected at low temperature (110 K) with an Agilent Technologies Supernova-E CCD diffractometer (Cu_{Ka} radiation, $\lambda = 1.5418$ Å, microfocus tube, multilayer mirror optics). Data were corrected for air and detector absorption, Lorentz and polarization effects;^[41] absorption by the crystal was treated with a semiempirical multiscan method.[42] The crystal was found to be a two-component twin (twin fractions 0.54:0.46). After de-twinning, the structure was solved by the charge-flip procedure.^[43] Refinement was carried out against all observations involving singles and composites of both twin domains by full-matrix least-squares methods based on F² against all unique reflections.^[44] All nonhydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. Hydrogen atoms on N were refined with all N–H bonds restrained equal with an esd of 0.02 Å. CCDC 913085 (3), 974356 ([(3)(thf)₂(dioxane)][B(C₆F₅)₄]₂), 972541 $([\mathbf{3}(Et_2O)_4][B(Ar^F)_4]_2)$, 913084 (5), 940651 ($\mathbf{3}(dca)_2$), 972542 ($[(\mathbf{3})_3]$ $[B(C_6F_5)_4]_2 \cdot 2.6 \text{ CH}_2\text{Cl}_2), \ 972543 \ ([(\textbf{1})_2(\textbf{3})][B(C_6F_5)_4]_2 \cdot 1.7 \text{ CH}_2\text{Cl}_2), \ 972544$ [(2)₂(3)][B(C₆F₅)₄]₂), and 913086 (5.4CH₂Cl₂) 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.

Details of the quantum chemical calculations

The density functional calculations used the B3LYP functional^[45] in combination with the 6-311G^{**} basis set.^[46] The calculations were performed with the program Gaussian 09.^[47]

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Keywords: aggregation \cdot guanidine \cdot hydrogen bonds \cdot oxidation \cdot self-assembly

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FULL PAPER

Hydrogen-bond sandwich, anyone? After oxidation of guanidinyl-functionalized aromatic compounds, the superbase is turned into a strong hydrogenbond donor and forms hydrogenbonded aggregates, which could be described as frozen stages on the way to hydrogen transfer (see figure).



Hydrogen Bonds

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Redox-Controlled Hydrogen Bonding: Turning a Superbase into a Strong Hydrogen-Bond Donor



Redox-Controlled Hydrogen Bonding

Hydrogen bonding can be greatly enhanced by oxidation of the hydrogen-bond donor component or reduction of the hydrogen-bond acceptor component, a strategy which could be applied for the design of "redox-controlled switches". In their Full Paper on page ■ ff. H.-J. Himmel et al. present the synthesis of a new redox-active guanidinyl-functionalized aromatic compound (GFA). Its oxidation turns the highly Brønsted basic molecule into a strong hydrogen-bond donor. Orange-colored aggregates are formed by reaction of the green-colored oxidized GFA with neutral GFAs. Reduction initiates deaggregation. A further increase of the basicity of the hydrogen-bond acceptor leads to deprotonation.