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Tuning the Properties of Redox-Active Guanidino-Functionalized Aromatic Ligands by Substitution: Experiment and Theory

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Substitution of the aromatic hydrogen atoms in the electron donors 1,2,4,5-tetrakis(tetramethylguanidino)benzene (1a) and 1,2,4,5-tetrakis(N,N'-dimethyl-N,N'-ethyleneguanidino)benzene (1b) by iodide (to give 2a and 2b) and nitro groups (to give 3a and 3b) afforded new redox-active ligands. Their properties (electron donor capacity, Brønsted basicity and op-

Introduction

1,4-Bis(dimethylamino)benzene and its derivatives are well-known organic electron donors,^[1] which can be easily oxidized to their intensely blue radical monocations or dications.^[2] Wurster-type systems have also been integrated in other architectures, which lead to, for example, crowns,^[3,4] cyclophanes^[5] and oligoanilines.^[6] 1,2,4,5-Tetraaminobenzene is also well known.^[7] and 1,2,4,5-tetrakis(dimethylamino)benzene and other derivatives have been introduced as even stronger electron donors.^[8] These compounds are generally oxidized directly to the dication. Recent work has shown that ion pairing is responsible for the difficulty in stabilizing the monocation radical,^[9] and the preparation of salts of the monocation has been made possible by the use of weakly coordinating anions. We have introduced guanidino-functionalized aromatic (GFA) compounds where several guanidino groups are in *para* positions to each other [GFA-*n*, where $n (\geq 4)$ denotes the number of guanidino groups] as a new class of strong organic electron donors and chelating ligands.^[10–15] The first compound of this class 1,2,4,5-tetrakis(tetramethylguanidino)benzene (1a, was Scheme 1).^[10] Its oxidation potential (two-electron oxidation) is -0.32 V vs. SCE (CH₃CN), thus 1a clearly is a stronger electron donor than 1,2,4,5-tetrakis(dimethylamino)benzene $[E_{1/2} (CH_3 CN) = -0.03 V \text{ vs. SCE}]^{[9]}$ The related compound 1b (Scheme 1) is slightly less basic than 1a

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tical spectra) have been analyzed and compared with the unsubstituted 1,2,4,5-tetrakis(guanidino)benzenes. The experimental results are supplemented by quantum chemical calculations. The first late-transition metal complex of the push-pull ligand 3a was prepared and characterized and its oxidation studied.

[estimated pK(BH⁺) values in CH₃CN solution of 25.3 for **1a** and 23.8 for **1b**] but is a superior electron donor $[E_{1/2}(CH_3CN) = -0.36 \text{ vs. SCE}].^{[12]}$



Scheme 1.

The reactivity of **1a** was assessed in several studies and some representative results are summarized in Figure 1.

Oxidation by I_2 furnished the semiconducting salt $1a(I_3)_2$.^[10,17] Several examples of dinuclear complexes, such as $[1a\{Cu(NCMe)_4\}_2](BF_4)_6$ and $[1a\{Cu(NO_3)_2\}_2][Cu-(NO_3)_4]$,^[11,16] showed that GFA-4 compounds are capable of forming stable complexes even after two-electron oxidation, in which they act as chelating ligands. Furthermore, trapped in dinuclear Cu^{II} complexes, the radical monocation $1a^{++}$ was stabilized.^[16] Hence $[1a\{Cu(NO_3)_2\}_2]NO_3$ features three strongly ferromagnetically coupled unpaired electrons (one on each copper atom and one on the bridging guanidine ligand) in its ground electronic state.^[16] Finally, 1a in $[1a(CuI)_2]$ was oxidized by I_2 (two-electron oxidation) to give the 1D polymer $[\{1a(CuI)_2\}(I_3)_2]_n$.^[17] This polymer was found to be an electrical semiconductor with a low (indirect) band gap of 1.05 eV. More semiconducting

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Figure 1. Some characteristic reactions of 1a.

1D coordination polymers have also been synthesized.^[18] For copper complexes, we were able to synthesize an almost complete electron-transfer series with complexes of the type $[Cu^{I}-GFA-4-Cu^{I}]$, $[Cu^{I}-GFA^{2+}-Cu^{I}]$ (polymeric), $[Cu^{II}-GFA-4-Cu^{II}]$, $[Cu^{II}-GFA-4-Cu^{II}]$ and $[Cu^{II}-GFA-4^{2+}-Cu^{II}]$.

The introduction of electron-withdrawing groups should lead to push-pull systems with distinct optical properties. In this work, we report the substitution of the remaining two aromatic hydrogen atoms in 1a and 1b by iodo or nitro groups to give the new electron donors 2a, 2b, 3a and 3b (Scheme 1). The synthesis, structure and electronic properties as well as some aspects of the reactivity of the new organic electron donors will be discussed and compared to those of 1a and 1b.

Results and Discussion

Quantum Chemical Calculations

Quantum chemical (DFT) calculations give an insight into the effect substitution could have on the redox properties of the guanidine electron donors and the $pK(BH^+)$ values. For the estimation of the electron donor capacity, two different indicators were considered, the first of which is based on thermodynamic considerations. Several model gas-phase electron transfer reactions between two of the six guanidines were examined (Scheme 2), and their ΔG^0 values (calculated using B3LYP/6-311G**) were compared.

The ΔG^0 indicator suggests that **1b** is the strongest and **3a** is the weakest electron donor. The electron donor capacity appears to decrease in the order 1b > 1a > 2b > 3b > 2a > 3a.



Scheme 2.

Another valuable indicator is the highest occupied molecular orbital (HOMO) energy, which is compared in Table 1. According to this indicator, the trend 1b > 1a >2b > 2a > 3b > 3a in the electron donor capacity was established. The order again suggests that 1b is the strongest and 3a is the weakest electron donor, but 2a and 3b have changed places in the series.

Table 1. Calculated HOMO and LUMO energies, the HOMO–LUMO energy gap (ΔE) and the calculated p*K*(BH⁺) value of the corresponding acid in CH₃CN.

| | E(HOMO) [eV] | E(LUMO) [eV] | $\Delta E [eV]$ | p <i>K</i> (BH ⁺) |
|----|--------------|--------------|-----------------|-------------------------------|
| 1a | -4.12 | 0.30 | 4.42 | 25.5 |
| 1b | -3.96 | 0.55 | 4.51 | 23.8 |
| 2a | -4.42 | -0.37 | 4.04 | 23.3 |
| 2b | -4.24 | -0.11 | 4.13 | 21.5 |
| 3a | -4.62 | -1.73 | 2.89 | 21.6 |
| 3b | -4.54 | -1.22 | 3.32 | 19.6 |
| | | | | |

A further parameter of importance for any application of the guanidine electron donors as building blocks in functional materials, is the HOMO–lowest unoccupied molecular orbital (LUMO) gap. The ability to control this gap over a large range through modification of the guanidine units in a relatively simple way would add to the attractiveness of this class of compounds. Although the absolute LUMO energy cannot be calculated accurately using simple DFT methods, the relative LUMO energies can be treated with more confidence. The HOMO–LUMO energy gaps are summarized in Table 1, and the gap could indeed be modified over a large range. Hence it is 4.42 eV in **1a** but only 2.89 eV in **3a**. Figure 2 shows the HOMO and LUMOs of **1a**, **2a** and **3a**. The HOMOs of all three guanidines look similar, whereas the LUMOs are localized to a large extent on the iodo and nitro groups in **2a** and **3a**.



Figure 2. Illustration of the HOMOs and LUMOs and their energies for 1a, 2a and 3a.

Finally, the $pK(BH^+)$ values in CH₃CN were estimated with the aid of an empirical formula introduced by Maksić et al.^[19] Solvent effects were considered with the conductorlike polarizable continuum model (CPCM). The resulting $pK(BH^+)$ values in CH₃CN for the corresponding acids are listed in Table 1. The compounds with cyclic guanidino groups exhibit lower values that their acyclic counterparts. Substitution of the C–H groups at the aromatic C₆ ring by C–I or C–NO₂ led to a marked decrease of the $pK(BH^+)$ value; a maximum of 25.5 was calculated for **1a**, and a minimum of 19.6 was reached for **3b**.

Synthesis and Characterization

Compounds 1a and 1b

Compounds **1a** and **1b** were synthesized according to a published procedure starting from 1,2,4,5-tetraaminobenzene, which was generated in situ from its HCl adduct, and the corresponding activated urea (activation with oxalyl chloride to give the Vilsmeier salts).^[10,12] Experiments led to the isolation and characterization of a byproduct of this reaction, the benzobisimidazole derivative **4** (Scheme 3 and Figure 3, a). The yield of **4** varied from 10–32%. A possible pathway is sketched in Scheme 3. According to this pathway, the common intermediate to both products is 1,4-bis-(tetramethylguanidino)-2,5-diaminobenzene, which is formed by the reaction of 1,2,4,5-tetraaminobenzene with two equivalents of the Vilsmeier salt 2-chloro-1,1,3,3-tetramethylformamidinium chloride, [(Me₂N)₂CCl]Cl.



Scheme 3.



Figure 3. a) Molecular structure of **4**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm]: N1–C2 140.14(16), N1–C4 133.05(17), N2–C1 139.41(16), N2–C4 136.68(16), N3–C4 136.17(16), C1–C2 141.24(19), C1–C3 138.44(17), C2–C3' 139.33(17), N4–C7 139.34(16), N4–C10 136.97(17), N5–C8 140.02(16), N5–C10 132.71(16), N6–C10 135.96(16), C7–C8 140.70(19), C7–C9 139.13(18), C8–C9' 139.18(17). b) Absorption and emission spectrum of **4** dissolved in MeOH. *I* denotes the normalized intensity.

The intermediate could either react with two further equivalents of the Vilsmeier salt to give 1a or it could eliminate NMe₂H at both "sides" of the molecule and undergo



Compounds 2a and 2b

Scheme 4 outlines the pathways to 2a and 2b. In the first step, the two-electron oxidation of 1a/b with I_2 furnished the triiodide salts.

Scheme 4.

The aromatic protons in these salts were substituted in the second step by reaction with I_2 in dimethylsulfoxide (DMSO). This reaction can be explained as follows: the adduct Me₂S·I₂ is formed by the I₂-catalyzed disproportionation of DMSO,^[20] and subsequently ionizes in polar DMSO



Figure 4. Molecular structures of **2a** and **2b**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [pm] and angles [°] for **2a**: C3–I1 210.4(2), N1–C1 140.7(3), N4–C2 141.5(3), N1–C4 130.0(3), N4–C9 129.0(3), N2–C4 137.9(3), N3–C4 137.6(3), N5–C9 138.1(3), N6–C9 139.0(3), C1–C2 141.3(3), C1–C3' 139.8(3), C2–C3 140.4(3), C1–N1–C4 121.19(19), C2–N4–C9 121.50(19). Selected bond lengths [pm] and angles [°] for **2b**: C2–I1 210.4(2), N1–C1 140.1(2), N4–C3 139.9(2), N1–C4 128.3(2), N4–C9 128.3(2), N2–C4 139.2(3), N3–C4 138.8(2), N5–C9 137.9(3), N6–C9 138.9(2), C1–C2 139.7(2), C2–C3 140.6(2), C1–C1 142.4(4), C3–C3 142.3(4), C1–N1–C4 120.66(16). C3–N4–C9 124.73(17).



to Me₂SI⁺ and I⁻. Halogenation of the aromatic ring by Me₂SI⁺ leads to the product. In addition to $2a(I_3)_2$ and $2b(I_3)_2$, small amounts of the monoiodated salts were isolated in crystalline form. Details of their molecular structures can be found in the Supporting Information. Finally, 2a and 2b were synthesized by reduction with hydrazine in *N*,*N*-dimethylformamide (DMF).^[21]

Both compounds crystallized from CH_2Cl_2 solutions overlaid with Et_2O , and their molecular structures are illustrated in Figure 4.

Compounds 3a and 3b

Nitration of **1a** with NO₂BF₄ in CH₃CN solution at 0 °C afforded **3a** (Scheme 5). Different to **1a**, which gave colourless crystals with a diamond-like shiny appearance (indicating a large refractive index), the push-pull system **3a** was isolated as deep red crystals.

1a / 1b + 2 NO₂BF₄ ----- 3a / 3b + 2 HBF₄

Scheme 5.

Figure 5 shows the molecular structure of 3a. A ball-andstick representation illustrates that the steric situation around the benzene ring is relatively relaxed. The NO₂ groups are not buried by the guanidino groups, but protrude. However, at 147.34(2) pm the C–NO₂ bond lengths are relatively long. A further important structural difference between 1a and 3a is the increase of the C1–C2–C3 angle from 122.81(12)° in 1a to 126.11(12)° in 3a.



Figure 5. a) Molecular structure of **3a**. Thermal ellipsoids drawn at the 50% probability level. Selected bond lengths [pm] and angles [°]: O1–N7 122.51(16), O2–N7 122.80(16), N1–C1 140.42(17), N1–C4 129.77(18), N2–C4 137.72(19), N3–C4 137.37(19), N4–C3 139.90(17), N4–C9 130.46(17), N5–C9 137.29(18), N6–C9 137.48(18), N7–C2 147.34(18), C1–C2 139.64(19), C1–C3 140.97(19), O1–N7–O2 123.35(12), C1–N1–C4 120.43(12), C3–N4–C9 121.09(12), C1–C2–C3 126.11(12). b) Spacefilling model. c) View along the C₆ ring.

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Similarly, **3b** was prepared by the nitration of **1b** with NO_2BF_4 , and its structure is shown in Figure 6. It also features relatively long C–NO₂ bonds [147.3(3) and 147.6(3) pm], and the C–C–C angle around the substituted C6/C3 atoms increases by 4°.



Figure 6. Molecular structure of **3b**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: N1–C1 140.2(3), N1–C7 129.9(3), N2–C7 136.0(3), N3–C7 136.9(3), N4–C2 141.0(3), N4–C12 129.5(3), N5–C12 138.1(3), N6–C12 137.9(3), N7–C4 140.6(3), N7–C17 128.6(3), N8–C17 136.9(3), N9–C17 138.6(3), N10–C5 140.1(3), N10–C22 129.4(3), N11–C22 138.6(3), N12–C22 137.2(3), N13–O1 122.0(2), N13–O2 123.2(2), N13–C3 147.3(3), N14–O3 122.6(2), N14–O4 122.2(2), N14–C6 147.6(3), C1–C 2 141.1(3), C1–C 6 139.5(3), C2–C3 139.1(3), C3–C4 139.2(3), C4–C5 141.3(3), C5–C6 138.9(3), O1–N13–O2 123.58(19), O3–N14–O4 124.43(19), C2–C3–C4 127.0(2), C1–C6–C5 127.1(2).

Optical Spectra

The UV/Vis spectra of all six guanidines contain intense bands due to $\pi \rightarrow \pi^*$ transitions localized on the benzene ring and electronic transitions that involve the guanidino groups (see Supporting Information). In the spectra of **3a** (Figure 7) and **3b**, a very broad band centred at 475 nm in **3a** and 448 nm in **3b** appeared, which was absent in the spectra of the other guanidines and most likely arises from charge-transfer transitions that involve both the guanidino donor and nitro acceptor groups.



Figure 7. Comparison of the UV/Vis spectra of 3a and $(3a)I_2$ in CH_2Cl_2 .

Protonation

The protonation steps in the titration curves overlapped heavily (see Supporting Information for an example). Therefore, the $pK(BH^+)$ values were estimated with the help of quantum chemical calculations and empirical correlations (Table 1). In most cases the protonated species were crystallized and structurally analyzed. Figure 8 shows part of the crystal structure of $[3aH_3]Cl_3 \cdot 3H_2O$ as an example.



Figure 8. a) Molecular structure of [3aH₃]Cl₃·3H₂O. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: N1-C1 140.9(3), N1-C7 136.6(3), N2-C7 132.5(3), N3-C7 133.5(3), N4-C2 142.5(3), N4-C12 134.9(3), N5-C12 133.4(3), N6-C12 133.5(3), N7-C4 141.2(3), N7-C17 135.0(3), N8-C17 133.8(3), N9-C17 133.4(3), N10-C5 137.6(3), N10-C22 131.8(3), N11-C22 136.3(3), N12-C22 135.0(3), C1-C2 139.4(3), C1-C6 140.0(3), C2-C3 140.6(3), C3-C4 138.3(3), C4-C5 142.4(3), C5-C6 141.3(3), N13-C3 148.1(3), N13-O1 120.8(3), N13-O2 122.4(3), N14-O3 123.6(2), N14-O4 122.2(3), O1-N13-O2 124.6(2), O3-N14-O4 124.08(19), 126.89(19), N2–C7–N3 C1-N1-C7 121.7(2), C2–N4–C12 125.03(19), N5-C12-N6 119.8(2), C4-N7-C17 121.29(19), N8-C17-N9 120.9(2), C5-N10-C22 121.42(19), N11-C22-N12 116.4(2). b) Illustration of the hydrogen-bonded network.

A hydrogen-bonded network, which involves cocrystallized water molecules, was established. Illustrations of the structures of other salts of protonated guanidines are included in the Supporting Information. Selected structural changes upon protonation are listed in Table 2. Protonation leads to a significant increase (of more than 5 pm) in the N=C bond lengths. At the same time, the C–NMe₂ bond lengths decrease.



Table 2. Average values of characteristic bond lengths [pm] in 1a, 2a, 3a, 1b, 2b and 3b before and after protonation.

| | 1a | $[1aH_4]Cl_4$ | $[1aH_2](PF_6)_2$ | 2a | $[2\mathbf{a}H_2]I_2$ | 3a | [3aH ₃]Cl ₃ | 1b | $[1b\mathrm{H}_4]\mathrm{Cl}_4$ | $[1bH_2](PF_6)_2$ | 2b | 3b |
|---------------------------|-------|---------------|-------------------|-------|-----------------------|-------|------------------------------------|-------|---------------------------------|-------------------|-------|-------|
| N=C | 128.9 | _ | 130.0(3) | 129.5 | 130.6(2) | 130.1 | 131.8(3) | 130.1 | _ | 128.2(2) | 128.3 | 129.4 |
| (H)N=C | _ | 135.9 | 134.4(3) | - | 135.7(2) | _ | 135.5 | | 134.7 | 133.1(3) | _ | _ |
| C-NMe ₂ | 138.9 | - | 137.4 | 138.2 | 137.0 | 137.5 | 135.7 | 137.2 | _ | 139.4 | 138.7 | 138.7 |
| (H)C– NMe ₂ | - | 133.4 | 133.7 | _ | 133.3 | _ | 133.4 | | 133.63 | 133.2 | - | _ |

Redox Properties

The cyclic voltammograms (CVs) of all six guanidine electron donors in CH_2Cl_2 are shown in Figure 9 (0.1 M Bu_4NPF_6 supporting electrolyte at a scan rate of 100 mV/s).



Figure 9. CVs of 1a, 2a, 3a, 1b, 2b and 3b.

The *E* values (relative to Fc/Fc⁺, see Supporting Information for curves relative to SCE) at the wave maxima are included in Table 3. In all cases, a two-electron oxidation wave was observed at negative potentials. Even on changing the electrolyte (e.g. NBu₄BPh₄ and other salts of relatively weakly coordinating anions), we were unable to distinguish between the two one-electron events. Quantum chemical calculations (B3LYP) of the gas-phase disproportionation of two equivalents of the radical monocation into one equivalent of the dication and the neutral guanidine resulted in a very large estimate of ΔG^0 of +253 kJ mol⁻¹. More work is necessary to identify the reason for the instability of the radical cations. In addition, the CVs for **1a**, **1b**,

2a and **2b** showed a one-electron wave due to oxidation to the trications at positive potentials. The corresponding waves for **3a** and **3b** are outside the window in which measurements are possible in CH₂Cl₂. The two-electron wave was relatively broad for **3a** and **3b**, which might suggest differences in the speed of electron transfer. According to the CV experiments, **1b** is the strongest electron donor with $E_{1/2} = -0.79$ V vs. Fc/Fc⁺ and **3a** is the weakest with $E_{1/2} = -0.54$ V vs. Fc/Fc⁺ in CH₂Cl₂ solutions.

Table 3. Summary of the CV results (*E* values [V] relative to Fc/ Fc⁺).

| First (t | wo-electro | on) wave | Second | (one-elect | ron) wave |
|----------|--|--|--|--|---|
| Eox | $E_{\rm red}$ | E _{1/2} | $E_{\rm ox}$ | E _{red} | $E_{1/2}$ |
| -0.71 | -0.82 | -0.76 | 0.72 | 0.65 | 0.68 |
| -0.74 | -0.85 | -0.79 | 0.70 | 0.62 | 0.66 |
| -0.54 | -0.64 | -0.59 | 0.88 | 0.82 | 0.85 |
| -0.55 | -0.67 | -0.61 | 0.82 | 0.75 | 0.79 |
| -0.27 | -0.54 | -0.41 | [a] | [a] | [a] |
| -0.33 | -0.56 | -0.45 | [a] | [a] | [a] |
| | $\begin{array}{c} -0.71\\ -0.74\\ -0.54\\ -0.55\\ -0.27\\ -0.33 \end{array}$ | $\begin{array}{c c} First (two-electron \\ \hline E_{ox} & E_{red} \\ \hline -0.71 & -0.82 \\ -0.74 & -0.85 \\ -0.54 & -0.64 \\ -0.55 & -0.67 \\ -0.27 & -0.54 \\ -0.33 & -0.56 \end{array}$ | First (two-electron) wave E_{ox} E_{red} $E_{1/2}$ -0.71 -0.82 -0.76 -0.74 -0.85 -0.79 -0.55 -0.67 -0.61 -0.27 -0.54 -0.41 -0.33 -0.56 -0.45 | First (two-electron) wave Second E_{ox} E_{red} $E_{1/2}$ E_{ox} -0.71 -0.82 -0.76 0.72 -0.74 -0.85 -0.79 0.70 -0.54 -0.64 -0.59 0.88 -0.55 -0.67 -0.61 0.82 -0.27 -0.54 -0.41 [a] -0.33 -0.56 -0.45 [a] | First (two-electron) wave Second (one-electron) E_{ox} E_{red} $E_{1/2}$ E_{ox} E_{red} -0.71 -0.82 -0.76 0.72 0.65 -0.74 -0.85 -0.79 0.70 0.62 -0.54 -0.64 -0.59 0.88 0.82 -0.55 -0.67 -0.61 0.82 0.75 -0.27 -0.54 -0.41 [a] [a] |

[a] Outside the solvent window.

This is in line with the calculated gas-phase electron donor capacity. The electron donor capacity decreases in the order 1b > 1a > 2b > 2a > 3b > 3a. The HOMOs (vide supra) were shown to look similar for the unsubstituted and substituted guanidines (Figure 2). Therefore, it is reasonable to correlate the HOMO energies with the measured potentials. The plot in Figure 10 indeed shows a linear relation-



Figure 10. $E_{1/2}$ values [V] for oxidation to the dication as a function of the HOMO energies [eV] of the neutral guanidines.

ship between the calculated HOMO energies and the measured $E_{1/2}$ values. We found the relationship E_{HOMO} [eV] = $-1.61 \cdot E_{1/2}$ [V] - 5.28.

Next, the twofold-oxidized electron donors were structurally characterized. To this end, salts were synthesized by the reaction of the neutral guanidines with I_2 . The anions were either I_3^- or I^- . Figure 11 displays the structures of $2b(I_3)_2$ and $3aI_2$ as examples.

a)



Figure 11. a) Molecular structure of 2b(I₃)₂. Ellipsoids are drawn at the 50% probability level. Selected distances [pm] and angles [°]: N1-C1 133.4(4), N1-C4 132.0(5), N2-C4 134.3(5), N3-C4 135.0(5), N4-C3 129.6(4), N4-C9 135.7(5), N5-C9 133.4(4), N6-C9 132.5(5), C1–C2 137.8(5), C1–C3 151.5(5), C3–C2' 142.7(5), C2-I1 210.0(4), I2-I3 291.38(9), I3-I4 290.96(10), I1...I2 385.6(1), C1-N1-C4 128.0(3), C3-N4-C9 128.8(3), N2-C4-N3 110.1(3), N5-C9-N6 112.5(3), I2-I3-I4 177.672(12). b) Molecular structure of 3aI₂. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [pm] and angles [°]: O1-N7 123.48(17), O2-N7 N1-C4 136.82(18), N2-C4 122.68(17), N1-C1 129.16(17), 132.81(18), N3-C4 134.62(19), N4-C2 132.02(17), N4-C9 135.58(17), N5-C9 134.30(18), N6-C9 133.85(19), N7-C3 C1–C3 142.27(19), C2-C3 146.56(17), C1-C2151.21(18), 138.81(18).

Some important structural differences between the neutral and dicationic guanidines are highlighted in Table 4. The most remarkable structural change is the elongation of the NC–CN bond lengths between the two adjacent carbon atoms in the central C_6 ring that are attached to the guanidino groups. Two-electron oxidation resulted in an increase of these bond lengths by more than 9 pm. The other four C–C bond lengths within the C_6 ring are similar, which indicates the bisallylic character of the dication.

The delocalization of the positive charges on to the guanidino groups causes a significant increase of 5 pm or more for the imino N=C bond lengths. Although the NC-CN bond lengths increased, the separations between the N atoms attached to two adjacent ring carbon atoms decreased sharply. Generally the effects were larger for the cyclic guanidines than for the acyclic ones. In the case of **1b**, the N···N separation was 297.7 pm before and 274.5 pm after two-electron oxidation.

Of particular interest are the changes in the optical properties upon oxidation. Two-electron oxidation was accompanied by intense colouration. For example, $[3a]I_2$ is dark red. The absorption spectrum of $[3a]I_2$ in CH₂Cl₂ is plotted with that of neutral **3a** in Figure 7.

Ligand Properties

Finally, we probed the suitability of the push-pull system **3a** as a ligand in preliminary experiments. The reaction of **3a** with CuI furnished the dinuclear complex $[3a(CuI)_2]$ (Scheme 6), and its structure is illustrated in Figure 12. The two Cu ions are displaced from the C₆ ring plane and adopt a *trans*-type structure with one Cu below and the other above the aromatic plane. The imino N=C bond lengths are elongated upon coordination from 129.77(18)/130.46(17) to 132.9(3)/133.3(3) pm. The changes are slightly smaller than those that occurred on protonation.

Scheme 6.

All of the bands in the absorption spectrum (Figure 13) experience a redshift upon coordination. Hence the bands at 255 and 321 nm in the spectrum of **3a** shift to 279 and 332 nm in that of $[3a(CuI)_2]$. The broad charge-transfer band at 474 nm shifts to 582 nm and increases in intensity.

The comparison between $[1a(CuI)_2]$ and $[3a(CuI)_2]$ (Table 5) reveals some differences, which could explain their different reactivities. All parameters indicate a weaker metal-ligand bond in $[3a(CuI)_2]$. Hence the average Cu–N distance is longer, and the imino N=C bond length is shorter (closer to the value in the free ligand) in $[3a(CuI)_2]$ than $[1a(CuI)_2]$. In addition, the shortest distance between

Table 4. Characteristic bond lengths [pm] of 1a, 2a, 3a, 1b, 2b and 3b and their changes upon two-electron oxidation [dication from the triiodide or iodide (in the case of 3a) and PF_6^- (in the case of 1b) salts].

| | 1a | 1a ²⁺ | 2a | 2a ²⁺ | 3a | 3a ²⁺ | 1b | 1b ²⁺ | 2b | 2b ²⁺ | 3b | 3b ²⁺ |
|-------------------------------------|------------|------------------|-----------|------------------|------------|------------------|------------|------------------|-----------|------------------|-----------|------------------|
| NC _{Ar} -C _{Ar} N | 140.87(2) | 149.1(4) | 141.3(3) | 150.6(7) | 140.97(2) | 151.21(2) | 141.34(2) | 150.6(4) | 142.4(4) | 151.5(5) | 141.1(3) | [a] |
| N=C | 128.77(2)/ | 133.9(3)/ | 129.0(3)/ | 133.7(6)/ | 129.77(2)/ | 135.58(2)/ | 128.66(2)/ | 133.7(3)/ | 128.3(2)/ | 132.0(5)/ | 129.9(3)/ | [a] |
| | 129.10(2) | 136.4(4) | 130.0(3) | 135.5(7) | 130.46(2) | 136.82(2) | 129.03(2) | 135.4(3) | 128.3(2) | 135.7(5) | 129.5(3) | |
| N…N | 287.5 | 275.6 | 281.1 | 273.1 | 287.3 | 272.2 | 297.7 | 274.5 | 284.0 | 271.6 | 293.0 | [a] |

[a] Not structurally characterized.



Figure 12. a) Molecular structure of $[3a(CuI)_2]$. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Cu–I 244.93(8), Cu–N1 204.63(19), Cu–N4 204.08(18), N1–C1 140.2(3), N1–C4 132.9(3), N2–C4 135.5(3), N3–C4 135.4(3), N4–C2 140.1(3), N4–C9 133.3(3), N5–C9 135.6(3), N6–C9 136.1(3), N7–C3 147.5(3), N7–O1 123.5(2), N7–O2 123.4(2), C1–C2 142.1(3), C1–C3' 140.4(3), C2–C3 140.5(3), N1–Cu–N4 81.26(7), N1–Cu–I 137.03(5), N4–Cu–I 141.60(5). b) View along the C₆ ring.



Figure 13. The UV/Vis spectra of 3a and [3a(CuI)₂] in CH₂Cl₂.

copper and the plane defined by the C₆ ring, $d(C_6-Cu)$, and the dihedral angle between the C₆ and N-Cu-N planes, \angle (C₆-N-Cu-N), are much larger in [**3a**(CuI)₂] than [**1a**(CuI)₂] (Figure 12, b).

Having synthesized [**3a**(CuI)₂], our next aim was its oxidation. The oxidation of [**1a**(CuI)₂] has previously been shown to give the semiconducting chain polymer [{**1a**(CuI)₂}-(I₃)₂]_n. In this case a molecular complex of the type [Cu^I– GFA-4–Cu^I] was oxidized into a [Cu^I–GFA-4²⁺–Cu^I]-type coordination polymer. According to band structure calculations, the already low band gap (experimental estimate 1.1 eV, calcd. 1.5 eV) could be further reduced by NO₂ substitution at the C₆ rings.^[18] However, the only product iso-

Table 5. Characteristic bond lengths [pm] and torsion angles [°] of $[1a(CuI)_2]$ and $[3a(CuI)_2]$.

| | [1a(CuI) ₂] | [3a (CuI) ₂] |
|-----------------------------------|-------------------------|----------------------------------|
| N=C | 141.5(2) | 140.2(3) |
| | 140.6(2) | 135.5(3) |
| Cu–N | 201.60(18) | 204.63(19) |
| | 201.68(16) | 204.08(18) |
| Cu–I | 244.15(7) | 244.93(8) |
| N…N | 268.4 | 266.1 |
| \angle (C ₆ -N-Cu-N) | 10.45 | 25.88 |
| $d(C_6-Cu)$ | 41.0 | 78.3 |

lated from the reaction between $[3a(CuI)_2]$ and I_2 was (3a)I₂. The Lewis basicity of 3a seems to be too low to allow copper coordination after two-electron oxidation. When a solution of $[3a(CuI)_2]$ was exposed to air for several days at r.t., we observed the formation of $(3a)I_2$ again. In addition, new mononuclear 5 was isolated, which consists of a C₃N₂ heterocycle (with two N=C double bonds) fused to a cyclopentadiene derivative (Figure 14). Compound 5 features three intact guanidino groups, two of which coordinate to one CuI₂. It was formed from $[3a(CuI)_2]$ by methane and copper elimination. In future, we will continue the oxidation experiments using different oxidation reagents (e.g. AgPF₆).



Figure 14. Molecular structure of **5**. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: C1–N1 132.7(4), C2–N4 129.6(4), N1–C7 136.3(4), N4–C12 138.0(4), N2–C7 132.1(4), N3–C7 134.6(4), N5–C12 133.2(4), N6–C12 133.2(4), C6–N7 129.1(4), C5–N14 138.6(4), C3–N13 136.8(4), C22–N10 128.6(4), C22–N12 142.8(4), C6–N12 135.6(4), C1–C2 151.0(4), C1–C5 138.9(4), C2-C3 141.0(5), Cu1–I1 254.45(6), Cu1–N1 210.0(3), Cu1–N4 215.4(3), N13–O1 126.7(3), N14–O3 125.1(4), C1–N1–Cu1 114.6(2), C2–N4–Cu1 114.3(2), N14–Cu1–I2 113.85(8), N1–Cu1–I1 116.79(7), N4–Cu1–I1 112.01(8), N1–Cu1–N4 77.98(10), I1–Cu1–I2 116.32(2).

Conclusions

The effect of substitution at the aromatic ring on the properties of guanidine electron donors was analyzed. The optical properties, Brønsted basicity and electron donor capacity of six guanidines were compared. The HOMO–LUMO gap of the guanidines is substantially influenced by substitution. Substitution with nitro groups led to intensely

coloured push-pull compounds. The estimated $pK(BH^+)$ values of the corresponding acids could be modified in a relatively large window by substitution $[pK(BH^+) = 19.6 -$ 25.5]. The structural changes upon protonation were studied and shown to affect the guanidino groups almost exclusively. The half potentials for the first (two-electron) oxidation/reduction waves varied between -0.76 and -0.41 V relative to Fc/Fc⁺. The oxidation potentials measured by cyclic voltammetry showed a linear correlation with the calculated HOMO energies. The dications that result from two-electron oxidation can be described in all cases as a pair of bisguanidinoallyl cations connected by two C-C single bonds. In preliminary experiments, the suitability of the guanidines as ligands was tested. The stability of [Cu^I–GFA-4–Cu^I]-type complexes were compared, and the redox chemistry of such complexes was analyzed. The results presented here demonstrate that the properties of the guanidine electron donors could indeed be altered over a large range by substitution at the aromatic ring system. The possibility of tuning the properties adds to the interest in these compounds for organic electronics and as building blocks in polymeric networks and conducting coordination polymers.

Experimental Section

General: All reactions were carried out under an Ar atmosphere using standard Schlenk techniques. All solvents were dried prior to use by standard methods. Compounds 1a, 1b and $2a(I_3)_2$ were prepared as described.^[10-12] IR spectra were recorded with a BIORAD Excalibur FTS 3000. NMR spectra were recorded with BRUKER Avance II 400 or BRUKER Avance DPX AC200 instruments. Elemental analyses were carried out at the Microanalytical Laboratory of the University of Heidelberg. UV/Vis spectra were measured with a Varian Cary 5000 spectrometer. Fluorescence measurements were recorded with a Varian Cary Eclipse machine. Electrochemical studies were carried out at r.t. using an EG&G model 273A potentiostat/galvanostat. The auxiliary electrode was a platinum wire and the working electrode was a glassy carbon disk. The reference electrode was an aqueous saturated calomel electrode. Calculations were carried out with the aid of the Gaussian 09^[22] program. Pure DFT calculations relied on the hybrid-method B3LYP (DFT using the Becke^[23] exchange functional and Lee-Yang-Parr^[24] correlation functional) with the 6-311G(d,p) basis set. Calculations on the solvent effect using CH₃CN (with static dielectric constant ε = 36.61 and dynamic dielectric constant of 1.806) were carried out using the CPCM.^[25]

Synthesis of 4: N,N,N',N'-Tetramethylurea (2.2 mL, 18.4 mmol) was dissolved in dry CHCl₃ (12 mL), and oxalyl chloride (8.0 mL, 91.0 mmol, 4.9 equiv.) was added dropwise to this solution. The reaction mixture was stirred for 16 h under reflux. The solvent was removed under vacuum, and the remaining solid was washed with Et₂O. The obtained 2-chloro-1,1',3,3'-tetramethylformamidium-chloride was dissolved in CH₃CN (48 mL) and added dropwise to a CH₃CN solution (20 mL) of 1,2,4,5-tetraaminobenzene (1.0 g, 3.5 mmol) and triethylamine (6.7 mL, 48.1 mmol) at 0 °C, and the mixture was stirred for 75 min at 0 °C. The precipitate was collected by filtration and washed with cold CH₃CN before being redissolved in HCl (10%). After addition of NaOH (20%), a white precipitate was formed. The resulting precipitate was collected by filtration

and washed with CH_3CN and Et_2O . Compound 4 (0.280 g, 1.2 mmol, 32%) was obtained as a pale greenish-white solid. Upon recrystallization from EtOH, colourless crystals were obtained. C₁₂H₁₆N₆ (244.30): calcd. C 59.00, H 6.60, N 34.40; found C 58.24, H 6.62, N 34.21. ¹H NMR (600.13 MHz, CD₃OD): δ = 7.11 (s, 2 H), 3.10 (s, 12 H) ppm. ¹³C{¹H} NMR (150.92 MHz, CD₃OD): δ = 157.76, 38.77 (CH₃) ppm. IR (CsI): \tilde{v} = 2951 (w), 2879 (w), 1590 (vs), 1515 (m), 1456 (s), 1428 (vs), 1379 (m), 1314 (m), 1233 (m), 1154 (m), 1064 (w), 1026 (w), 922 (m), 881 (s), 837 (m), 694 (w), 591 (w) cm⁻¹. UV/Vis (CH₃OH, $c = 2.78 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ε , $dm^3 mol^{-1} cm^{-1}$) = 324 (2.82 × 10⁴) nm. MS (FAB+): m/z (%) = 245 (100) $[4H]^+$, 215 (12). Crystal data for $C_{12}H_{16}N_6$ ·2EtOH: $C_{16}H_{28}N_6O_2$, $M_r = 336.44$, $0.20 \times 0.15 \times 0.15$ mm³, monoclinic, space group $P2_1/c$, a = 10.805(2), b = 13.699(3), c = 12.278(3) Å, $\beta = 99.28(3)^{\circ}$, V = 1793.6(6) Å³, Z = 4, $d_{calc} = 1.246$ Mg m⁻³, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T =100 K, θ_{range} 1.91 to 30.02°. Reflections measd. 10236, indep. 5236, $R_{\text{int}} = 0.0458$. Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0499$, w $R_2 =$ 0.1130.

Synthesis of $1b(I_3)_2$: To a solution of 1b (0.06 g, 0.12 mmol) in CH₂Cl₂ (9 mL) was added a solution of I₂ (0.09 g, 0.35 mmol) in CH_2Cl_2 (10 mL). The colour of the mixture turned deep green. After stirring for 20 min at r.t., the solvent was removed in vacuo and the remaining green solid dissolved in CH₃CN. Black crystals of $2(I_3)_2$ (0.09 g, 0.07 mmol, 64%) of a metallic appearance were obtained from a concentrated solution of CH₃CN at r.t. C₂₆H₄₂I₆N₁₂ (1284.10): calcd. C 24.32, H 3.30, N 13.09; found C 24.50, H 3.39, N 12.94. ¹H NMR (399.89 MHz, CD₃CN): δ = 5.26 (s, 2 H, CH), 3.70 (s, 8 H, CH₂), 3.61 (s, 8 H, CH₂), 2.74 (s, 24 H, CH₃) ppm. ¹³C{¹H} NMR (100.56 MHz, CD₃CN): δ = 165.38, 158.47, 100.14 (CH), 48.67 (CH₂), 33.24 (CH₃) ppm. IR (CsI): $\tilde{v} =$ 2940 (w), 2882 (w), 1623 (s), 1562 (vs), 1508 (vs), 1466 (vs), 1412 (s), 1374 (s), 1351 (vs), 1285 (s), 1239 (m), 1204 (m), 1088 (w), 1026 (vs), 971 (s), 898 (w), 825 (w), 781 (m), 744 (s), 653 (w), 616 (w), 583 (w), 556 (w) cm⁻¹. UV/Vis (CH₂Cl₂, $c = 1.43 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ϵ , dm³mol⁻¹ cm⁻¹) = 294 (10.16 × 10⁴), 368 (5.84 × 10⁴), 592 (0.07×10^4) nm. MS (ESI): m/z (%) = 648 (10) [1b + I]⁺, 324 (100) $[1b + I]^{2+}$, 261 (97) $[1b]^{2+}$, 232 (92) $[1b-C_3H_7N]^{2+}$, 174 (30) $[1b]^{3+}$.

Synthesis of 1b(PF₆)₂: Compound 1b (0.063 g, 0.121 mmol) was dissolved in CH₃CN (6 mL) and stirred for 1 d at r.t. in air. To the resulting green solution was added NH₄PF₆ (0.039 g, 0.239 mmol). After the addition of Et_2O , dark crystals of $1b(PF_6)_2$ (0.067 g, 0.082 mmol, 67%) were obtained. $C_{26}H_{42}F_{12}N_{12}P_2$ (812.62): calcd. C 38.43, H 5.21, N 20.68; found C 38.46, H 5.20, N 20.56. ¹H NMR (399.89 MHz, CD₃CN): δ = 3.69–3.59 (m, 16 H, CH₂), 2.73 (s, 24 H, CH₃) ppm. ¹³C{¹H} NMR (100.56 MHz, CD₃CN): δ = 165.41, 158.47, 100.13 (CH), 48.62 (CH₂), 33.17 (CH₃) ppm. IR (CsI): $\tilde{v} = 2924$ (w), 1628 (m), 1571 (s), 1515 (vs), 1477 (s), 1411 (w), 1355 (s), 1284 (m), 1240 (w), 1027 (m), 973 (m), 841 (vs), 799 (w), 734 (m), 557 (s) cm⁻¹. UV/Vis (CH₃CN, c = $0.71 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ϵ , dm³ mol⁻¹ cm⁻¹) = 225 (3.20×10⁴), 279 (1.40×10^4) , 419 (3.93×10^4) , 605 (0.05×10^4) nm. MS (ESI): m/z (%) = 667 (82) [1b + PF₆]⁺, 261 (100) [1b]²⁺. Crystal data for $C_{26}H_{42}F_{12}N_{12}P_2$: $M_r = 812.66, 0.35 \times 0.30 \times 0.30 \text{ mm}^3$, monoclinic, space group $P2_1/c$, a = 9.7430(19), b = 10.600(2), c = 17.158(3) Å, $\beta = 96.16(3)^{\circ}$, $V = 1760.2(6) \text{ Å}^3$, Z = 2, $d_{\text{calc}} = 1.533 \text{ Mgm}^{-3}$, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T =100 K, θ_{range} 2.06 to 29.49°. Reflections measd. 8286, indep. 4851, $R_{\text{int}} = 0.0557$. Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0684$, w $R_2 =$ 0.1891.

Synthesis of $2b(I_3)_2$: To a solution of $1b(I_3)_2$ (0.043 g, 0.03 mmol) in DMSO (20 mL) was added I₂ (0.007 g, 0.03 mmol). The reaction



mixture was stirred for 1 h under reflux. The solvent was removed under vacuum. Upon recrystallization from CH₃CN, dark crystals of $2b(I_3)_2$ (0.031 g, 0.02 mmol, 66%) were obtained. $C_{26}H_{40}I_8N_{12}$ (1535.88): calcd. C 20.33, H 2.62, N 10.94; found C 20.41, H 2.62, N 10.95. ¹H NMR (600.13 MHz, CD₃CN): δ = 3.72–3.61 (m, 16 H, CH₂), 2.71 (s, 24 H, CH₃) ppm. ¹³C{¹H} NMR (150.92 MHz, CD₃CN): δ = 163.52, 157.17, 79.33, 48.46 (CH₂), 33.15 (CH₃) ppm. IR (CsI): $\tilde{v} = 2925$ (w), 2866 (w), 1643 (s), 1567 (vs), 1507 (vs), 1409 (s), 1373 (m), 1330 (vs), 1293 (s), 1266 (s), 1233 (m), 1169 (w), 1087 (w), 1033 (s), 954 (w), 843 (w), 749 (m), 705 (w), 663 (w), 634 (w), 569 (m), 547 (w) cm⁻¹. UV/Vis (CH₂Cl₂, c = $1.02 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ϵ , dm³ mol⁻¹ cm⁻¹) = 294 (8.11×10⁴), 368 (4.86 × 10⁴) nm. MS (ESI): m/z (%) = 774 (100) [2b]⁺, 387 (66) $[2b]^{2+}$. Crystal data for $C_{26}H_{40}I_8N_{12}$: $M_r = 3071.80$, $0.30 \times 0.20 \times 0.20$ mm³, triclinic, space group $P\bar{1}$, a = 10.027(2), b = 10.361(2), c = 11.286(2) Å, $a = 65.68(3)^{\circ}$, $\beta = 81.27(3)^{\circ}$, $\gamma =$ 84.36(3)°, V = 1055.3(4) Å³, Z = 1, $d_{calc} = 2.417$ Mg m⁻³, Mo- K_{α} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 2.00 to 29.99°. Reflections measd. 23683, indep. 6160, R_{int} = 0.0458. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0325$, w $R_2 = 0.0697$.

Synthesis of 2a: To a solution of $2a(I_3)_2$ (0.103 g, 0.067 mmol) in DMF (2 mL) was added hydrazine monohydrate (0.1 mL) under an argon atmosphere. The mixture was stirred at r.t. for 1 h. The resulting precipitate was collected by filtration and washed with CH₃CN. The resulting yellow solid was dissolved in HCl (10%). After addition of NaOH (20%), the solution was extracted three times with CH₂Cl₂. The combined organic phases were dried with K_2CO_3 , and the solvent was removed under vacuum to yield 2a (0.034 g, 0.044 mmol, 65%) as a yellow powder. $C_{26}H_{48}I_2N_{12}$ (782.55): calcd. C 39.91, H 6.18, N 21.48; found C 39.76, H 6.08, N 21.35. ¹H NMR (600.13 MHz, CD₂Cl₂): δ = 2.68 (s, 48 H, CH₃) ppm. ¹³C{¹H} NMR (150.92 MHz, CD₂Cl₂): δ = 158.98, 138.80, 96.63, 39.85 (CH₃) ppm. IR (CsI): $\tilde{v} = 2919$ (w), 2801 (w), 1584 (vs), 1499 (m), 1452 (m), 1422 (m), 1407 (m), 1366 (s), 1235 (w), 1189 (m), 1135 (s), 1065 (w), 1042 (w), 1015 (m), 949 (w), 910 (m), 809 (m), 756 (w), 723 (w), 687 (w), 610 (w) cm⁻¹. UV/Vis (CH₂Cl₂, $c = 1.8 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ε , dm³ mol⁻¹ cm⁻¹) = 255 (4.77 × 10⁴), 339 (0.99×10^4) nm. MS (FAB⁺): m/z (%) = 783 (100) [(**2a**)H]⁺, 737 (69) $[2a-HN(CH_3)_2]^+$. Crystal data for $C_{26}H_{48}I_2N_{12}$: $M_r = 782.56$, $0.30 \times 0.20 \times 0.20$ mm³, monoclinic, space group $P2_1/n$, a =9.900(2), b = 16.157(3), c = 11.044(2) Å, $\beta = 113.29(3)^{\circ}$, V =1622.6(6) Å³, Z = 2, $d_{calc} = 1.602 \text{ Mg m}^{-3}$, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 2.34 to 30.21°. Reflections measd. 27257, indep. 4763, $R_{int} = 0.0525$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0285$, w $R_2 = 0.0654$.

Synthesis of 2b: To a solution of $2b(I_3)_2$ (0.152 g, 0.099 mmol) in DMF (2 mL) was added hydrazine monohydrate (0.07 mL) under an argon atmosphere. The mixture was stirred at r.t. for 1 h. The resulting precipitate was collected by filtration and washed with CH₃CN. The resulting yellow solid was dissolved in HCl (10%). After addition of NaOH (20%), the solution was extracted three times with CH₂Cl₂. The combined organic phases were dried with K_2CO_3 , and the solvent was removed under vacuum to yield 2b (0.053 g, 0.068 mmol, 69%) as a yellow powder. $C_{26}H_{40}I_2N_{12}$ (774.49): calcd. C 40.32, H 5.21, N 21.70; found C 40.53, H 5.17, N 21.40. ¹H NMR (399.89 MHz, CD₂Cl₂): δ = 3.24–3.14 (m, 16 H, CH₂), 2.62 (s, 24 H, CH₃) ppm. ¹³C{¹H} NMR (100.55 MHz, CD₂Cl₂): *δ* = 153.55, 137.18, 98.39, 48.85 (CH₂), 34.50 (CH₃) ppm. IR (CsI): $\tilde{v} = 2924$ (w), 2846 (w), 1636 (vs), 1488 (m), 1439 (w), 1418 (m), 1390 (m), 1285 (m), 1244 (m), 1236 (m), 1194 (w), 1167 (m), 1048 (m), 1033 (w), 991 (w), 968 (w), 939 (s), 825 (w), 739 (w), 659 (w), 637 (w), 608 (w) cm⁻¹. UV/Vis (CH₂Cl₂, c = $7.0 \times 10^{-6} \text{ mol } \text{L}^{-1}$): λ_{max} (ϵ , dm³ mol⁻¹ cm⁻¹) = 254 (12.13×10⁴), 345 (2.37 × 10⁴) nm. MS (ESI⁺): m/z (%) = 775 (100) [(**2b**)H]⁺, 388 (11) [(**2b**)2H]²⁺. Crystal data for C₂₆H₄₀I₂N₁₂: M_r = 774.50, 0.30 × 0.30 × 0.30 mm³, monoclinic, space group C2/c, a = 12.663(3), b = 14.440(3), c = 16.619(3) Å, β = 98.06(3)°, V = 3008.8(0) Å³, Z = 4, d_{calc} = 1.710 Mgm⁻³, Mo- K_a radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} 2.34 to 30.21°. Reflections measd. 8512, indep. 4394, R_{int} = 0.0220. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0266, w R_2 = 0.0716.

Synthesis of 3a: NO₂BF₄ (0.398 g, 3.0 mmol) was dissolved in CH₃CN (24 mL) at 0 °C and added dropwise to a suspension of 1a (0.362 g, 0.68 mmol) in CH₃CN (11 mL). The reaction mixture was stirred for 0.5 h at 0 °C. Removal of the solvent in vacuo led to a brown-red solid, which was redissolved in water and HCl (10%). After addition of NaOH (20%), the solution was extracted three times with CH2Cl2. The combined CH2Cl2 phases were dried with K₂CO₃, and the solvent was removed under vacuum. Upon recrystallization from CH₃CN, deep red crystals of [C₆(NO₂)₂- ${NC(NMe_2)_2}_4$ (0.062 g, 0.1 mmol, 14%) were obtained. $C_{26}H_{48}N_{14}O_4$ (620.75): calcd. C 50.31, H 7.79, N 31.59; found C 50.02, H 7.69, N 31.31. ¹H NMR (600.13 MHz, CD₂Cl₂): δ = 2.65 (s, 48 H, CH₃) ppm. ¹³C NMR (150.90 MHz, CD₂Cl₂): δ = 160.22, 140.18, 130.61, 39.56 (CH₃) ppm. IR (CsI): $\tilde{v} = 2990$ (w), 2928 (w), 2889 (w), 2808 (w), 1569 (vs), 1516 (vs), 1474 (s), 1457 (s), 1426 (s), 1378 (vs), 1213 (s), 1144 (vs), 1059 (m), 1025 (m), 968 (s), 917 (m), 801 (s), 720 (m), 676 (w), 644 (w) cm⁻¹. UV/Vis (CH₂Cl₂, c = $2.80 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ϵ , dm³ mol⁻¹ cm⁻¹) = 255 (3.81 × 10⁴), $321 (1.73 \times 10^4)$, $394 (0.12 \times 10^4)$, $474 (0.12 \times 10^4)$ nm. MS (FAB^+) : m/z (%) = 621 (100) $[3a + H]^+$. Crystal data for 3a $(C_{26}H_{48}N_{14}O_4): M_r = 620.78, 0.30 \times 0.25 \times 0.25 \text{ mm}^3$, monoclinic, space group $P2_1/n$, a = 8.3330(17), b = 18.865(4), c = 10.629(2) Å, $\beta = 97.83(3)^{\circ}$, $V = 1655.3(6) \text{ Å}^3$, Z = 2, $d_{\text{calc}} = 1.245 \text{ Mg m}^{-3}$, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T =100 K, θ_{range} 2.16 to 30.03°. Reflections measd. 9548, indep. 4825, $R_{\text{int}} = 0.0405$. Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0502$, w $R_2 =$ 0.1247.

Synthesis of 3b: NO₂BF₄ (0.095 g, 0.72 mmol) was dissolved in CH₃CN (10 mL) at 0 °C and added dropwise to 1b (0.091 g, 0.17 mmol) in CH₃CN (8 mL). The reaction mixture was stirred for 0.5 h at 0 °C. Removal of the solvent in vacuo led to a brownred solid, which was redissolved in water and HCl (10%). After addition of NaOH (20%), the solution was extracted three times with CH₂Cl₂. The combined CH₂Cl₂ phases were dried with K₂CO₃, and the solvent was removed under vacuum. Upon recrystallization from CH₃CN, orange crystals of **3b** (0.009 g, 0.012 mmol, 7%) were obtained. C₂₆H₄₀N₁₄O₄ (612.70): calcd. C 50.97, H 6.58, N 32.01; found C 51.04, H 6.43, N 32.18. ¹H NMR (600.13 MHz, CD₂Cl₂): δ = 3.25–3.16 (m, 16 H, CH₂), 2.65 (s, 24 H, CH₃) ppm. ¹³C NMR (150.90 MHz, CD₂Cl₂): δ = 155.19, 141.28, 128.81, 48.68 (CH₂), 34.11 (CH₃) ppm. IR (CsI): v = 2937 (w), 2872 (w), 2827 (w), 1628 (s), 1523 (s), 1488 (s), 1450 (m), 1394 (s), 1280 (vs), 1245 (m), 1220 (s), 1138 (w), 1120 (w), 1075 (w), 1060 (w), 1035 (m), 955 (vs), 861 (w), 815 (m), 752 (m), 720 (w), 707 (w), 640 (m), 628 (m), 586 (w), 544 (w) cm⁻¹. UV/Vis (CH₂Cl₂, $c = 4.90 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ϵ , $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 252 (3.31×10^4) , 328 (1.14×10^4) , 448 (0.14×10^4) nm. MS (FAB⁺): m/z (%) = 613 (100) [**3b** + H]⁺. Crystal data for **3b**·4CH₃CN: $C_{34}H_{52}N_{18}O_4$, $M_r = 776.94$, $0.30 \times 0.20 \times 0.15$ mm³, triclinic, space group $P\overline{1}$, a = 10.823(2), b = 10.984(2), c = 17.317(4) Å, a =100.64(3)°, $\beta = 91.06(3)$ °, $\gamma = 90.91(3)$ °, V = 2022.5(7) Å³, Z = 2, $d_{\text{calc}} = 1.276 \text{ Mgm}^{-3}$, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, $\theta_{range} 2.04$ to 27.49°. Reflections measd. 16880, indep. 9176, $R_{int} = 0.0494$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 =$ $0.0698, wR_2 = 0.1987.$

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Synthesis of [(3a)H₃]Cl₃: Et₂O·HCl (0.1 mL, 2 M) was added to 3a (0.016 g, 0.02 mmol) dissolved in CH₂Cl₂ (10 mL). After stirring for 20 min at r.t., the resulting yellow precipitate was collected by filtration and washed with CH₂Cl₂. Upon recrystallization from CH₃CN/Et₂O, orange crystals of [(3a)H₃]Cl₃·3H₂O (0.012 g, 0.015 mmol, 61%) were obtained. C₂₆H₅₁Cl₃N₁₄O₄·3H₂O (784.18): calcd. C 39.82, H 7.33, N 25.01; found C 39.88, H 7.11, N 24.92. ¹H NMR (600.13 MHz, CD₃CN): δ = 2.85 (s, 48 H, CH₃) ppm. ¹³C NMR (150.90 MHz, CD₃CN): δ = 40.44 (CH₃) ppm. IR (CsI): $\tilde{v} = 3402$ (w), 2936 (w), 1636 (vs), 1542 (vs), 1474 (m), 1423 (m), 1395 (m), 1360 (w), 1341 (w), 1302 (w), 1241 (m), 1228 (m), 1170 (m), 1161 (m), 1147 (w), 1065 (w), 1041 (w), 1020 (w), 910 (w), 895 (w), 799 (w), 780 (w) cm⁻¹. UV/Vis (CH₂Cl₂, c = $0.77 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ϵ , dm³ mol⁻¹ cm⁻¹) = 307 (2.68 × 10⁴), 456 (0.28×10^4) nm. MS (FAB⁺): m/z (%) = 621 (100) [3a + H]⁺, 311 (30) $[3a + 2H]^{2+}$. Crystal data for $[(3a)H_3]Cl_3 \cdot 3H_2O$: $C_{26}H_{57}Cl_3N_{14}O_7$, $M_r = 784.21$, $0.25 \times 0.20 \times 0.20$ mm³, triclinic, space group $P\bar{1}$, a = 11.059(2), b = 12.725(3), c = 16.208(3) Å, a =84.57(3)°, $\beta = 87.80(3)°$, $\gamma = 66.23(3)°$, $V = 2078.0(7) Å^3$, Z = 2, $d_{\text{calc}} = 1.253 \text{ Mgm}^{-3}$, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, $\theta_{range} 2.07$ to 27.90°. Reflections measd. 18077, indep. 9860, $R_{int} = 0.0427$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 =$ $0.0577, wR_2 = 0.1449.$

Synthesis of (3a)I₂: I₂ (0.005 g, 0.039 mmol) was dissolved in CH₂Cl₂ (2 mL) and added dropwise to 3a (0.007 g, 0.012 mmol) in CH₂Cl₂ (5 mL). The mixture was stirred for 2 h at r.t. The solvent was removed under vacuum, and the resulting solid was redissolved in CH₃CN. On addition of Et₂O, dark red crystals of (3a)I₂ (0.01 g, 0.011 mmol, 92%) were obtained. $C_{26}H_{48}I_2N_{14}O_4$ (874.56): calcd. C 35.71, H 5.53, N 22.42; found C 35.69, H 5.52, N 22.44. ¹H NMR (600.13 MHz, CD_2Cl_2): $\delta = 3.04$ (s, 48 H, CH_3) ppm. ¹³C NMR (150.90 MHz, CD_2Cl_2): $\delta = 166.14$, 146.37, 127.25, 41.73 (CH₃) ppm. IR (CsI): $\tilde{v} = 2934$ (w), 1636 (m), 1593 (s), 1545 (vs), 1514 (vs), 1498 (s), 1470 (s), 1429 (m), 1402 (s), 1381 (s), 1334 (w), 1305 (m), 1282 (s), 1189 (m), 1169 (m), 1077 (w), 988 (w), 921 (w), 899 (w), 801 (w), 756 (w), 713 (w), 653 (w) cm⁻¹. UV/Vis (CH₂Cl₂, $c = 1.14 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ε , dm³ mol⁻¹ cm⁻¹) = 269 (4.49×10^4) , 390 (4.13×10^4) , 532 (0.30×10^4) nm. MS (FAB⁺): m/z (%) = 621 (100) [**3a** + H]⁺, 531 (12) [**3a**-2NO₂], 469 (62). Crystal data for $(3a)I_2$: $C_{26}H_{48}I_2N_{14}O_4$, $M_r = 874.58$, $0.35 \times 0.30 \times 0.30$ mm³, triclinic, space group $P\bar{1}$, a = 9.5230(19), b= 10.351(2), c = 10.837(2) Å, $a = 75.73(3)^\circ$, $\beta = 81.95(3)^\circ$, $\gamma =$ 63.26(3)°, V = 924.0(4) Å³, Z = 1, $d_{calc} = 1.572$ Mg m⁻³, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 2.25 to 32.92°. Reflections measd. 12246, indep. 6785, R_{int} = 0.0215. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0271$, $wR_2 = 0.0619$.

Synthesis of (3b)(I₃)₂: I₂ (0.014 g, 0.11 mmol) was dissolved in CH₂Cl₂ (2 mL) and added dropwise to 3b (0.011 g, 0.018 mmol) in CH₂Cl₂ (6 mL). The mixture was stirred for 2 h at r.t. The resulting precipitate was collected by filtration and washed with CH₂Cl₂. Upon recrystallization from CH₃CN, dark crystals of (3b)2I₃ (0.02 g, 0.015 mmol, 80%) were obtained. $C_{26}H_{40}N_{14}O_4I_6$ (1374.10): calcd. C 22.73, H 2.93, N 14.27; found C 23.16, H 3.04, N 14.34. ¹H NMR (600.13 MHz, CD₃CN): δ = 3.68–3.65 (m, 16 H, CH₂), 2.76 (s, 24 H, CH₃) ppm. ¹H NMR [600.13 MHz, (CD₃)₂-SO]: δ = 3.72–3.65 (m, 16 H, CH₂), 2.76 (s, 24 H, CH₃) ppm. ¹³C NMR [150.90 MHz, (CD₃)₂SO]: δ = 162.57, 147.19, 125.36, 47.80 (CH2), 32.38 (CH₃) ppm. IR (CsI): v = 2958 (w), 2881 (w), 1669 (s), 1578 (vs), 1551 (vs), 1504 (s), 1474 (m), 1412 (m), 1373 (m), 1341 (s), 1291 (s), 1236 (w), 1198 (w), 1077 (w), 1005 (m), 966 (w), 926 (w), 815 (w), 776 (w), 745 (m), 648 (w), 580 (w), 496 (w), 454 (w) cm⁻¹. UV/Vis (CH₂Cl₂, $c = 1.44 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ε ,

dm³mol⁻¹ cm⁻¹) = 256 (3.01×10⁴), 295 (7.97×10⁴), 372 (6.73×10⁴) nm. MS (ESI⁺): m/z (%) = 306 (100) [**3b**]²⁺.

Synthesis of [3a(CuI)2]: Compound 3a (0.022 g, 0.036 mmol) and CuI (0.015 g, 0.081 mmol) in CH₃CN (10 mL) were stirred for 1 h at r.t. The resulting dark blue precipitate was collected by filtration and washed with CH₃CN and Et₂O to afford [3a(CuI)₂] (0.022 g, 0.022 mmol, 61 %). C₂₆H₄₈Cu₂I₂N₁₄O₄ (1001.65): calcd. C 31.18, H 4.83, N 19.58; found C 31.11, H 4.88, N 18.93. ¹H NMR (200.13 MHz, CD₂Cl₂): δ = 2.81 (s, 48 H, CH₃) ppm. IR (CsI): \tilde{v} = 2938 (w), 2876 (w), 1521 (vs), 1466 (s), 1417 (s), 1406 (s), 1391 (s), 1346 (w), 1240 (w), 1207 (s), 1152 (s), 1113 (w), 1066 (w), 1037 (m), 991 (s), 909 (m), 800 (m), 733 (w), 711 (m), 696 (w), 643 (w), 610 (w) cm⁻¹. UV/Vis (CH₂Cl₂, $c = 1.42 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ε , $dm^3 mol^{-1} cm^{-1}$ = 279 (3.16×10⁴), 332 (2.81×10⁴), 582 (0.30× 10⁴) nm. MS (FAB⁺): m/z (%) = 811 (14) [(3a)CuI + H]⁺, 621 (32) $[3a + H]^+$, 460 (60) $[(3a)H-HNC{N(CH_3)_2}_2-HN(CH_3)_2]^+$. Crystal data for $[3a(CuI)_2]$: $C_{26}H_{48}Cu_2I_2N_{14}O_4$, $M_r = 1001.66$, $0.20 \times 0.20 \times 0.16$ mm³, triclinic, space group $P\bar{1}$, a = 7.595(2), b =10.824(2), c = 11.725(2) Å, $a = 90.52(3)^{\circ}$, $\beta = 91.21(3)^{\circ}$, $\gamma =$ 103.67(3)°, V = 936.3(6) Å³, Z = 1, $d_{calc} = 1.776$ Mg m⁻³, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 2.58 to 30.05°. Reflections measd. 9893, indep. 5471, R_{int} = 0.0242. Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0282$, w $R_2 = 0.0658$.

Synthesis of 5: In contrast to that of [1a(CuI)₂], the oxidation of $[3a(CuI)_2]$ with I₂ led to decomposition of the complex. In the case of $[3a(CuI)_2]$, only oxidized ligand $(3a)I_2$ was obtained. The slow oxidation of [3a(CuI)₂] in CH₂Cl₂ or CH₃CN solutions at r.t. in air led quantitatively in 3 d to $(3a)I_2$ and 5, which was crystallized from CH₂Cl₂/hexane. ¹H NMR (200.13 MHz, CD₃CN): δ = 3.10 (s, 3 H), 3.00 (s, 12 H), 2.95 (s, 12 H), 2.93 (s, 12 H), 2.81 (s, 6 H) ppm. IR (CsI): $\tilde{v} = 2930$ (w), 1645 (s), 1603 (s), 1578 (s), 1516 (m), 1459 (m), 1410 (s), 1352 (w), 1315 (m), 1292 (m), 1258 (w), 1225 (m), 1169 (m), 1144 (w), 1065 (w), 1036 (w), 928 (m), 901 (w) cm⁻¹. UV/ Vis (CH₂Cl₂, $c = 1.10 \times 10^{-5} \text{ mol } \text{L}^{-1}$): λ_{max} (ϵ , dm³mol⁻¹ cm⁻¹) = 377 (1.87×10⁴), 457 (0.87×10⁴) nm. MS (ESI⁺): m/z (%) = 605 (100) $[5 - Cu - 2I]^+$. Crystal data for 5·2CH₂Cl₂: C₂₇H₄₉Cl₄Cu- $I_2N_{14}O_4$, $M_r = 1092.94$, $0.20 \times 0.20 \times 0.20$ mm³, monoclinic, space group $P2_1/n$, a = 9.542(2), b = 39.561(8), c = 11.920(2) Å, $\beta =$ 106.31(3)°, V = 4318.5(15) Å³, Z = 4, $d_{calc} = 1.681$ Mg m⁻³, Mo- K_a radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} 2.06 to 27.92°. Reflections measd. 20337, indep. 10326, R_{int} = 0.0224. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0341$, w $R_2 = 0.0839$.

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- K_a radiation. The temperature was set to 100 K. The data collected were processed using the standard Nonius software.^[26] 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.^[27,28] Graphical handing of the structural data during solution and refinement was performed with XPMA.^[29] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations.

CCDC-848628 (for 4), -848623 [for $1b(PF_6)_2$], -770431 [for $2b(I_3)_2$], -770441 (for 2a), -848627 (for 2b), -848621 (for 3a), -848624 (for 3b), -848622 (for [3aH_3]Cl_3), -848625 [for (3a)I_2], and -848626 (for [3a(CuI)_2]) 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.

Supporting Information (see footnote on the first page of this article): Molecular structures of $[(4)H_2]Cl_2$, $[(1a)H_2](PF_6)_2$, $[(1b)H_2](PF_6)_2$, $[(1b)H_4]Cl_4$, $[(2a)H_2]I_2$ and monoiodated salts of 1a and 1b. Titration curve of 1b. UV/Vis spectra and CVs of the six GFAs vs. Fc/Fc⁺. CVs for 3a at different scan rates. Synthetic details for $[(4)H_2]Cl_2$, $[(1b)H_4]Cl_4$ and $[(1b)H_2](PF_6)_2$.

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