Proton-Coupled Electron Transfer (PCET) with 1,4-Bisguanidino-Benzene Derivatives: Comparative Study and Use in Acid-Initiated C-H Activation

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Abstract: Proton-coupled electron transfer (PCET) is of key importance in modern synthetic chemistry. Redox-active guanidines were established by our group as valuable alternatives to toxic high-potential benzoquinones in a variety of different PCET reactions. In this work, the PCET reactivity of a series of 1,4-bisguanidino-benzenes varying in their redox potentials and proton affinities is evaluated. The relevant redox and protonation states are fully characterized, and the compounds sorted with respect to their PCET reactivity by comparative PCET experiments supplemented by quantum-chemical calculations. Depending on the studied reactions, the driving force is either electron transfer or proton transfer; thereby the influence of both processes on the overall reactivity could be assessed. Two of the PCET reagents are applied in representative oxidative aryl-aryl coupling reactions, namely the intramolecular coupling of 3,3''-4,4''-tetrathymethoxy-o-terphenyl to give the corresponding triphenylene, the intermolecular coupling of N-ethylcarbazole to give \( \text{NN}'\text{-diethyl-3,3''-bicarbazole} \), and in the oxidative lactonization of 2-[4-methoxyphenyl]methylbenzoic acid. Under mild conditions, the reactions proceed fast and efficient. Only small amounts of acid are needed, in clear contrast to the corresponding coupling reactions with traditional high-potential benzoquinones such as DDQ or chloranil requiring a large excess of a strong acid.

Introduction

Proton-coupled electron transfer (PCET) plays a central role in modern synthetic chemistry, as it allows for example the selective oxidation of organic compounds and other useful reactions. In biology, PCET is involved in essential processes such as photosynthesis and a variety of redox enzymatic reactions. The PCET chemistry of coordination compounds, for example oxo complexes of metals in high oxidation states, that are transformed in PCET reactions to hydroxy- or aqua-complexes, metal oxide clusters such as the decatungstate anion \([\text{WO}_6\text{O}_{18}]^{4−}\), and of organic PCET reagents, for example quinones, TEMPO and other aminoxyl radicals, as well as Hantzsch esters and dihydropyridine derivatives, are well documented. By separating the electron acceptor/donor site from the proton acceptor/donor site, the two decisive parameters for the thermodynamics of PCET, the redox potential and the acid constant (proton affinity), could be tuned separately ("bidirectional" PCET).

In the last years, our group established redox-active guanidines, comprising guanidino-functionalized aromatics (GFAs) and urea azines, as versatile organic PCET reagents and redox catalysts. The compound 1,2,4,5-tetakis(tetramethyguanidino)-benzene (ttmgb, Scheme 1) is the archetypical example for a GFA, being an electron donor in its reduced, neutral state, but a remarkably potent oxidant in its oxidized, dicationic state, if electron transfer is coupled with proton transfer. Here, the high Brønsted basicity of the reduced, neutral state \((pK_a \text{ ca. 25.3 for (ttmgb)} \text{ in CH}_3\text{CN})\) contributes significantly to the driving force. The scope of the PCET reactivity of redox-active guanidines in organic synthesis could be greatly expanded in the presence of an excess of a strong acid. Hence, redox-active guanidines allow efficient aryl-aryl coupling reactions of aromatic compounds with relatively high redox potential up to at least 1.2 V vs. ferrocenium/ferrocene \((\text{Fc}^+ / \text{Fc})\). Scheme 1 shows as example the conversion of 3,3'',4,4''-tetrathymethoxy-o-terphenyl (oxidation potential of 0.74 V vs. \(\text{Fc}^+ / \text{Fc} \)) with one equivalent of \((\text{ttmgb})\text{(BF}_4\text{)}_2\) to the corresponding triphenylene coupling product in almost quantitative yield, requiring a large excess of a strong acid \((\text{HBF}_4\cdot\text{OEt}_2)\).

Recently we showed that oxidized bisguanidine 1,4-bis(tetramethyguanidino)-benzene GFA2 \(^+\) (see Lewis structure in Figure 1a) is a stronger oxidant in PCET reactions than the oxidized tetraguisuguanidine GFA2 \(^+\) [30]. Therefore, it is attractive to study the PCET chemistry of redox-active bisguanidines in more detail. In this work, the PCET reactivity of the five different 1,4-bisguanidino-benzene derivatives sketched in Figure 1 is compared. Of these, GFA2, GFA4 and GFA5 are new, while GFA1 [33]...
and GFA3 were previously reported. In comparative (2e, 2H) PCET reactions, the oxidized GFA1+ is reacted with the reduced, diprotonated form of another bisguanidine. Depending on the guanidino groups, these reactions are either driven by electron-transfer (while proton transfer is unfavorable) or by proton-transfer (while electron-transfer is unfavorable); thereby, information about the reaction mechanism could be obtained by comparing the PCET reactivity. Finally, GFA1+ and GFA4+ are applied as PCET reagents in representative intra- and intermolecular aryl-aryl coupling reactions, and in an oxidative lactonization. (The reasons for the choice of these two compounds is given below.) In sharp contrast to high-potential benzoquinones and also ttmgb, only a small amount of acid is required to initiate fast and efficient reactions.
Results and Discussion

Synthesis and characterization

The three new bisguanidines GFA2, GFA4 and GFA5 were synthesized from the corresponding diamino precursors. Reaction of 2-methoxy-1,4-diaminobenzene with 2-chloro-1,1,3,3-tetramethylformamidinium chloride gave GFA2. For the preparation of GFA4 and GFA5, 1,4-diaminobenzene was reacted with 2-chloro-1,3-dimethyl-1H-benzo[d]imidazol-3-ium tetrafluoroborate or 2-chloro-1,3-dimethylperimidinium tetrafluoroborate (Scheme 2).

Crystals of sufficient quality for structural analysis with single-crystal X-ray diffraction (XRD) were obtained for GFA2 and GFA4. Figure 2 illustrates the solid-state structures of the two new bisguanidines, and selected structural parameters are compiled in Tables 1 and 2. In line with the structures of other guanidino-substituted aromatics, the central CN$_3$ unit of each guanidino group is highly tilted with respect to the aromatic plane. A detailed analysis of this issue for GFA1 was published previously by our group, showing that this conformation is,

![Scheme 2. Synthesis of the three new redox-active bisguanidines GFA2, GFA4 and GFA5.](image)

![Figure 2. Illustration of the structures of the neutral bisguanidines GFA2 and GFA4 in the solid state. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted. Colour code: C grey, N blue, O red.](image)

| Table 1. Selected bond lengths (in Å) measured for GFA2 and (GFA2 + 2H)(PF$_6$)$_2$ in the solid state. |
|---|---|---|
| bond | GFA2 | (GFA2 + 2H)(PF$_6$)$_2$ |
| a | 1.408(2) | 1.422(2) |
| b | 1.295(2) | 1.350(2) |
| c | 1.378(2)/1.390(2) | 1.338(2)/1.330(2) |
| d | 1.398(2) | 1.386(2) |
| e | 1.390(2) | 1.385(3) |
| f | 1.389(2) | 1.389(2) |
| g | 1.409(2) | 1.398(2) |
| h | 1.385(2) | 1.389(2) |
| i | 1.404(2) | 1.404(2) |
for electronic reasons, highly favored energetically with respect to the conformation with co-planar CN and aromatic planes.

Redox chemistry

Experimental results

Prior to chemical oxidation experiments, we carried out cyclic voltammetry to obtain information about the redox potentials. Figure 3 compares the cyclic voltammograms for the five GFAs studied in this work, and Table 3 summarizes the \( E_{1/2} \) and \( E_{ox} \) values derived from these measurements. The curves for GFA1 - GFA4 were recorded in CH\(_2\)Cl\(_2\) solutions. In the case of GFA5, the low solubility of the oxidized form hampered the determination of the redox potential in CH\(_2\)Cl\(_2\) solution (dashed curve in Figure 3). Therefore, cyclic voltammetry measurements were repeated with the salt GFA5(PF\(_6\)) of the oxidized form (see below for its synthesis and characterization) in CH\(_2\)CN solution (neutral GFA5 is poorly soluble in this solvent), yielding sharp waves due to a quasi-reversible two-electron redox process when the measurements started in reduction direction. The cyclic voltammograms of GFA1 and GFA2 clearly show a single reversible two-electron redox event; the first and the second electron are removed at equal potential. For GFA3, the waves are broader, indicating splitting of the two-electron redox process into two one-electron events with \( E_{1/2} \) values of approximately \(-0.31\) V for the redox couple GFA3\(^{2+}/\)GFA3\(^0\) and approximately \(-0.21\) V for the redox couple GFA3\(^{3+}/\)GFA3\(^{2+}\). The potential separation of the two one-electron redox events increases for GFA4, with clearly separated \( E_{1/2} \) values of \(-0.25\) V for the redox couple GFA4\(^{2+}/\)GFA4\(^0\) and \(-0.06\) V for the redox couple GFA4\(^{3+}/\)GFA4\(^{2+}\). From these values, one could estimate the disproportionation of GFA4\(^{3+}\) to GFA4 and GFA4\(^{2+}\) to be endergonic by 18 kJ mol\(^{-1}\) with an equilibrium constant \( K_{disp} \) of \(6.1 \times 10^{-4}\) (using the formula \( \Delta G = -RT \ln K_{disp} \) and \( K_{disp} = \exp(-[F/RT] \Delta E_{1/2}) \)).

Cyclic voltammetry measurements were also carried out in CH\(_2\)CN solution. The following redox potentials were obtained: \( E_{1/2} = -0.21\) V (\( E_{ox} = -0.18\) V) for GFA1, \( E_{1/2} = -0.30\) V (\( E_{ox} = -0.27\) V) for GFA2, \( E_{1/2} = -0.24\) V (\( E_{ox} = -0.20\) V) for GFA3, and (as already mentioned) \( E_{1/2} = -0.15\) V (\( E_{ox} = -0.12\) V) for GFA5. In all these cases, two-electron redox processes were found.

However, in the case of GFA4, the low solubility in CH\(_2\)CN prohibited measurements in this solvent.

Two electrons and two protons are exchanged in PCET reactions between the dicaticionic, oxidized form of one and the doubly-protonated, reduced form of the other bisguanidine (see below). Therefore the value \( \Delta G = -F [E_{1/2}(1^{1+}) + E_{1/2}(2^{2+})] \) was calculated to compare the two-electron acceptor properties.
leading to the order for increasing “two-electron acceptor strength” (decreasing $-F \langle [E_{1/2}(1^+) + E_{1/2}(2^+)] \rangle$ value): GFA2 $< \text{GFA3} < \text{GFA1} < \text{GFA4} < \text{GFA5}$. Chemical oxidation was carried out with two equivalents of Fc(PF$_6$)$_2$. In all cases, the products of two-electron oxidation were isolated as stable, storable solid compounds. Figure 4 illustrates the solid-state structures of the new compounds GFA4(PF$_6$)$_2$ and GFA5(PF$_6$)$_2$. Selected bond lengths are included in Tables 2 and 4. As expected, the N–C imino bond length of the neutral GFA increases significantly upon oxidation (e. g. from 1.287(2) Å in GFA4 to 1.376(3) Å in GFA4(PF$_6$)$_2$). By contrast, the N–C bond connecting the guanidino group to the aromatic ring decreases (from 1.412(2) Å in GFA4 to 1.302(2) Å in GFA4(PF$_6$)$_2$). The large differences in the C–C bond lengths within the C$_6$ ring of the oxidized molecules signal loss of the aromatic system, in line with the Lewis structure shown for GFA1$^{2+}$ in Figure 1.

Finally, we prepared 1:1 mixtures between a neutral bisguanidine and the salt of the corresponding doubly-oxidized compound in CH$_3$CN solution and recorded UV-vis as well as EPR spectra. The appearance of an EPR signal and strong new absorptions in the visible region of the UV-vis spectra indicated the presence of the radical monocationic bisguanidine in significant amount, formed in a comproportionation reaction (despite of the absence of any sign of one-electron redox processes in the cyclic voltammograms). For example, Figure 5 displays the UV-vis spectrum of the green 1 : 1 mixture of GFA4 and GFA4(PF$_6$)$_2$, showing strong bands centered at 699 nm (very broad) and 426 nm that are absent in the spectrum of GFA4 or GFA4(PF$_6$)$_2$ alone. Moreover, the inset shows the EPR spectrum measured for this mixture (broad, unstructured signal at g = 2.00). TD-DFT calculations (B3LYP/def2-TZVP) predicted strong electronic transitions at 718 and 386 nm (Figure 6), in excellent agreement with the experiment. Plots of the isodensity surfaces for the orbitals involved in the transition at 718 nm are included in Figure 6, being π-orbitals delocalized over the complete molecule.

In the case of the radical monocation GFA3$^{2+}$, prepared similarly by mixing equimolar amounts of GFA3 and GFA3(PF$_6$)$_2$, bands at 575 nm (with a shoulder at 542 nm) and 404 nm appeared. Here, TD-DFT calculations (B3LYP/def2-TZVP) predicted electronic transitions at 543/501 and 365/346 nm, again in good agreement with the experimental values (see Figure 6). The blue shift of the lowest-energy absorption of GFA3$^{2+}$ compared to GFA4$^{2+}$ could be explained by the reduced size of the π-electron system.

All 1:1 mixtures between the neutral and dicationic redox states showed EPR signals assigned to the radical monocations. In the case of GFA1$^{2+}$ and GFA5$^{2+}$, a distinct hyperfine coupling (HFC) to hydrogen and nitrogen nuclei is visible (Figure 7), with

![Figure 4. Illustration of the solid-state structures of the bisguanidine dications GFA4$^{2+}$ and GFA5$^{2+}$, together with two PF$_6^-$ counterions, obtained upon oxidation of the neutral compounds. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted. Colour code: C grey, N blue, P red, F green.](image)

| Table 3. E$_{1/2}$ and E$_{ox}$ values (in V vs. the Fc$^+/Fc$ couple) from cyclic voltammetry measurements in CH$_3$Cl$_2$ solution (Faraday constant F = 9.648456·10$^8$ C mol$^{-1}$). |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Compound       | $E_{1/2}$ (GFA$^{2+}$ / GFA) | $E_{1/2}$ (GFA$^{2+}$ / GFA$^{3+}$) | $E_{ox}$ (GFA$^{2+}$ / GFA) | $E_{ox}$ (GFA$^{3+}$ / GFA$^{4+}$) |
| GFA1           | -0.23/ -0.14    | -0.23/ -0.14    | +44.4 kJ mol$^{-1}$  |
| GFA2           | -0.30/ -0.22    | -0.30/ -0.22    | +57.9 kJ mol$^{-1}$  |
| GFA3           | -0.31/ -0.27    | -0.21/ -0.14    | +50.2 kJ mol$^{-1}$  |
| GFA4           | -0.25/ -0.18    | -0.06/ 0.00     | +29.9 kJ mol$^{-1}$  |
| GFA5            | -0.15/ -0.12    | -0.15/ -0.12    | +28.9 kJ mol$^{-1}$  |

[a] Measurements for GFA5(PF$_6$)$_2$ in CH$_3$CN due to low solubility in CH$_3$Cl$_2$.

![Table 4. Selected bond lengths (in Å) measured for (GFA5 + 2H)(PF$_6$)$_2$ and GFA5(PF$_6$)$_2$ in the solid state.](image)
a line spacing of 1.8 G. For the other radical monocations, the HFC is not clearly resolved and hidden under broad, unstructured signals. The presence of more than 20 lines indicates hyperfine coupling to the four equivalent aromatic H atoms and the two equivalent N atoms directly attached to the C\(_6\) ring, producing in theory (2 \cdot 2 \cdot 1/2 + 1)(2 \cdot 4 \cdot 1/2 + 1) = 25 lines.

**Quantum-chemical studies**

Structures and electronic energies were calculated with the B3LYP functional together with the def2-TZVP basis set, since this combination was shown to give reliable results in previous studies with redox-active guanidines.\(^{[27,29,30]}\) Thermal contributions were calculated with the B3LYP functional and SV(P) basis set. The solvent effect was considered with the conductor-like screening model (COSMO), with a relative permittivity \(\varepsilon_r = 37.5\) (CH\(_3\)CN). (See Supporting Information for more details.) The calculations reproduced accurately the experimental solid-state structures (see Supporting Information for details). The thermodynamics calculated for the pure electron transfer reactions between the oxidized form GFA1(PF\(_6\))\(_2\) and one of the neutral, reduced bisguanidines GFA2-GFA5 (the anions were included in the calculations)\(^{[30]}\) are compiled in Table 5. For GFA2 and GFA3, the Gibbs free reaction energies are negative, meaning that they are stronger two-electron donors than GFA1. This result is in line with the cyclic voltammetry measurements for which the term \(-F \cdot [(E_{1/2}(1st) + E_{1/2}(2nd))]\), being approximately the standard Gibbs free energy change for the reaction GFA\(^+\) + 2 e\(^-\) \rightarrow GFA, is more positive for GFA2 and GFA3 than for GFA1. By contrast, the Gibbs free reaction energies are positive for GFA4 and GFA5, again in line with the results of the cyclic voltammetry measurements, showing that GFA4 and GFA5 are weaker two-electron donors than GFA1.

**Protonation**

**Experimental results**

All guanidines could be doubly protonated with two equivalents of NH\(_4\)PF\(_6\). The new salts (GFA2 + 2H)(PF\(_6\))\(_2\), (GFA4 + 2H)(PF\(_6\))\(_2\) and (GFA5 + 2H)(PF\(_6\))\(_2\) were crystallized from concen-

Figure 5. a) From left to right: Photos of cuvettes with CH\(_3\)CN solutions of GFA4, GFA4(PF\(_6\))\(_2\) and an equimolar mixture of GFA4 and GFA4(PF\(_6\))\(_2\). b) UV-vis spectra of GFA4, GFA4(PF\(_6\))\(_2\) and an equimolar mixture of GFA4 and GFA4(PF\(_6\))\(_2\) in CH\(_3\)CN solutions. The EPR spectrum of the 1:1 mixture in CH\(_2\)Cl\(_2\) is shown in the inlet.

Figure 6. Comparison between the UV-vis spectra of 1:1 mixtures of GFA3 and GFA3(PF\(_6\))\(_2\) (black curve) and of GFA4 and GFA4(PF\(_6\))\(_2\) (red curve) in CH\(_3\)CN solutions. The spectra were normalized to the maximum of absorption of the lowest-energy transition. Simulations of spectra for GFA3\(^+\) and GFA4\(^+\) on the basis of TD-DFT calculations (B3LYP/def2-TZVP) are reproduced below the experimental spectra. In addition, isodensity plots for the two orbitals involved in the lowest-energy electronic transition of GFA4\(^+\) at 718 nm are plotted (SOMO to LUMO transition, 52a\(_u\)(beta) \rightarrow 53a\(_g\)(beta)).
Figure 7. EPR spectra of the radical monocations GFA1** and GFA5**, formed from 1:1 mixtures of GFA1** and GFA1 and of GFA5** and GFA5, respectively, in CHCl₃ solutions (concentrations ca. 5·10⁻³ mol·L⁻¹) at room temperature.

Table 5. Calculated electronic energy, enthalpy at 0 K and Gibbs free energy at 298 K for pure electron transfer reactions (B3LYP functional in combination with the stated basis set, solvent effect modelled with the conductor-like screening model (COSMO)). Anions included in the calculations.

| Reaction | SV(P) | TZVP[a] | TZVP[b] |
|----------|-------|---------|---------|
| ΔE       |       |         |         |
| ΔH       |       |         |         |
| ΔG       |       |         |         |
| GFA1(PF₆)⁺ + GFA2 ↔ GFA1 + GFA2(PF₆)₂ | -65.7 | -54.1  | -28.4  |
| ΔE       |       |         |         |
| ΔH       |       |         |         |
| ΔG       |       |         |         |
| GFA1(PF₆)⁺ + GFA3 ↔ GFA1 + GFA3(PF₆)₂ | -59.9 | -48.2  | -22.6  |
| ΔE       |       |         |         |
| ΔH       |       |         |         |
| ΔG       |       |         |         |
| GFA1(PF₆)⁺ + GFA4 ↔ GFA1 + GFA4(PF₆)₂ | -53.1 | -41.5  | -15.9  |
| ΔE       |       |         |         |
| ΔH       |       |         |         |
| ΔG       |       |         |         |
| GFA1(PF₆)⁺ + GFA5 ↔ GFA1 + GFA5(PF₆)₂ | -1.6  | -1.9   | +24.6  |
| ΔE       |       |         |         |
| ΔH       |       |         |         |
| ΔG       |       |         |         |

[a] Zero-point energy and thermal contributions calculated with the SV(P) basis set.

Table 6. Electronic energy, enthalpy at 0 K and Gibbs free energy at 298 K for monoprotonation of the bisguanidines calculated with density functional calculations with the B3LYP functional and the stated basis set. The table also includes the thermodynamics for proton transfer from GFA1 to GFA2 in which the PF₆⁻ counterions were included.

| Reaction | SV(P) | TZVP[a] | TZVP[b] |
|----------|-------|---------|---------|
| ΔE       |       |         |         |
| ΔH       |       |         |         |
| ΔG       |       |         |         |
| GFA1 + H⁺ ↔ (GFA1 + H)⁺ | -1104.1 | -1110.0 |         |
| ΔE       |       |         |         |
| ΔH       |       |         |         |
| ΔG       |       |         |         |
| GFA2 + H⁺ ↔ (GFA2 + H)⁺ | -1065.0 | -1070.1 |         |
| ΔE       |       |         |         |
| ΔH       |       |         |         |
| ΔG       |       |         |         |
| (GFA1 + H)PF₆⁺ ↔ GFA1 + (GFA2 + H)PF₆⁻ | -1038.1 | -1044.0 |         |
| ΔE       |       |         |         |
| ΔH       |       |         |         |
| ΔG       |       |         |         |
| GFA3 + H⁺ ↔ (GFA3 + H)⁺ | -1082.8 | -1085.1 |         |
| ΔE       |       |         |         |
| ΔH       |       |         |         |
| ΔG       |       |         |         |
| GFA4 + H⁺ ↔ (GFA4 + H)⁺ | -1063.4 | -1067.4 |         |
| ΔE       |       |         |         |
| ΔH       |       |         |         |
| ΔG       |       |         |         |
| GFA5 + H⁺ ↔ (GFA5 + H)⁺ | -1038.2 | -1042.0 |         |

[a] Zero-point energy and thermal contributions calculated with the SV(P) basis set.
and an adjacent PF$_6^-$ counterion from the experimental solid-state structures of the doubly protonated bisguanidines. A complete survey of the structures that follow from different starting geometries (different positions of the PF$_6^-$ counterion around the monoprotonated bisguanidine) was not undertaken due to the immense computational cost of such a survey. Therefore, we could not completely exclude a considerable error for calculations that include anions. On the other hand, the addition of the counterions is generally advisable in COSMO calculations.$^{[27,29,30]}$

We also calculated the thermodynamics of double-proton exchange between (GFA$_1^+2H$)(PF$_6^-$)$_2$ and one of the other neutral bisguanidines; the values could be obtained by subtracting the values for the proton-coupled electron transfer (PCET, see Table 7 in the next section) from the values for pure electron transfer (Table 5). A discussion follows in the next section.

Figure 8. Illustration of the structures of the doubly protonated bisguanidines in the solid state. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted. Hydrogen bonding between the dications and the PF$_6^-$ counterions is highlighted by dashed lines.

Table 7. Electronic energy, enthalpy at 0 K and Gibbs free energy at 298 K for proton-coupled electron transfer reactions calculated with density functional calculations with the B3LYP functional.

| Reaction | $\Delta E$ | $\Delta H^0$ | $\Delta G_{298}$ |
|----------|------------|-------------|-----------------|
| (GFA$_1^+2H$)(PF$_6^-$)$_2$ | -41.4 | -36.1 | -28.0 |
| (GFA$_3^+2H$)(PF$_6^-$)$_2$ | -82.9 | -77.4 | -66.7 |
| (GFA$_5^+2H$)(PF$_6^-$)$_2$ | -54.9 | -53.3 | -49.4 |

| $\varepsilon_r$ | SV(P) | TZVP$^{[a]}$ |
|----|-------|-----------------|
| 1 | -40.4 | -28.0 |
| 37.5 | -35.1 | -22.7 |
| 75.0 | -27.4 | -15.0 |

| $\varepsilon_r$ | SV(P) | TZVP$^{[a]}$ |
|----|-------|-----------------|
| 1 | -74.5 | -58.0 |
| 37.5 | -69.0 | -52.5 |
| 75.0 | -58.2 | -41.8 |

| $\varepsilon_r$ | SV(P) | TZVP$^{[a]}$ |
|----|-------|-----------------|
| 1 | -51.9 | -48.6 |
| 37.5 | -48.8 | -45.5 |
| 75.0 | -37.3 | -34.1 |

| $\varepsilon_r$ | SV(P) | TZVP$^{[a]}$ |
|----|-------|-----------------|
| 1 | -51.8 | -49.4 |
| 37.5 | -50.2 | -47.8 |
| 75.0 | -47.8 | -43.4 |

[a] Zero-point energy and thermal contributions calculated with the SV(P) basis set.
Comparative PCET reactivity

Experimental results

Next we inspected PCET reactions between the salt GFA1(PF$_6$)$_2$, containing the twofold-oxidized form GFA1$^{2+}$, with the reduced, doubly-protonated form of another bisguanidine. An example, reaction between GFA1$^{2+}$ and (GFA4$+$2H)$^{2+}$, is shown in Scheme 3. In all cases, GFA1$^{2+}$ was reduced and twofold protonated to give (GFA1$+$2H)$^{2+}$, and the reduced, twofold-protonated reaction partner deprotonated and oxidized to the dication. Hence, the results indicate that the salt GFA1(PF$_6$)$_2$ is the strongest oxidant in PCET reactions.

The conversion was followed by $^1$H NMR spectroscopy to gain (qualitative) information about the reaction rates (see Figure 9). The reaction between GFA1$^{2+}$ and (GFA5$+$2H)$^{2+}$ was completed almost instantly; therefore it is not included in Figure 9. Reaction between GFA1$^{2+}$ and (GFA4$+$2H)$^{2+}$ required 20 min for 93% conversion under the chosen conditions. Reaction between GFA1$^{2+}$ and (GFA3$+$2H)$^{2+}$ was slower; 93% conversion was reached after 180 min, and 99% after 300 min. The lowest reaction rate was measured for the reaction between GFA1$^{2+}$ and (GFA2$+$2H)$^{2+}$, requiring more than 800 min for 70% conversion (see Supporting Information for a complete curve). In all experiments, no reaction intermediate appeared in the NMR spectra.

Moreover, we followed the reaction between GFA1$^{2+}$ and (GFA4$+$2H)$^{2+}$ by UV-vis spectroscopy. The dication GFA4$^{2+}$ formed in this reaction could easily be traced by its characteristic electronic absorption at 495 nm (Figure 10). No bands due to reaction intermediates were detected. Hence, the NMR and UV-vis spectroscopic measurements clearly show that an intermediate arising from the transfer of only one proton and/or electron is not formed in significant amount. In further UV-vis experiments, we tried to achieve pseudo-first order conditions by applying an excess of GFA1(PF$_6$)$_2$ (10, 20 and 40 eq.). Clearly, the rate constant increases with increasing concentration of GFA1(PF$_6$)$_2$ (see Supporting Information for details). However, an analysis showed that the kinetics does not follow a simple second-order rate law. The two reactants are both dications. Therefore, the approach of the two reactants to give a hydrogen-bonded complex is opposed by a strong electrostatic barrier, and also a barrier due to solvent reorganization, contributing to the overall reaction rate.

![Scheme 3. Example PCET reaction between GFA1(PF$_6$)$_2$ and (GFA4$+$2H)(PF$_6$)$_2$ studied to sort the five bisguanidines with respect to their PCET reactivity.](image)

![Figure 9.](image)

![Figure 10. a) UV-vis spectra for the PCET reaction between GFA1(PF$_6$)$_2$ and (GFA4$+$2H)(PF$_6$)$_2$ in CH$_3$CN at room temperature, both applied in a concentration of 4·10$^{-3}$ mol·l$^{-1}$. The reaction is completed within 80 min under the applied conditions.](image)
Quantum-chemical calculations

Table 7 summarizes thermodynamic state functions calculated for the considered PCET reactions. The \( \Delta G \) values for the PCET reactions between the oxidized, dicationic redox state GFA\( ^{1+} \) and the reduced, diprotonated form of another bisguanidine are included as red bars in Figure 11. In all cases, negative \( \Delta G \) values were obtained, meaning that the reaction in which the doubly protonated, reduced bisguanidine is oxidized to the dicationic, oxidized bisguanidine is exergonic. This result is in full agreement with the experimental results showing that all these reactions take place in the predicted direction. Figure 11 directly compares the Gibbs free energy change of reactions in which only electron transfer occurs (blue bars) with reactions involving both electron and proton transfer (both at \( \varepsilon_r = 37.5 \)).

In the case of GFA4 and GFA5, pure electron transfer leading to oxidation of the two bisguanidines by GFA1(PF\( _6 \)\( ^{2+} \)) are endergonic. Nevertheless, oxidation of (GFA4 + 2H\(^+\)) as well as (GFA5 + 2H\(^+\)) by GFA1\(^{1+}\) via PCET are exergonic reactions, and the experiments showed that these reactions are even particularly fast. Compounds GFA4 and GFA5 are considerably weaker Brønsted bases than GFA1. The lower Brønsted basicity leads to an exergonic reaction if electron transfer is coupled with proton transfer. The high reaction rate implies that the proton-transfer step decisively contributes to the overall rate.

According to the experiments, the reaction between (GFA2 + 2H)(PF\( _6 \))\(^{2+} \) and GFA1(PF\( _6 \))\(^{2+} \) is the slowest reaction. It also is the reaction that exhibits the highest (least negative) Gibbs free energy change. However, the experimentally observed order in the reaction rates does not fully correlate with the calculated order for the thermodynamics of the (2e\(^-\), 2H\(^+\)) PCET reactions. Hence, reaction with (GFA3 + 2H\(^+\))\(^{2+} \) is slower than reaction with (GFA4 + 2H\(^+\))\(^{2+} \), in opposition to the trend in the Gibbs free energy changes. This result again points to the importance of proton transfer for the reaction rate, since GFA4 is a weaker proton acceptor (see Table 6) but also a weaker electron donor (see Table 5) compared with GFA3.

In a previous study we showed that the reaction between GFA1 and 10-methyl-9,10-dihydroacridane (AcrH\( _2 \)) follows a mechanism in which an electron transfer equilibrium is followed by proton transfer.[26] Both the rate of the electron transfer step and that of the proton transfer step enter into the overall rate equation, that could be formulated as \( k_{\text{et}} = k_{\text{et}} (k_{\text{et}} + k_{\text{et}}) \), where \( k_{\text{et}} \) is the rate constant for proton transfer, and \( k_{\text{et}} \) and \( k_{\text{et}} \) are the rate constants for electron transfer and back electron transfer regenerating the reactants, respectively. Similar results were also reported for the reaction between tetrachloro-1,4-benzoquinone (chloranil) and AcrH\( _2 \) in acetonitrile.[28] Most likely, the PCET reactions between the bisguanidines studied herein follow a similar mechanism. However, as mentioned previously, the equilibrium constant for the formation of the initial hydrogen-bond complex also enters into the rate equation, since the approach of the two dicationic reaction partners is opposed by a high barrier due to electrostatic repulsion and solvent reorganization.

In summary, the experimental and quantum-chemical results show that GFA1 is the strongest oxidant in PCET reactions of the five considered bisguanidines. However, it is not the strongest oxidant in pure electron transfer reactions, since GFA4 and GFA5 exhibit higher redox potentials.

Test reactions for applications in preparative chemistry

In the final section of this work, we demonstrate the use of the two oxidized bisguanidines GFA1\(^{2+} \) and GFA4\(^{2+} \) as PCET reactants in typical intra- and intermolecular aryl-aryl coupling reactions, and in an oxidative lactonization reaction. We selected these two bisguanidines for the following reasons: (i) GFA1\(^{2+} \) is the strongest oxidant in PCET reactions of all five considered bisguanidines. (ii) GFA4\(^{2+} \) is a stronger oxidant than GFA1\(^{2+} \) in pure electron-transfer reactions, but exhibits a lower proton affinity. By comparing the reactivity of GFA1\(^{2+} \) and GFA4\(^{2+} \), the importance of both factors on the PCET reactivity could be analysed. (iii) GFA4\(^{2+} \) displays a characteristic band in the visible region (at 495 nm) that could be used to follow the conversion by UV-vis spectroscopy. The test reactions do not intend to demonstrate the scope of reactivity of these GFAs (see previous papers on this issue[29,30]). The aims are to complete the analysis of the reactivity differences between GFA1 and GFA4, giving information on the reaction mechanism, and to answer the question about the required amount of acid for reaction initiation, highlighting the advantages of GFA reagents in PCET reactions with respect to high-potential quinones. We used HBF\(_4\)-OEt\(_2\) as acid and CH\(_3\)CN as solvent; the E\(_1\)O\(_2\) signals in the 'H NMR spectra could be used to verify the amount of added acid. In the case of the two coupling reactions, the conversion could not be followed easily by NMR spectroscopy due to the intermediate formation of radical species. Therefore, the conversion/yield was determined after work-up (see Supporting Information for details).

**Figure 11.** Comparison between the reaction Gibbs free energy \( \Delta G \) for the oxidation of the neutral, reduced bisguanidines by GFA1(PF\( _6 \))\(^{2+} \) (dicationic, oxidized form) in a pure electron transfer reaction (blue bars) and in a PCET reaction (red bars) from B3LYP/def2-TZVP calculations with COSMO (\( \varepsilon_r = 37.5 \)).
**Intramolecular oxidative coupling of 3,3’’-4,4’’-tetramethoxy-o-terphenyl**

We already reported the reaction of GFA1(PF₆)₂ with 3,3’’-4,4’’-tetramethoxy-o-terphenyl (oxidation potential of +0.74 V vs. Fc⁺/Fc) to give the corresponding triphenylene (Table 8).[30] Herein, we compare the reactions with GFA1(PF₆)₂ and GFA4(PF₆)₂ as PCET reagent, carried out in CH₂CN solution at room temperature. In both cases, the addition of a strong acid is needed, but only 12.5 mol% HBF₄·OEt₂ are sufficient for clean, efficient coupling. The results are summarized in the table integrated in Table 8. The conversion was determined by NMR spectroscopy after a work-up procedure yielding a mixture of the coupling product and the reduced, deprotonated bisguanidine (see Supporting Information for detailed information). Reaction with GFA1(PF₆)₂ was faster than with GFA4(PF₆)₂. With 0.13 equivalents of HBF₄·OEt₂, 88% of the coupling product was obtained after 6 h at room temperature for reaction with GFA1(PF₆)₂, but only 80% after 25 h at room temperature for reaction with GFA4(PF₆)₂. The best results were obtained for reaction at 333 K with GFA1(PF₆)₂ and 1.3 equivalents of HBF₄·OEt₂ (96% after 10 min reaction time). For comparison, reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) requires a huge amount of a strong acid (e.g. methanesulfonic acid in CH₂Cl₂ for two reactions with GFA1(PF₆)₂ and GFA4(PF₆)₂ in combination with 0.1 equivalents of QCl₂ and 98% for reaction with GFA4(PF₆)₂). To show that the coupling product could be quantitatively separated from the bisguanidine, the mixture was dissolved in Et₂O and the bisguanidine protonated by addition of HCl·OEt₂ for two reactions with GFA1(PF₆)₂ and GFA4(PF₆)₂ (see Supporting Information for details). After filtration over celite the NMR spectrum of the filtrate showed the sole presence of the coupling product. The remaining residue consists of the twofold-protonated bisguanidine, that could be dissolved in CH₂CN (and re-oxidized to the PCET reagent if desired).

**Intermolecular oxidative coupling of N-ethylcarbazole**

An $E_{1/2}$ value of +1.12 V vs. SCE (+0.66 V vs. Fc⁺/Fc) was measured for N-ethylcarbazole. Venkatakrishnan et al. showed that reaction of DDQ or chloranil with N-ethylcarbazole gives quantitative conversion (>99%) of the bicarbazole coupling product (reaction in Scheme 4) in very short time when carried out in CH₂Cl₂ solution; however the addition of a large excess of methanesulfonic acid was required (1:10 v/v methanesulfonic acid:CH₂Cl₂ solvent mixture).[40] In the reactions with GFA1 and GFA4, addition of only 1.25 eq. of an acid (HBF₄·OEt₂) was required. The reactions were carried out in CH₂CN at room temperature. After 30 min reaction time and a work-up procedure (see Supporting Information for details), the bicarbazole coupling product was obtained in excellent conversion of 97% for reaction with GFA1(PF₆)₂ and 98% for reaction with GFA4(PF₆)₂.

**Oxidative lactonization of 2-[(4-methoxyphenyl)ethyl]-benzoic acid**

Finally, we tested the oxidative lactonization of 2-[(4-methoxyphenyl)ethyl]-benzoic acid to give 3-(4-methoxyphenyl)-1(3H)-isobenzofuranone. This reaction was shown to proceed in high (NMR) yield with tetrachloro-o-benzoquinone (QCl₂, Table 9) in the presence of a hydrogen-bond donor or a redox catalyst. Nocera, Jacobsen et al. reported reaction with 1.3 equivalents of the benzoquinone and several different hydrogen-bond donor compounds in CH₂Cl₂ solution at 4 °C; the best results (98% NMR yield after 24 h) were obtained with 0.1 eq. of the hydrogen-bond donor HBD sketched in Table 9.[41] Greb et al. used 1.3 equivalents of QCl₂ in combination with 0.1 equivalents of the special silicon redox catalyst Si(Cat^+)(SQ^2)₂ (see Table 9) to obtain >95% NMR yield, again in CH₂Cl₂ at 4 °C after 24 h reaction time.[42] Moreover, a photo-catalytic reaction in CH₂CN solution at room temperature with 5 mol% DDQ and 50 mol% tert-butyl nitrite was reported, using dioxygen from air as terminal oxidant.[43] The mixture was irradiated for 24 h by a blue compact fluorescent lamp with $\lambda = 450 \pm 50$ nm light. The conversion was high, but a mixture of the phthalide product together with the hydroxylated phthalide was obtained.[44] In our initial experiments, we used one equivalent of GFA1(PF₆)₂ or GFA4(PF₆)₂, and also one equivalent of HBF₄·OEt₂.

![Intramolecular Aryl-Aryl Coupling Reaction of 3,3’’-4,4’’-Tetramethoxy-O-Terphenyl](image-url)

**Table 8. Intramolecular aryl-aryl coupling reaction of 3,3’’-4,4’’-tetramethoxy-o-terphenyl. The stated conversion was determined after work-up, leading to a mixture of the coupling product and the reduced, twofold-protonated GFA from which the coupling product could be quantitatively separated by filtration over celite (see Supporting Information for details).**

| PCET reagent  | eq. of HBF₄·OEt₂ | Temperature/time | Conversion |
|---------------|-----------------|-----------------|------------|
| GFA1(PF₆)₂    | 0.13            | 298 K, 6 h      | 88%        |
| GFA1(PF₆)₂    | 1.3             | 333 K, 10 min   | 96%        |
| GFA4(PF₆)₂    | 0.13            | 298 K, 6 h      | 63%        |
| GFA4(PF₆)₂    | 0.13            | 298 K, 25 h     | 80%        |
| GFA4(PF₆)₂    | 1.1             | 298 K, 1.5 h    | 86%        |
Reaction was carried out in CH$_3$CN at room temperature, giving 98 % NMR yield for reaction with GFA1(PF$_6$)$_2$ after 40 min reaction time and also 98 % with GFA4(PF$_6$)$_2$, but only after 5 h reaction time. The conversion, directly estimated from the NMR spectra of the reaction mixture, for the two PCET reagents is compared in Figure 12, showing that reaction is much faster with GFA1(PF$_6$)$_2$. Hence the results of the test reactions are in line with the results of the comparative PCET reactions between two of the GFAs. Although GFA4 exibits the higher redox potential compared with GFA1, it reacts slower in PCET reactions. As detailed above, this result could be explained by the lower Brønsted basicity of GFA4. Thereby, the experi-
Proton-coupled electron transfer (PCET) is of immense importance in redox-enzymatic reactions in biology and also in synthetic chemistry. In this work we analyse the effect of proton transfer step. Thereby, comparative PCET reactions proton affinities showed that the driving force for PCET derivatives was considered. First, the new molecules were synthesized and characterized in all relevant charge and conversion if electron transfer is accompanied with proton transfer for the overall reaction rate. The results of our combined experimental and quantum-chemical analysis clearly decode the importance of the two parameters, redox potential and Bronsted basicity, for the PCET properties of redox-active bisguanidines, and depict the possibilities for their fine tuning.

Finally, two bisguanidino-benzene compounds were applied in typical intra- and intermolecular aryl-aryl coupling reactions and in an oxidative lactonization. All these reactions proceeded almost quantitatively at mild conditions. The amount of acid that was needed to initiate the reactions (one or even only 0.13 equivalents) was much lower than in traditional procedures relying on high-potential quinones. Hence, the results of this work demonstrate the huge potential of redox-active guanidines as valuable alternatives to toxic high-potential quinones for use as PCET reagents.

Figure 12. Conversion vs. time plots for lactonization of 2-[(4-methoxyphenyl)methyl]-benzoic acid with GFA1(PF$_6$) ($\bullet$), GFA3(PF$_6$) ($\triangle$), or GFA4(PF$_6$) ($\square$) from NMR spectroscopic measurements. See Supporting Information for the complete curve with 1 eq. GFA4(PF$_6$).

Conclusions
Proton-coupled electron transfer (PCET) is of immense importance in redox-enzymatic reactions in biology and also in synthetic chemistry. In this work we analyse the effect of modifications at the guanidino groups and the aromatic core on the PCET properties of redox-active bisguanidines. For this systematic study, a series of five 1,4-bisguanidino-benzene derivatives was considered. First, the new molecules were synthesized and characterized in all relevant charge and protonation states. The analysis of the redox potentials and proton affinities showed that the driving force for PCET reactions is either the electron transfer (redox) step or the proton transfer step. Thereby, comparative PCET reactions between the five bisguanidines provided (qualitative) information about the mechanisms of PCET reactions. Interestingly, comparative reactions, being endergonic in the case of pure electron transfer, turned to be most exergonic with fastest conversion if electron transfer is accompanied with proton transfer. The differences in the Bronsted basicities explain these results, highlighting their decisive role for the thermodynamics and demonstrating the important contribution of the proton transfer step for the overall reaction rates. The results of our
discussion above).

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Conflict of Interest
The authors declare no conflict of interest.

Keywords: C–H activation · guanidines · proton affinity · proton-coupled electron transfer · redox potential

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