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Oxidation

Redox-Active Guanidines in Proton-Coupled Electron-Transfer Reactions: Real Alternatives to Benzoquinones?

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Abstract: Guanidino-functionalized aromatics (GFAs) are readily available, stable organic redox-active compounds. In this work we apply one particular GFA compound, 1,2,4,5-tetrakis(tetramethylguanidino)benzene, in its oxidized form in a variety of oxidation/oxidative coupling reactions to demonstrate the scope of its proton-coupled electron transfer (PCET) reactivity. Addition of an excess of acid boosts its oxidation power, enabling the oxidative coupling of substrates with redox potentials of at least +0.77 V vs. Fc^+/Fc. The green recyclability by catalytic re-oxidation with dioxygen is also shown. Finally, a direct comparison indicates that GFAs are real alternatives to toxic halo- or cyano-substituted benzoquinones.

Proton-coupled electron transfer (PCET) is important for biological and bioinspired (photosynthetic) processes as well as synthetic chemistry,[1–3] and has been studied intensively mechanistically.[4,5] Quinones are especially versatile organic PCET reagents. Their redox-properties and the pK_a values of their corresponding hydroquinones can be varied by the introduction of substituents,[6–8] and also by electronic excitation.[9,10] Figure 1 shows as examples the three benzoquinones BQ, CA and DDQ. The 1 e^- redox potentials (E_{red} vs. Fc^+/Fc) of DDQ (+0.14 V) and CA (−0.35 V) are significantly higher than that of BQ (−0.88 V).[8] However, the reduction of the pK_a value of the reduced form that accompanies the increase of E_{red} of the oxidized form leads to a certain "leveling" effect on the PCET reactivity.[7,8] Benzoquinones with a relatively high oxidation potential, for example, CA and DDQ, are used in a number of PCET reactions as stoichiometric oxidation reagents, often in combination with a strong acid,[11–13] and in some reactions also catalytically, for example, DDQ together with nitrite.[14] Low-potential *p*-benzoquinone derivatives were used as redox-mediators in biomimetic catalysis and as redox catalysts (often together with transition metal complexes).[15–17] Moreover, low-potential *o*-quinone-type catalysts were recently shown to enable manifold (bioinspired) aerobic oxidations.[18–26]

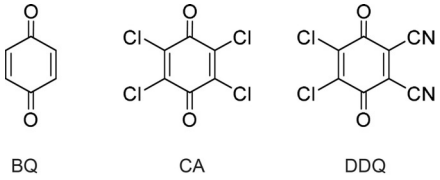

Figure 1. Lewis structures of *p*-benzoquinone (BQ), chloranil (CA), and 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ).

Despite of the outstanding success story of quinones, some drawbacks oppose their large-scale applications. Hence cyano- or halo-substituted benzoquinones like **CA** are highly toxic, as they induce reactive oxygen species and oxidative stress, showing an inflammatory response both in vivo and in vitro.[27] Moreover, the recycling of the quinones is sometimes problematic due to side reactions.[11] Strong oxidizing reagents are required for high-potential quinones. For low-potential quinones catalytic oxidation of the hydroquinone with dioxygen is possible,[28] but could be hampered by the formation of quinhydrones (the 1:1 complex between benzoquinone and hydroquinone exhibits a binding energy of more than 20 kJ mol^{-1})[29] at high concentrations.[28]

We recently developed a new class of PCET reagents, namely redox-active guanidines, that do not have these disadvantages.[30–33] One example is 1,2,4,5-tetrakis-(tetramethylguanidino)benzene (**1**), which could be readily oxidized to the dication $\mathbf{1}^{2+}$ (Scheme 1). The loss of aromaticity upon oxidation leads to significantly different C–C bond distances in the C_6 ring and a distinct colour change from pale yellow for neutral **1** to intense green for the dication $\mathbf{1}^{2+}$. Proton-coupled electron transfer (PCET) reactions of oxidized 1,2,4,5-tetrakis(tetramethylguanidino)benzene ($\mathbf{1}^{2+}$, Scheme 1)[34] with some inorganic (thiol to disulfides, phosphines to diphosphines)[31] and organic substrates with relatively low redox-potential (e.g., phenols to biphenols, catechols to benzoquinones) were already reported.[31,32] The π-system of $\mathbf{1}^{2+}$ accepts the electrons and the nitrogen lone pairs accept the protons. Using a copper co-catalyst, $\mathbf{1}^{2+}$ could be used as an organocatalyst with dioxygen as the terminal oxidant.[32] The pK_a value of ca. 25.3 for $(\mathbf{1}+H)^+$ in CH_3CN sharply decreases upon oxidation. Interestingly, green $\mathbf{1}^{2+}$ still is a Lewis[35] and Brønsted base, and is protonated with HBF_4·Et_2O to blue $(\mathbf{1}+H)^{3+}$ and orange

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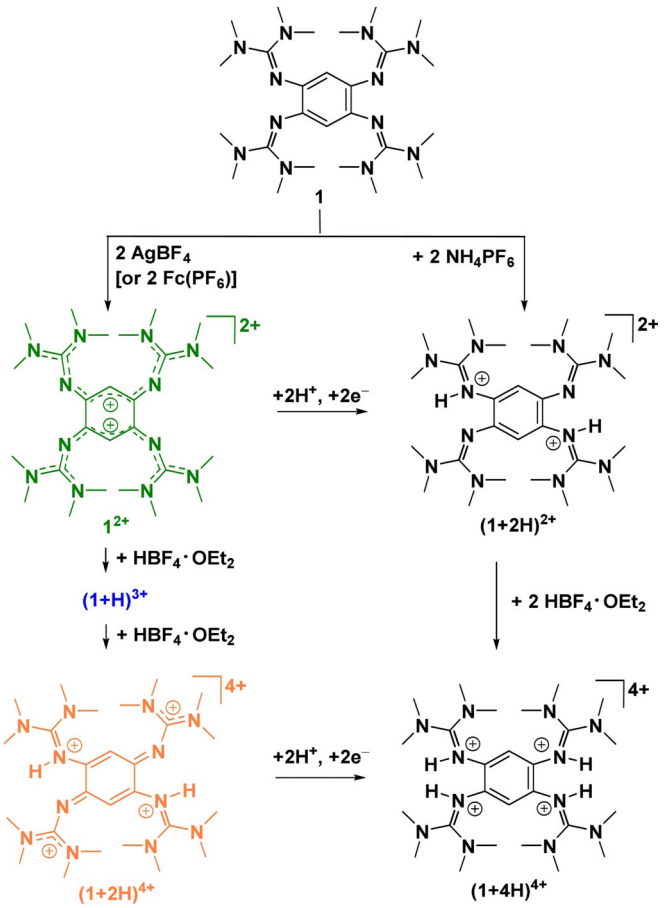


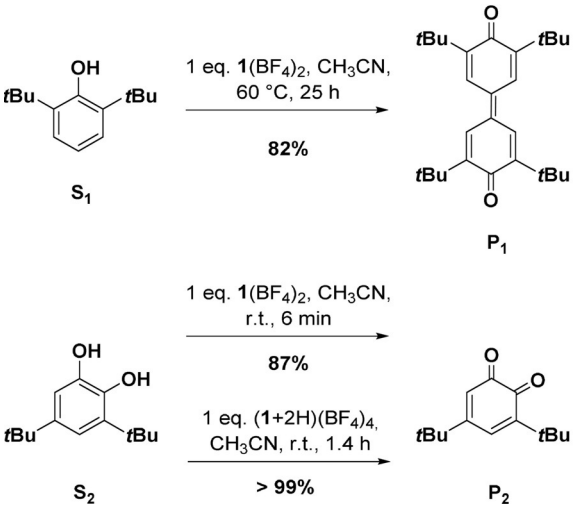
Scheme 1. Lewis structures of characterized, stable states, starting with neutral 1,2,4,5-tetrakis(tetramethylguanidino)-benzene (**1**), relevant for the PCET reactivity. The colors characteristic for the oxidized states are highlighted.

$(\mathbf{1}+2\,H)^{4+}$ (with a pK_a value of ca. 13 in CH_3CN close to CF_3COOH, Scheme 1).[36] The reduction potential increases from $\mathbf{1}^{2+}$ ($E_{1/2}=-0.73$ V vs. Fc^+/Fc in CH_3CN) to $(\mathbf{1}+2H)^{4+}$ by ca. 0.7 V.[36]

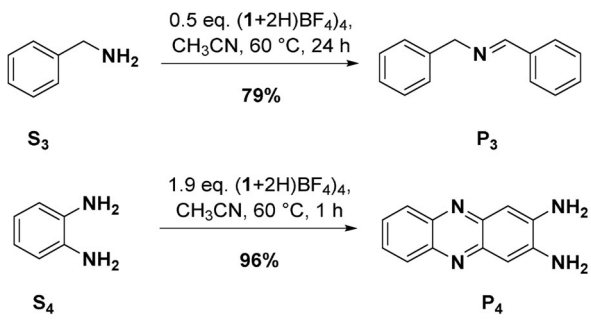
Herein, we demonstrate the wide scope of its PCET reactivity, especially in combination with strong acids. Nine oxidative coupling/ oxidation reactions were studied with substrates that differ largely in their redox potentials. In addition, we show that efficient regeneration of the PCET reagent $\mathbf{1}(BF_4)_2$ is possible by catalytic oxidation with dioxygen. Finally, we compare its PCET properties with benzoquinones.

The salts $\mathbf{1}(BF_4)_2$ (oxidized GFA) and $(\mathbf{1}+2\,H)(BF_4)_4$ (oxidized and protonated GFA)[36] as well as $\mathbf{1}(BF_4)_2$ in combination with an excess of the strong acid $HBF_4{\cdot}OEt_2$ were applied. The substrates are grouped in low-potential [Eqs. (1–4)] and high potential substrates [Eqs. (5–9)], for example, +0.52 V for NPh_3 ($\mathbf{S_6}$),[37] +0.66 V for 4,4′-dibromo-triphenylamine ($\mathbf{S_7}$), +0.74 V for 3,3′′,4,4′′-tetramethoxy-*o*-terphenyl ($\mathbf{S_9}$),[13b] and +0.77 V vs. Fc^+/Fc for 4-nitro-triphenylamine ($\mathbf{S_8}$).[38] To allow for a direct comparison, all reactions were carried out in CH_3CN solution. The yields were estimated from NMR signal integration (see the Supporting Information).

Oxidative coupling of 2,6-di-*tert*-butyl-phenol ($\mathbf{S_1}$) to the diketone ($\mathbf{P_1}$) gives best results (82% yield) with $\mathbf{1}(BF_4)_2$ [Eq. (1)] rather than $(\mathbf{1}+2\,H)(BF_4)_4$. Oxidation of 3,5-di-*tert*-butyl-catechol ($\mathbf{S_2}$) to the *o*- benzoquinone ($\mathbf{P_2}$) is fast with $\mathbf{1}(BF_4)_2$, but gives slightly better yields with $(\mathbf{1}+2\,H)(BF_4)_4$ [Eq. (2)]. Both reactions are presumably initiated by deprotonation. Catechol deprotonation is favored by the intramolecular O–H···O bridge in the resulting monoanion.[7,39]



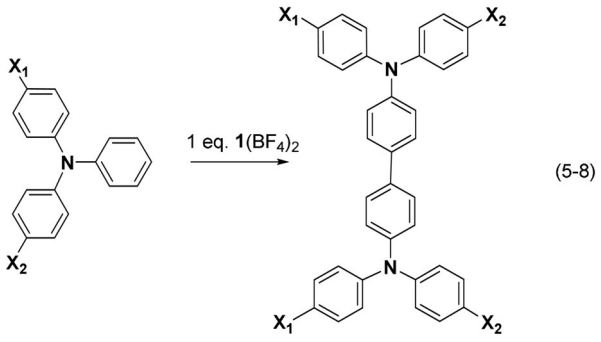
The oxidative coupling of benzylamine ($\mathbf{S_3}$) to give *N*-(phenylmethylene)benzenemethanamine ($\mathbf{P_3}$) and the oxidation of *o*-phenylene-diamine ($\mathbf{S_4}$) to give 2,3-diaminophenazine ($\mathbf{P_4}$) give best results with $(\mathbf{1}+2\,H)(BF_4)_4$ (79% respectively 96% yield, see Eqs. (3) and (4)]. With $\mathbf{1}(BF_4)_2$, these reactions are much slower, giving less than 10% yield after 25 h at 60 °C (see the Supporting Information for details). UV/Vis and ^1H NMR spectra (see the Supporting Information) indicate that $(\mathbf{1}+2\,H)^{4+}$ first protonates the amine, in line with the acidity of $(\mathbf{1}+2\,H)^{4+}$.[36]



When benzylamine oxidation was repeated with 0.5 equivalents of $\mathbf{1}(BF_4)_2$ and slightly more than 1 equivalent of NH_4PF_6, the reaction proceeded with a similar rate and slightly better yield (84%).

Next we inspected the reactivity toward substrates with higher redox potentials, requiring the addition of excess acid. Happily, oxidative coupling of triphenylamine and derivatives with electron-withdrawing and -donating groups [$\mathbf{S_5}$–$\mathbf{S_8}$, Eq. (5)–(8)] is accomplished in less than 2.3 h with excellent

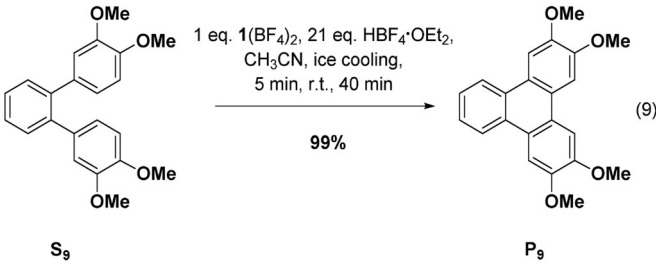
yields with a combination of $\mathbf{1}(BF_4)_2$ (equimolar amount) and excess $HBF_4{\cdot}OEt_2$ (see the Supporting Information). The results demonstrate the superior functional-group tolerance of such coupling reactions. UV/Vis experiments showed the presence of reaction intermediates, arising from substrate oxidation (see the Supporting Information).[12h,40,41] In principle, the triphenylamine derivatives could be protonated by the strong acid. However, in all cases fast oxidation was observed, indicating that protonation plays no significant role.



(5-8)

		conditions	yield	
X_1 = OMe, X_2 = H	$S_5 \rightarrow P_5$	21 eq. $HBF_4{\cdot}OEt_2$, CH_3CN, ice cooling, 5 min, r.t., 1.9 h	90%	(5)
X_1 = H, X_2 = H	$S_6 \rightarrow P_6$	20 eq. $HBF_4{\cdot}OEt_2$, CH_3CN, ice cooling, 5 min, r.t., 25 min	>99%	(6)
X_1 = Br, X_2 = Br	$S_7 \rightarrow P_7$	24 eq. $HBF_4{\cdot}OEt_2$, CH_3CN, ice cooling, 10 min, r.t., 1.4 h	95%	(7)
X_1 = NO_2, X_2 = H	$S_8 \rightarrow P_8$	23 eq. $HBF_4{\cdot}OEt_2$, CH_3CN, ice cooling, 20 min, r.t., 2.3 h	95%	(8)

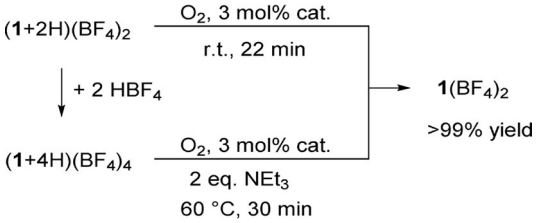
Finally, we tested an intramolecular oxidative coupling reaction of 3,3′′,4,4′′-tetramethoxy-*o*-terphenyl (**S_9**) [Eq. (9)], a substrate with a high oxidation potential of 0.74 V vs. Fc^+/Fc. Application of 1 equivalent of $\mathbf{1}(BF_4)$ with an excess of $HBF_4{\cdot}OEt_2$ leads to 99% triphenylene coupling product.



(9)

Obviously, $(\mathbf{1}+2H)(BF_4)_4$ forms from $\mathbf{1}(BF_4)_2$ upon acid addition, but the oxidation potential of these organic substrates is still higher than the reduction potential of $(\mathbf{1}+2H)(BF_4)_4$.[36] Hence the addition of excess acid boosts the oxidation power, as also found for benzoquinones in aqueous[42,43] and aprotic solutions.[12b,h,k,44,45]

The guanidinium salt could easily be separated from the reaction mixture. We already showed that $(\mathbf{1}+2H)^{2+}$ can be quantitatively reconverted to $\mathbf{1}^{2+}$ by catalytic oxidation with dioxygen.[32] In new experiments we tested the recyclability of $\mathbf{1}(BF_4)_2$ from the reduced tetraprotonated compound $(\mathbf{1}+4H)(BF_4)_4$, that is formed in the experiments with $(\mathbf{1}+2H)(BF_4)_4$ or an excess of acid. Indeed, quantitative formation of $\mathbf{1}(BF_4)_2$ (NMR studies, see the Supporting Information) within 30 min at 60 °C was achieved by catalytic oxidation with dioxygen in the presence of 2 equivalents of NEt_3 (Scheme 2) with a simple, commercially available catalyst (3 mol% of a 1:1 mixture of $CuCl_2/[Cu(H_2O)_6](BF_4)_2$), independent of the concentration of $(\mathbf{1}+4H)(BF_4)_4$ (62, 17, and 8 mmol L^{-1}). A complex formation between the product ($\mathbf{1}^{2+}$) and the reactant [$(\mathbf{1}+2H)^{2+}$ or even $(\mathbf{1}+4H)^{4+}$], as observed in the case of benzoquinone (quinhydrone complex), is prohibited by strong electrostatic repulsion.

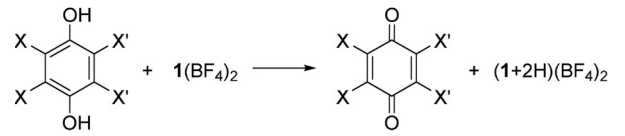


Scheme 2. Regeneration of $\mathbf{1}(BF_4)_2$ from the reduced and two- or fourfold protonated forms (cat. = $[CuCl_2/Cu(H_2O)_6(BF_4)_2]$).

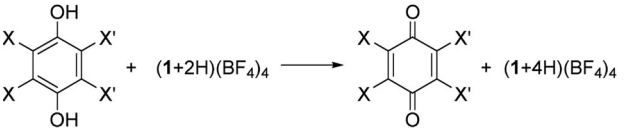
The reaction between dihydro-benzoquinone and $\mathbf{1}^{2+}$ in CH_3CN leads quantitatively in 35 min at r.t. to BQ,[31] showing that $\mathbf{1}^{2+}$ is a stronger PCET reagent than BQ. To gain more information, we calculated the energetics of the reactions in Table 1 by using the B3LYP functional in combination with a def2-SV(P) or def2-TZVP basis set. The solvent effect was estimated with the conductor-like screening model (COSMO) at a relative permittivity ε_r of 40. Calculations with and without BF_4^- counter-ions gave similar results (see the Supporting Information); we here present results with BF_4^-. According to these calculations, $\mathbf{1}(BF_4)_2$ is similar to BQ with respect to the thermodynamics of its PCET reactions, and slightly weaker than CA. On the other hand, $(\mathbf{1}+2H)(BF_4)_4$ is a significantly stronger PCET reagent than all three quinones BQ, CA and DDQ.

The effect of hydrogen-bonding and protonation on the redox-potential of quinones in aqueous and aprotic solutions[41,46] was already studied. Moreover, estimates for the pK_a value of protonated BQ were reported (e.g., from Pourbaix diagrams).[47,48] On the other hand, monoprotonation of BQ in significant amounts requires the use of superacidic HF/AsF_5 and low temperature, since the salt $(BQ+H)AsF_6$ decomposes already above −60 °C.[49] By contrast, $(\mathbf{1}+2H)(BF_4)_4$ is a storable compound, being stable in the solid state and in solution at ambient conditions.[36] Consequently, the double-proton transfer from $(\mathbf{1}+2H)(BF_4)_4$ to BQ to give $\mathbf{1}(BF_4)_2$ and $(BQ+2H)(BF_4)_2$ (exhibiting almost symmetric F···H–O bonds between

Table 1. Reaction energies, enthalpies (at 0 K) and Gibbs free energies (at 298 K) for the reaction between the benzoquinones BQ, CA or DDQ and $\mathbf{1}(BF_4)_2$ respectively $(\mathbf{1}+2H)(BF_4)_4$ from B3LYP + COSMO/def2-TZVP calculations at $\varepsilon_r = 1$ and 40.



	X	X′	ΔE [kJ mol^{-1}]		ΔH (0 K) [kJ mol^{-1}]	ΔG (298 K) [kJ mol^{-1}]
			$\varepsilon_r = 1$	$\varepsilon_r = 40$	$\varepsilon_r = 1$	$\varepsilon_r = 1$
BQ	H	H	−1.8	9.9	1.5	6.0
CA	Cl	Cl	9.9	12.9	12.7	15.2
DDQ	Cl	CN	45.2	59.8	47.3	48.2



	X	X′	ΔE [kJ mol^{-1}]		ΔH (0 K) [kJ mol^{-1}]	ΔG (298 K) [kJ mol^{-1}]
			$\varepsilon_r = 1$	$\varepsilon_r = 40$	$\varepsilon_r = 1$	$\varepsilon_r = 1$
BQ	H	H	−82.3	−67.4	−76.2	−71.0
CA	Cl	Cl	−70.6	−64.3	−65.0	−61.8
DDQ	Cl	CN	−35.3	−17.5	−30.4	−28.8

cation and anion, with F–H: 1.360 Å and O–H: 1.059 Å) was calculated (B3LYP + COSMO/def2-TZVP) to be associated with a high positive reaction energy of +251 kJ mol^{-1} at $\varepsilon_r = 40$. Accordingly, no reaction was observed when $(\mathbf{1}+2H)(BF_4)_4$ was dissolved together with BQ in CH_3CN. Interestingly, $(BQ+2H)(BF_4)_2$ decomposes in the calculations for $\varepsilon_r = 1$ by fluoride abstraction from the anion to a complex $BQ(HF)_2(BF_3)_2$ (see the Supporting Information). Moreover, $(CA+2H)(BF_4)_2$ defines no minimum structure at both $\varepsilon_r = 1$ and 40, but converges again to the product of fluoride abstraction, $CA(HF)_2(BF_3)_2$ (Figure 2). The reaction between $(\mathbf{1}+2H)(BF_4)_4$ and CA to give, instead of protonated **CA**, the favoured complex $CA(HF)_2(BF_3)_2$ exhibits a reaction energy of +317 kJ mol^{-1} at $\varepsilon_r = 40$.

In summary we demonstrated the preeminent PCET reactivity and efficient recyclability (by green oxidation of $(\mathbf{1}+2H)(BF_4)_2$ or $(\mathbf{1}+4H)(BF_4)_4$ with dioxygen) of the tetrakisguanidine $\mathbf{1}(BF_4)_2$. This PCET reagent is readily synthesized (in two steps starting from commercially available 1,2,4,5-tetraaminobenzene-tetrahydrochloride), easy to handle, and thermally stable.[30,34,36,50] The results show that the combination of $\mathbf{1}(BF_4)_2$ with a strong acid allows the fast and near quantitative oxidative coupling of substrates with high redox potentials (at least +0.77 V vs. Fc^+/Fc) at mild conditions, making the compound a real alternative to traditionally applied toxic benzoquinone derivatives.

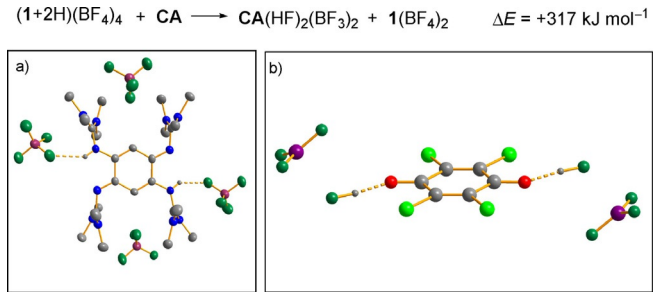


Figure 2. a) Comparison between the experimentally derived structure of the stable compound $(\mathbf{1}+2H)(BF_4)_4$ in the solid state (a) and the structure of the $CA(HF)_2(BF_3)_2$ complex obtained in the attempt to calculate the analogue two-fold-protonated CA with two BF_4^- counter-ions (b).

Conflict of interest

The authors declare no conflict of interest.

Keywords: guanidine · oxidation · oxidative coupling · proton-coupled electron transfer · redox reaction

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