

Oxidizing Agents

Completing the Redox-Series of Silicon Trisdioxolene: *ortho*-Quinone and Lewis Superacid Make a Powerful Redox CatalystRezisha Maskey, Christoph Bendel, Jonas Malzacher, and Lutz Greb*^[a]

Abstract: Quinones are mild oxidants, the redox potentials of which can be increased by supramolecular interactions. Whereas this goal has been achieved by hydrogen bonding or molecular encapsulation, a Lewis acid-binding strategy for redox amplification of quinones is unexplored. Herein, the redox chemistry of silicon tris(perchloro)dioxolene **1** was studied, which is the formal adduct of *ortho*-perchloroquinone Q^{Cl} with the Lewis superacid bis(perchlorocatecholato)silane **2**. By isolating the anionic monoradical $1^{\cdot-}$, the redox-series of a century-old class of compounds was completed. Cyclic voltammetry measurements revealed that the redox potential in **1** was shifted by more than 1 V into the anodic direction compared to Q^{Cl} , reaching that of “magic blue” or NO^+ . It allowed oxidation of challenging substrates such as aromatic hydrocarbons and could be applied as an efficient redox catalyst. Remarkably, this powerful reagent formed *in situ* by combining the two commercially available precursors $SiCl_4$ and Q^{Cl} .

The amplification of the redox potential of quinones by supramolecular interactions has been the subject of recent efforts. Tetrahalogenated *para*-quinones were shown to operate as potent single-electron oxidants if encapsulated as guests in Pd_2L_4 cages, catalyzing various cycloaddition reactions (Figure 1A).^[1] Moreover, Jacobsen and co-workers demonstrated that the redox potential of Q^{Cl} is increased by dicationic bis(amidinium)salts acting as dual hydrogen-bond donors (Figure 1B).^[2] However, the increase of redox potentials by the binding of Lewis acids has not been studied yet. Silicon tris(perchloro)dioxolene **1**, the two-electron-oxidized form of a century-old class of dianions 1^{2-} , is an easily prepared neutral triplet diradical and the first non-metal centered open-shell

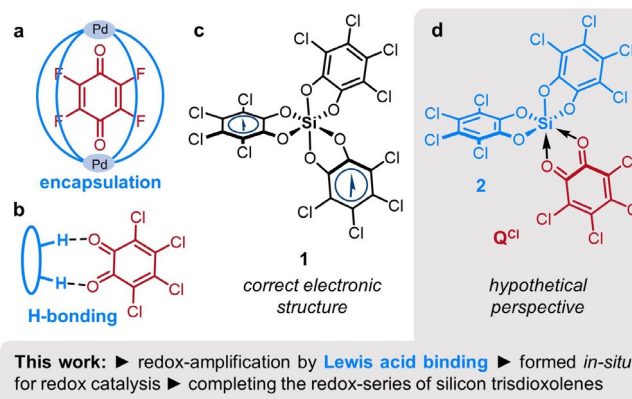


Figure 1. a) Activation of *p*-fluoroquinone by host-guest encapsulation in Pd-cages. b) Activation of Q^{Cl} through binding to a hydrogen-bond donor. c) Neutral diradical silicon tris(perchloro)dioxolene **1**, and d) its hypothetical representation as Q^{Cl} bound to the Lewis superacid **2**.

semiquinonate (Figure 1C).^[3] By taking a hypothetical perspective, **1** can be considered as *ortho*-perchloroquinone, Q^{Cl} , coordinated to the Lewis superacid bis(perchlorocatecholato)silane **2** (Figure 1D).^[4] In the present work, we study the redox properties of **1** and, by doing so, we elaborate this third concept to turn quinones into potent two-electron acceptors by Lewis acid binding. This strategy resembles the combination of XeF_2 or F_2 with fluoride ion acceptors,^[5] but offers substantially easier handling than that of those highly corrosive and toxic reagents. Beyond, it touches the emerging field of frustrated radical pairs and offers a new means for redox catalysis.^[6] Remarkably, **1** can be prepared from the two commercially available compounds $SiCl_4$ and Q^{Cl} *in situ* and acts as a powerful oxidant and highly efficient catalyst. Furthermore, these studies lead to the isolation of the monoradical anion $1^{\cdot-}$, ultimately completing the redox series of the century-old substance class of silicon triscatecholates.^[3a]

To gather first insights into the redox properties of **1**, we started with a guiding cyclic voltammetry (CV) measurement of the two-electron-reduced, most stable form $[NBu_4]_2[1]$ (Figure 2A). Fluorinated electrolytes like NBu_4PF_6 or NBu_4BARF_{24} in CH_2Cl_2 were avoided due to potential defluorinating side reactions mediated by Lewis superacidic products. With NBu_4BARF_{20} (0.1 M) as the electrolyte, the cyclic voltammogram of $[NBu_4]_2[1]$ revealed two separated, non-reversible oxidation waves at 0.45 and 0.86 V vs. Fc/Fc^+ (Figure S17). We attributed those peaks to the redox couples $1^{2-}/1^{\cdot-}$ and $1^{\cdot-}/1$, respectively. The substantial peak separation allowed to estimate the comproportionation constant ($K \approx 8 \times 10^6$), which encouraged

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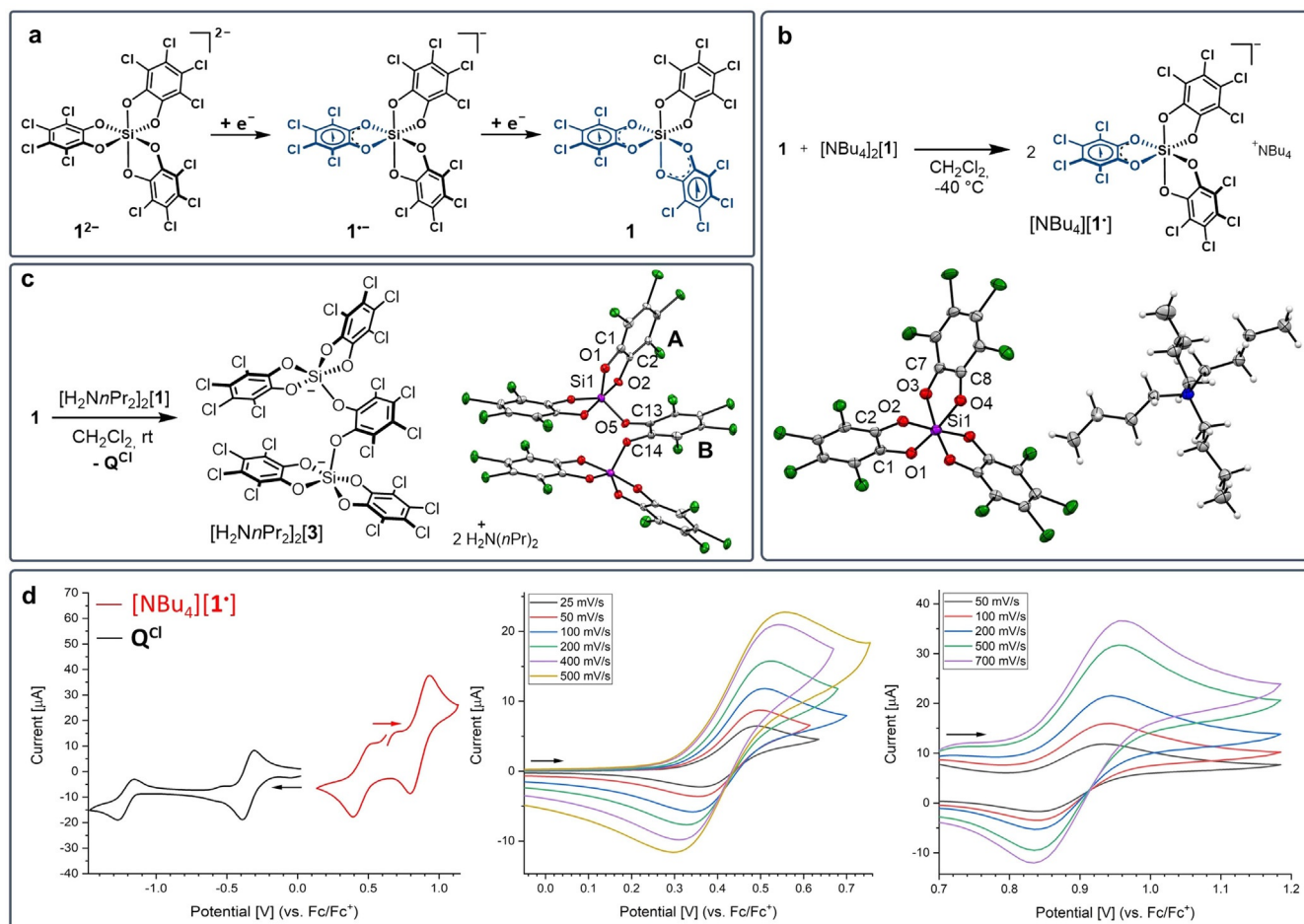


Figure 2. a) Lewis structures of the involved redox-isomers 1^{2-} , 1^{1-} and 1 . b) Synthesis of 1^{1-} by comproportionation, together with SCXRD molecular structure (ellipsoids are set at 50% probability, selected bond length [Å]: O1–C1 1.284(3), O2–C2 1.277(3), O3–C7 1.350(3), O4–C8 1.342(3), C1–C2 1.447(4), C7–C8 1.397(3), O1–Si1 1.868(2), O2–Si1 1.884(2), O3–Si1 1.761(2), O4–Si1 1.743(2)). c) Synthesis of 3^{2-} by liberation of Q^{Cl} with SCXRD structure (ellipsoids are set at 50% probability, cations omitted for clarity, selected bond length [Å]: O1–C1 1.362(4), O2–C2 1.353(5), O5–C13 1.367(4), C1–C2 1.395(5), C13–C14 1.394(6), O1–Si1 1.689(3), O2–Si1 1.796(3), O5–Si1 1.671(3)). d) Left: cyclic voltammogram of $[\text{NBu}_4][1^{\cdot-}]$ (red trace) and Q^{Cl} (black trace) in dichloromethane, referenced against Fc/Fc^+ , $[\text{NBu}_4][\text{BARf}_{20}]$ (0.1 M), 500 and 100 mV s^{-1} , respectively. Right: pseudo-reversible peaks for both oxidation events of at different scan-rates (25–700 mV s^{-1}) under similar conditions.

us to access the hitherto elusive silicon trisdioxolene monoradical anion 1^{1-} by reacting 1 with 1^{2-} . Indeed, mixing of equimolar amounts of 1 and $[\text{NBu}_4]_2[1]$ in CH_2Cl_2 at low temperatures led to the formation of a green crystalline species whose analytical features were in line with 1^{1-} (Figure 2B). The anionic part of the salt was ^{13}C NMR silent, whereas electron paramagnetic resonance (EPR) spectroscopy revealed a strong featureless signal ($g=2.0064$), indicating an $S=1/2$ state. UV/Vis spectroscopy of $[\text{NBu}_4][1^{\cdot-}]$ showed the characteristic absorption bands for an open-shell semiquinonate ligand and several weak intervalence charge transfer bands (IVCT) in the near-IR (NIR)-region (Figure S39). Typical C–O stretching modes for catecholate and semiquinonate were visible in the IR-spectra, but different from those of 1 or 1^{2-} (Figure S36).^[7] Single-crystal X-ray diffraction (SCXRD) of the crystalline compound confirmed the correct spectroscopic interpretation (Figure 2B).

The measured bond lengths were used to calculate the metrical oxidation states of the dioxolene units according Brown's procedure (see supporting information).^[8] Those parameters

confirm the Lewis formulation of 1^{1-} , with two dianionic catecholato ligands ($\text{C}-\text{O}_{\text{avg}}=1.35 \text{ \AA}$) and one monoanionic open-shell semiquinonate ($\text{C}-\text{O}_{\text{avg}}=1.28 \text{ \AA}$), and are in line with those of transition metal dioxolene complexes of identical ligand oxidation states.^[7,9]

An alternative reaction outcome was observed during the attempted comproportionation reaction of 1 and 1^{2-} with the protic counter cation $[\text{H}_2\text{N}(\text{nPr})_2]^+$ (Figure 2C). Instead of the electron transfer described above, the release of Q^{Cl} and the formation of a new diamagnetic species was observed by ^{13}C NMR spectroscopy. SCXRD of the reaction product revealed the formation of a diamagnetic, dianionic product 3^{2-} , in which two units of 2 are bridged by a dianionic catecholate (Figure 2C). Apparently, ligand scrambling is favored over electron transfer through hydrogen bond activation by the protic cation $[\text{H}_2\text{N}(\text{nPr})_2]^+$. Very interestingly, the ^{13}C NMR spectrum of 3^{2-} was showing only one set of catecholate signals at room temperature, indicating a fast exchange of the terminal catecholates **a** with bridging catecholate **b** (Figure 2C). Indeed,

DFT-computations of the corresponding exchange pathway revealed a very low exchange barrier of $\Delta G^\ddagger = 50 \text{ kJ mol}^{-1}$ (Figure S48). This high fluxionality once more underscores the dynamic covalent chemistry of the Si–O bond in silicon catecholates, but for the first time, this exchange is observed spectroscopically.^[10]

Next, we turned our attention back to the redox properties of the system. CV measurements on the monoradical anion $[\text{NBu}_4][1^\cdot]$ provided two quasi reversible redox peaks at 0.43 and 0.88 V (Figure 2D, red trace), in line with the peaks already observed for the dianion $[\text{NBu}_4]_2[1]^{2-}$. The well-separated peaks qualify the compound as Robin–Day class II/III mixed-valence compounds.^[11] This interpretation also agrees with the IVCT observed experimentally for **1** and 1^\cdot in the NIR-region and highlights the potential of silicon to act as a bridging unit for the construction of metal-free electronic devices.^[12] Having the electrochemical parameters, a comparison of the redox potentials of **1** with that of Q^{Cl} could be made (Figure 2D, black trace). A massively shifted redox potential by about 1.2 V into the anodic direction becomes apparent. Hence, the effect evoked by binding of Q^{Cl} to **2** outperforms the anodic shift of approximately 1.0 V for *p*-quinones caused by Pd-cages encapsulation (Figure 1C),^[11] or of approximately 0.6 V with Q^{Cl} coordinated to dicationic hydrogen-bond donors (Figure 1D),^[2] and illustrates the effectiveness of Lewis superacid-binding strategy for redox amplification.

EPR-spectroscopic monitoring of reactions with substrates of known redox potentials served to bracket the potential of **1**.^[13] Indeed, successful oxidations were observed by mixing **1** with thianthrene (0.84 V vs. Fc/Fc^+) and tris(4-bromophenyl)amine (0.72 V vs. Fc/Fc^+ , „magic blue“) in CH_2Cl_2 . An upper bound was encompassed by the reaction with tris(2,4-dibromo-phenyl)amine (1.12 V vs. Fc/Fc^+). Although the formation of the corresponding aminium radical cation could not be detected by EPR spectroscopy, substantial line broadening of the ^1H NMR aromatic signals of the phenylamine indicated electron transfer processes occurring. Accordingly, the experimental findings ranged the redox potential of **1** between tris(2,4-dibromo-phenyl)amine and thianthrene (0.86–1.12 V vs. Fc/Fc^+), in line with the electroanalytical results. Next, the oxidation of alkyl-substituted benzenes was followed by EPR spectroscopy. Given the fleeting nature of those radical cations, their isolation was not attempted.^[14] Formation of the corresponding radical cations was observed for hexamethylbenzene, pentamethylbenzene, and 1,2,3,4-tetramethylbenzene by the appearance of characteristic hyperfine coupling patterns (Figures S31 and S32). With mesitylene (1,3,5-trimethylbenzene), no reaction occurred. Since the oxidation potentials of alkyl-benzenes are poorly documented, they were determined in CH_2Cl_2 with 0.1 M NBu_4PF_6 as electrolyte (Table S1). Remarkably, these values were exceeding the oxidative power of **1**. We explain this observation by the possibility of **1** to engage in proton-coupled electron transfer and the rapid follow chemistry of the oxidation products. Interestingly, the π – π -stacked complexes observed between **1** and less strong electron donors, such as benzene, can be considered as precursor complexes for the herein observed electron transfer.^[4]

After investigations on the redox chemistry of **1** applied in stoichiometric fashion, we were keen to know whether **1** holds the potential to act as a redox catalyst. As a model reaction, an intramolecular oxidative lactonization was chosen (Figure 3A).^[2] Quantitative conversion of 2-(4-methoxybenzyl)benzoic acid **4** into the corresponding lactone **5** was achieved with a catalyst loading of 5 mol% of **1** and 1.3 equiv. of Q^{Cl} at room temperature in less than 2 h. Thus, **1** shows improved efficiency than the hydrogen-bond donor system (Figure 1D), well in line with the more positive redox-shifting effect for Q^{Cl} .^[2] The mechanistic proposal consists of a net $2\text{H}^+ / 2\text{e}^-$ delivery from the substrate to **1**, with the formed *o*-tetrachlorocatechol $\text{H}_2\text{Cat}^{\text{Cl}}$ being replaced by another Q^{Cl} , redelivering **1**.^[2] This assumption finds support by the respective signals of 1 equiv. of $\text{H}_2\text{Cat}^{\text{Cl}}$ in the NMR spectra (Figure S43). Given the straightforward synthesis of **1** by the combination of SiI_4 with Q^{Cl} , we attempted to form the catalyst **1** in situ. Remarkably, transformation of **4** to **5** succeeded in similar efficiency by pre-mixing 5 mol% of SiI_4 and 1.3 equiv. of Q^{Cl} before adding the substrate (Figure 3a). It is by no means required to pre-isolate **1**.

To probe the generality of **1** to act as redox-catalyst, other reactions were tested. Methoxy substituted terphenyl **6** underwent quantitative dehydrogenative coupling with 10 mol% of **1** after 24 h at room temperature. (Figure 3b). Moreover, dihydroanthracene was oxidized to anthracene, but the product reacted faster than the starting material, resulting in secondary oxidation products (Figure S47).

In conclusion, we describe the redox chemistry of silicon tris-dioxolenes and complete its redox series. In doing so, we establish the strategy of Lewis acid-induced redox amplification of *ortho*-quinones. Cyclic voltammetry and guiding redox reactions disclose a potential of $E_{1/2} \approx 1.0 \text{ V vs. Fc}/\text{Fc}^+$, rendering **1**

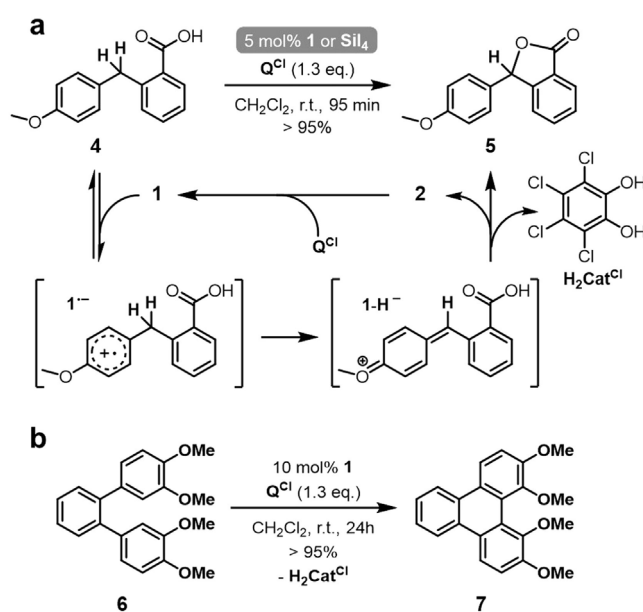


Figure 3. a) Redox-catalytic transformation of **4** into **5**, either with 5 mol% of **1** or with in situ formed **1** from 5 mol% SiI_4 and Q^{Cl} (+30 min pre-mixing). b) Dehydrogenative coupling of **6** by redox catalyst **1**.

as strong an oxidant as “magic blue” or NO^+ . However, in contrast to such oxidants that might possess limitations due to their charged nature, non-innocence, or a tedious synthesis, **1** stands out as a neutral oxidant that is obtained by the simple combination of the two commercially available compounds SiI_4 and Q^{Cl} . Proof-of-concept reactions exemplify **1** as an efficient redox catalyst, that can be generated in situ. We foresee the combination of Q^{Cl} and SiI_4 and, more generally, the concept of Lewis acid-binding induced redox amplification as a powerful tool for challenging transformations and catalysis, wherever high oxidation potentials are needed.

Experimental Section

Crystallographic data: Deposition numbers 2035360, 2035361 and 2035362 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of interest

The authors declare no conflict of interest.

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