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Completing the Redox-Series of Silicon Trisdioxolene: *ortho*-Quinone and Lewis Superacid Make a Powerful Redox Catalyst

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Abstract: Quinones are mild oxidants, whose redox potentials 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, we study the redox chemistry of silicon tris(perchloro)dioxolene **1** – the formal adduct of *ortho*-perchloroquinone Q^{Cl} with the Lewis superacid bis(perchlorocatecholato)silane **2**. By isolating the anionic monoradical $1^{\bullet-}$, we complete the redox-series of a century-old class of compounds. Cyclic voltammetry measurements reveal that the redox potential in **1** is shifted by more than 1 V into the anodic direction compared to Q^{Cl} , reaching that of "magic blue" or NO^+ . It allows oxidation of challenging substrates such as aromatic hydrocarbons and can be applied as an efficient redox catalyst. Remarkably, this powerful reagent forms *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, NOCERA and JACOBSEN 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 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 as 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 $1^{\bullet-}$, ultimately completing the redox series of the century-old substance class of silicon triscatecholates.^[3a]

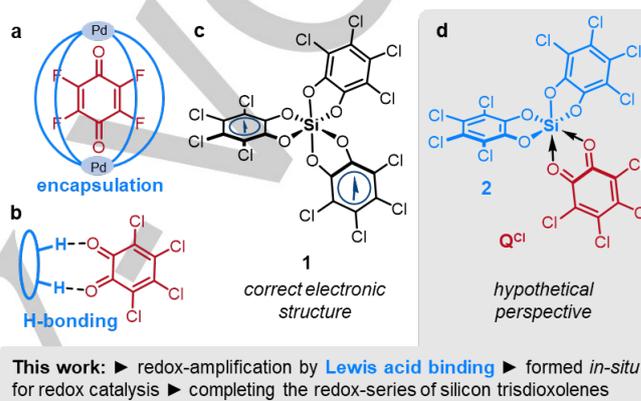


Figure 1. a) Activation of *p*-fluoroquinone by host-guest encapsulation in Pd -cages. b) Activation of Q^{Cl} through binding to a hydrogen-bond donor. c) Neutral diradical silicon tris(perchloro)dioxolene **1**, and d) its hypothetical representation as Q^{Cl} bound to the Lewis superacid **2**.

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 V and 0.86 V vs. Fc/Fc^+ (Figure S17). We attributed those peaks to the redox couples $1^{2-}/1^{\bullet-}$ and $1^{\bullet-}/1$, respectively. The substantial peak separation allowed to estimate the comproportionation constant ($K \approx 8 \times 10^6$), which encouraged us to access the hitherto elusive silicon trisdioxolene monoradical anion $1^{\bullet-}$ by reacting **1** with 1^{2-} . Indeed, mixing of equimolar amounts of **1** and $[NBu_4]_2[1]$ in CH_2Cl_2 at low temperatures lead to the formation of a green crystalline species whose analytical features were in line with $1^{\bullet-}$ (Figure 2B). The anionic part of the salt was ^{13}C -NMR silent, whereas EPR spectroscopy revealed a strong featureless signal ($g = 2.0064$), indicating an $S=1/2$ state. UV-Vis spectroscopy of $[NBu_4][1^{\bullet-}]$ showed the characteristic absorption bands for an open-shell semiquinonate ligand and several weak intervalence charge transfer band (IVCT) in the 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).

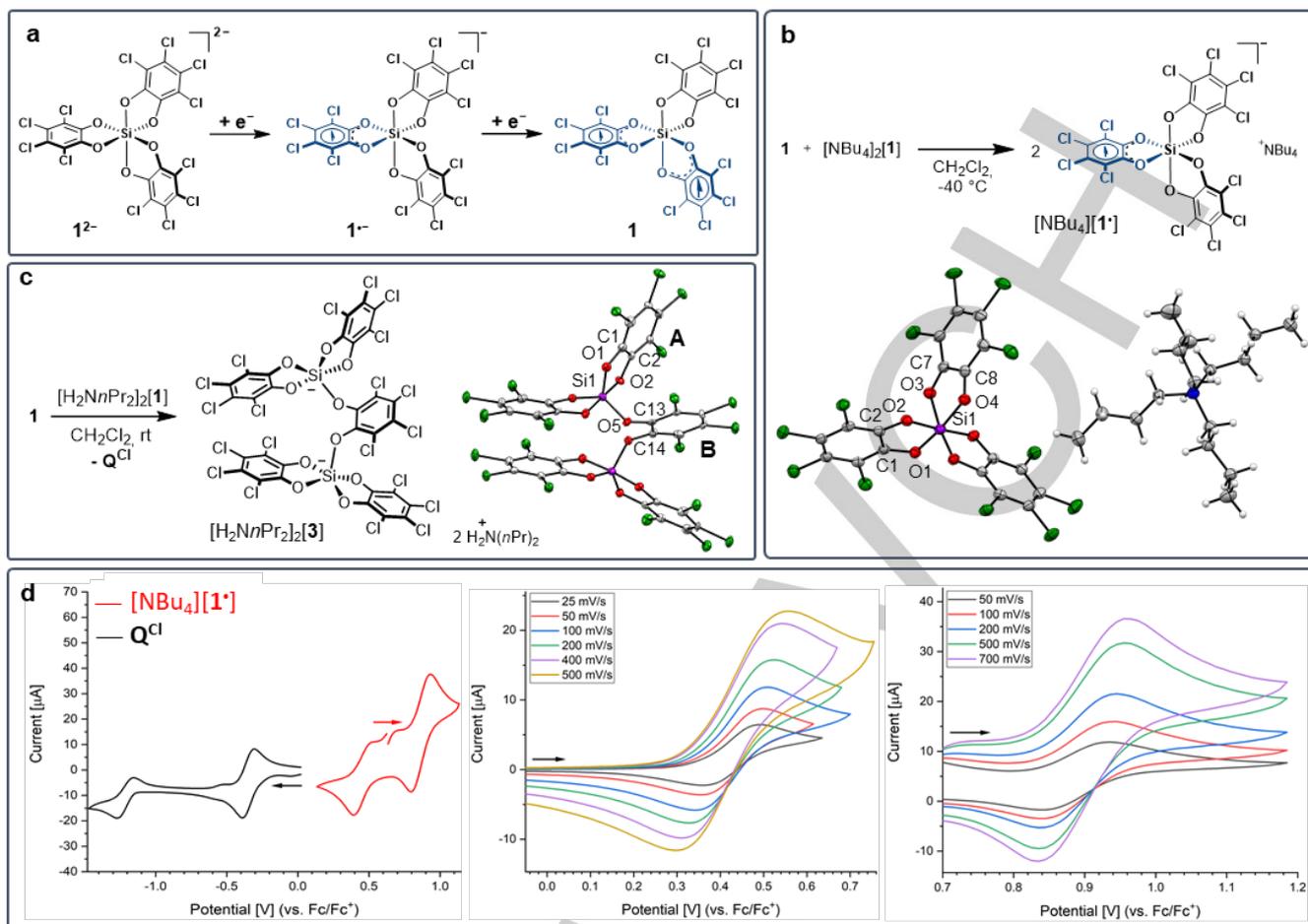


Figure 2. a) Lewis structures of the involved redox-isomers 1^{2-} , 1^{1-} and 1 . b) Synthesis of 1^{1-} by comproportionation, together with SCXRD molecular structure (ellipsoids are set at 50% probability, selected bond length [Å]: O1-C1 1.284(3), O2-C2 1.277(3), O3-C7 1.350(3), O4-C8 1.342(3), C1-C2 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 $[NBu_4][1^{1-}]$ (red trace) and Q^{Cl} (black trace) in dichloromethane, referenced against Fc/Fc^+ , $[NBu_4][BArF_2]$ (0.1 M), 500 mV/s and 100 mV/s, respectively. Right: Pseudo-reversible peaks for both oxidation events of at different scan-rates (25 mV/s – 700 mV/s) under similar conditions.

The measured bond lengths were used to calculate the metrical oxidation states of the dioxolene units according Brown's procedure (see supporting information).^[9] Those parameters confirm the Lewis formulation of 1^{1-} , with two dianionic catecholato ligands ($C-O_{avg} = 1.35 \text{ \AA}$) and one monoanionic open-shell semiquinonate ($C-O_{avg} = 1.28 \text{ \AA}$), 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 $[H_2N(nPr)_2]^+$ (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 $[H_2N(nPr)_2]^+$. Very interestingly, the ^{13}C NMR spectrum of 3^{2-} was showing only *one* set of catechol signals at room temperature, indicating a fast exchange of the terminal

catecholates **a** with bridging catechol **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 $[NBu_4][1^{1-}]$ provided two quasi reversible redox peaks at 0.43 V and 0.88 V (Figure 2D, red trace), in line with the peaks already observed for the dianion $[NBu_4]_2[1]$. 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^{1-} 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 ~ 1.0 V for *p*-quinones caused by Pd-cages encapsulation (Figure 1C),^[1] or of ~ 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 CH₂Cl₂. An upper bound was encompassed by the reaction with tris(2,4-dibromophenyl)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-dibromophenyl)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/S32). With mesitylene (1,3,5-trimethylbenzene), no reaction occurred. Since the oxidation potentials of alkyl-benzenes are poorly documented, they were determined in CH₂Cl₂ with 0.1 M NBu₄PF₆ 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 eq. of Q^{Cl} at r.t. in less than 2h. 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 $2H^+/2e^-$ delivery from the substrate to **1**, with the formed *o*-tetrachlorocatechol H_2Cat^{Cl} being replaced by another Q^{Cl} , redelivering **1**.^[2] This assumption finds support by the respective signals of 1 eq. of H_2Cat^{Cl} in the NMR spectra (Figure S43). Given the straightforward synthesis of **1** by the combination of Sil_4 with Q^{Cl} , we attempted to form the catalyst **1** *in situ*. Remarkably, transformation of **4** to **5** succeeded in similar efficiency by premixing 5 mol% of Sil_4 and 1.3 eq. of Q^{Cl} before adding the substrate (Figure 3a). It is by no means required to pre-isolate **1**.

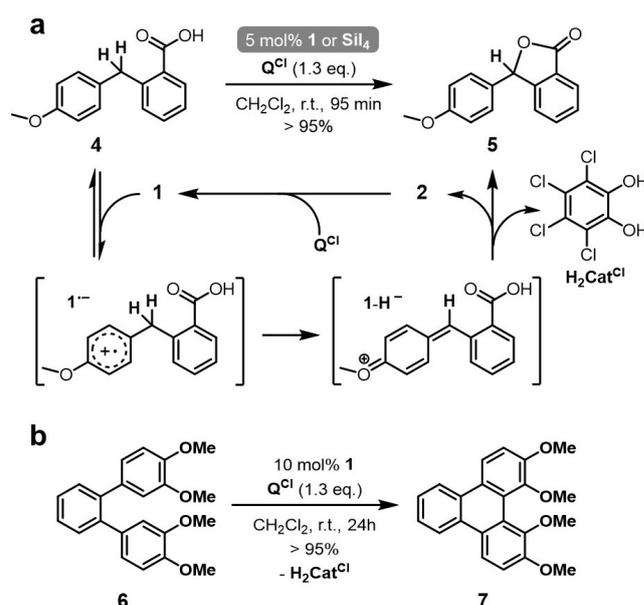


Figure 3. a) Redox-catalytic transformation of **4** into **5**, either with 5 mol% of **1** or with *in situ* formed **1** from 5 mol% Sil_4 and Q^{Cl} (+ 30 min premixing). b) Dehydrogenative coupling of **6** by redox catalyst **1**.

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 24h at r.t. (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 trisdioxolenes 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 $E_{1/2} \approx 1.0$ V vs. Fc/Fc⁺, rendering **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 Sil_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 Sil_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.

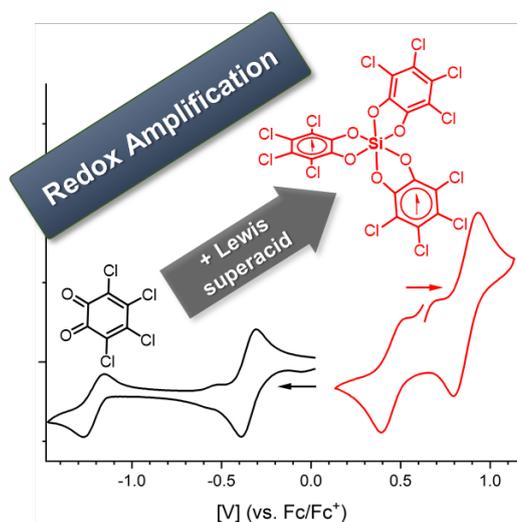
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Keywords: electron transfer • main group elements • oxidation • quinones • redox catalysis

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Completing the Redox-Series of Silicon Trisdioxolene – The redox chemistry of silicon tris(perchlorodioxolene) is studied and the series completed by the isolation of the monoradical anion. The neutral diradical state turns out as a remarkably potent oxidant (as strong as "magic blue" or NO⁺) and redox catalyst, which can be generated from SiI₄ and *ortho*-chloranil *in situ*. In a more general sense, this study serves as a blueprint for the redox-amplification of *ortho*-quinones by Lewis acid binding.

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