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Triptycene 1,2-Quinones and Quinols. Permeable Crystalline Redox-Active Molecular Solids

Sophie Langis-Barsetti, Thierry Maris, and James D. Wuest

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Abstract

Suitably designed quinones and quinols are promising modules for the programmed construction of ordered redox-active molecular solids. To explore this potential, we have synthesized compounds **1–4**, in which multiple 1,2-benzoquinone and 1,2-quinol units are attached to a triptycene core. The resulting molecules have topologies that disfavor efficient packing, and structural studies show that they crystallize to form open networks held together by characteristic attractive intermolecular forces, including O-H···O hydrogen bonds, C-H···O interactions, π stacking, and dipolar interactions. Remarkably, the resulting solids are permeable and can undergo reversible redox reactions without loss of crystallinity. Our work may thereby help lead to the design of robust carbon-based batteries with electrodes derived from quinones, quinols, and other redox-active molecules abundantly produced by nature.

Introduction

Quinones and hydroquinones (known historically as quinols) play a uniquely important role in chemistry, in part because of their widespread occurrence in nature and their characteristic ability to engage in redox reactions.^{2,3} In addition, these compounds take part in diverse intermolecular interactions and thereby show strongly associative behavior, allowing them to serve as useful modules in the programmed construction of ordered molecular materials.⁴ In particular, the participation of these compounds in charge-transfer interactions and π -stacking has been used to produce assemblies with radicals^{5,6} and with aromatic compounds.^{7–9} Quinones and quinols can also form hydrogen-bonded networks with a variety of partners, including heterocycles,^{8,10} phenols,^{9,11–15} and other classes of compounds.^{16–18} The first example of the phenomenon of co-crystallization, reported by Wöhler in 1844,¹⁹ was produced by combining 1,4-benzoquinone and 1,4-hydroquinone in a 1:1 ratio. The resulting structure, known as quinhydrone, features an open network held together by a combination of hydrogen bonds and charge-transfer interactions.^{20–22}

However, surprisingly little effort has been made so far to build on this promising foundation by designing more complex quinones and quinols for use in the modular construction of new molecular materials.^{23–27} Moreover, the chemistry of 1,4-benzoquinones and hydroquinones has been explored much more extensively than that of the isomeric 1,2-benzoquinones and their reduced forms,²⁸ despite the potential of all of these compounds to engage in similar intermolecular interactions and to serve as modules in supramolecular construction.^{29,30} In particular, the historic work of Wöhler provides a strong motivation for studying the co-crystallization of 1,2-benzoquinones with catechols, but little work of this type has been

reported.^{31–32} We have therefore undertaken a study to assess the utility of 1,2-benzoquinones and the corresponding catechols in the modular assembly of complex redox-active molecular structures held together by hydrogen bonds, charge-transfer interactions, and other forces. Of particular interest is the possibility of using such modules to make porous crystalline solids for use as electrodes in carbon-based batteries.^{33–36}

In addition to being redox-active, 1,2-benzoquinones can also take part in Diels-Alder reactions, leading to the formation of dimers.^{37,38} or by undergoing sequences of hydration, tautomerization, and autoxidation to give hydroxy-substituted 1,4-benzoquinones and other products.^{39,40} To avoid these degradative pathways, we elected to study suitably substituted 1,2benzoquinones. Moreover, to favor the formation of open networks created by modular assembly, we decided to attach multiple 1,2-benzoquinone and catechol units to molecular cores with shapes designed to inhibit efficient packing. In this way, we identified triptycene(trisquinone) 1 and reduced forms 2-4 as compounds of particular interest as modules for supramolecular construction. Triptycenes are attractive choices because their characteristic rigid trigonal topology interferes with close molecular packing and thereby favors the formation of open structures with significant volume available for the inclusion of guests.⁴¹ Moreover, triptycenes 1-4 provide relatively simple symmetric structures that incorporate multiple 1,2benzoquinone and catechol units, all freely exposed on the molecular periphery in a way that lets them form characteristic intermolecular interactions without significant interference. Simpler triptycenes with quinone and catechol moieties have been prepared by White and MacLachlan for use in constructing molecular assemblies,^{42,43} but no structural analyses of the triptycenes themselves have been reported.



Results and Discussion

Syntheses of Triptycenes 1–4. Ghanem et al. reported using BBr₃ to convert the known hexamethoxytriptycene **5** into triptycene(triscatechol) **4** (Scheme 1), but no characterization of the product was reported.⁴⁴ We prepared triscatechol **4** from precursor **5** by a modified procedure in which only three equivalents of BBr₃ were used, because the demethylation of *ortho* methoxy substituents is known to occur via cyclic borate intermediates.⁴⁵ In triptycene derivatives, controlled stepwise oxidation of the three aromatic rings is possible because electronic effects are communicated transannularly.^{46,47} Notably, Chen and collaborators reported the progressive oxidation of an analogue of triscatechol **4** with nitric acid by varying the concentration of oxidant and the length of contact.⁴⁷ Nitric acid was also used by Han and coworkers to prepare an analogue of trisquinone **1**, but they reported only a partial characterization of the product.⁴⁸ To avoid possible side reactions involving nitration and ring opening,⁴⁹ and to better control the extent of oxidation, we decided to treat triscatechol **4** with other agents, and we achieved the synthesis of compounds **1–3** in a selective manner, as summarized in Scheme 1.

Scheme 1



Although 1,4-benzoquinones are typically less powerful oxidants than their 1,2-benzoquinone counterparts,^{50,51} each catechol unit in triscatechol **4** is substituted by an electron-donating tetrahydroxy-9,10-dihydroanthracenyl scaffold, and 1,4-benzoquinone can in fact be used to effect a single oxidation to give monoquinone **3** in 77% yield. Oxidation to produce bisquinone **2** occurred in 79% yield when triscatechol **4** was treated with tetrachloro-1,2-benzoquinone (*o*-chloranil), whereas *p*-chloranil was ineffective. These reactions are highly selective, and only a single product of oxidation was observed in the crude mixtures. No significant amounts of starting material, intermediates, or over-oxidized compounds were observed, even after extended periods of time or in the presence of excess oxidant. Finally, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidized triscatechol **4** to give trisquinone **1** in 61% yield. Compounds **1–4** all proved to be stable in the solid state, although triscatechol **4** is slightly air-sensitive, and quinones **1–3** decomposed slowly in solution, especially when exposed to heat or light.⁵² All characterizations were therefore performed using freshly prepared solutions, and crystallizations were carried out in the dark.

Absorption and Emission Properties of Triptycenes 1–4. Absorption and emission spectra of compounds 1–4 are shown in Figure 1. All four compounds absorb near 290 nm, and the band shifts bathochromically from trisquinone 1 to triscatechol 4 as electron-donating catechol units are added to the triptycene core. Quinones 1–3 show additional absorption near 380 nm, leading to spectra that superimpose the characteristic features of catechol itself ($\lambda_{max} = 277$ nm) and those of 1,2-benzoquinone ($\lambda_{max} = 273$, 377 nm).^{53,54} Monoquinone 3 also exhibits an important charge-transfer band around 480 nm, which is typical of triptycene donor-acceptor systems,^{46,47,55} and bisquinone 2 shows a band that is similar but less intense. Emission spectra for compounds 2–4 reflect the relative positions of their absorption bands near 290 nm. Emission from trisquinone 1 is bathochromically shifted, but spectra of compound 1 were recorded in DMF to circumvent poor solubility in CH₃CN, and the observed shift may be solvent-induced.



Figure 1. Absorption spectra (left) and normalized emission spectra (right) of solutions of triptycene(trisquinone) 1 (green), bisquinone 2 (blue), monoquinone 3 (red), and triscatechol 4

(black). Compound 1 was dissolved in DMF, and compounds 2–4 were dissolved in CH₃CN, with $\lambda_{ex} = 280$ nm for compounds 1 and 2, $\lambda_{ex} = 290$ nm for compound 3, and $\lambda_{ex} = 300$ nm for compound 4.

Structure of Triptycene(trisquinone) 1. Layering CH₃CN on a solution of trisquinone **1** in DMSO induced the formation of red crystals, which were found to belong to the hexagonal space group $P6_3$. Additional crystallographic information is summarized in Table 1, and a representation of the structure appears in Figure 2. Dipolar interactions between canted oxygen atoms and dienes (3.03 Å for the shortest C···O distance) underlie organization of molecules of compound **1** to form sheets (Figure 2a). Adjacent sheets are linked in an offset arrangement by C-H···O interactions (2.46–2.48 Å) involving oxygen atoms and hydrogen atoms of the quinone units (Figure 2b), thereby defining parallel hexagonal channels. The channels contain disordered molecules of CH₃CN, and 17% of the total volume of the crystals is accessible to guests.^{56–58} Direct removal of the guests under reduced pressure leads to the loss of crystallinity, and we have not yet been able to prepare a guest-free crystalline solid constructed from trisquinone **1**.



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Figure 2. Representations of the structure of crystals of triptycene(trisquinone) **1** grown from DMSO/CH₃CN. (a) View down the *c*-axis showing two adjacent offset sheets, one with all molecules drawn in blue. The offset sheets define parallel hexagonal channels. (b) View down the *b*-axis showing molecules in five adjacent sheets and revealing how the sheets are connected by C-H…O interactions. The most significant interactions are represented by broken lines. Unless otherwise indicated, atoms of carbon are shown in gray, atoms of hydrogen in white, and atoms of oxygen in red. Included molecules of solvent are omitted.

 Table 1. Crystallographic data for triptycenes 1–4.

Compound	1 • CH ₃ CN	2 • 1.5 dioxane	3 • 3.5 dioxane	4 ^a	
crystallization medium	DMSO/CH ₃ CN	dioxane/PhMe	dioxane/hexane	Me-THF	
formula	$C_{20}H_8O_6 \bullet C_2H_3N$	$C_{20}H_{10}O_6 \bullet 1.5 C_4H_8O_2$	$C_{20}H_{12}O_6 \bullet 3.5 C_4H_8O_2$	$C_{20}H_{14}O_{6}$	
crystal system	hexagonal	monoclinic	monoclinic	hexagonal	
space group	P63	$P2_1/c$	<i>I</i> 2/a	$P\overline{6}2c$	
a (Å)	15.7405(3)	17.2624(5)	24.0009(11)	13.3732(7)13.3732(7)10.8212(7)	
<i>b</i> (Å)	15.7405(3)	8.6308(2)	8.5212(4)		
<i>c</i> (Å)	11.9054(3)	16.1531(5)	31.560(2)		
α (°)	90	90	90	90	
β (°)	90	109.286(2)	93.151(2)	90	
γ (°)	120	90	90	120	
$V(Å^3)$	2554.53(12)	2271.57(11)	6444.8(6)	1676.0(2)	
Ζ	6	4	8	2	
$\rho_{\rm calcd}$ (g cm ⁻³)	1.503	1.399	1.354	0.694 ^b	
<i>T</i> (K)	150	150	150	150	
μ (mm ⁻¹)	1.503	0.574	0.560	0.276	
$R_1, I > 2\sigma$	0.0968	0.0539	0.0811	0.0488	
R_1 , all data	0.1035	0.1298	0.2113	0.1623	
$\omega R_2, I > 2\sigma$	0.2556	0.0654	0.1295	0.0493	
ωR_2 , all data	0.2804	0.1397	0.2532	0.1635	

no. measured reflections	38684	29785	40908	37342
no. independent reflections	3924	4327	5526	1279
no.obs.reflections $I >$ $2\sigma(I)$	3184	3615	3431	1248

^a Guests not identified unambiguously by crystallography are omitted from the composition.

^b Calculated without contributions from guests.

Structure of Triptycene(bisquinone) 2. The addition of toluene, chloroform, or ether to a saturated solution of bisquinone 2 in dioxane afforded rectangular dark orange crystals. Analysis by X-ray diffraction established that the crystals belonged to the monoclinic space group $P2_1/c$. Crystallographic parameters are provided in Table 1, and views of the structure appear in Figure 3. Molecules of compound 2 are connected by O-H···O hydrogen bonds (O···O distance = 2.735Å) between quinone and catechol units to form undulating tapes. The tapes are further linked into sheets by C-H···O interactions (H···O distance = 2.50 Å) involving the bridgehead hydrogens and quinone moieties (Figure 3a). The sheets in turn are paired by additional C-H···O interactions (H···O distance = 2.38 Å) and by dipolar interactions between oxygen atoms and electron-deficient carbon atoms incorporated in the quinone units (2.90 Å for the shortest C···O distance). It is interesting to note that the quinone units involved as donors in these dipolar interactions are planar, whereas the acceptor quinones are not, and their adjacent carbonyl groups form a dihedral angle of 17°. Additional cohesion within the sheets is provided by short $C \cdots O$ interactions (2.77 Å) involving the oxygen atoms of well-ordered molecules of included dioxane and electron-deficient carbon atoms in the distorted quinone units. Pairs of sheets are isolated from one another by layers of partly ordered molecules of dioxane (Figure 3b). In total, 42% of the volume of the crystal is accessible to guests.⁵⁶



Figure 3. Representation of the structure of crystals of triptycene(bisquinone) **2** grown from dioxane/toluene. (a) View showing how undulating hydrogen-bonded tapes are further linked by C-H \cdots O interactions to form sheets. Two individual tapes are highlighted in blue, and the most significant intermolecular interactions are represented by broken lines. (b) View down the *b*-axis showing how paired sheets are isolated from one another by layers of dioxane. One individual sheet is highlighted in blue, and all molecules of dioxane appear in red. Unless stated otherwise, atoms of carbon are shown in gray, atoms of hydrogen in white, and atoms of oxygen in red.

Crystallization of bisquinone **2** from a mixture of THF and hexane provided a pseudopolymorph in which the quinone units are less strikingly deformed.⁵⁹ As a result, the torsion observed in the structure of crystals grown from dioxane may not be an inherent feature of compound **2** but may rather be a consequence of molecular packing or the result of multiple C···O interactions involving dioxane. However, distorted 1,2-benzoquinones have been noted by other researchers; for example, Fukin et al. observed a torsion angle of 34° between the carbonyl groups in 4,5dimethoxy-3,6-di-*tert*-butyl-1,2-benzoquinone.⁶⁰

Structure of Triptycene(monoquinone) 3. Allowing vapors of hexane to diffuse into a solution of monoquinone 3 in dioxane induced the formation of dark red plates, which were found to belong to the monoclinic space group I^{2}/a . Additional crystallographic data are presented in Table 1, and views of the structure are shown in Figure 4. Like bisquinone 2, monoquinone 3 crystallizes to form a structure built from sheets separated by layers of included molecules of dioxane. Molecules of compound 3 form pairs held together by π -stacking of quinone units (centroids separated by 3.65 Å) and by C-H··· π interactions involving hydrogen atoms of guinone units and the π -systems of catechol units (H···centroid distance = 2.38 Å). The pairs are further linked into sheets by multiple intermolecular O-H···O hydrogen bonds and C-H···O interactions (Figure 4). In particular, bifurcated O-H···O hydrogen bonds (O···O distances of 2.86 and 2.89 Å) are formed along the *b*-axis, with the two oxygen atoms of quinone units acting as a bidentate acceptor and an OH group of catechol units acting as donor. In addition, C-H···O interactions along the *b*-axis link oxygen atoms of quinone units with aromatic hydrogens and bridgehead hydrogens (H···O distances of 2.42 and 2.63 Å). Along the *a*-axis, intermolecular O-H···O hydrogen bonds between catechol units (O···O distance = 2.81 Å) and C-H···O interactions between catechol oxygen atoms and aromatic hydrogen atoms (H...O distance = 2.56 Å) reinforce the sheets. The structure is also strengthened by interactions of monoquinone **3** with oxygen atoms of included molecules of dioxane, which form O···H-O hydrogen bonds with catechol units ($O \cdots O$ distance = 2.76 Å), $O \cdots C$ interactions with quinone units ($O \cdots$ centroid

distance = 2.78 Å), and various O···H-C interactions. Approximately 59% of the volume of the crystal is accessible to guests.⁵⁶



Figure 4. Representation of the structure of crystals of triptycene(monoquinone) **3** grown from dioxane/hexane. (a) View showing how π -stacked pairs are further associated by multiple O-H…O hydrogen bonds and C-H…O interactions to form sheets. An individual pair is highlighted in blue, and various intermolecular interactions are represented by broken lines. (b) View down the *b*-axis showing how sheets are isolated from one another by layers of dioxane. One individual sheet is highlighted in blue, and all molecules of dioxane appear in red. Unless stated otherwise, atoms of carbon are shown in gray, atoms of hydrogen in white, and atoms of oxygen in red.

Structure of Triptycene(triscatechol) 4. Cooling a saturated solution of triscatechol 4 in methyltetrahydrofuran (Me-THF) yielded colorless needles that were found to belong to the hexagonal space group $P\overline{6}2c$. Other crystallographic data are provided in Table 1, and

representations of the structure appear in Figure 5. Molecules of compound 4 can be considered to be packed in sheets in the *ab*-plane without forming any noteworthy intra-sheet interactions (Figure 5a), but adjacent sheets are linked along the *c*-axis by multiple O-H…O hydrogen bonds (O…O distances in the range 2.71–2.73 Å). In this way, each molecule of triscatechol 4 participates in a total of six intermolecular O-H…O hydrogen bonds.



Figure 5. Representation of the structure of crystals of triptycene(triscatechol) **4** grown from Me-THF. (a) Side view of part of three offset sheets, showing how molecules in adjacent sheets are connected by $O-H\cdots O$ hydrogen bonds. Molecules in one sheet are highlighted in blue, and hydrogen bonds are represented by broken lines. (b) Space-filling view along the *c*-axis showing the presence of trilobate channels defined by two adjacent sheets, with one sheet highlighted in blue. Unless stated otherwise, atoms of carbon are shown in gray, atoms of hydrogen in white, and atoms of oxygen in red. Disordered molecules of included solvent are not shown.

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Adjacent sheets are offset in a way that defines large trilobate channels (Figure 5b). The channels are filled with disordered molecules of solvent, and 63% of the total volume of the crystals is accessible to guests.⁵⁶ Larger fractions of guest-accessible volumes have been observed in other molecular crystals, particularly those of proteins.^{61–63} However, the structure of triptycene(triscatechol) **4** is noteworthy because the molecule has a simple, open, symmetric topology and consists of only 26 non-hydrogen atoms. Our observations underscore the inherent difficulty of finding effective ways to pack molecules that have awkward topologies and must simultaneously take part in multiple directional interactions. Molecules of this type are typically programmed by their topologies and interactions to form open networks with significant volumes available for the inclusion of guests.

In addition to the structures described above in detail, pseudopolymorphs with similar molecular organization were also obtained by crystallizing triscatechol **4** from dioxane/hexane and by crystallizing bisquinone **2** and monoquinone **3** from THF/hexane.⁵⁹ The additional pseudopolymorphs differ primarily in the extent of inclusion of molecules of solvent. In particular, structures produced by crystallization from dioxane are more highly solvated than those obtained from THF, possibly because the extra atom of oxygen in dioxane provides an additional site of hydrogen bonding. In all cases, molecules of triptycenes **1–4** are linked by interactions typical of quinones and quinols, including O-H…O hydrogen bonds, C-H…O interactions, π -stacking, and dipolar interactions.^{4,23} Crystals obtained under all conditions include molecules of solvent and typically have large guest-accessible volumes in the form of channels or layers. We attribute this behavior to the relatively rigid trigonal geometry of the triptycenyl core of compounds **1–4**, which cannot be packed efficiently in ways that allow the

quinone and quinol units to engage in their preferred modes of association. As a result, normal patterns of crystallization are disrupted, and molecules of compounds **1–4** are forced to create open networks with significant fractions of volume occupied by guests. Moreover, because the compounds cannot crystallize in ways that simultaneously satisfy the demands of topology and directional intermolecular interactions, there is no overriding preference for a particular pattern of molecular organization, and the compounds have significant opportunities to crystallize in various pseudopolymorphic forms.

The prototypical 1:1 co-crystallization of 1,4-benzoquinone and hydroquinone to give quinhydrone led us to attempt co-crystallizations of different triptycenes 1–4. Of special interest to us were co-crystallizations of pairs in which the numbers of complementary quinone and quinol units are properly balanced. Unfortunately, however, attempted co-crystallization of trisquinone 1 and triscatechol 4 was thwarted by disproportionation (Scheme 2), and pronounced differences in solubility prevented us from co-crystallizing compounds 2 and 3. Disproportionation also occurred in mixtures containing compounds 1 and 3 or compounds 2 and 4 (Scheme 2).

Scheme 2



Redox Properties of Triptycenes 1–4 in Solution. The highly selective syntheses of mono-, bis-, and trisquinones **1–3** by controlled oxidation prompted us to study the electrochemical behavior of the compounds in more detail. Cyclic voltammograms of solutions of trisquinone **1** and triscatechol **4** in DMF are presented in Figure 6. Redox potentials were assessed by square-wave voltammetry to allow the potential of non-reversible events to be measured more accurately. Square-wave voltammograms are shown in Figure 7, and redox potentials are summarized in Table 2, along with the properties of 1,2-benzoquinone and catechol as model compounds. The effect of transannular interactions on the redox properties of triptycene derivatives of 1,4-benzoquinone is well documented.^{46,64–66} This behavior is mirrored in our

redox data for related triptycene derivatives of 1,2-benzoquinone, and three distinct redox events were found for all compounds 1–4.



Figure 6. Cyclic voltammograms of solutions of triptycene(trisquinone) **1** (Figure 6a) and triptycene(triscatechol) **4** (Figure 6b) in DMF (~1 mM) containing tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The voltammograms were recorded at a scan rate of 100 mV/s, and potentials are reported with respect to the ferrocene/ferrocenium couple.



Figure 7. (a) Square-wave voltammograms showing the reduction waves of solutions of compounds 1-3 (top to bottom) in DMF containing 1% MeCOOH. (b) Square-wave voltammograms showing the oxidation waves of compounds 2-4 from top to bottom. All voltammograms were recorded in DMF solutions (~1 mM) containing tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The voltammograms were recorded at a scan rate of 20–50 mV/s, and potentials are reported with respect to the ferrocene/ferrocenium couple.

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Table 2. Redox potentials of triptycenes 1–4.^a

Compound	Reduction (V)	Oxidation (V)
1,2-Benzoquinone	-0.78 -0.69 ^b	-
Trisquinone 1	-1.05, -0.79, -0.58 -0.91, ^b -0.63, ^b -0.49 ^b	-
Bisquinone 2	-0.79, ^b -0.64 ^b	0.48
Monoquinone 3	-0.75 ^b	0.35, 0.49
Triscatechol 4	-	0.16, 0.35, 0.50
Catechol	-	0.49

^aMeasured by square-wave voltammetry in DMF solutions (~1 mM) containing tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. Potentials are reported with respect to the ferrocene/ferrocenium couple.

^b Values recorded in DMF solutions containing 1% MeCOOH.

Quinones typically undergo one-electron reduction in aprotic media.^{50,51,67-69} Solutions of triptycene(trisquinone) **1** in DMF exhibit three reversible reduction waves corresponding to the formation and oxidation of semiquinone anions. Addition of MeCOOH shifts reduction to slightly more positive potentials, increases the intensity of the signals, and leads to a loss of reversibility. We attribute these changes to a transition to a two-electron process in which the resulting catecholate dianion is rapidly protonated by MeCOOH and is therefore no longer available for the return wave. The redox behavior of quinones and quinols is notoriously complex, however, and more detailed studies will be necessary to confirm the origin of our observations. In pure DMF, the reduction profiles of bisquinone **2** and monoquinone **3** appeared

to be complicated by the effect of intra- and intermolecular proton transfers, and the addition of MeCOOH simplifed the voltammograms. Under these conditions, an irreversible reduction wave was observed for each quinone unit at potentials similar to those needed to reduce trisquinone **1**. In all media examined, the first reductions of triptycenequinones **1** and **2** occurred at a lower potential than that observed for 1,2-benzoquinone.⁵³ This behavior presumably results from the electron-withdrawing effect of other quinone units in the compounds.

Cyclic voltammograms of compounds 2–4 in DMF show one, two, and three irreversible oxidation waves, respectively, and addition of MeCOOH had little effect on the oxidation profiles. The irreversibility of the transformations is most likely due to deprotonation of the highly unstable protonated quinones formed during the oxidation.^{66–69} Oxidation potentials are consistent throughout the triptycene series, with equivalent oxidations taking place at nearly identical potentials for each compound. The substituted 9,10-dihydroanthracene scaffold can be seen to act as an electron-donating group, with all oxidation potentials being below those of catechol itself.

Redox Reactions of Triptycenes 1–4 as Crystalline Solids. Our structural studies of compounds 1–4 establish that the triptycenyl topology, along with the characteristic ability of quinones and quinols to engage in multiple intermolecular interactions, gives rise to the formation of open networks composed of redox-active molecules. This special combination of features suggested that materials derived from compounds 1–4 might be able to serve as electrodes in carbon-based batteries and led us to study their redox behavior in the solid state. We found that exposure to vapors of H_2NNH_2 reduced quinones 1–3 to triscatechol 4, both in

solution and in the solid state. Correspondingly, vapors of HNO_3 (produced by 70% aqueous acid) could be used to oxidize solid samples of catechols 2–4. Under these conditions, the redox reactions take place without the formation of significant amounts of by-products. Moreover, the progress of reactions can be assessed by visual inspection because the color of samples changes. For example, when dark purple crystals of the THF solvate of monoquinone 3 (Figure 8a) were exposed to vapors of H₂NNH₂, triscatechol 4 was formed as a colorless solid that retained the morphology of the initial crystals (Figure 8b). No significant cracking was observed, and the resulting product was shown by polarized light microscopy to retain crystallinity. X-ray powder diffraction confirmed that the product of solid-state reduction is microcrystalline, and comparison with the characteristic pattern produced by crystals of monoquinone 3 established that the initial molecular organization is retained despite the change in composition (Figure 9). As a result, solid-state reduction under these conditions produces triscatechol 4 in crystalline form, with the molecules now arranged as they were in crystals of monoquinone 3. Notably, the resulting structure of triscatechol 4 is not the same as that of crystals grown directly from solution. Analogous oxidations could be carried out by treating the Me-THF solvate of triscatechol 4 with HNO_3 to form monoquinone 3. However, preventing the initial product from undergoing further oxidation was challenging, and the product was less highly crystalline.



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Figure 8. Micrographs showing a dark purple crystal of monoquinone 3 grown from THF/hexane (Figure 8a) and a colorless crystal of triscatechol 4 resulting from solid-state reduction caused by exposure to vapors of H_2NNH_2 (Figure 8b).

5 10 15 20 25 30 35 40 45 50 20 (degrees)

Figure 9. Comparison of the X-ray powder diffraction pattern (black trace) of a microcrystalline sample of triscatechol **4** (as produced by the solid-state reduction of crystals of monoquinone **3**) with the simulated pattern derived from the crystal structure of the THF solvate of compound **3** (red trace).

To understand how such processes occur, we examined the structure of the THF solvate of monoquinone **3** in detail and confirmed that it resembles the pseudopolymorphic solvate of dioxane (Figure 4). Again, π -stacking of quinone units creates pairs that are further linked into sheets by multiple intermolecular O-H···O hydrogen bonds and C-H···O interactions (Figure





Figure 10. Representation of the structure of crystals of triptycene(monoquinone) 3 grown from THF/hexane. (a) View showing how π -stacked pairs are further joined by O-H···O hydrogen bonds and C-H···O interactions to form sheets. An individual π -stacked pair is highlighted in blue, and other significant intermolecular interactions are represented by broken lines. (b) View along the *c*-axis showing how sheets are connected by O-H…O hydrogen bonds and how molecules of THF are included between the layers. One individual sheet is highlighted in blue, and all molecules of THF appear in red. (c) View along the *a*-axis, showing layers in the *ac*plane in which included molecules of THF occupy parallel channels (green). Unless otherwise stated, atoms of carbon are shown in gray, atoms of hydrogen in white, and atoms of oxygen in red.

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Topotactic processes in which crystals of small molecules react with added agents to give new compounds in crystalline form are very rare.^{70–73} Moreover, we are not aware of any previous reports showing that transformations of this type can be carried out reversibly. Topotactic processes accompanied by changes in chemical composition cannot be dismissed as mere chemical curiosities; in fact, they promise to help solve key problems in emerging areas of technology. Of particular importance is the challenge of creating a new generation of green batteries that are cheap, rechargeable, and entirely derived from renewable carbon-based resources. In such devices, redox reactions must take place reversibly without substantially altering molecular organization in the electrodes.

Previous examples of topotactic processes occurring with changes in chemical composition suggest that molecular packing must normally be inefficient, so that external agents can penetrate the initial crystals and by-products can exit. Moreover, the crystals must be held together by intermolecular interactions that are strong enough to inhibit dissolution, disfavor unwanted molecular reorientation, and maintain the integrity of the crystals despite internal stresses generated by compositional and structural changes. In crystals of monoquinone **3**, the volume accessible to guests defines layers composed of parallel individual channels with the approximate dimensions 4×6 Å² (Figure 10c). These channels include THF and are therefore wide enough to allow smaller molecules such as H₂NNH₂ and HNO₃ to diffuse throughout the crystal and to reduce or oxidize molecules of monoquinone **3**.

Exposing crystals of compound **3** to vapors of H_2NNH_2 for periods longer than those needed to effect complete conversion into triscatechol **4** caused fracturing along the longest axis (Figure

S1). Indexing the crystal faces revealed that the fractures are aligned with the planes containing channels of THF. This finding is consistent with the hypothesis that H₂NNH₂ penetrates the crystals by entering the channels, replaces molecules of THF, and reduces host 3 to triscatechol
4. These changes introduce stresses that are most easily relieved by fracturing the crystals along the planes of weakest bonding, which are those rich in included molecules of solvent.

Processes in which single crystals of simple molecular compounds are transformed by exposure to a suitable reagent into structurally related crystals of a different compound are highly uncommon. Moreover, no such transformations are known to be reversible or to involve interconversion of the constituent molecules by redox reactions. For these reasons, our results offer important evidence that it may be possible to engineer carbon-based rechargeable batteries analogous to the current generation of lithium-ion analogues, but with inorganic electrodes replaced by molecular solids that can undergo reversible redox processes without disruptive structural changes. Earlier studies have highlighted the potential of quinones and their reduced forms to serve as components in carbon-based batteries.^{33–36,74,75} Our work takes a significant further step by showing how suitable quinones and quinols can be designed so that they form robust permeable crystals able to take part in reversible redox reactions without significant changes in molecular organization. In future work, we hope to reveal how related materials can be derived inexpensively from the large number of quinonoid compounds produced renewably by nature.

Conclusions

Suitably designed quinones and their reduced forms can serve as modules for the rational construction of ordered redox-active carbon-based solids. Our study of triptycenes **1–4** has revealed that attaching multiple quinone and quinol units to cores chosen to disfavor efficient packing can give rise to compounds that are programmed to form open networks held together by characteristic attractive intermolecular forces, including O-H…O hydrogen bonds, C-H…O interactions, π -stacking, and dipolar interactions. Remarkably, the resulting materials can undergo reversible redox reactions without losing crystallinity. In this way, our work helps define a path leading to the design of robust rechargeable carbon-based batteries incorporating electrodes derived from quinones, quinols, and other redox-active molecules that are abundantly produced by nature.

Experimental Section

Anhydrous oxygen-free solvents were obtained by passage through columns packed with activated alumina and supported Cu catalyst (Glass Contour, Irvine, CA). Reagents and all other solvents were purchased from commercial sources and used without further purification unless otherwise indicated. 1,2-Benzoquinone⁷⁶ and hexamethoxytriptycene **5**⁴⁴ were synthesized according to published procedures. A full characterization of known compound **4** is presented below to provide data not included in earlier publications.

NMR spectra were recorded at 20 °C, using a spectrometer operating at 400 MHz for ¹H NMR spectra and at 100 MHz for ¹³C NMR spectra. Chemical shifts are reported in parts per million relative to tetramethylsilane, with the signal of residual undeuterated solvent used as an internal standard. Cyclic voltammograms were obtained using solutions in dry N₂-sparged dimethylformamide (DMF) or in DMF containing 1% acetic acid, with tetrabutylammonium hexafluorophosphate (TBAP) as the supporting electrolyte (0.1 M). The working electrode was a glassy carbon electrode, the counter-electrode was a Pt wire, and the pseudo-reference electrode was an Ag wire. The concentration of the compounds examined was ~1 mM, and ferrocene/ferrocenium was used as an internal standard.

2,3,6,7,14,15-Hexahydroxytriptycene (4). Compound **4** was synthesized by modifying the method reported by Ghanem et al.⁴⁴ A solution of 2,3,6,7,14,15-hexamethoxytriptycene (**5**; 2.01 g, 4.63 mmol) in dichloromethane (100 mL) was stirred at 0 °C under N₂ and treated dropwise with a solution of BBr₃ (1.0 M, 16 mL, 16 mmol) in dichloromethane. The mixture was stirred at 25 °C for 18 h, treated with water, and stirred for 15 min. The resulting precipitate was separated by filtration, washed with water, and dried under vacuum to give 2,3,6,7,14,15-hexahydroxytriptycene (**4**; 1.47 g, 4.20 mmol, 91%) as a nearly colorless solid. Further purification could be achieved by crystallization from hot dioxane. Single crystals for analysis by X-ray diffraction were grown by adding hexane to a saturated solution of compound **4** in dioxane or by cooling a saturated solution in Me-THF: mp > 300 °C; FTIR (ATR) 3542, 3462, 3278, 3191, 1610, 1485, 1449 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.40 (s, 6H), 6.71 (s, 6H), 4.88 (s, 2H); ¹³C {¹H} NMR (100 MHz, DMSO-*d*₆) δ 141.0, 137..8, 111.6, 51.0; UV-Vis (CH₃CN) λ_{max} (ε) 305 (18,700); Emission (THF, λ_{ex} 300 nm) λ_{em} 326 nm; SWV (DMF, NBu₄PF₆) $E_{1/2}$ 0.16,

0.35, 0.50 V (Fc/Fc⁺); HRMS (APCI-TOF) m/z [M - H]⁻ calcd for C₂₀H₁₃O₆ 349.0712, found 349.0714.

6,7,14,15-Tetrahydroxy-9,10-dihydro-9,10-[1,2]benzenoanthracene-2,3-dione (3). 1.4-Benzoquinone (0.232 g, 2.15 mmol) was added to a suspension of 2,3,6,7,14,15hexahydroxytriptycene (4; 0.509 g, 1.45 mmol) in THF (10 mL). The mixture was stirred at 25 °C for 20 h, and volatiles were then removed by evaporation under reduced pressure. The residue was triturated with water, and the resulting dark purple solid was separated by filtration and dried under vacuum to afford 6,7,14,15-tetrahydroxy-9,10-dihydro-9,10-[1,2]benzenoanthracene-2,3dione (3; 0.385 g, 1.11 mmol, 77%). Further purification could be achieved by crystallization induced by allowing vapors of hexane to diffuse slowly into a saturated solution of compound 3 in THF in the dark: mp > 300 °C; FTIR (ATR) 3397, 3254, 3129, 3054, 2956, 2808, 1673, 1639, 1617, 1590, 1572, 1499, 1460 cm⁻¹;¹H NMR (400 MHz, DMSO- d_6) δ 9.01 (s, 4H), 6.81 (s, 4H), 6.24 (s, 2H), 5.03 (s, 2H); ${}^{13}C{}^{1}H$ NMR (100 MHz, DMSO- d_6) δ 180.3, 153.4, 144.8, 130.3, 119.6, 111.9, 48.9; UV-Vis (CH₃CN) λ_{max} (ϵ) 291 (8090), 435 (5640); Emission (CH₃CN, λ_{ex} 290 nm) λ_{em} 324 nm; SWV (DMF/AcOH 1%, NBu₄PF₆) $E_{1/2}$ -0.75, 0.35, 0.49 V (Fc/Fc⁺); HRMS (APPI-TOF) m/z [M + H]⁺ calcd for C₂₀H₁₃O₆ 349.0712, found 349.0711.

14,15-Dihydroxy-9,10-dihydro-9,10-[1,2]benzenoanthracene-2,3,6,7-tetraone (2). *o*-Chloranil (0.352 g, 1.43 mmol) was added to a suspension of 2,3,6,7,14,15-hexahydroxytriptycene (4; 0.198 g, 0.565 mmol) in anhydrous oxygen-free dioxane (10 mL). The mixture was stirred at 25 °C for 20 h, and volatiles were then removed by evaporation under reduced pressure. The residue was then triturated with dichloromethane, and the resulting dark

orange solid was separated by filtration, washed with dichloromethane, and dried under vacuum to afford 14,15-dihydroxy-9,10-dihydro-9,10-[1,2]benzenoanthracene-2,3,6,7-tetraone (**2**; 0.155 g, 0.448 mmol, 79%). Further purification could be achieved by crystallization induced by allowing vapors of toluene, ether, or chloroform to diffuse slowly into a saturated solution of compound **2** in dioxane in the dark: mp > 300 °C; FTIR (ATR) 3371, 3079, 2954, 1682, 1658, 1645, 1595, 1576, 1507, 1454 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.36 (s, 2H), 6.84 (s, 2H), 6.42 (s, 4H), 5.04 (s, 2H); ¹³C {¹H} NMR (100 MHz, DMSO-*d*₆) δ 179.3, 150.1, 146.8, 126.0, 122.9, 112.4, 48.3; UV-Vis (CH₃CN) λ_{max} (ε) 280 (4100), 383 (4480), 480 (1230); Emission (CH₃CN, λ_{ex} 280 nm) λ_{em} 311 nm; SWV (DMF/AcOH 1%, NBu₄PF₆) *E*_{1/2} -0.79, -0.64, 0.48 V (Fc/Fc⁺); HRMS (ESI-TOF) *m/z* [M - H]⁻ calcd for C₂₀H₉O₆ 345.0399, found 345.0390.

9,10-Dihydro-9,10-[1,2]benzenoanthracene-2,3,6,7,14,15-hexaone (1). 2,3-Dichloro-5,6dicyano-1,4-benzoquinone (1.55 g, 6.83 mmol) was added to a suspension of 2,3,6,7,14,15hexahydroxytriptycene (**4**; 0.198 g, 0.565 mmol) in anhydrous oxygen-free THF (15 mL) under an atmosphere of N₂. The mixture was stirred at 25 °C for 20 h, and the resulting suspension was filtered. The filtrate was washed with THF and dried under vacuum to afford 9,10-dihydro-9,10-[1,2]benzenoanthracene-2,3,6,7,14,15-hexaone as a yellow solid (**1**; 0.119 g, 0.346 mmol, 61%). Further purification to afford red crystals of compound **1** could be achieved by allowing CH₃CN to diffuse slowly into a saturated solution in DMSO: mp > 300 °C; FTIR (ATR) 3060, 3078, 2954, 1682, 1658, 1645, 1595, 1576, 1507, 1454 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.57 (s, 6H), 5.04 (s, 2H); ¹³C {¹H} NMR (100 MHz, DMSO-*d*₆) δ 178.8, 147.1, 125.5, 48.1; UV-Vis (DMF) λ_{max} (ε) 281 (10,100), 380 (6740); Emission (DMF, λ_{ex} 280 nm) λ_{em} 339 nm; SWV (DMF,

NBu₄PF₆) $E_{1/2}$ -1.03, -0.79, -0.60 V (Fc/Fc⁺); HRMS (APCI-TOF) m/z [M]⁻ calcd for C₂₀H₈O₆, 344.0321, found 344.0317.

Solid-State Redox Reactions. Freshly prepared dark purple crystals of monoquinone **3**, grown from solutions in THF, were placed in a 4 mL vial, which was then transferred to a 20 mL vial containing 1 mL of hydrazine hydrate. The larger vial was then sealed with a cap, and after about 15 min vapors of hydrazine had reached the crystals and begun to react. As soon as the solid sample had turned completely colorless, the small vial was removed, and the crystals were placed on the stage of a polarized-light microscope. As shown in the Supporting Information, the crystals retained their initial morphology, displayed birefringence, and yielded a well-resolved X-ray powder diffraction pattern. However, individual crystals were not sufficiently ordered to allow their structure to be determined by single-crystal X-ray diffraction. All other solid-state redox experiments were carried in a similar way, and the identity of the products was confirmed by recording their NMR spectra, which matched those of authentic samples.

Notes

The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: X. Description of representative solid-state redox experiments, ¹H and ¹³C NMR spectra of

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triptycenes 1–4, voltammograms, absorption/emission spectra, and additional crystallographic details, including ORTEP drawings (PDF). Structural data for compounds 1–4 (CIF).

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