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# Articles

## Do Catechol Derivatives Electropolymerize?

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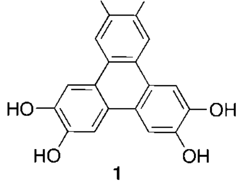
ABSTRACT: Several recent reports have claimed that catechol and its derivatives undergo electropolymerization when oxidized to form poly(*o*-phenylene)s. We demonstrate that the products of these electrochemical reactions are likely triphenylene derivatives rather than polymeric materials.

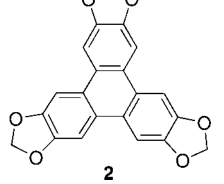
Recently, Xu and co-workers reported that the oxidation of 1,2-methylenedioxybenzene (MDOB) leads to the formation of a conjugated polymer, PMDOB (Figure 1).[1] These researchers subsequently claimed that electrochemical oxidation of catechol similarly leads to the formation of the polymer PoDHB.[2] We found both of these claims extremely surprising, since it has been known for several decades that catechol and its ether and ketal derivatives cyclotrimerize to form triphenylenes when chemically[3–6] or electrochemically oxidized.[7–9] Owing to their importance as liquid crystalline materials,[10] molecular-scale devices,[11–13] and molecular receptors,[6,9,14] triphenylene derivatives of this type have received considerable attention over the past 30 years. Although their chemical and electrochemical syntheses from catechol derivatives have been widely explored and exploited,[15] we are aware of no previous reports that indicate that appreciable quantities of poly(*o*-phenylene)s are formed via the oxidation of catechol derivatives, even under conditions that are almost identical to those employed by Xu et al. These considerations led us to investigate these systems in closer detail.

Before proceeding further, we need to first examine the evidence that the products identified as PMDOB and PoDHB are, in fact, polymers. Determination of molecular weight is a crucial step in the identification of a species as a polymer. Unfortunately, Xu and co-workers have not reported carrying out either mass spectrometry (e.g., MALDI-TOF, electrospray) or any other experiments (size exclusion chromatography, light scattering, osmometry, changes in viscosity, etc.) routinely used to assess the molecular weight of a polymeric material. The authors do present indirect evidence for the proposed polymer structures in the form of the diminished solubility, electrochromism, and the optical properties of the oxidation products. However, none of these properties uniquely characterize polymeric systems. Low solubility is also a feature of polycyclic aromatic molecules, and hexalkoxytriphenylenes have been shown to exhibit electrochromism similar to that reported for PMDOB.[16,17] The increases in conjugation inferred from the absorption and emission spectra also do not necessarily indicate the formation of conjugated polymers because triphenylene derivatives also possess extended conjugation. We will return to the optical properties of these products shortly.

Although no conclusive evidence has been provided to demonstrate that the oxidation products obtained are polymers, Xu and co-workers do present data that strongly indicate that these species are *not* polymeric. Both of the $^1$H NMR spectra reported for “PMDOB” and “PoDHB” are inconsistent with those expected for polymers. The peaks observed in the $^1$H NMR spectrum of a high molecular weight polymer should be considerably broadened, whereas those reported were narrow, suggesting that the products were low molecular weight species. Low molecular weight polymers can also be ruled out since these species would be lower symmetry and would have more complicated spectra than those observed; signals associated with end groups should also be easily detectable in the spectra, yet no such peaks were found. The spectra shown are, however, in keeping with what one would expect for discrete, relatively low molecular weight species and are entirely consistent with what one would expect for triphenylene derivatives. It should also be noted that the aromatic peaks for these oxidation products are shifted downfield relative to the monomer peaks, which is contrary to the observation made for oligo(*o*-phenylenes) reported in the literature. Such oligomers tend to adopt a helical $\pi$-stacked structure, which leads to an upfield shift of the aromatic protons relative to the monomers.[18,19]



**1**



**2**

On the basis of the above observations, we suggest that the species identified as PoDHB and PMDOB are instead the triphenylenes **1** and **2**, respectively. The optical properties of these products strongly support this assignment. Hexaalkoxytriphenylenes exhibit highly structured absorption spectra in solution, with an intense absorption at ~280 nm and several weaker bands at longer wavelengths up to around 360 nm. Significantly, the number, position, and relative intensities of

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**Figure 1.** Proposed structure of oxidation products of catechol and MDOB.

**Scheme 1. Preparation of Compound 2**

$$\mathbf{1}\ \xrightarrow[\substack{K_2CO_3\\ DMF}]{CH_2BrCl}\ \mathbf{2}\ \xleftarrow[CH_2Cl_2]{FeCl_3}\ \mathbf{MDOB}$$

*(route a)* *(route b)*

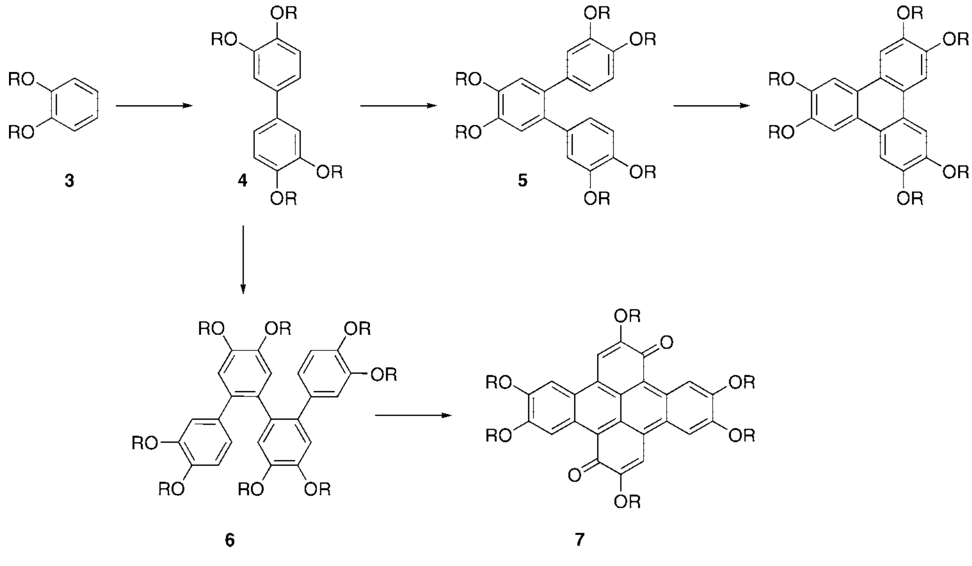
the peaks observed in the absorption spectra of 2,3,6,7,10,11-hexaalkoxytriphenylenes almost exactly match those observed for the oxidation product of MDOB.[11,13,14,16,20,21] This close resemblance is to be expected if the product is **2**, as the optical properties of triphenylene derivatives are relatively insensitive to solvent polarity and the nature of the alkyl groups attached to the oxygens.[21] The fluorescence spectra of the oxidation products reported by Xu et al. are similarly in excellent agreement with the numerous spectra of triphenylene derivatives reported in the literature.[13,14,21] The qualitative observation that the doped product is a dark green color in the solid state also conforms to the description given by Simonet and co-workers for oxidized triphenylene derivatives.[8] Finally, it should be noted that there is literature precedent for the preparation of compound **1** from the direct chemical oxidative cyclization of catechol.[5,22]

Given these observations, we decided to prepare triphenylenes **1** and **2** via independent routes in order to compare their properties to those of the oxidation products obtained by Xu and co-workers. Hexahydroxytriphenylene **1** is a known compound that has been extensively studied, but to the best of our knowledge its spectroscopic properties have not been reported in DMSO, the solvent used in the characterization of "PoDHB". Compound **1** was prepared by hydrolysis of 2,3,6,7,10,11-hexamethoxytriphenylene following literature procedures; the latter compound, incidentally, is obtained from the oxidative cyclotrimerization of veratrole. The properties of **1** are in agreement with those reported in the literature,[4,23] and mass spectrometry (MALDI-TOF) confirmed that the product was the triphenylene **1**. The $^1$H NMR spectrum of this compound in DMSO exhibits two peaks: a sharp peak at 7.60 ppm and a broad peak at 9.28 ppm; this agrees well with Xu and co-workers' report of a single peak at 7.65 ppm. The 9.28 ppm peak observed in our spectrum likely corresponds to the hydroxyl protons; the observation of these protons depends strongly on the experimental conditions, and therefore its apparent[24] absence from the spectrum of "PoDHB" is consistent with its identification as **1**. This is reinforced by the $^{13}$C NMR spectrum of **1**, which in DMSO has three peaks at 107.7, 121.7, and 145.2 ppm, which are virtually identical to the peaks reported by Xu and co-workers at 107.8, 121.9, and 145.0 ppm. Such a close agreement strongly suggests that PoDHB and triphenylene **1** are the same compound.

We next turned our attention to compound **2**. The characterization of this compound does not appear to have been reported in the literature.[25] We prepared this compound via two independent routes: (a) reaction of compound **1** with bromochloromethane and (b) $FeCl_3$ oxidation of MDOB (Scheme 1). The products were characterized by $^1$H and $^{13}$C NMR, mass spectrometry, UV−vis absorption,and emission spectroscopy. The products obtained via these two approaches were identical to one another. This last point is significant, since it demonstrates that **2** can be prepared from the oxidative cyclization of MDOB. This is the major product formed from this reaction, and we observed no evidence of linear oligomeric materials by mass spectrometry.

Like the oxidation product reported by Xu and co-workers, triphenylene **2** is insoluble in all organic solvents examined except for DMSO, in which it is only sparingly soluble. The $^1$H NMR of this compound exhibits two peaks at 6.17 and 8.17 ppm, which agree with the values reported by Xu (6.17 and 8.15 ppm). As expected, the $^{13}$C NMR of **2** has four peaks, which appear at 101.3, 101.9, 124.5, and 147.4 ppm. In comparison, Xu and co-workers found three peaks at 101, 109, and 147 ppm. These two spectra therefore share two peaks in common: one at 147 ppm and another in the vicinity of 101 ppm. In part, the disparity between these results may arise due

**Scheme 2. Known Oxidative Reaction Pathways for Catechol Derivatives**



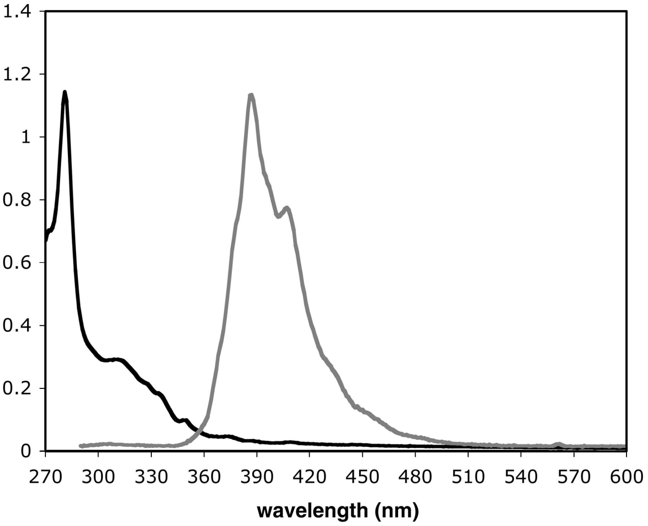


**Figure 2.** UV−vis absorption (black) and emission (gray) spectra for a 10 $\mu$M solution of compound **2** in DMSO.

to the poor signal-to-noise ratio apparent in the spectrum reported for PMDOB (see Figure 6b in ref 1b), which could account for the failure to observe a second peak near 101 ppm as well as the signal at 124.5 ppm. It is somewhat harder to rationalize the observation of a peak at 109 ppm in the spectrum of the product identified as PMDOB with no corresponding peak in the spectrum of **2**. Again, the low solubility of this material may be the cause, since at very low concentrations of the analyte even trace quantities of a more soluble impurity may lead to spurious signals in the NMR. Obviously, however, such arguments must be treated with caution.

Further evidence that "PMDOB" and **2** are the same compound comes from a comparison of the UV−vis absorption and emission spectra obtained in DMSO. Both the absorption and emission spectra of **2** (Figure 2) appear to be nearly identical to those of the oxidation product of MDOB (Figures 3 and 7 of ref 1b). As these spectra contain considerable fine structure, it is highly unlikely that such a close match is merely coincidence. These spectra, taken in conjunction with the NMR and solubility results, provide striking evidence that the "polymer" obtained by Xu and co-workers is the triphenylene derivative **2**.

From a mechanistic standpoint, it is not surprising that the formation of a triphenylene derivative is strongly preferred over the formation of acyclic polymers or oligomers (Scheme 2). In the initial stages, it is expected that catechol derivatives (**3**) will dimerize to form biphenyls (**4**).[26] These biphenyls preferentially react with monomers, likely forming the *o*-terphenyls (**5**),[27,28] which then cyclize efficiently to triphenylenes.[15,29] Entropically, the intramolecular cyclization of **5** will be heavily favored over intermolecular chain growth reactions. This cyclization is also enthalpically favored by the aromatic character of the central ring and the greater conjugation of the planar triphenylene relative to nonplanar[18,19] acyclic oligomers. Even when the biphenyl **4** is oxidized in the absence of **3**, i.e., conditions where terphenyl formation is precluded, a planar polycylic structure **7** is formed in high yields, presumably via the tetraphenyl oligomer **6**.[28,30,31] Thus, even if polymeric *o*-phenylenes were to be formed, they would likely be unstable toward oxidative cyclization.

In conclusion, our results strongly suggest that the oxidation products obtained from catechol and its acetal derivative MDOB are not polymeric materials as earlier claimed, but are instead the triphenylene derivatives **1** and **2**. These findings are fully consistent with the enormous body of research that has been published over the past 40 years on the synthesis of triphenylenes via the oxidation of catechol derivatives. These results highlight the difficulties associated with the preparation of poly(*o*-phenylenes), which remain an elusive class of conjugated polymers.

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**Supporting Information Available:** Full synthetic and analytical details for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) We say "apparent" absence because it is unclear from the data presented in ref 3 whether chemical shifts as high as 9.3 ppm were examined.

(25) Interestingly, it appears that Simonet and co-workers may have prepared this compound electrochemically using conditions similar to those described in ref 1, but their attempts to characterize this product were frustrated by its exceedingly poor solubility, which is one of this compound's distinguishing characteristics. In the same report, several other, much more soluble, triphenylene derivatives were prepared and characterized using the same conditions. See ref 7f.

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