

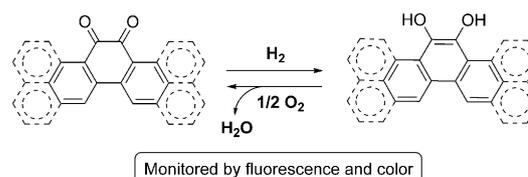
# Redox Switching of Orthoquinone-Containing Aromatic Compounds with Hydrogen and Oxygen Gas

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**Abstract:** Unique redox switching of orthoquinone-containing pentacyclic aromatic compounds with molecular hydrogen and oxygen in the presence of a palladium nanoparticle catalyst (SAPd) is disclosed. These molecules were predicted by *in silico* screening before synthesis. Efficient protocols for the synthesis of orthoquinone-containing aromatic compounds by palladium-mediated homocoupling and the benzoin condensation reaction were developed. Clear switching between orthoquinone and aromatic hydroquinone compounds was observed on the basis of their photoluminescence properties. Furthermore, the twist strain of the orthoquinone moiety could induce dramatic changes in color and emission.

Highly conjugated polyaromatic compounds have been widely applied in the development of fluorescent materials, semiconductor materials, organic electroluminescence devices, and organic solar-cell devices. For this purpose, a wide variety of polyaromatic organic compounds have been designed. Various switching technologies of the  $\pi$ -conjugated molecules have also been reported, such as photochromism,<sup>[1]</sup> thermochromism,<sup>[1]</sup> electrochromism,<sup>[2]</sup> piezochromism,<sup>[3]</sup> solvatochromism,<sup>[4]</sup> and halochromism,<sup>[5]</sup> as well as redox-mediated chromism induced by electricity<sup>[2]</sup> or chemical reagents.<sup>[6]</sup> The key issue for the design of molecules exhibiting redox switching is the introduction of functional groups that enable interconversion between the oxidized and reduced states (OFF and ON). We were convinced that aromatic compounds containing an orthoquinone moiety

were interesting candidates for redox switching, because the orthoquinone could be reduced to the corresponding hydroquinone, and the hydroquinone could also be quickly oxidized to the quinone (Scheme 1).<sup>[7]</sup> Thus, two different states of a  $\pi$ -



**Scheme 1.** Proposed redox-switching system.

conjugated system could be produced by a redox reaction. For the establishment of a redox system, usually oxidizing and reducing reagents, such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), NaBH<sub>4</sub>, and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, are required.<sup>[6]</sup> However, the side products derived from these reagents are potential problems for a reversible redox system. For a clean and reversible redox system, molecular hydrogen and oxygen would be ideal reagents. Thus, gaseous hydrogen and oxygen could be used for the hydrogenation of the orthoquinone to the hydroquinone in the presence of a metal catalyst. In contrast, gaseous oxygen could be used for the oxidation of the hydroquinone to the orthoquinone.<sup>[8]</sup> In this proposed environmentally friendly redox system based on molecular hydrogen and oxygen, the main side product is removable water, and this system could be made reversible without purification. Furthermore, this technology could possibly be applied to the development of photoluminescent materials that respond to switching between hydrogen and oxygen gas or to gas sensors for the detection of hydrogen and/or oxygen by the monitoring of fluorescence. To our knowledge, only one example of the redox switching of a coumarin derivative as an optical material has been reported, for which a combination of oxygen and photoenergy were used for oxidation, and hydrogen was used in the presence of a Pd catalyst for reduction.<sup>[9]</sup> Herein, we describe a unique redox-switching system of newly proposed orthoquinone-containing pentacyclic aromatic compounds with molecular hydrogen and oxygen in the presence of a palladium nanoparticle catalyst, a sulfur-modified gold-supported palladium catalyst (SAPd).

Our ideal molecules for the establishment of a redox-switching system should show clear switching properties between fluorescence emission and fluorescence quenching, and between a colored state and a colorless state. To discover possible candidates, we screened several orthoquinone-con-

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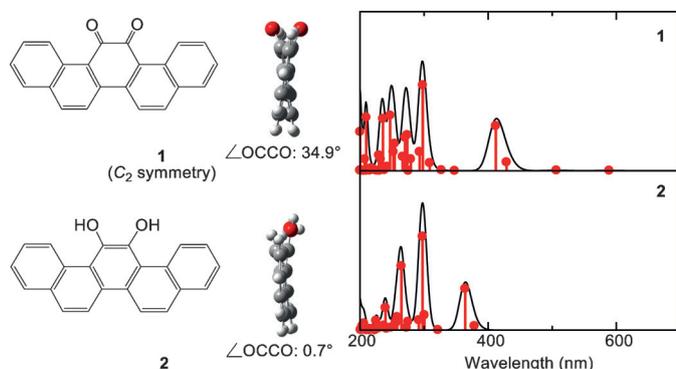
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taining aromatic compounds *in silico* to estimate their fluorescence and UV/Vis spectra. We then carried out geometry optimization and predicted the UV/Vis and fluorescence spectra of picene-13,14-dione (**1**)<sup>[10]</sup> and picene-13,14-diol (**2**) by using density functional theory (DFT) and time-dependent (TD) DFT methods (B3PW91 functional,<sup>[11]</sup> 6-311 + G(2d) basis set). In the calculated UV/Vis spectra, the maximum absorptions of **1** and **2** in CHCl<sub>3</sub> were estimated to occur at

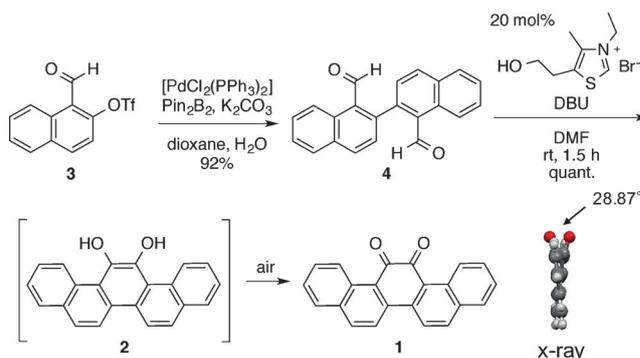


**Figure 1.** Optimized structure and estimated UV/Vis spectra of **1** and **2**.

412 and 378 nm, respectively (Figure 1). The visible color of **1** in CHCl<sub>3</sub> was expected to be yellow. Moreover, it was assumed that **2** in CHCl<sub>3</sub> was colorless. The maximum fluorescence wavelength of **1** and **2** in CHCl<sub>3</sub> was calculated to be 719 (oscillator strength,  $f=0.002$ ) and 464 nm ( $f=0.117$ ), respectively. As the oscillator strength of **1** was very small, this molecule would not have the property of fluorescence. On the other hand, **2** was expected to show blue fluorescence. From the results obtained, we predicted that the pentacyclic picene derivatives **1** and **2**, containing orthoquinone and hydroquinone moieties in the center, would show switching properties in color and fluorescence. Furthermore, the comparison of each calculated most stable structure of **1** and **2** indicated a large difference between the twist strain at the C–C bond of the orthoquinone moiety in **1** and the hydroquinone moiety in **2**. Thus, the twist strains of **1** and **2** were 34.91 and 0.71°, respectively (Figure 1; see Table S1 in the Supporting Information). Calculation of the nucleus-independent chemical shift (NICS)<sup>[12]</sup> by using the GIAO<sup>[13]</sup> method indicated that these strains affected the deconjugation of **1** and controlled the ON/OFF status of photoluminescence. The NICS is defined as the negative value of the absolute shielding computed at a ring center (NICS(0)) or at 1 Å above a ring center (NICS(1)).<sup>[14]</sup> The NICS(0) and NICS(1) values in **1** were estimated to be +13.2 and +5.5 ppm, respectively. These were large positive values reflecting an antiaromatic character. On the other hand, the NICS(0) and NICS(1) values in **2** were calculated to be –10.0 and –9.6 ppm, respectively. These values indicated that **2** had an aromatic character. The results of the theoretical calculation suggested that the  $\pi$ -conjugated system was broken by distortion in the center of **1**.

After completion of the calculation studies, we synthesized **1** (Scheme 2). The benzoin-condensation precursor **4** was prepared by the modified protocol developed by Wang et al.<sup>[15]</sup> The known triflate **3**<sup>[16]</sup> was treated with catalytic bis(triphenylphosphine)palladium(II) dichloride (10 mol %), bis(pinacolato)diboron (0.6 equiv), and potassium carbonate (3.0 equiv; dioxane, H<sub>2</sub>O, rt→90°C, 2 h) to provide the homocoupling product **4** in 92% yield. The key benzoin condensation reaction of **4** with 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazol-3-ium bromide (20 mol %)<sup>[8b,17]</sup> and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.0 equiv; DMF, rt, 1.5 h) gave the desired hydroquinone **2**. The yielded hydroquinone **2** was rapidly oxidized in air (oxygen) to afford **1** in quantitative yield as single crystals. X-ray crystal-structure analysis showed that the angle of twist strain on the C–C bond belonging to the orthoquinone moiety in **1** was 28.87°. Importantly, the angle was almost the same as that found by calculation. Furthermore, orthoquinone **1** did not show fluorescence, and the visible color of **1** in the solution state (in CHCl<sub>3</sub>, AcOEt, THF, EtOH, or toluene) was yellow, as indicated by the UV/Vis spectrum (see Figure S1 in the Supporting Information).

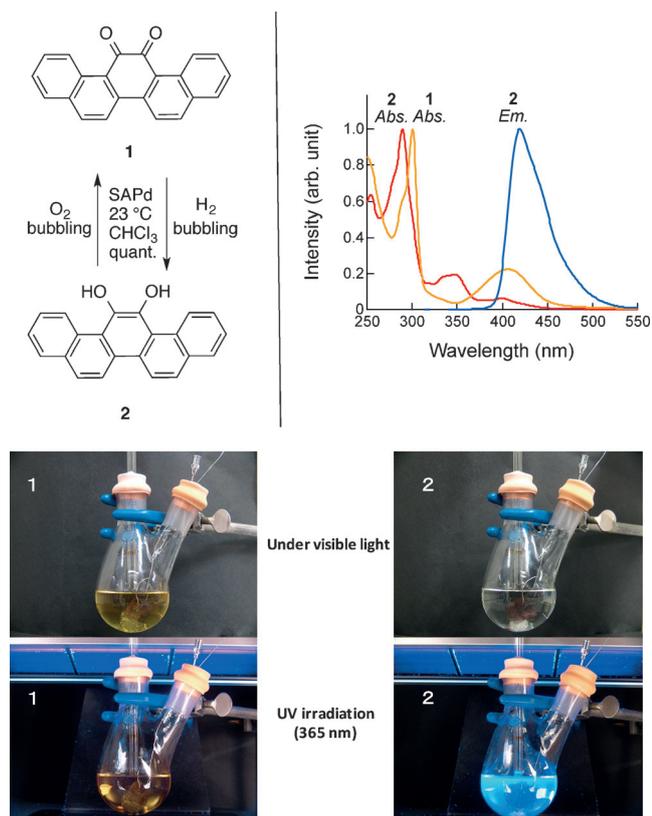
The redox switching of **1** with molecular hydrogen and oxygen was investigated. Generally, a heterogeneous cata-



**Scheme 2.** Synthesis and X-ray crystal structure of **1**. DMF = *N,N*-dimethylformamide.

lyst, such as Pd/C, is used to reduce a quinone to a hydroquinone. However, the heterogeneous conditions were not suitable for monitoring the optical properties of our system. The SAPd developed by Arisawa and co-workers was used to solve this problem.<sup>[18]</sup> The Pd nanoparticles in the SAPd are tightly supported on a gold-mesh sheet. Thus, optical properties, such as UV/Vis and fluorescence spectra *in situ*, can be observed clearly. Furthermore, it can be easily taken out of the reaction vessel with a pair of tweezers and is also recyclable.

When the reduction of orthoquinone **1** was carried out in the presence of SAPd with hydrogen gas bubbled through the mixture in CHCl<sub>3</sub> at ambient temperature, the desired hydroquinone **2** was obtained quantitatively (Figure 2; the reaction time of the reduction could be controlled by the surface area of SAPd). The yellow color of **1** disappeared as the reaction progressed. In contrast, clear blue fluorescence under irradiation with UV light (365 nm) appeared toward

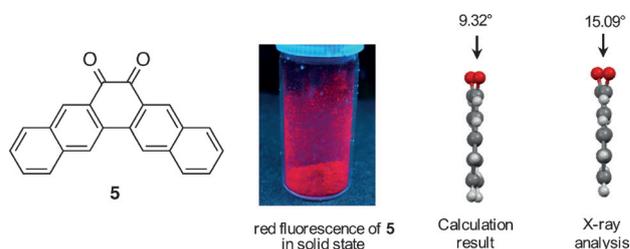


**Figure 2.** Redox switching of **1** and **2** with H<sub>2</sub> and O<sub>2</sub> gas. The absorption spectra of **1** and **2** and the fluorescence spectrum of **2** in CHCl<sub>3</sub> (excitation wavelength: 290 nm) are shown. All spectra were normalized at the maximum. The molar absorption coefficient at the maximum absorption of **1** and **2** is  $2.91 \times 10^4$  and  $5.45 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively.

the end of the reaction (see movies in the Supporting Information). In the fluorescence spectrum of **2**, blue emission was observed at the maximum fluorescence wavelength of 419 nm (Figure 2; see also Figure S2). These results indicated that the fluorescence of **2** resulted from the extension of the  $\pi$ -conjugated system by the transformation of the orthoquinone into a hydroquinone. All optical properties of **1** and **2** agreed with the estimations of the *in silico* study (Figure 1). The subsequent reverse oxidation of the hydroquinone **2** to the orthoquinone **1** proceeded smoothly when hydrogen gas was simply exchanged for oxygen gas; the colorless solution changed to yellow, and the blue fluorescence was quenched. As a result, clean and reversible redox switching with hydrogen and oxygen gas was established.

Next, the details of the oxidation conditions were investigated (see Table S2). The aerobic oxidation for the conversion of **2** into **1** could be carried out in quantitative yield, even though a longer reaction time was required. On the other hand, when the oxidation reaction occurred in the absence of SAPd, the required reaction time was twice that under the standard conditions. These results indicated that SAPd acted not only as a catalyst for hydrogenation but also as a catalyst for oxidation. The use of SAPd in redox reactions has not been described previously.

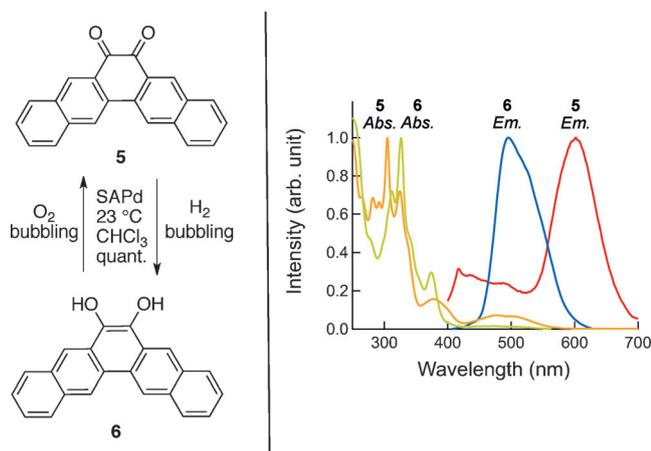
After the establishment of a redox system with picene derivatives, our focus shifted to the optical properties of other pentacyclic fused aromatic compounds, including the effect of twist strain. For this investigation, pentaphen-6,7-dione (**5**)<sup>[19]</sup> was chosen on the basis of theoretical calculations (Figure 3).



**Figure 3.** Structure and red fluorescence of pentaphen-6,7-dione (**5**).

This molecule was calculated to be almost planar; the twist strain on the C–C bond belonging to the orthoquinone moiety in **5** was 9.32°, which is considerably smaller than in **1** (see Table S3). Furthermore, as the NICS(0) and NICS(1) values in **5** were estimated to be +12.1 and +4.0 ppm, respectively, **5** has antiaromatic character. In the TD DFT calculation, the maximum absorption of **5** in CHCl<sub>3</sub> was calculated to be 540 nm. Additionally, the maximum fluorescence wavelength of **5** in CHCl<sub>3</sub> was estimated to be 558 nm ( $f=0.115$ ). Thus, fluorescence emission was expected in **5**, whereas **1** does show fluorescence, although both compounds have the same molecular formula. According to the theoretical calculation, there are almost no differences between **1** and **5** in their orbital energies. However, the sequence of molecular orbitals is different. Although the LUMO in **1** is a similar  $\pi^*$  orbital to that in **5**, the HOMO in distorted **1** is an *n*-type orbital with a lone pair in the plane for the two oxygen atoms, whereas the HOMO in planar **5** is a  $\pi$  orbital without a lone-pair orbital for the two oxygen atoms. The molecular orbital corresponding to the HOMO in **1** is the HOMO-3 in **5**. Therefore, it is assumed that the oscillator strength of the HOMO–LUMO ( $n$ - $\pi^*$ ) transition in **1** is very small, and that of the HOMO–LUMO ( $\pi$ - $\pi^*$ ) transition in **5** is very large, thus resulting in a huge difference expected in the UV/Vis and fluorescence spectra. As a result, by the molecular design aimed at controlling the twist strain, we can also tune the optical properties of orthoquinone derivatives drastically.

Compound **5** was synthesized smoothly by a similar strategy to that used for **1** (see details in the Supporting Information). The obtained product **5** formed a red crystal, and the small twist strain on the C–C bond belonging to the orthoquinone moiety in **5** was proved by X-ray crystal-structure analysis (angle: 15.09°; Figure 3). The UV/Vis and fluorescence spectra of **5** in CHCl<sub>3</sub> are shown in Figure 4. Although there is a discrepancy in the wavelengths of maximum fluorescence between observation (602 nm) and calculations (558 nm), huge differences in the optical properties of the picene derivative **1** and the pentaphene derivative **5** were clearly observed. In particular, the red fluorescence of **5** is remarkable for a simple pentacyclic aromatic compound containing an orthoquinone. Our preliminary calculation



**Figure 4.** Redox switching of **5** and **6**. The absorption and fluorescence spectra of **5** (excitation wavelength: 371 nm) and **6** (excitation wavelength: 355 nm) in  $\text{CHCl}_3$  are shown. All spectra were normalized at the maximum. The molar absorption coefficient at the maximum absorption of **5** and **6** is  $4.7 \times 10^4$  and  $3.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively.

indicated that the intermolecular interaction induced a red-shift in the fluorescence spectrum of **5**. Significantly, compound **5** also emitted the red fluorescence (620 nm) in the solid state (see Figure S3), thus indicating that **5** readily aggregated even in the solution state. The redox switching of **5** with molecular hydrogen and oxygen was investigated (Figure 4). When the reduction of orthoquinone **5** was carried out by bubbling hydrogen gas through the solution in the presence of SAPd, the desired hydroquinone **6** was formed in a quantitative yield, and the color of the solution changed from orange to yellow. At the same time, the fluorescence color under irradiation with UV light (365 nm) changed from red to green (see also Figure S4). In the fluorescence spectrum, the maximum fluorescence wavelength of hydroquinone **6** was 495 nm, which is 107 nm shorter than that of **5**. The reverse oxidation from **6** to **5** with oxygen gas proceeded smoothly under our established conditions to complete the reversible redox switching of the pentaphene derivatives **5** and **6**.

In conclusion, a unique redox-switching system composed of orthoquinone-containing aromatic compounds in combination with hydrogen and oxygen gas was discovered. In this study, the *in silico* screening of orthoquinone-containing aromatic compounds was an effective approach to estimate the visible color, fluorescence, and aromaticity of a selection of candidate molecules. Efficient synthetic protocols, including a palladium-catalyzed homocoupling reaction followed by a benzoin condensation reaction, were established for the preparation of the orthoquinone-containing aromatic compounds, and a reversible and clean redox system based on molecular hydrogen and oxygen was established. SAPd was found to be an effective redox catalyst that was suitable not only for the monitoring of visible color and fluorescence but also for recycling. The redox chromism of the picene derivatives **1** and **2** showed perfect ON/OFF switching of their visible color and fluorescence as a result of differences in aromaticity and the twist strain of the molecules. Further-

more, unique red fluorescence of **5** in the solid and in solution was discovered. Finally, we demonstrated that the twist strain of the orthoquinone moiety could induce dramatic changes in color and emission. Further applications of the developed redox system to gas sensors, reductant and oxidant sensors, luminescent materials, and redox semiconductor materials are currently under development.

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**Keywords:** hydroquinones · materials science · quinones · redox switching · twist strain

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