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Reduction of Emeraldine Base Form of Polyaniline by Pillar[5]arene Based on Formation of Poly(pseudorotaxane) Structure

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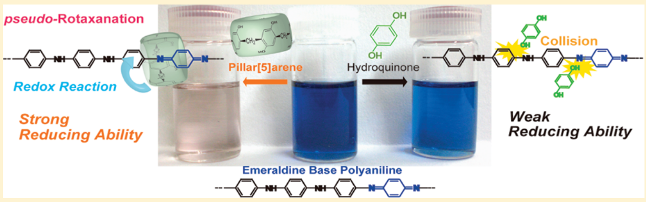
S Supporting Information

ABSTRACT: We report on the reduction of polyaniline (PANI) by pillar[5]arene based on the formation of the poly(pseudorotaxane) structure. When pillar[5]arene was mixed with emeraldine base (EB) form of PANI, a blue solution color resulting from the EB form of PANI was diluted over time, and became completely colorless after 180 min. The FT-IR spectrum of the mixture of the EB form of PANI and pillar[5]arene displayed a new band at 1646 cm^{-1}, which was assigned the C=O stretching band of benzoquinone. These results indicate that both oxidation of the hydroquinone units of pillar[5]arene and reduction of the EB form of PANI were induced by mixing the EB form of PANI and pillar[5]arene. Pillar[5]arene showed a stronger reducing ability than the unit model of hydroquinone. The ROE correlations between the methylene bridge protons of pillar[5]arene and the benzene protons of PANI indicated that the PANI chain was included into the pillar[5]arene cavity. Formation of the poly(pseudorotaxane) structure between PANI and pillar[5]arene was the main reason for the strong reducing ability of the EB form of PANI.



INTRODUCTION

Polyaniline (PANI) is one of the most investigated conducting polymers owing to its unique features such as its versatile redox properties, environmental stability and reversible doping.[1−9] PANI exists in four major forms (Figure 1a).[3−9] In its fully reduced form, it is known as a leucoemeraldine base (LB) and is characteristically transparent. In its fully oxidized form, it is termed a pernigraniline base (PB) and possesses a dark violet color. Half-oxidized PANI has an emeraldine base (EB) form and is blue in color. Protonation of the EB form of PANI results in the green, electrically conducting emeraldine salt (ES) form. Reversible interconversion between these different forms of PANI is controllable electrically and chemically, and induces color changes. The color change is particularly interesting in sensing applications,[9] since it matches detection capabilities of the human eye. The chemical interconversion of these different forms is achieved by treatment with reducing and oxidizing agents. Treating the EB form of PANI with the oxidizing agent ammonium persulfate results in its interconversion to the fully oxidized PB form of PANI.[7] Reduction of the EB form of PANI is achieved by treatment with the reducing agent hydrazine hydrate.[7] In this study, we report on the interesting reducing behavior of a macrocyclic ring compound "pillar[5]arene"[10−23] (Figure 1b) for the EB form of PANI. Pillar[5]arene was first synthesized and named by our research group in 2008.[10] Its composition is similar to that of typical calixarenes;[24−28] however, pillar[5]arene has repeating units connected by methylene bridges at the *para*-position and so has a unique symmetrical pillar architecture different from the basket-shaped structure of *meta*-bridged calixarenes. As pillar[5]arene is a cyclic pentamer composed of hydroquinone units, it shows the characteristic properties of hydroquinone. One of the interesting properties of pillar[5]arene is its electron donating property. Owing to the electron donating property of hydroquinone, the inner cavity of pillar[5]arene is an electron-rich space, and pillar[5]arene forms complexes with electron-accepting guest molecules such as viologen and pyridinium salt derivatives.[10,11,21,22] Following the host−guest complexation between pillar[5]arene and viologen derivatives, we synthesized poly(pseudorotaxanes)[19] and polyrotaxanes[20] constructed from pillar[5]arene as a cyclic component and viologen polymer as a polymeric chain. The other characteristic property of hydroquinone is its reducing ability. Hydroquinone is easily oxidized and converts to *p*-benzoquinone and has therefore been used as a reducing agent.[29−31] In this study, we use pillar[5]arene as a macrocyclic reducing agent for the EB form of PANI. We report on the interesting reducing ability of pillar[5]arene resulting from the formation of poly(pseudorotaxane) constructed from PANI and pillar[5]arenes.

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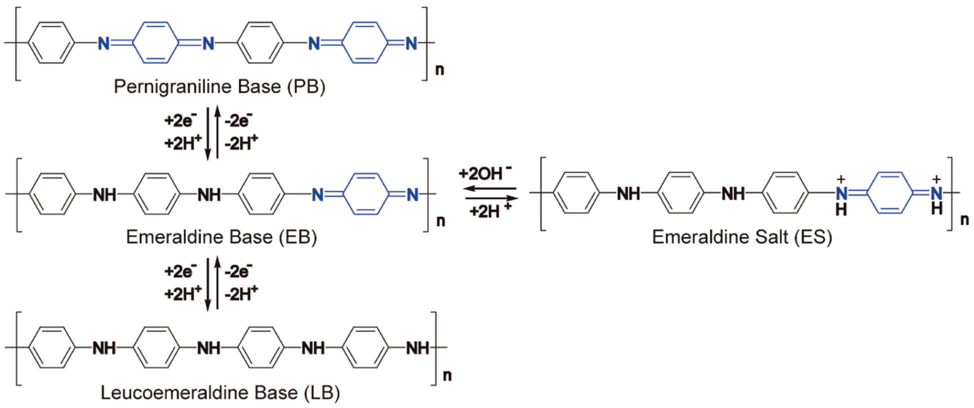
(a) Polyaniline



(b) Pillar[5]arenes

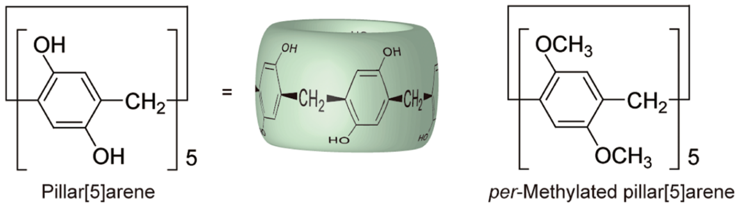


Figure 1. (a) Oxidation−reduction chemistry of polyaniline and (b) pillar[5]arenes.

RESULTS AND DISCUSSION

The EB form of PANI (M_w = 20 000) shows an absorption band at 640 nm (Figure 2a). Initially, upon addition of pillar[5]arene, the absorption band did not change but, was found to decrease over time and disappeared after 180 min. This color change could be observed directly by the human eye. At 0 min, the solution was blue from the EB form of PANI (Figure 2a, inset i). The blue color became diluted with time, and after 180 min the solution was colorless (Figure 2a, inset ii). These spectral changes with pillar[5]arene are very similar to those observed previously for the reduction of the EB form of PANI using hydrazine,[7] indicating that PANI is reduced from the EB to the LB form upon addition of pillar[5]arene. The absorption spectra exhibited an isosbestic point at 389 nm, indicating the presence of the two species of the EB and LB forms of PANI in solution. Figure 2b shows the emission spectra of a mixture of the EB form of PANI and pillar[5]arene. No emission was observed in the initial stage. However, after 180 min, an emission appeared at 416 nm. It was reported that the emission from the EB excited state was self-quenched by the adjacent quinolid groups, whereas the LB form of PANI exhibited a strong emission centered at ca. 410 nm.[4] Therefore, the observation also supports the theory that the EB form is reduced fully to the LB form of PANI through oxidation of the hydroquinone units of pillar[5]arene as confirmed by FT-IR measurements (Figure 3). The new peak appeared at 1646 cm^{-1} in the film cast from a mixture of the EB form of PANI and pillar[5]arene in DMSO (Figure 3c), whereas there were no peaks in this region in the films cast from a solution of each of the EB form of PANI (Figure 3a) and the pillar[5]arene (Figure 3b) in DMSO. The new band observed in the mixture was assigned the C═O stretching band of benzoquinone, indicating oxidation of the hydroquinone units of pillar[5]arene with the EB form of PANI. It is apparent that pillar[5]arene acts as a reducing agent for EB form of PANI. The color change was not induced by mixing *per*-methylated pillar[5]arene (Figure 2b) and the EB form of PANI (Supporting Information), indicating that the hydroquinone units of pillar[5]arene were therefore necessary for the redox reaction.

Parts a and b of Figure 4 show the UV−vis and emission spectra of the solutions with constant concentration of the EB form of PANI and varying concentrations of pillar[5]arene. The samples were left for 12 h to achieve equilibrium. The absorption band at 640 nm decreased in intensity (Figure 4a) and the emission at 414 nm increased with the increase in concentration of pillar[5]arene (Figure 4b). The EB form was reduced to the LB form of PANI as the amounts of pillar[5]arene increased. The stoichiometry between pillar[5]arene and PANI was estimated by Job plot. As a repeating unit model of PANI, aniline tetramer was used. As with a mixture of EB form PANI and pillar[5]arene, the absorption band at 589 nm for aniline tetramer decreased with increasing concentration of pillar[5]arene. The stoichiometry between aniline tetramer and pillar[5]arene determined by Job plot was 1:1 (Supporting Information). One quinoid ring was contained in an aniline tetramer molecule. Thus, the redox reaction is based on donation and acceptance of electrons between one hydroquinone unit in a pillar[5]arene molecule and one quinoid ring in an aniline tetramer molecule.

Control experiments were carried out to investigate the reduction mechanism. Pillar[5]arene is a cyclic pentamer composed of hydroquinone units, and reduction of the EB form of PANI with a unit model of hydroquinone was examined. Upon addition of hydroquinone, the absorption band from the EB form of PANI decreased slightly (Figure 5a), but the blue solution color hardly changed (Figure 5a, inset ii, and changes in the intensities of the absorption bands with hydroquinone were much smaller than those with pillar[5]arene (Figure 4a). The changes in absorption band intensity at 640 nm upon addition of pillar[5]arene and hydroquinone are plotted in Figure 5b. Even for small amount of

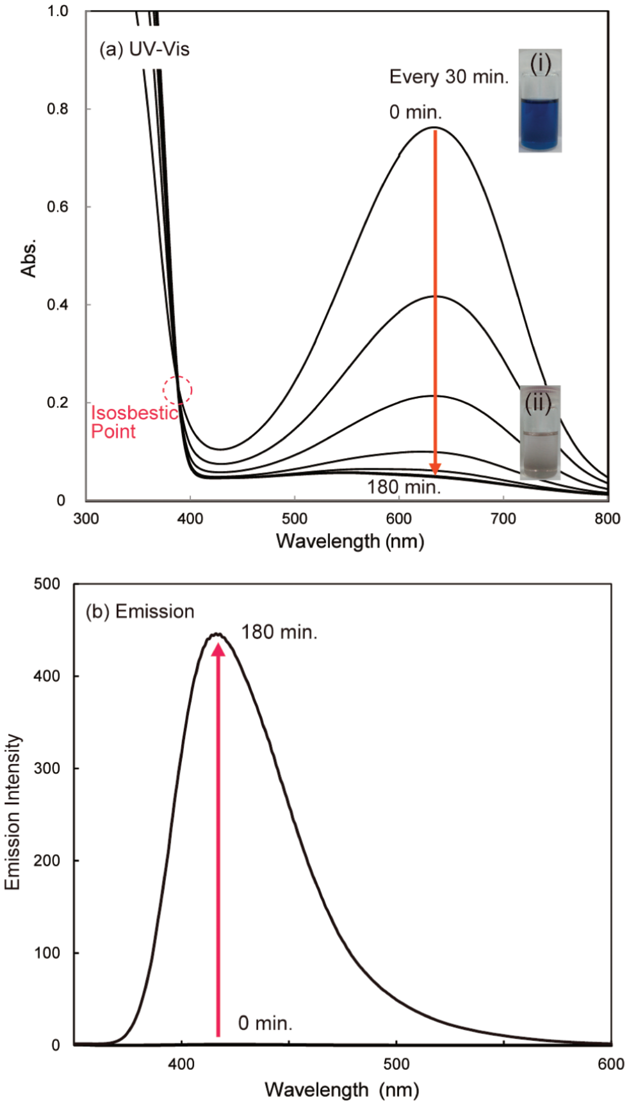


Figure 2. (a) UV−vis and (b) emission spectra of a mixture of the EB form of PANI (12.5 μM, M_w = 20 000) and pillar[5]arene (62.5 μM) in NMP as a function of time. Insets i and ii are photos of the solution after mixing at 0 and 180 min, respectively.

pillar[5]arene, the absorption intensity decreased considerably and, at the saturated state, decreased by almost 90%. On the other hand, in the unit model of hydroquinone, the absorption intensity decreased by 40% at the saturated state. These data indicate that the reducing ability of pillar[5]arene is much stronger than that of hydroquinone.

Figure 6 shows the cyclic voltammograms of hydroquinone and pillar[5]arene. In the potential range 0 to 1.5 V vs SCE, hydroquinone showed a typical oxidation peak at 1.01 V (Figure 6b).[32] In pillar[5]arene (Figure 6a), the position of the oxidation peak was similar to that in hydroquinone, indicating that oxidation of the five hydroquinone units in pillar[5]arene occurred separately and the oxidation activity was similar to the unit model of hydroquinone. From the results, the cyclic structure of pillar[5]arene should be important for reducing the EB form of PANI. To clarify this, the ROESY NMR measurement of a mixture of the EB form of PANI and pillar[5]arene was carried out (Figure 7).

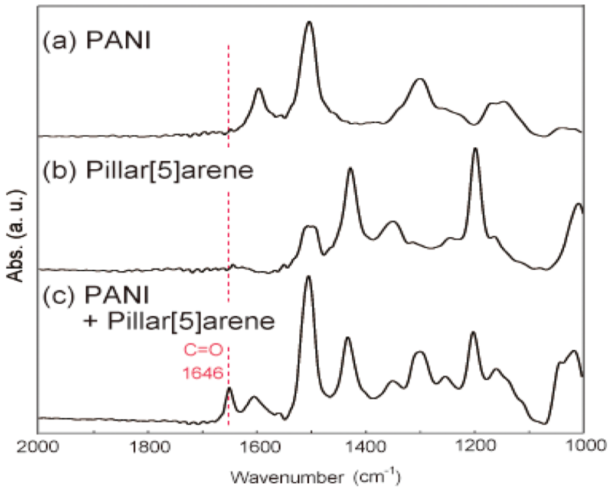


Figure 3. FT-IR spectra of (a) the EB form of PANI, (b) pillar[5]arene, and (c) a mixture of the EB form of PANI and pillar[5]arene. The samples were prepared by casting on NaCl plates.

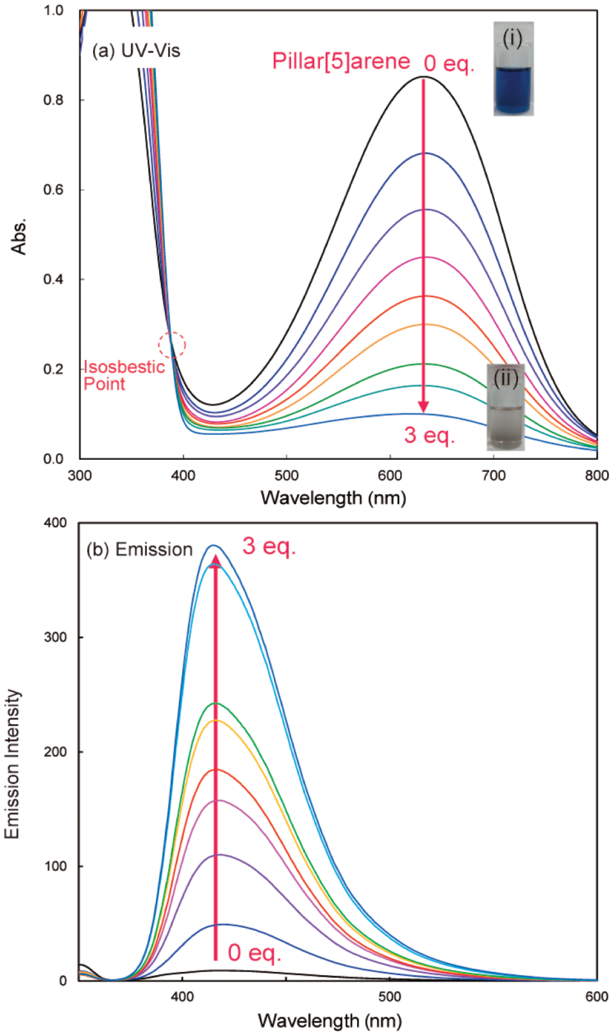


Figure 4. (a) UV−vis and (b) emission spectra of a mixture of the EB form of PANI (12.5 μM) and pillar[5]arene (0−3 equiv to a repeating unit in PANI) in NMP. The samples were left for 12 h to achieve equilibrium. Insets ii and i are photos of the solution with and without pillar[5]arene (3 equiv), respectively.

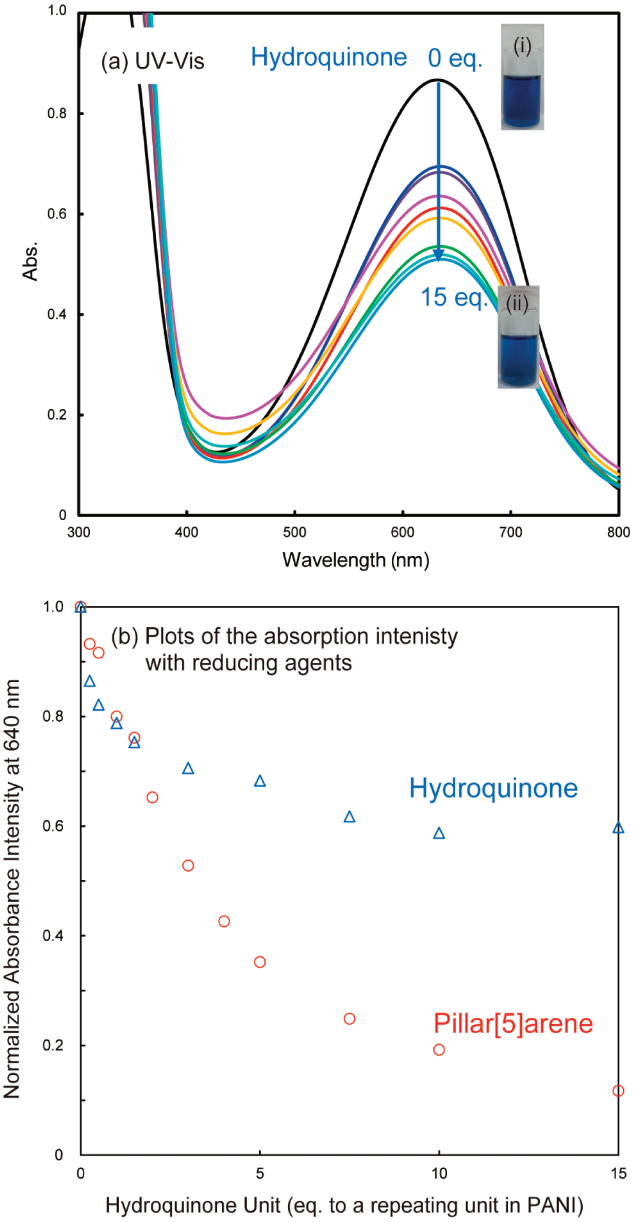


Figure 5. (a) UV−vis spectra of the EB form of PANI (12.5 mM) upon addition of hydroquinone (0−15 equiv to a repeating unit in PANI) in NMP. Insets ii and i are photos of the solution with and without hydroquinone (15 equiv), respectively. (b) Plots of the normalized absorption intensity by adding pillar[5]arene (red circles) and hydroquinone (blue triangles).

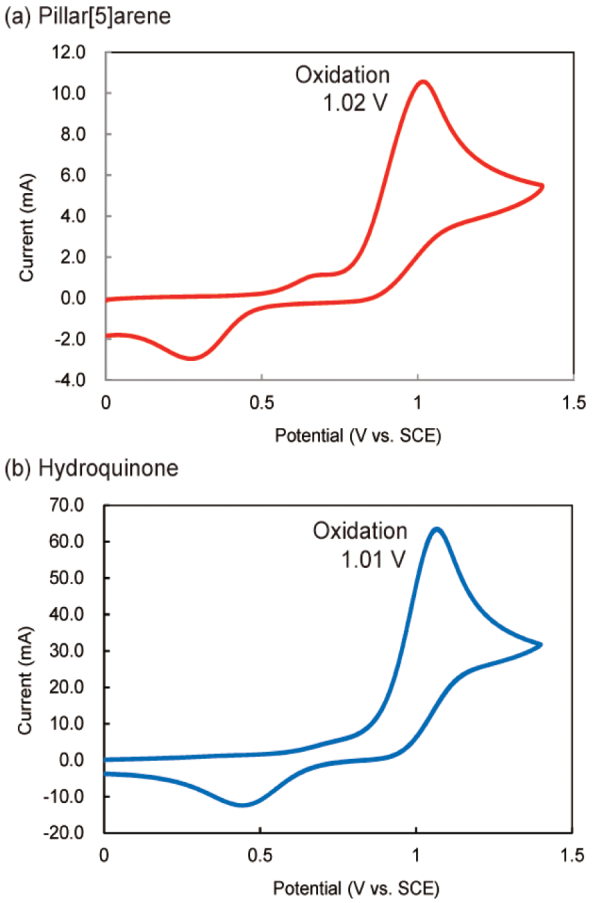


Figure 6. Cyclic voltammograms of (a) pillar[5]arene (1 mM) and (b) hydroquinone (5 mM) in 0.1 M Bu$_4$NPF$_6$/acetonitrile at a scan rate of 100 mV/s using Pt working electrode (ϕ = 1.6 mm).

The sample was left for 12 h to complete the reduction of the EB form of PANI. Observation of the ROE correlations between the methylene bridge protons of pillar[5]arene (peak B) and the benzene protons of PANI (peak a) indicated that the PANI chain was included into the pillar[5]arene cavity.[33] Formation of a poly(pseudorotaxane) structure constructed from PANI and pillar[5]arene was confirmed. From these observations, the proposed reduction mechanism is shown in Figure 8. In the unit model of hydroquinone, reduction of the EB form of PANI took place to a small extent by collision between hydroquinone and the EB form of PANI (Figure 8a). But reduction via collision is inefficient in reducing the EB form of PANI, and thus the reducing ability of hydroquinone for the EB form of PANI is quite weak. In contrast, in the cyclic structure of pillar[5]arene, formation of the poly(pseudorotaxane) structure between PANI and pillar[5]arenes (Figure 8b), which was confirmed by 2D ROESY NMR, is efficient in reducing the EB form of PANI. The poly(pseudorotaxane) structure is ideal for moving the reducing agent pillar[5]arene close to the oxidized substrate EB form of the PANI chain.

■ CONCLUSIONS

We found that pillar[5]arene acted as a strong reducing agent for the EB form of PANI and the formation of the poly(pseudorotaxane) structure changed the optical property of PANI significantly. PANI-based poly(pseudorotaxane)s[34−40] using cyclodextrins[34−36] and cucurbiturils[37,38] as cyclic components have been synthesized, but formation of the cyclodextrin and cucurbituril based poly(pseudorotaxane)s did not induce these optical changes. Thus, the optical changes induced by the pseudorotaxanation between the EB form of PANI and pillar[5]arene is the first example of its kind. The other interesting point is that the pillar[5]arene showed a stronger reducing ability than the unit model of hydroquinone. Formation of the poly(pseudorotaxane) structure between PANI and pillar[5]arene was the main reason for the strong reducing ability of the EB form of PANI. To the best of our knowledge, enhancing the ability of the reducing agent by formation of the supramolecular structure

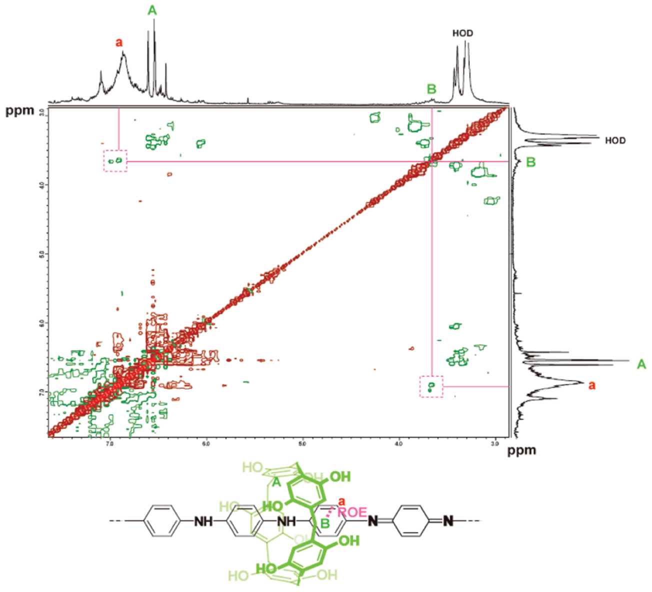


Figure 7. 2D ROESY analysis of a mixture of pillar[5]arene (13.3 mM) and the EB form of PANI (26.7 mM, M_w = 20 000) in DMSO-d_6 at 25 °C.

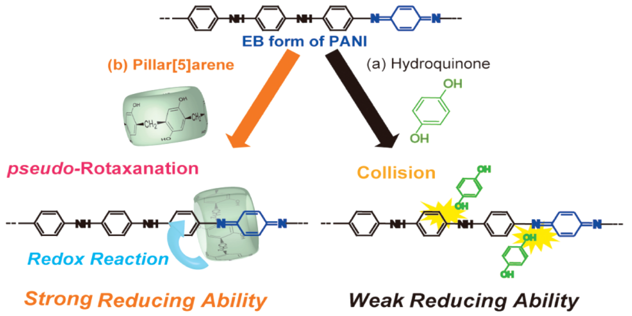


Figure 8. Proposed structures in the reduction mechanism of the EB form of PANI using (a) hydroquinone and (b) pillar[5]arene as reducing agent.

is the also first example. Use of this macrocyclic compound as a reducing agent is not well-known, and thus the macrocyclic pillar[5]arene will be applied as a reducing agent for various redox-active substances.

■ EXPERIMENTAL SECTION

Materials. All solvents and reagents were used as supplied. EB form of PANI (M_w = 20 000) was purchased from Aldrich. *per*-Methylated pillar[5]arene, pillar[5]arene, and aniline tetramer were synthesized according to the literature.[12,41]

Measurements. The ^{1}H NMR spectra were recorded at 500 MHz with a JEOL-ECA 500 spectrometer. Fluorescence spectra were recorded on a Hitachi F-2500 fluorescence spectrometer at room temperature. UV−vis absorption spectra were recorded with a JASCO V-630. For fluorescence and UV−vis measurements, 1 cm quartz cuvets were used. Cyclic voltammetry measurements were recorded on an ALS 600A Electrochemical Analyzer with 0.1 M Bu_4NPF_6/acetonitrile at a scan rate of 100 mV/s using a Pt working electrode (ϕ = 1.6 mm). The FT-IR spectra were obtained using a JASCO FT-IR460 plus infrared spectrometer.

■ ASSOCIATED CONTENT

S Supporting Information. UV−vis spectra of a mixture of EB form of PANI and *per*-methylated pillar[5]arene as a function of time and Job plot for aniline tetramer and pillar[5]arene. This material is available free of charge via the Internet at http://pubs.acs.org.

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