Aromaticity Relocation in Perylene Derivatives upon Two-electron Oxidation to Form Anthracene and Phenanthrene


Dedication

Abstract: We prepared perylene dication $1^{2+}$ and $2^{2+}$ by using "capped" perylene derivatives, and successfully obtained the single crystals of perylene dication $1^{2+}$, for the first time, which enables us to perform its structural analysis. We realized that the substituted aryl groups on perylene control the positions of positive charges, thus the remaining electronic system satisfies Clar's sextet rule toward the highest number of localized sextets. Experimental and theoretical evidences proved that Clar's aromatic $\pi$-sextet rule could be applied even for the dicationic perylenes in a very simple way.

Figure 2. a) X-ray crystal structure of pyrene with HOMA values (in bold),[7] b) one of the Kekulé resonance structures of pyrene, c) Clar structure of pyrene. The carbon designation is described in b).

We have reported that the sterically hindered pyrene could be oxidized with SbCl$_5$ to give the persistent pyrene dication.[6] Thus, an excellent crop of dark blue colored crystals of 1,3,6,8-tetrakis(4-mesityloxyphenyl)pyrene dication suitable for X-ray studies were obtained (Figure 2).[7] To the best of our knowledge, this is the first X-ray crystal structure of pyrene dication.

Figure 1. a) X-ray crystal structure of pyrene with HOMA values (in bold),[7] b) one of the Kekulé resonance structures of pyrene, c) Clar structure of pyrene.

Supporting information for this article is available via a link at the end of the document.

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[1] The concept makes it possible to explain various physical and chemical properties of polycyclic aromatic hydrocarbons (PAHs). Accordingly, if more than one structure can be drawn for a given electronic system, those of them, which have the highest number of localized sextets, are the most stable structures. For instance, pyrene consists of four fused benzene rings. Figure 1 shows X-ray and Kekulé structures of pyrene and the structure with localized sextets denoted as the circles within the rings. There is a good correspondence with the experimental C=C bond lengths observed in X-ray structure and the one predicted by the sextet rule. From the single crystal X-ray structural analysis, it is expected that the structure in Figure 1b is more stable relative to the other resonance contributors at the ground state. In fact, the lateral rings in pyrene are significantly more aromatic than two inner benzene rings shown by the indicators of aromaticity, harmonic oscillator model of aromaticity (HOMA)[2] and nucleus independent chemical shift (NICS)[3] values (vise infra). Recently we have reported synthesis and physical properties of the tetrakis-mesityloxy-substituted tetrabenzoperypentacene, in which the local aromaticity absolutely depicted eight benzene rings according to the sextet rule.[4]

Although PAHs are very common in chemistry, their isolated cationic and dicationic species are practically unavailable in normal experimental conditions due to their remarkable reactivity. Cation radicals and dications are important intermediates in organic synthesis, appearing in the molecular electronic and optical materials for a wide range of applications.[5] As an interesting example, Bettinger has discovered the fact that dications of higher linear acenes are formed more easily in sulfuric acid.[6]
lengths at the inner benzenes become rather close to naphthalene, giving higher HOMA values (Figure 2). These experimental results show a correlation with theoretical calculations (Figure S14). The NICS is another aromaticity index. However, the NICS values for charged systems tend to be high due to the electron deficient situation (Figure S19).

The two-electron oxidation changes the electronic system of pyrene into that of naphthalene — according to this finding, thus we have quenst for a double image of the other PAH as well. Here, we select perylene as a particular example to highlight the aromaticity relocation.

While perylene anions and dianions can be isolated in the moderate experimental conditions, the cationic and dicationic counterparts are unstable due to their high reactivity. The oxidation of the unsubstituted perylene having an amine bridge at a bay-area results in the formation of directly-linked dimers.

Therefore, in order to investigate the isolated cationic species, it is necessary to cap the most reactive positions by the substituents. We have prepared 3,9- and 3,10-diarylperylenes 1 and 2 by the Suzuki–Miyaura cross-coupling between 4-borylanisole and dibromoanperlenes 3 and 4, respectively (Scheme 1). These compounds have been fully characterized by $^1$H and $^{13}$C NMR, high-resolution MALDI-TOF mass spectroscopy, and single crystal X-ray analysis (SI).

![Scheme 1. Synthesis of perylene derivatives 1 and 2. (a) Br$_3$, benzene. (b) p-MeOPhB(OH)$_2$, K$_2$CO$_3$, Pd catalyst. Ar = p-methoxy-phenyl.](image)

UV-vis absorption spectra of 1 and 2 in toluene are shown in Figure 3. Compared to the pristine perylene ($\lambda_{\text{max}} = 439$ nm), 1 and 2 exhibit red-shifted and broader absorption ($\lambda_{\text{max}} = 461$ and 462 nm, respectively), suggesting the certain electronic communication between the perylene and phenyl units.

Compounds 1 and 2 show reversible oxidative waves in cyclic voltammetry at +0.41 and +0.79 V for 1, and +0.42 and +0.78 V for 2 (versus Fc/Fc$^*$, Figure S24). Compared to the first oxidation potential of the pristine perylene (0.54 V vs Fc/Fc$^*$), those of compounds 1 and 2 shifted to lower potentials. The reversible oxidation encouraged us to investigate the ability of 1 and 2 for the generation of the stable cationic and dicaticonic species.

The generation of the cationic and dicaticonomic species of 1 and 2 was carried out with NOSbF$_6$ (1 eq. and 2 eq., respectively) in CH$_2$Cl$_2$/CH$_3$CN. The UV-vis-NIR absorption spectra are shown in Figure 3. After addition of 1 eq. of NOSbF$_6$ to 1, the intense bands at 432 nm and 458 nm decreased, whereas new bands in visible region at 743 and 595 nm and the NIR region at 1002 nm arose. The absorption spectrum is the same as that of the electrochemically oxidized 1 at +0.52 V (versus Fc/Fc$^*$) (Figure S12). The calculated absorptions for 1$^+$ performed by time-dependent density functional theory (TD-DFT) at the BLYP35/SVP (with CPCM solvent model implementations in MeCN) using the Gaussian 09 package roughly agree with the experimental data. The excitation at 879 nm region is responsible for the observed absorption of 1$^+$ at 1002 nm. Addition of 1 eq. of NOSbF$_6$ to 2 made the intense bands at 434 nm and 462 nm decreased, whereas new bands in visible region at 714 nm and the NIR region at 969 nm arose (Figure 3b). This absorption spectrum is also the same as that of the electrochemically oxidized 2 at +0.56 V (versus Fc/Fc$^*$) (Figure S13). The predicted absorptions for 2$^+$ are in accordance with the experimental data. The calculated absorption at 818 nm is responsible for the observed absorption of 2$^+$ at 969 nm and the one at 685 nm corresponds to the experimental absorption at 714 nm.

![Figure 3. UV-vis-NIR absorption spectra of (a) 1 (black), 1$^+$ (red), and 1$^{2+}$ (blue) (4.4 $\times$ 10$^{-4}$ M) and (b) 2 (black), 2$^+$ (red), and 2$^{2+}$ (blue) (1.8 $\times$ 10$^{-5}$ M) along with the calculated oscillator strength, formed under the oxidation with NOSbF$_6$ in CH$_2$Cl$_2$/CH$_3$CN at room temperature.](image)

Upon further addition of NOSbF$_6$ (totally 2 eq.), 1$^{2+}$ was oxidized to form the dicaticonomic species 1$^{3+}$, resulting in the appearance of visible band at 631 nm (Figure 3a), and the
disappearance of the ESR signals. These indicate that the singlet state of \(1^{2+}\) is more stable than triplet state. For dication \(1^{2+}\), the simulated absorption agrees with the experimental data. The excitation at 802 nm is responsible for the observed absorption of \(1^{2+}\) at 631 nm. This excitation is associated with from HOMO to LUMO with the oscillator strength of 1.39.

We have tried to make single crystals of \(1^{2+}\). By using similar conditions to the pyrene dication, dark blue crystals of \(1^{2+}⋅2\text{SbCl}_6\) from anhydrous dichloromethane and heptane were obtained (Figure 4).[10] The crystal structure of \(1^{2+}⋅2\text{SbCl}_6\) revealed that the counter anions are positioned above and below the perylene plane. The dihedral angles of phenyl units in \(1^{2+}\) are 35°. Compared to the neutral state, the phenyl groups tilted about 26°. The quinoidal structure of methoxyphenyl groups should contribute to stabilize dicationic state. Although there are literatures on the charged perylenes,[10,11] this is the first X-ray crystal structure of perylene dication, thus the first experimental structural analysis of perylene dication.

By the electronic system rearrangement upon the two-electron oxidation, the bond lengths at C4-C5, C6-C6a, C10-C11, and C12-C12a in \(1\) become longer and those at C3a-C4, C5-C6, C6a-C6b, C6b-C12d, C9b-C12d, C9b-C10, C11-C12, and C12a-C12b become shorter, being close to anthracene. Here, the planes constructed from C1, C2, and C3, and C7, C8 and C9 in \(1^{2+}\) are twisted against the planar central anthracene core by 10° (Figure S23). The bond length alternations from 1 to \(1^{2+}\) and the twist of the lateral 3C units in \(1^{2+}\) indicate the large change of its electronic system. HOMA values for \(1\) and \(1^{2+}\) on the basis of crystal structures are well-correlated with the theoretical calculations (Figure S18). Consequently the aromaticity of the perylene (larger HOMA values) relocates from the (two) naphthalene parts into the anthracene unit upon the two-electron oxidation (bold in Figure 4 and Scheme 2).

Further addition of NOSbF$_5$ (totally 2 eq.) to \(2\) resulted in the formation of dicarboxylic species \(2^{2+}\). The appearance of visible band at 700 nm (Figure 3b) and the disappearance of the ESR signals indicate that the singlet state of \(2^{2+}\) is more stable than triplet state. The ground state of dicarboxylic species was also estimated to be singlet by the DFT calculations. The excitation at 724 nm is responsible for the observed absorption of \(2^{2+}\) at 700 nm. This excitation is associated from HOMO to LUMO with the oscillator strength of 1.71. In spite of many attempts, the crystals of \(2^{2+}\) suitable for X-ray measurement could not be obtained so far. Theoretical calculations for \(2^{2+}\) predict similar behavior to \(1^{2+}\); the bond lengths at C4-C5, C6-C6a, C10-C11, and C12-C12a become longer and those at C3a-C4, C5-C6, C6a-C6b, C6b-C12d, C9b-C12d, C9b-C10, C11-C12, and C12a-C12b become shorter, being close to phenanthrene (Figure S16 and Scheme 2).

Considering the resonance contributors of the perylene dication, we realized that the substituted aryl groups control the positions of positive charges, thus the remaining electronic system is willing to satisfy Clar's sextet rule. Eventually the

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**Figure 4.** Crystal structure of a) \(1^{2+}⋅2\text{SbCl}_6\), and the bond lengths (Å) and the calculated HOMA values of b) \(1\) and c) \(1^{2+}⋅2\text{SbCl}_6\). Thermal ellipsoids are scaled at 50% probability.
pristine aromaticity relocates into another unit upon the two-electron oxidation toward the highest number of localized sextets, called “Clar structure” (Scheme 2).

Finally, we have double-checked MO diagrams of 12+ in detail in order to understand the apparent vibronic structure in the absorption spectrum of 12+ at 387, 372, 358, and 346 nm (Figure 3a). At a glance, this characteristic spectral shape is recognizable to π-π* transition of anthracene (λ casi = 377, 358, 341, and 326 nm in CH2Cl2). Curiously, this absorption is assigned to be from HOMO to LUMO+2 of 12+, and their orbital coefficients involve those of HOMO and LUMO of anthracene (dotted squares in Figure 5). These facts inspire us to research the reactivity of perylene dications as the doubly positive charged anthracene. This is our next target.

![Figure 5. MO diagrams of perylene dication 12+ (singlet). Inset shows the frontier orbital of anthracene.](image-url)

In summary, multiple experimental and theoretical evidences proved that the Clar’s rule is still valid to explain and predict the structure and reactivity of dicationic PAHs in a very simple way. In the case of 3,9-diarylperylene, we could find the anthracene structure in the doubly positive-charged conditions, while the phenanthrene skeleton appeared in two-electron oxidized 3,10-diarylperylene. As a matter of facts, 12+ illustrated the characteristics vibronic absorption spectrum around 350 nm. The aromaticity relocation would also occur in other PAHs. Radical cations and dications are not only important intermediates in organic transformations, but also crucial for a wide range of materials because of their intriguing electronic and optical properties. The characteristic absorption spectra of charged PAHs can be seen as their fingerprints, making it possible to identify the compound even in the interstellar medium. We are actively investigating larger PAHs upon oxidation to explore the reactivity of the charged PAHs.

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**Keywords:** aromaticity • oxidation • dication • bond length alternation • perylene

[13] It has been demonstrated by multiple research groups that B3LYP delocalizes the charge in π-conjugated systems. a) M. Renz, K. Theillacker, C. Lambert, M. Kaupp, J. Am. Chem. Soc. 2009, 131,


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