

# Pyrrole-Fused Azacoronene Family: The Influence of Replacement with Dialkoxybenzenes on the Optical and Electronic Properties in Neutral and Oxidized States

Masayoshi Takase,<sup>\*,†</sup> Tomoyuki Narita,<sup>†</sup> Wataru Fujita,<sup>†</sup> Motoko S. Asano,<sup>†</sup> Tohru Nishinaga,<sup>\*,†</sup> Hiroaki Benten,<sup>‡</sup> Kenji Yoza,<sup>§</sup> and Klaus Müllen<sup>\*,||</sup>

<sup>†</sup>Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

<sup>‡</sup>Department of Polymer Chemistry, Graduate School of Science and Engineering, Kyoto University, Katsura, Nishikyo, Kyoto 615-8510, Japan

<sup>§</sup>Bruker AXS, Yokohama, Kanagawa 221-0022, Japan

<sup>||</sup>Max-Planck-Institute for Polymer Research, Ackermannweg 10, Mainz 55128, Germany

## Supporting Information

**ABSTRACT:** A novel pyrrole-fused azacoronene family was synthesized via oxidative cyclodehydrogenation of the corresponding hexaarylbenzenes as the key step, and the crystal structures of tetraazacoronene **3b** and triazacoronene **4a** were elucidated. The photophysical properties for neutral compounds **1–4** were investigated using steady-state UV–vis absorption/emission spectroscopy and time-resolved spectroscopy (emission spectra and lifetime measurements) at both room temperature and 77 K. The observation of both fluorescence and phosphorescence allowed us to estimate the small  $S_1$ – $T_1$  energy gap ( $\Delta E_{S-T}$ ) to be 0.35 eV (**1a**), 0.26 eV (**2a**), and 0.36 eV (**4a**). Similar to the case of previously reported hexapyrrolohexaazacoronene **1** (HPHAC), electrochemical oxidation revealed up to four reversible oxidation processes for all of the new compounds. The charge and spin delocalization properties of the series of azacoronene  $\pi$ -systems were examined using UV–vis–NIR absorption, ESR, and NMR spectroscopies for the chemically generated radical cations and dications. Combined with the theoretical calculations, the experimental results clearly demonstrated that the replacement of pyrrole rings with dialkoxybenzene plays a critical role in the electronic communication, where resonance structures significantly contribute to the thermodynamic stability of the cationic charges/spins and determine the spin multiplicities. For HPHAC **1** and pentaazacoronene **2**, the overall aromaticity predicted for closed-shell dications  $1^{2+}$  and  $2^{2+}$  was primarily based on the theoretical calculations, and the open-shell singlet biradical or triplet character was anticipated for tetraazacoronene  $3^{2+}$  and triazacoronene  $4^{2+}$  with the aid of theoretical calculations. These polycyclic aromatic hydrocarbons (PAHs) represent the first series of nitrogen-containing PAHs that can be multiply oxidized.



## INTRODUCTION

Enormous interest exists in the development of  $\pi$ -electron materials because they exhibit electronic, optoelectronic, and magnetic properties that are suitable for their potential application in molecular electronics.<sup>1–3</sup> Compared to  $\pi$ -conjugated polymers, polycyclic aromatic hydrocarbons (PAHs) exhibit molecular structures and molecular weights that provide advantages in investigations of their fundamental structure–property relationships.<sup>1b,3</sup> From these points of view, several approaches, such as the peripheral modification of known PAHs,<sup>4</sup> the reorganization of fusion patterns,<sup>5–7</sup> and the introduction of curvature,<sup>8,9</sup> have been adopted to produce novel  $\pi$ -electron materials.

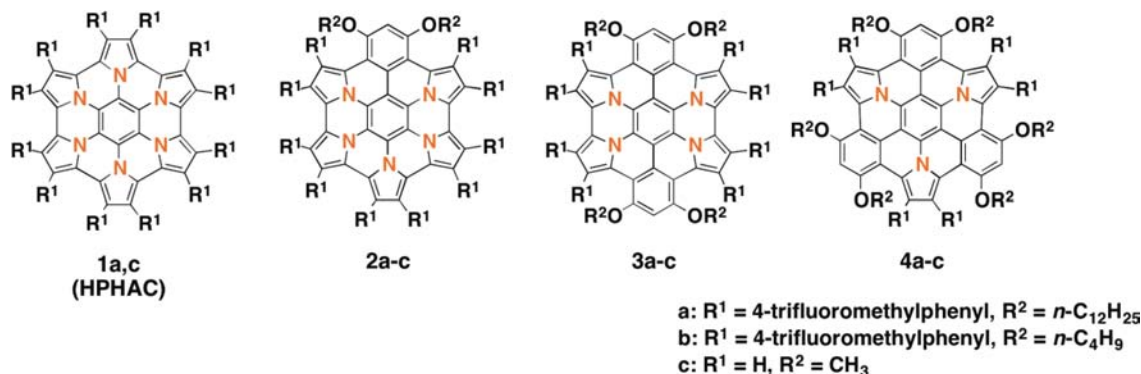
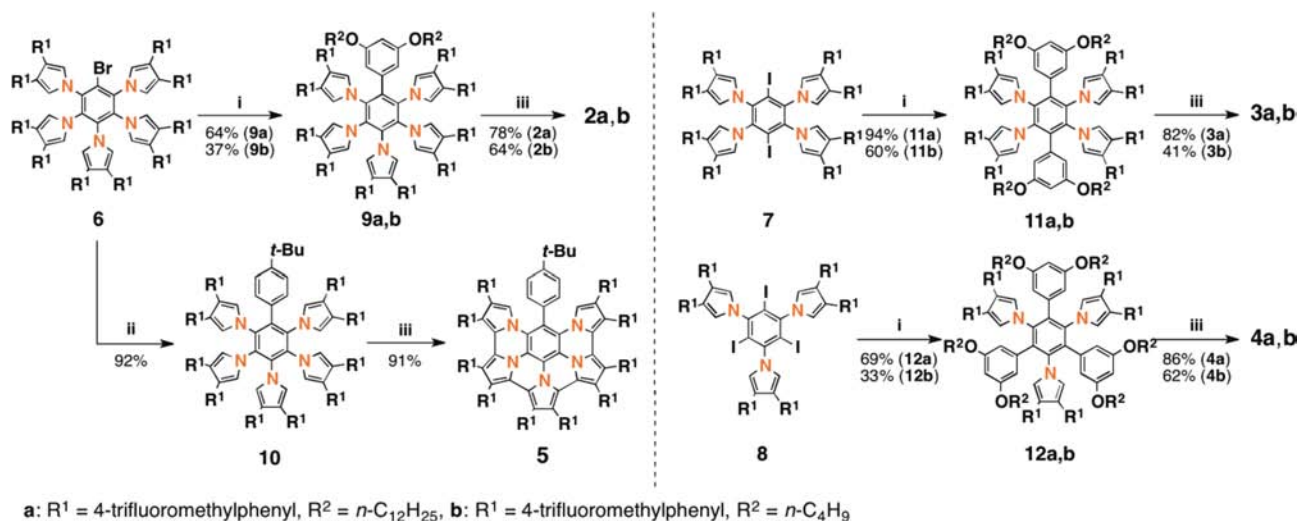
The introduction of heteroatoms, such as nitrogen, into PAHs strongly affects the electronic structures, as has been observed in the case of N-doped carbon materials.<sup>10</sup> Similar to PAHs that incorporate sulfur,<sup>11</sup> nitrogen-containing  $\pi$ -electron

materials with well-defined structures typically have advantageous synthetic routes and/or chemical stabilities compared to recently developed PAHs that contain heteroatoms such as boron, silicon, and phosphorus.<sup>12</sup> As examples of N-doped PAHs, coronene,<sup>13–16</sup> acene,<sup>17–20</sup> triphenylene,<sup>21,22</sup> and other PAH-based  $\pi$ -systems<sup>23,24</sup> have been synthesized. The presence of imino nitrogens increases the overall electron-accepting properties compared to hydrocarbon- and other heteroatom-containing analogues. Therefore, it is well-known that all-carbon triphenylenes are p-type and hexaazatriphenylenes are n-type semiconductors.<sup>22</sup> In addition, metal-ion complexation<sup>15,21a,d</sup> and alkylation/arylation<sup>11g,24,25</sup> can functionalize N-doped PAHs.

Received: March 6, 2013

Published: May 12, 2013

Chart 1. Pyrrole-Fused Azacoronene Family Investigated in This Paper

Scheme 1. Synthesis of Pyrrole-Fused Azacoronenes 2a,b–4a,b and Partially Fused 5<sup>a</sup>

<sup>a</sup>Reagents and conditions: (i) (3,5-dialkoxyphenyl)boronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, Aliquat 336, in toluene and H<sub>2</sub>O; (ii) 4-(*tert*-butylphenyl)boronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, Aliquat 336, in toluene and H<sub>2</sub>O; (iii) FeCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>NO<sub>2</sub>.

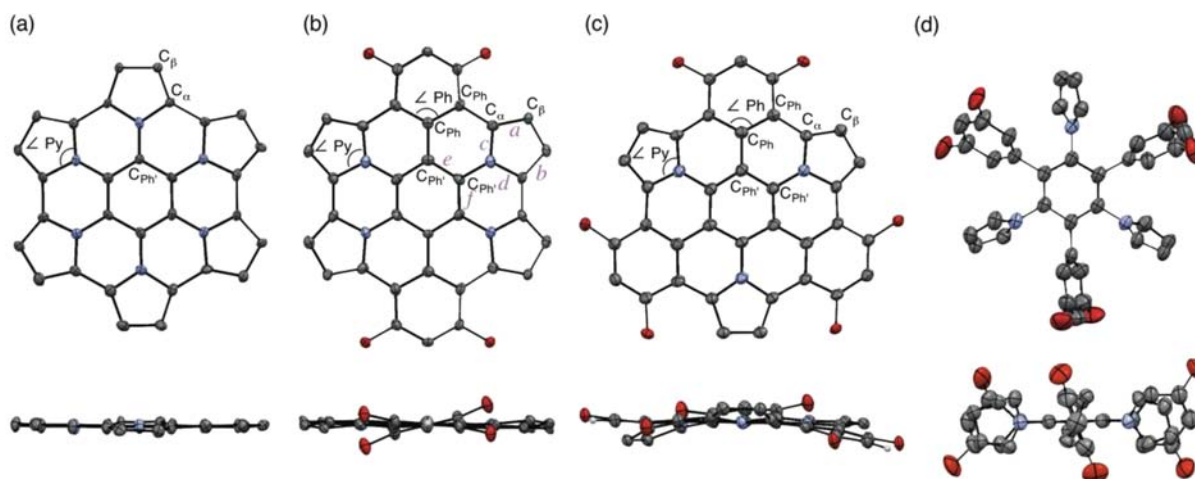
In contrast to the above-mentioned N-doped  $\pi$ -systems that possess electron-accepting pyridine-type nitrogens, pyrrole and its derivatives contain electron-donating nitrogen atoms. Because this nitrogen offers two electrons to the five-membered ring, pyrrole is an aromatic and electron-rich compound. Some biological materials, pigments,<sup>26</sup> and conductive polymers based on the pyrrole-containing  $\pi$ -system<sup>27</sup> have been investigated, but few variations are known compared to the number of variations in the pyridine-type  $\pi$ -system. Synthetic studies on large pyrrole-containing  $\pi$ -systems are rather limited to the porphyrin and phthalocyanine derivatives.<sup>28</sup> Therefore, we recently demonstrated that cyclodehydrogenation of hexapyrrolobenzene effectively yielded a fused structure (i.e., hexapyrrolohexaazacoronene **1** (HPHAC)),<sup>16</sup> where six pyrroles were circularly connected (Chart 1). The crystal structure of dication **1**<sup>2+</sup> clearly revealed that the quinoidal structures of the fused-pyrrole moiety played a critical role in stabilizing the oxidation state.

In the present study, we have designed and synthesized a series of pyrrole-fused azacoronenes **2–4** in which some of the pyrrole rings of HPHAC are replaced with dialkoxybenzenes. The nature of the charge distribution, the delocalization, and the charge carriers is one of the most important subjects in conjugated polymers.<sup>29</sup> Therefore, *linear* conjugated oligomers with mixed-valence or charged states have attracted funda-

mental interest as model systems for charge-transfer and charge-conductive phenomena.<sup>27a,b,d,e,30,31</sup> However, the  $\pi$ -systems that include five- and six-membered rings within the same PAHs have never been investigated systematically. The marriage of these aromatics should influence their redox properties and the electronic nature of their oxidation states as well as the photophysical properties of their neutral states. Herein, we report chemical features of the series of nitrogen-containing PAHs that possess small S<sub>1</sub>–T<sub>1</sub> energy gaps and can be multiply oxidized with different spin multiplicities in their dication states.

## RESULTS AND DISCUSSION

**Synthesis.** In a manner similar to that used for a hydrocarbon analogue (i.e., hexa-*peri*-hexabenzocoronene (HBC)),<sup>32</sup> the synthesis of a series of new pyrrole-fused azacoronenes **2–4** was conducted following our previously published procedure,<sup>16</sup> where oxidative cyclodehydrogenation is the key step (Scholl reaction).<sup>32,33</sup> As shown in Scheme 1, the hexaaryl precursors **9–12** were prepared by selective nucleophilic aromatic substitutions (S<sub>N</sub>Ar) of the corresponding fluoroarenes with  $\beta$ -diarylpyrrole to yield **6–8**<sup>34</sup> followed by successive Suzuki–Miyaura coupling. Final planarization with FeCl<sub>3</sub> afforded targets **2–4** in good yields (41–86%). Notably, the 3,5-dialkoxyphenyl group appears to be required for



**Figure 1.** Crystal structures of (a) **1a**,<sup>16</sup> (b) **3b**, (c) **4a**, and (d) **12b**. Thermal ellipsoids are at 50% probability. Solvent molecules, H atoms, and peripheral alkyl and aryl groups are omitted for clarity.

**Table 1.** Selected Mean Bond Lengths (Å)<sup>a</sup> and Inner Angles (deg)<sup>a</sup> for **1a**, **3b**, **4a**, and **12b** from the Crystal Structures

	$C_{\beta}-C_{\beta}$	$C_{\alpha}-C_{\beta}(a)$	$N-C_{\alpha}(c)$	$C_{\beta}-C_{\beta}$	$C_{\alpha}-C_{\alpha}$	$N-C_{Ph'}$	$C_{Ph'}-C_{Ph'}(e)$	$C_{Ph'}-C_{Ph'}(f)$	$C_{\alpha}-C_{Ph}$	$C_{Ph}-C_{Ph'}$	$C_{Ph}-C_{Ph}$	$\angle Py$	$\angle Ph$
<b>1a</b> <sup>b</sup>	1.438(1)	1.390(1)	1.395(1)	1.483(1)	1.366(1)	1.371(1)	—	—	—	—	—	113.5(1)	—
<b>3b</b>	1.438(4)	1.398(3)	1.387(3)	1.447(5)	1.380(3)	1.399(3)	1.478(4)	1.430(6)	1.434(3)	1.434(3)	112.6(4)	122.8(4)	
<b>4a</b>	1.436(4)	1.389(3)	1.395(2)	—	1.381(3)	1.396(3)	1.464(3)	1.448(1)	1.416(3)	1.416(3)	111.5(2)	123.4(3)	
<b>12b</b>	1.435(5)	1.362(2)	1.401(2)	—	1.426(3)	1.400(2)	—	1.488(3)	1.384(3)	1.384(3)	107.8(1)	120.4(1)	

<sup>a</sup>The values were averaged for  $C_{6v}$  (**1a**),  $D_{2h}$  (**3b**),  $D_{3h}$  (**4a**), and  $C_3$  (**12b**) symmetry. The estimated standard deviations (esd) of mean values were calculated from the experimental esd values using the following equation:  $\delta(l) = 1/(\sum(1/\delta_i^2))^{1/2}$ . <sup>b</sup>Reference 16.

complete planarization of the azacoronene core. When Scholl reaction was performed with **10**, which possesses a 4-*tert*-butylphenyl group instead of a 3,5-dialkoxyphenyl group, partially fused **5** was obtained as the main product (91%) even though the completely fused structure was also detected by matrix-assisted laser desorption ionization (MALDI) mass spectrometry. Insight into this different reactivity was obtained from the molecular orbitals near the highly occupied molecular orbital (HOMO). For **9c**, the HOMO (−5.56 eV) is localized on all of the peripheral pyrrole and dialkoxyphenyl groups; however, the HOMO (−5.51 eV) of **10** shows localization of the MO on the pyrrole rings primarily at the meta- and para-positions from the 4-alkylphenyl group. This result indicates a low probability of the localization of radical cations required to lead to complete planarization. A MO similar to that of **9c** appears at HOMO−3 (−5.58 eV) for **10** (Figure S2 in Supporting Information). The <sup>1</sup>H NMR resonances of the phenyl ring between the two alkoxy groups shifted downfield (i.e.,  $\Delta\delta = 0.43$  (**2a**), 0.41 (**3a**), and 0.18 (**4a**) ppm, respectively), which reflects the complete planarization and the effective  $\pi$ -electron conjugation. As revealed in the previous  $\pi$ -system **1** (HPHAC),<sup>16</sup> the azacoronenes **2a–4a** were also thermally and photochemically stable (Figures S3 and S13 in SI).

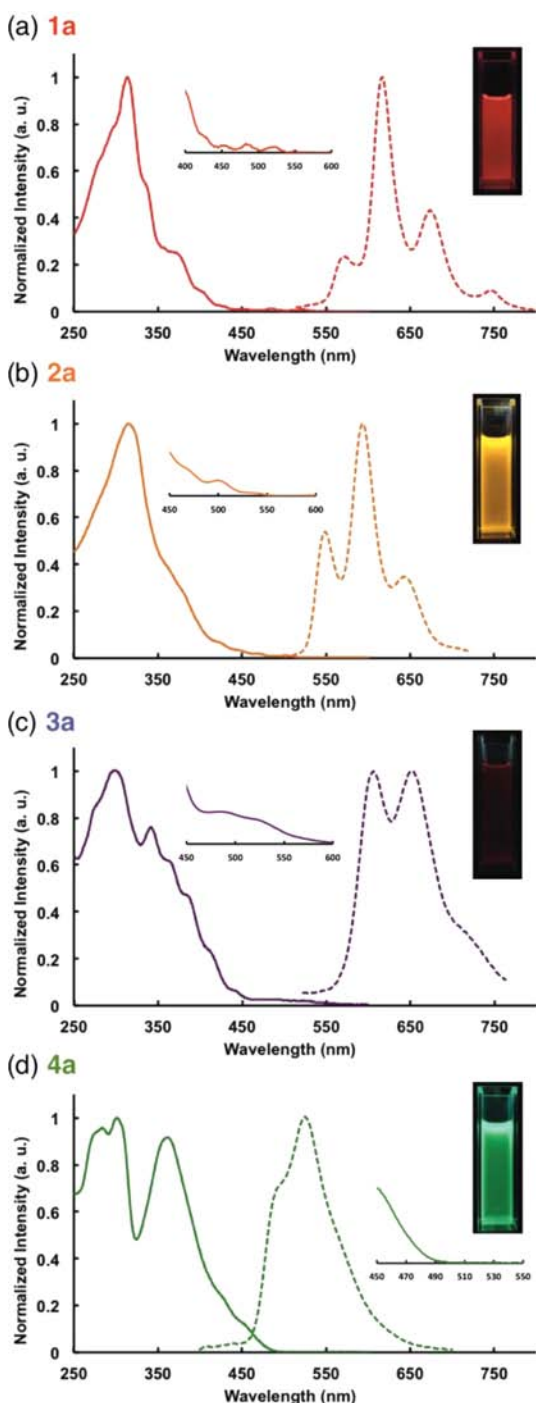
**X-ray Crystal Structures.** Single-crystal X-ray structure determinations were performed on **3b**, **4a**, and **12b** (Figure 1). The planarized azacoronene structures of **3b** and **4a** were confirmed by X-ray crystallography, whereas a  $C_3$ -symmetric propeller structure was observed for **12b**. The  $\pi$ -systems of **3b** and **4a** were only slightly strained due to the bulky substitutions on the pyrrole and benzene rings (Figure S4 in SI), and no  $\pi$ - $\pi$

interactions were observed (Figure S5 in SI). Table 1 shows the selected geometrical parameters of **1a**, **3b**, **4a**, and **12b**. Briefly, in association with the planarization, the bond lengths of the peripheral moieties of the original pyrrole (Py) (i.e.,  $C_{\alpha}-C_{\beta}(a,b)$ ) and the phenyl (Ph) group (i.e.,  $C_{Ph}-C_{Ph}$ ) increase, whereas the bond lengths between the central benzene (Ph') and the peripheral aryl groups (i.e.,  $N-C_{Ph'}$  and  $C_{Ph}-C_{Ph'}$ ) tend to decrease with little changes in the central benzene unit (i.e.,  $C_{Ph'}-C_{Ph'}(e,f)$ ). The inner mean angles of the original aryl groups become wider compared to those of **12b**.

**Photophysical Properties in the Neutral States.** The UV–visible absorption and emission spectra of **1a–4a** in  $CH_2Cl_2$  are shown in Figure 2, and their optical properties are summarized in Table 2. As shown in the insets of Figure 2, the small molar extinction coefficients ( $\epsilon$  for the 0–0 transition in the range of 1400–2300 mol<sup>−1</sup> L cm<sup>−1</sup>) indicate that the transitions from the ground to the excited singlet state ( $S_0 \rightarrow S_1$ ) are partially allowed for **1a–3a**, which is typical phenomena for disc-shaped molecules with high symmetry.<sup>5a,55</sup> A similar trend was also observed for **4a**; however, the  $S_0 \rightarrow S_1$  transition is allowed with a 10-fold larger  $\epsilon$  than those of **1a–3a**. The solutions were all light-yellow in color but showed colorful emissions from red to green as the number of pyrrole rings decreased from **1** to **4** (Figure 2, insertion). The fluorescence quantum yields ( $\Phi_F$ ) were ~2% for **1a**, **2a**, and **4a** and 0.1% for **3a**. The small  $k_f \approx 1 \times 10^6$  s<sup>−1</sup> calculated from the  $\Phi_F$  and the fluorescence lifetimes ( $\tau_F$ ) of **1a–3a** are well correlated to the partially allowed  $S_0 \rightarrow S_1$  transitions observed in their absorption spectra (Table 2).

To investigate the triplet state properties of the azacoronene family, emission spectra and lifetimes were measured in 2-





**Figure 2.** Absorption (solid line) and emission (dotted line) spectra of azacoronenes **1a–4a** in  $\text{CH}_2\text{Cl}_2$  at room temperature. Insets show enlargements of the cutoff region of the absorption spectra and photographs of the solutions under irradiation with UV light (254 nm).

methyltetrahydrofuran (MTHF) rigid glass at 77 K. Figure 3 shows the prompt emission spectra of **1a–4a** in MTHF at both 298 and 77 K and phosphorescence spectra at 77 K. Here, the fluorescence spectra at 77 K can be obtained by subtracting the corresponding phosphorescence fraction from the prompt emission spectra. Notably, the  $S_1$ – $T_1$  energy gaps ( $\Delta E_{S-T}$ ), which is less than 0.36 eV, were smaller than those of condensed PAHs, including HBC (0.5 eV),<sup>36</sup> chrysene (0.9 eV), and naphthalene (1.5 eV) (Figure S9 in SI).<sup>37</sup> The small

$\Delta E_{S-T}$  should play a critical role in the efficient formation of the triplet state in the azacoronenes<sup>38</sup> because they lack heavy atoms and involve no clear  $n$ – $\pi^*$  transition around the  $S_1$  states (Figures S10 and S11 in SI).<sup>39</sup>

The relative phosphorescence intensity and the phosphorescence lifetime ( $\tau_p$ ) varied drastically for **1a–4a**. The noticeable phosphorescence and the long  $\tau_p$  (1100 ms) from **4a** at 77 K can be explained by the reduced  $T_1 \rightarrow S_0$  intersystem crossing due to its large  $E_T$  because the  $E_T$  estimated from the phosphorescence 0–0 transition decreased from 2.25 eV (**4a**) to 2.03 eV (**2a**) and 1.95 eV (**1a**). The lack of phosphorescence of **3a** may be due to a smaller  $E_T$ , which results in a larger  $T_1 \rightarrow S_0$  intersystem crossing rate compared to that of **1a**.

**Electrochemistry.** To investigate the redox properties, cyclic voltammograms (CV) were measured in  $\text{CH}_2\text{Cl}_2$  (Figure 4, Table 3). Similar to HPHAC **1a**, whose CV exhibited three reversible oxidation peaks,<sup>16</sup> partially substituted **2a–4a** exhibited up to four reversible oxidation peaks under the measurement conditions (Figure 4). Differential pulse voltammetry experiments confirmed that each wave corresponded to the transfer of a single electron (Figure S14 in SI). Notably, although the first two peaks for all of compounds have similar oxidation potentials, the differences between the second and third peaks ( $\Delta E^{\text{ox3-ox2}}$ ) are smaller in the order of **1a** > **2a** > **3a**  $\cong$  **4a**, which is consistent with the trend observed in the DFT results (Figure 5). On the basis of the structural differences, the introduction of dialkoxybenzenes instead of pyrrole rings decreases onsite Coulombic repulsion in the step from dication to trication; however, it does not change their first two oxidation potentials. Therefore, an investigation of the electronic properties in these oxidation states was then performed with chemically generated radical cations and dications.

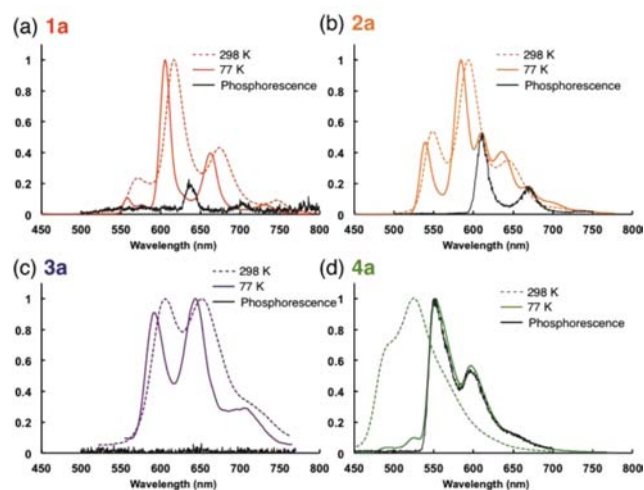
**Chemical Oxidations and Crystal Structure of  $4b^{2+}$ .** Chemical oxidation was conducted with  $\text{SbCl}_5$  in  $\text{CH}_2\text{Cl}_2$  at room temperature. Figure 6 shows the absorption spectra of the radical cation and dication states of **1a** and **2b–4b**.<sup>40</sup> When the oxidant was added incrementally to the solutions, the spectra changed dramatically with isosbestic points, which strongly supports the sequential oxidation of the  $\pi$ -systems from a neutral to a radical cation ( $M^{\bullet+}$ ) and then to a dication ( $M^{2+}$ ) (Figure S15 in SI). Therefore, neither disproportionation from two radical cation species into neutral and dication species nor  $\pi$ -dimer formation between two radical cation species<sup>30e,g,31e,h</sup> nor follow-up chemical reactions, including decomposition, were observed under the measurement conditions.

In the course of the chemical oxidation of a series of compounds, single crystals suitable for the X-ray single-crystal structure analyses were obtained for  $4^{2+}$  in the  $4b^{2+}(\text{SbCl}_6^-)_2$  form. The presence of two counteranions clearly identified the dication state, and similar to the neutral structure of **4a**, the azacoronene moiety was nearly planar (Figure 7). Notably, a comparison of the mean bond lengths near the pyrrole units of neutral **4a** and dication  $4b^{2+}$  indicates a contribution from the quinoidal structures of  $4^{2+}$ , which was previously reported for  $1^{2+}(\text{SbCl}_6^-)_2$ <sup>16</sup> (for  $4b^{2+}(\text{SbCl}_6^-)_2$ ,  $N$ – $C_\alpha$  1.389(3),  $C_\alpha$ – $C_\beta$  1.413(3),  $C_\beta$ – $C_\beta$  1.412(5), and  $C_\alpha$ – $C_{Ph}$  1.438(3) Å). In addition, the mean bond length of  $O$ – $C_{Ph}$  (1.336(3) Å) for the dication decreased compared to that of the neutral form (1.358(2) Å). Therefore, the resonance structures—the so-called benzenoid and quinoid structures—contribute significantly to the stabilization of the cationic charges where

Table 2. Optical Parameters of 1a–4a<sup>a</sup>

		absorption				emission					Stokes shifts (cm <sup>-1</sup> )	$\Delta E_{S-T}$ (eV)	
		$\lambda_{\max}^b$ (nm)	$\epsilon$	$E_S^c$ (eV)	$\lambda_{\max}^b$ (nm)	$E_T^c$ (eV)	$\Phi_F^d$	$\tau_F$ (ns)	$k_f^e$ (10 <sup>6</sup> s <sup>-1</sup> )	$k_n + k_{isc}^f$ (10 <sup>7</sup> s <sup>-1</sup> )			$\tau_D$ (ms)
1a	rt <sup>g</sup>	521	1429	2.30	571	1.95	0.015	16 <sup>h</sup>	0.91 <sup>h</sup>	6.0 <sup>h</sup>	100	1531 <sup>h</sup>	0.35
	77 K <sup>h</sup>	517			557	2.03	39			250	1370		
2a	rt <sup>g</sup>	504	1584	2.29	548	2.03	0.018	15 <sup>h</sup>	1.2 <sup>h</sup>	6.6 <sup>h</sup>	–	403 <sup>h</sup>	0.26
	77 K <sup>h</sup>	500			540	–	23			–	81		
3a	rt <sup>g</sup>	528	2322	2.18	602	–	0.001	1.1 <sup>h</sup>	0.88 <sup>h</sup>	88 <sup>h</sup>	–	2740 <sup>h</sup>	–
	77 K <sup>h</sup>	518			597	–	2.5			–	2176		
4a	rt <sup>g</sup>	451	15670	2.61	493 (sh)	–	0.017	6.3 <sup>h</sup>	2.7 <sup>h</sup>	16 <sup>h</sup>	–	1854 <sup>h</sup>	0.36
	77 K <sup>h</sup>	456			525	2.25	6.6			1100	1693		

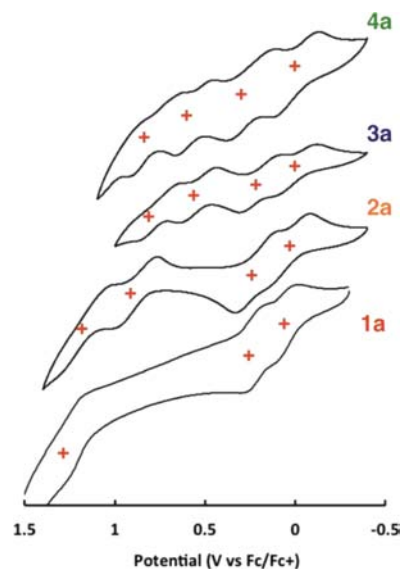
<sup>a</sup> $\Phi_F$ , quantum yield of fluorescence;  $\tau_F$ , lifetime of fluorescence;  $k_f$ , radiative rate constant;  $k_n$ , nonradiative decay rate constant;  $k_{isc}$ , intersystem crossing rate constant. <sup>b</sup>The 0–0 transition wavelength. <sup>c</sup>Calculated from the 0–0 transition wavelength. <sup>d</sup>Determined by comparison with quinine sulfate in 0.5 M H<sub>2</sub>SO<sub>4</sub> ( $\Phi = 0.51$ ). <sup>e</sup> $k_f = \Phi_F/\tau_F$ . <sup>f</sup> $k_n + k_{isc} = (1/\tau_F) - k_f$ . <sup>g</sup>Measured in CH<sub>2</sub>Cl<sub>2</sub>. <sup>h</sup>Measured in MTHF.



**Figure 3.** Prompt emission spectra of 1a–4a in MTHF at 298 K (dotted colored line) and 77 K (solid colored line) and phosphorescence spectra at 77 K (black solid line). The phosphorescence fractions were collected from the time domain from 15.0 to 15.1 ms after excitation.

heteroatoms with large electronegativities, such as nitrogen and oxygen, support the localization of cations.

**Electronic Properties in the Oxidized States.** To investigate the electronic properties of the cationic species, electron spin resonance (ESR) spectra were measured for the radical cations of 1a and 2b–4b with the solutions prepared under the above-mentioned conditions. Broad but flat single-line signals were observed for all of the azacoronenes, which indicates the presence of delocalized radical cations ( $g = 2.0023–2.0034$  and  $\Delta H = 0.24–0.30$  mT, Figure S16 in SI). In contrast, the dications of 1a and 2b–4b were all ESR-silent at room temperature, and thus NMR spectra were measured to examine the closed- or open-shell nature. In the presence of Fe(C<sub>5</sub>H<sub>4</sub>Ac)<sub>2</sub>·AgBF<sub>4</sub>,<sup>41</sup> 1.0 mM CD<sub>2</sub>Cl<sub>2</sub> solutions of all of the dications were prepared with a 1.0 M CD<sub>3</sub>CN solution of NOSbF<sub>6</sub>, and the absorption spectra were monitored. As previously reported for 1a<sup>2+</sup>,<sup>16</sup> sharp <sup>1</sup>H NMR spectrum of 2b<sup>2+</sup> was obtained with low-field shifts at room temperature (Figure S17 in SI). These ESR and NMR results clearly demonstrated the closed-shell nature of 2b<sup>2+</sup>, which is consistent with the results for 1a<sup>2+</sup>. The <sup>1</sup>H NMR spectra of 3b<sup>2+</sup> and 4b<sup>2+</sup> showed severe broadening in the aromatic region under the same conditions in the range of 233–298 K.<sup>42</sup> Therefore, super-



**Figure 4.** Cyclic voltammograms of 1a–4a in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mM). Conditions: concentration, 1.0 mM; supporting electrolyte, 0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>; working electrode, Pt; reference electrode, Ag/AgNO<sub>3</sub>; counterelectrode, Pt wire; scan rate, 100 mV/s, potentials, vs Fc/Fc<sup>+</sup>.

**Table 3.** Oxidation Potentials ( $E^{\text{ox}}$ ) of 1a–4a in CH<sub>2</sub>Cl<sub>2</sub>

	$E_{1/2}^{\text{ox}1}$ (V)	$E_{1/2}^{\text{ox}2}$ (V)	$E_{1/2}^{\text{ox}3}$ (V)	$E_{1/2}^{\text{ox}4}$ (V)	$\Delta E^{\text{ox}3-\text{ox}2}$ (V)
1a	0.04	0.23	1.23	1.80 (p.a.) <sup>a</sup>	1.00
2a	0.03	0.22	0.88	1.17	0.66
3a	0.00	0.21	0.54	0.76	0.33
4a	0.00	0.25	0.56	0.77	0.31

<sup>a</sup>Quasi-reversible. Potential was estimated by differential pulse voltammetry (DPV).

conducting quantum interference device (SQUID) measurements were performed for the powder sample of 4b<sup>2+</sup>(SbCl<sub>6</sub><sup>-</sup>)<sub>2</sub>, which resulted in nearly zero magnetic susceptibilities at 100–300 K (Figure S18 in SI).<sup>42</sup> On the basis of the ESR, NMR, and SQUID results, the triazacoronene dication 4b<sup>2+</sup> is supposed to be an open-shell singlet biradical.<sup>7,43</sup> The DFT calculations of 4b<sup>2+</sup> with the crystal structure geometry also support the experimental results. Therefore, a comparison of the energies for the three possible configurations revealed that the singlet biradical state was most stable compared to the other closed-shell and triplet states (Table 4), which will be discussed in the next section.<sup>44</sup>

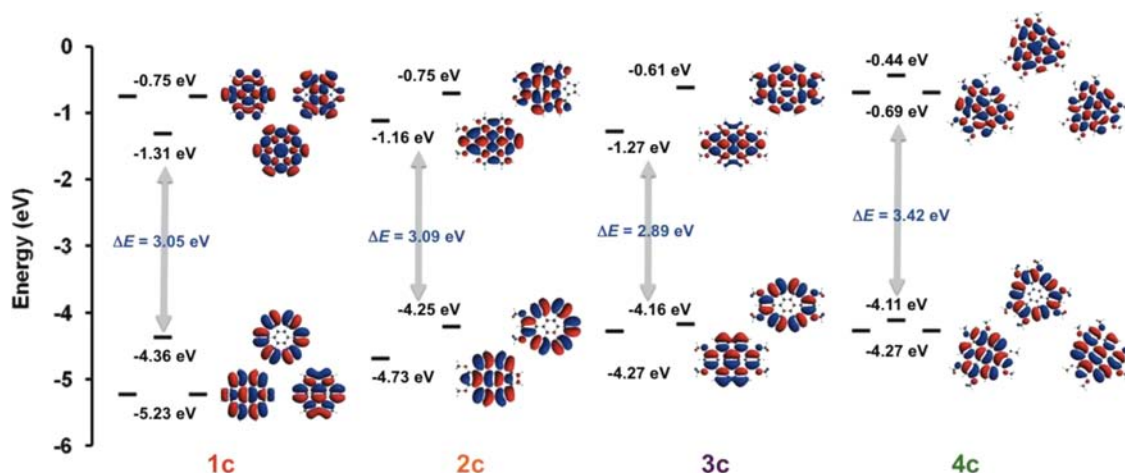


Figure 5. Molecular orbital diagrams of **1c**–**4c** calculated at the B3LYP/6-31G(d) level of theory.

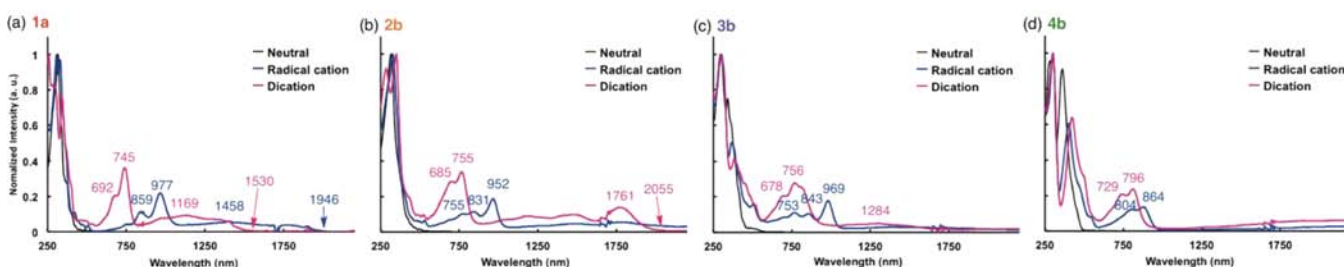


Figure 6. Absorption spectra of the radical cations and dications of **1a** and **2b**–**4b** (1.0 mM) generated by the presence of 1.5 and 3.0 equiv of  $\text{SbCl}_5$  in  $\text{CH}_2\text{Cl}_2$  at room temperature.

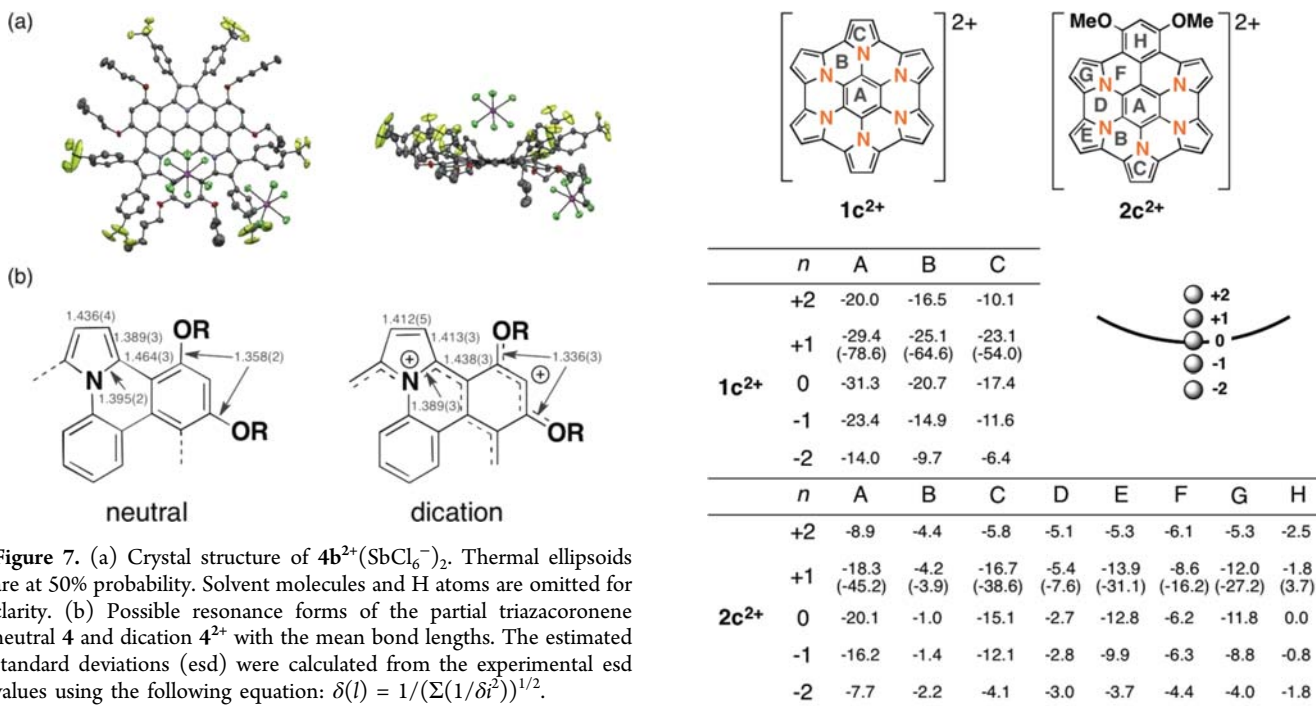


Figure 7. (a) Crystal structure of  $\mathbf{4b}^{2+}(\text{SbCl}_6^-)_2$ . Thermal ellipsoids are at 50% probability. Solvent molecules and H atoms are omitted for clarity. (b) Possible resonance forms of the partial triazacoronene neutral **4** and dication  $\mathbf{4}^{2+}$  with the mean bond lengths. The estimated standard deviations (esd) were calculated from the experimental esd values using the following equation:  $\delta(l) = 1/(\sum(1/\delta_i^2))^{1/2}$ .

For the experimentally confirmed closed-shell dications  $\mathbf{1a}^{2+}$  and  $\mathbf{2a}^{2+}$ , nucleus-independent chemical shift (NICS) values<sup>45</sup> were evaluated to study the aromaticity using DFT calculations. The total MO contributions to the  $zz$  (i.e., out-of-plane) component of the NICS tensor ( $\text{NICS}(1)_{zz}$ ) are also depicted (Figure 8).<sup>46</sup> The NICS results for  $\mathbf{1c}^{2+}$  showed large negative values for all of the calculated points. Interestingly, the values

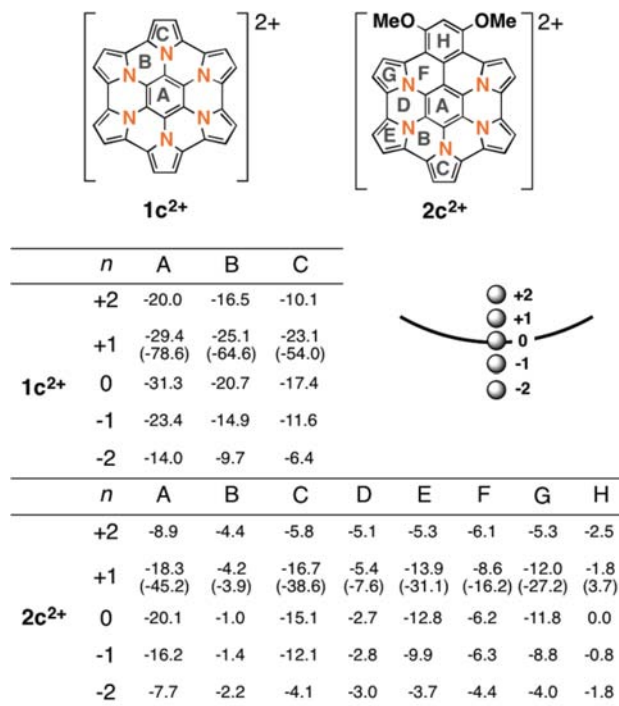


Figure 8. NICS( $n$ ) values ( $\text{NICS}(1)_{zz}$ ) of the dications  $\mathbf{1c}^{2+}$  and  $\mathbf{2c}^{2+}$  at various points. The calculations were performed at GIAO/HF/6-311+G(d,p)//B3LYP/6-31G(d) level of theory. Values of  $n = +2$  to  $-2$  are distances in Å from the ring centers of each ring. The optimized structures of  $\mathbf{1c}^{2+}$  and  $\mathbf{2c}^{2+}$  are slightly bent with symmetries of  $C_{6v}$  and  $C_s$ , respectively (Figure S19 in SI).



were distinct in the concave area. Furthermore, the largest absolute values were obtained at the center of the azacoronene and became smaller toward the periphery (from A to C ring), which suggests that the overall aromatic character for  $1c^{2+}$  resulted from the quinoidal resonance structures of the fused-pyrrole moiety.<sup>16</sup> A similar trend was also observed for  $2c^{2+}$  but with much smaller absolute values. In analogy to  $1c^{2+}$ , the center points above and below the A ring had relatively large absolute values, and those in the outer dialkoxybenzene (i.e., the H ring) were negligibly small due to the quinoidal structure. The introduction of dialkoxybenzene thus appears to prohibit the cyclic  $\pi$ -conjugation in the dication states, resulting in smaller NICS values, which, in turn, indicates weaker aromatic character of  $2c^{2+}$  compared to that of  $1c^{2+}$ . These aromatic characteristics most likely support the discriminatively large differences (i.e., onsite Coulombic repulsion) between the second and third oxidation potentials ( $\Delta E^{\text{ox3-ox2}}$ ) of **1a** and **2a** described above. Once azacoronenes are oxidized to the dication states, aromatic stabilization of the  $\pi$ -system is obtained by overall bond alternation (i.e., resonance), which leads to difficulty in the third oxidation steps.

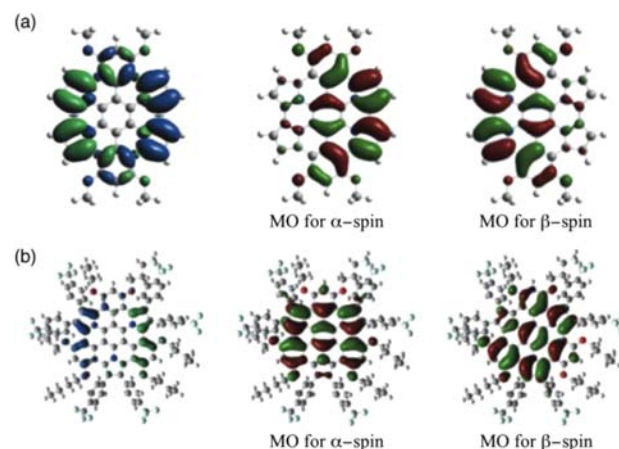
**DFT Consideration of the Spin Multiplicity of the Dications.** To shed some light on the spin multiplicity of the dications, especially of the NMR- and ESR-silent  $3b^{2+}$  and  $4b^{2+}$  dications, theoretical calculations of the energies for the three possible configurations were conducted using DFT: a restricted wave function with a closed-shell configuration (R), an unrestricted wave function with an open-shell singlet configuration (singlet biradical: U), and an unrestricted wave function with an open-shell triplet configuration (T). Table 4

**Table 4. Relative Energies in kcal mol<sup>-1</sup> for the Dication of 1c–4c and 4b in the Spin-Restricted Singlet (R), Spin-Unrestricted Singlet (U), and Triplet (T) States at the B3LYP/6-31G(d) level**

	$\Delta E(\text{R-U})$	$\Delta E(\text{T-U})$	$\Delta E(\text{T-R})$
$1c^{2+}$	0.04	16.44	16.39
$2c^{2+}$	0.00	6.13	6.13
$3c^{2+}$	3.56	0.15	-3.40
$4c^{2+}$	0.01	-2.24	-2.25
$4b^{2+a}$	3.10	4.75	1.65

<sup>a</sup>The geometry was obtained from the single-crystal structures.

summarizes the relative energies of these three states. Although the energy differences of the closed-shell and open-shell singlet ( $\Delta E_{\text{R-U}} = \Delta E_{\text{RB3LYP}} - \Delta E_{\text{UB3LYP}}$ ) of  $1c^{2+}$  and  $2c^{2+}$  were nearly equal, those of the open-shell triplet and closed-shell singlet ( $\Delta E_{\text{T-R}}$ ) favored the stabilities of their closed-shell singlets, which were consistent with the experimental results that indicated the closed-shell nature of  $1a^{2+}$  and  $2a^{2+}$ . For  $3c^{2+}$ , the open-shell singlet biradical and triplet states were in agreement with the NMR results and were evaluated to be stable compared to the closed-shell singlet by 3.6 and 3.4 kcal mol<sup>-1</sup>, respectively. A comparison between the open-shell triplet and singlet ( $\Delta E_{\text{T-U}}$ ) indicated that the singlet biradical state of  $3c^{2+}$  had a slightly lower energy than the triplet state. The  $\langle S^2 \rangle$  value of 0.59 for the singlet state also supports the biradical character of  $3c^{2+}$ . Notably, the spin-density maps of the singly occupied molecular orbital (SOMO) and the MOs for the  $\alpha$ - and  $\beta$ -spins were disjointed by the dialkoxybenzenes (Figure 9a and Figure S20 in SI). Similar phenomena for the singlet biradical states have been previously reported.<sup>7,31g,43</sup>



**Figure 9.** Spin-density maps of SOMO and molecular orbitals for the  $\alpha$ - and  $\beta$ -spins of (a)  $3c^{2+}$  and (b)  $4b^{2+}$  in the singlet biradical states. Isovalues are  $0.0004 \text{ e } \text{\AA}^{-3}$  for the spin densities and  $0.02 \text{ e } \text{\AA}^{-3}$  for the MOs. The geometry of  $4b^{2+}$  was obtained from the single-crystal structures.

Triazacoronene dication  $4c^{2+}$  exhibited a stable triplet state compared to the closed-shell singlet and singlet biradical states by  $\sim 2.3 \text{ kcal mol}^{-1}$ , even though the experimental characterizations and the single-point calculations based on the crystal structure geometry of  $4b^{2+}$  revealed that the singlet biradical was the most stable state. According to the DFT results for  $4c^{2+}$ , the bond lengths and the inner angles of the peripheral aryl moieties are averaged in a symmetric fashion of  $D_{3h}$ ,  $C_{2v}$  and  $C_s$  for R, U, and T, respectively. The spin-density maps and the MOs for  $4b^{2+}$  with the crystal structure geometry possess a symmetry plane as demonstrated in Figure 9b, which indicates the comparative similarity to the symmetries of the calculated open-shell states ( $C_{2v}$  or  $C_s$ ) than the  $D_{3h}$  of the closed-shell state. In general, open-shell singlet biradical character appears at an intermediate interaction strength of two spins. In this context, the closed-shell nature of the pyrrole-rich  $1^{2+}$  and  $2^{2+}$  can be concluded to be caused by the quinoidal resonance structure of the fused-pyrrole moiety. The replacement of the pyrrole ring with dialkoxybenzene tends to prohibit the spin-spin interaction, which leads to the singlet biradical and triplet characteristics of azacoronenes  $3^{2+}$  and  $4^{2+}$ .<sup>47</sup>

## SUMMARY AND CONCLUSION

We have demonstrated the comprehensive synthesis and characterization of a series of pyrrole-fused azacoronenes, which differs in the size and symmetry of their  $\pi$ -systems. Similar to the case of the hydrocarbon analogue (i.e., HBC), the synthesis of the planarized disc structures was conducted on the basis of the oxidative cyclodehydrogenation reactions of the corresponding hexaarylbenzenes. The introduction of two alkoxy groups at the meta-positions on the benzene ring was found to effectively promote the key coupling reaction between not only the pyrrole-pyrrole rings but also the pyrrole-benzene rings, which provided an opportunity to study the optical and electronic properties in their neutral and oxidized states. Reflecting their different  $\pi$ -conjugation system, the stepwise substitution of the pyrrole with dialkoxybenzene rings drastically altered the optical properties. Their small  $\Delta E_{\text{S-T}}$  values ( $< 0.36 \text{ eV}$ ) may be of fundamental importance in the area of molecular photonics because thermally activated  $T_1 \rightarrow S_1$  intersystem crossing can be possible without use of high

excitation power density or the coherent laser for triplet–triplet annihilation (TTA) process.<sup>48</sup>

Although the fusion of the pyrrole and dialkoxybenzene rings does not induce discriminative differences in the spin delocalization nature for their radical cation species, the electronic properties of the dication species differ substantially. Hexaazacoronene  $1^{2+}$  and pentaazacoronene  $2^{2+}$  clearly exhibited a closed-shell nature, whereas tetraazacoronene  $3^{2+}$  and triazacoronene  $4^{2+}$  exhibited an open-shell nature. For the pyrrole-rich compounds, higher oxidation states (more than trication) became difficult to achieve due to the resonance structures of  $1^{2+}$  and  $2^{2+}$ . From these observations, we concluded that fusion of the pyrrole rings facilitates charge/spin delocalization, which is consistent with the results of the polypyrrole study: in other words, the introduction of dialkoxybenzenes instead of pyrrole rings within the pyrrole-fused azacoronene family tends to prohibit the charge/spin interaction in their dication states. Therefore, replacement of the pyrrole rings with dialkoxybenzenes induces the higher oxidation states and contributes to the appearance of “weakly interacting” spins with open-shell character. In line with our strategy to fuse hybrid aromatics, the further functionalization of polycyclic aromatic hydrocarbons (PAH) would be beneficial for molecular electronics and spintronics with well-defined structures.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and the characterization data for all new compounds; Figure S2–S20, atomic coordinations of the optimized structures of **1c–4c** in neutral and dication states (B3LYP/6-31G(d)), and X-ray data for **3b**, **4a**, **12b**, and **4b**<sup>2+</sup>(SbCl<sub>6</sub><sup>-</sup>)<sub>2</sub> (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

mtakase@tmu.ac.jp (M.T.); nishinaga-tohru@tmu.ac.jp (T.N.); muellen@mpip-mainz.mpg.de (K.M.).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work is supported by a Grant-in-Aid for Scientific Research (No. 22350021 and No. 23750045) from MEXT, Japan, and a research grant from the Noguchi Institute and the Asahi Glass Foundation. We thank Prof. Kotohiro Nomura (Tokyo Metropolitan University) for valuable discussions and Prof. Shinzaburo Ito (Kyoto University) for photophysical measurements.

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(38) As one of the characteristic properties, delayed fluorescence (DF) was observed for the azacoronenes possibly via thermally activated  $T_1 \rightarrow S_1$  intersystem crossing. Detailed measurements are in progress to decide the dominant process, which will be published elsewhere.

(39) The theoretical calculations performed using the time-dependent DFT (TD-DFT) method predict the existence of a higher excited triplet state  $T_q$  at an energy between  $S_1$  and  $T_1$ . The  $T_2$  state is predicted for **2c** and **3c**, and nine quantized triplet states are predicted for **4c** (Figure S10 in SI). If one or more higher triplet states exist between  $T_1$  and  $S_1$  (i.e.,  $T_q$  intermediate), the total rate of intersystem crossing ( $k_{isc}$ ) from the  $S_1$  to the triplet manifold is  $k_{isc} = \sum_q (k_{isc})_q$  where  $(k_{isc})_q$  is the  $S_1 \rightarrow T_q$  intersystem crossing rate. Therefore, the efficient ISC from  $S_1$  to the triplet manifold via higher excited triplet states  $T_q$  is expected for **4c**, which would explain larger  $k_n + k_{isc}$  of **4a** compared to those of **1c** and **2c**.

(40) When we used  $Fe(ClO_4)_3 \cdot 6H_2O$  as an oxidant in a mixture of  $CH_2Cl_2$  and  $CH_3CN$  (4:1, v/v), up to tetracation, trication, and dication species were observed for **4a**, **3a**, and **2a**, respectively. See Supporting Information, S15.

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(47) One reviewer pointed out the importance of the structural origin of the open-shell characters. Therefore, we have added some of possible resonance (quinoidal) forms based on the crystal and DFT calculation results in Supporting Information (S20), although we understand it is extremely difficult at the moment to explain the existence of an open-shell state and the spin multiplicity from the resonance structures.

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