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Engineering Control over the Conformation of the Alkyne–Aryl Bond by the Introduction of Cationic Charge

Takashi Terashima, Takuya Nakashima, and Tsuyoshi Kawai*

Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan

tkawai@ms.naist.jp

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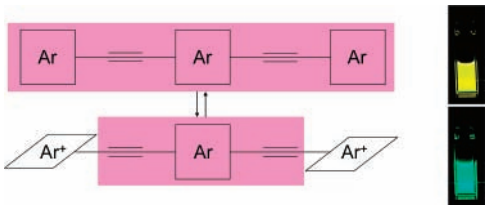
ABSTRACT



A novel arylene–ethynylene molecule has been synthesized. This molecule is more stable in a coplanar form than in a twisted form as in the cases of typical arylene–ethynylene molecules. When the cationic charge was introduced into the π-conjugated system, the perpendicularly twisted form became more stable than the coplanar state. The conformational change was controlled by introduction and removal of cationic charge, confirmed by the absorption and fluorescence spectroscopy and DFT calculation.

Arylene−ethynylene derivatives, such as 1,4-bis(phenylethynyl)benzene, 9,10-bis(phenylethynyl)anthracene, and the analogues oligomers and polymers[1] are recently attracting substantial interest due to their fairly high charge transport capability and highly efficient luminescent properties. A number of potential applications have been proposed such as displays,[2] sensors,[3] and molecular electronic conducting wires.[4] The origin of these fascinating properties is mainly attributed to their extended linear π-system and consequently to the relative intramolecular orientation of planar aromatic rings.

The structure−property relationships of the arylene−ethynylene derivatives have been studied extensively.[5] In most molecules and polymers, the coplanar structure over the neighboring aryl groups is the most stable both in the ground state and in the excited state, which affords the well-extended π-conjugation system. The energy barrier for the rotation about the alkyne−aryl bond is relatively low in the ground state,[6] and the energy difference between the fully coplanar structure and the perpendicularly twisted structure has been estimated to be less than kT of room temperature.[5c] Therefore, the rotation around the ethynyl group and the rapid exchange between the coplanar form and the twisted form

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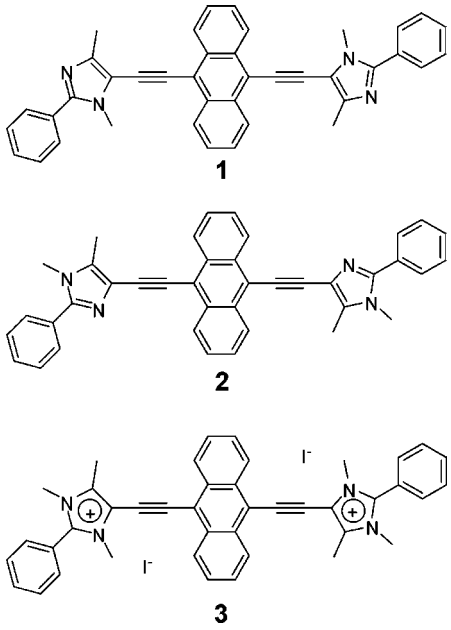
are allowed. The conformational change of 1,4-bis(phenylethynyl)benzene derivatives resulting from the rotation about the central axis has been reported to modulate the conducting properties at the single molecular level.[7] Several groups have achieved a certain degree of configurational control between the coplanar form and the twisted form in the sterically restricted system such as Langmuir−Blodgett films,[8] self-assembled monolayers,[9] intramolecular tethering,[10] and liquid crystalline aggregates.[11] From the viewpoint of the molecular switching materials, stimuli-responsive molecular units whose coplanarity can be modulated by external stimulation are worth studying. For example, Yamamoto et al. have prepared unique π-conjugated polymers based on the arylene−ethynylene structure containing the imidazole group, and protonation of the imidazole unit in the main chain has resulted in the blue shift of the HOMO−LUMO absorption band. They suggested reversible modulation of the coplanarity of the main chain with the reversible transformation between imidazole and imidazolium.[12a] However, to the best of our knowledge, none has performed systematic study on the conformational modulation of the arylene−ethynylene unit by the reversible protonation−deprotonation of the arylene groups. In the present study, we report a new bisimidazolyl-ethynyl anthracene whose π-conjugation system is controlled by means of the molecular conformation along the alkyne−aryl bonds.

Chart 1. Compounds **1**−**3**



Compound **1** whose chemical structure is shown in Scheme S-1 (Supporting Information) was synthesized by the cross-coupling reactions of 9,10-dibromoanthracene and ethynylated imidazole derivatives.[13] Compounds **2** and **3** were also synthesized as the reference compounds. The molecular structures and optical properties of these compounds are summarized in Chart 1 and Table 1, respectively.

Table 1. Experimental and Calculated Photophysical Properties

	1	**2**	**3**
observed λ_{abs} (nm)	511	490	476
observed ϵ ($M^{-1}\cdot cm^{-1}$)	4.5×10^4	6.0×10^4	4.8×10^4
observed λ_{em} (nm)	555	531	497
emission quantum yield (ϕ)	0.72	0.80	0.80
emission lifetime (ns)	2.7	3.4	2.9
calcd λ_{abs}[a] (nm)	567	523	470
calcd dihedral angle[b]	14°	4°	89°

[a] Calcd UV−vis spectra and [b] calcd dihedral angles between anthracene and imidazole were estimated by Gaussian03. All other conditions are presented in the Supporting Information.

Compounds **1** and **2** show characteristic absorption bands at 511 and 490 nm and fluorescence emissions at about 555 and 531 nm, respectively. It should be noted that these molecules show clear fluorescence emission with quantum yields as high as 80%. The characteristic emission wavelength and absorption maximum wavelength of the compound **2** are markedly shorter than those of compound **1**. This difference in the HOMO−LUMO gap energy might

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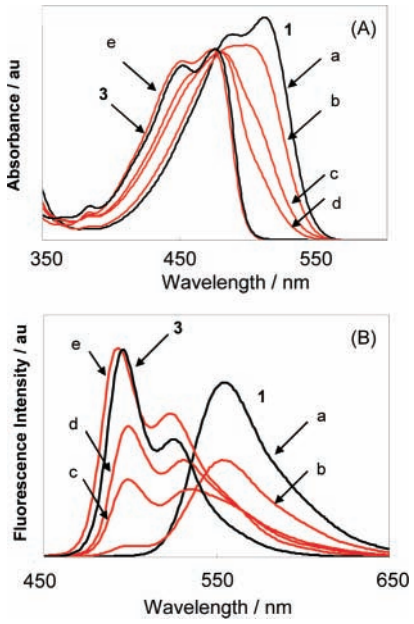

Figure 1. (A) Absorption spectra of **1** with TFA concentrations of (a) 0, (b) 0.4, (c) 6.3, (d) 25.0, and (e) 2500 mM and **3** in DMSO. (B) Fluorescence spectra of **1** with TFA concentration of (a) 0, (b) 0.4, (c) 6.3, (d) 25.0, and (e) 2500 mM and **3** in DMSO excited at 360 nm. [**1**] = 5.0 μM. [**3**] = 5.0 μM.

be attributed to the restricted π-conjugational expansion in compound **2** originated from the disconnection of the π-conjugation at the imidazole groups. Considering the resonance structure of **3** whose delocalized π-electron structure seems to be a hybrid of **1** and **2**, the intermediate wavelength is expected. However, both absorption and emission peaks of **3** appeared at shorter wavelengths than those of compounds **1** and **2**. These results suggest that π-conjugation length is not necessarily determined by the π-electron resonance structure on imidazolium under assumption of the coplanar structure. Fluorescence lifetime studies[13] revealed that the emission decay from each compound exhibited monoexponential decay, confirming the presence of a single emitting species.

As shown in Figure 1a, when TFA, as a proton source, was added, the absorption peak at 511 nm was suppressed and an another absorption band appeared at the shorter wavelength continuously. Finally, the absorption peak almost coincided with that of **3**. The resulting spectrum reverted to the starting spectrum by the addition of triethylamine (TEA) as a base, indicating the reversible switching in the absorption spectrum. The presence of quasi-isosbestic points at 360 and 477 nm supported the reversible quasi-two-component equilibrium reaction, showing difficulty in distinguishing between the mono- and the diprotonated forms. In a fluorescence mesurement, the peak at 555 nm decreased and a new fluorescence band appeared at around 493 nm, finally coinciding with that of **3**. A significant color change from yellow to greenish blue was visibly observed. The fluorescence spectrum also reverted to the starting spectrum by the addition of TEA, also indicating the reversible switching of fluorescence. These blue shifts in both fluorescence and absorption spectra indicate that the π conjugation length becomes short upon the protonation in both the ground and the excited states. Taking the symmetrical structure into account from the change in the ^{1}H NMR spectra of **1** caused by the addition of TFA-*d*,[13] diprotonation of **1** was concluded. The absorption and fluorescence spectra of the protonated form of compound **2** in the presence of TFA were also the same as those of compound **3**. That is, the protonated forms of compounds **1** and **2** have electronic and, thus, geometrical structures similar to those of compound **3**.

To evaluate the origin of the spectral blue shifts in the imidazolium form, we performed quantum mechanical calculations of the geometrical and electrical structure and the basic photochemical properties for compounds **1**−**3** by DFT[14] and TDDFT[15] methods at the B3LYP/DGDZVP level. For the calculation, the Gaussian03[16] suite of programs was used. From the most stable optimized geometries of **1**−**3** depicted in Figure 2, the approximate dihedral angles

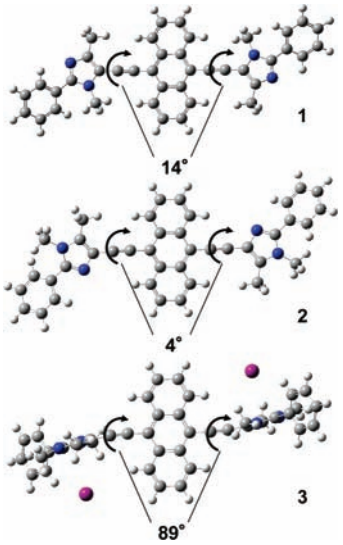

Figure 2. DFT-based optimized structures of **1**−**3** and dihedral angles between anthracence and imidazole, respectively.

between the anthracene and the imidazole unit were evaluated to be 14° for **1** and 4° for **2**, which correspond to the coplanar structure. Meanwhile, the dihedral angle for **3** was 89°, which indicates a perpendicularly twisted form. The energy difference between the most stable form and the unstable twisted or coplanar forms was evaluated to be significantly larger than the kT at room temperature (0.6 kcal/mol) for each molecule, to shift the population over the conformations.[13]

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(16) *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003. See Supporting Information for the full reference.

The dihedral angles between the phenyl group and the imidazolium group of compounds **1** and **2** were also significantly smaller than those of compound **3**. HOMO and LUMO orbitals of compound **1** markedly expand throughout the molecule, and those of compound **2** expand between imidazoles. The HOMO-6 and LUMO orbitals of compound **3**, which are responsible for the absorption band at 476 nm, are confined in the ethynyl anthracene unit (Figure 3). It

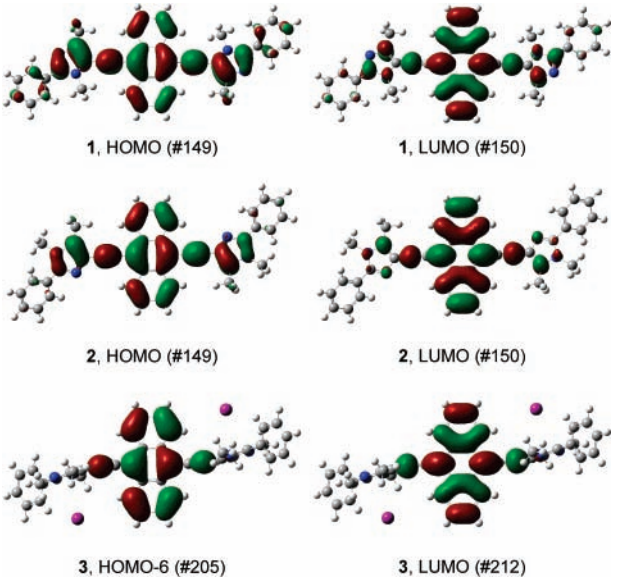

Figure 3. Frontier orbitals of compounds **1**−**3** calculated by the B3LYP/DGDZVP DFT method.

should be noted that the orbitals HOMO∼HOMO-5 were localized on the iodide ion and that the transitions between the iodide ion and the molecule showed almost zero oscillator strengths. The TDDFT calculations predicted the distinct blue shift of the absorption by the transformation from the imidazole form to the imidazolium form (Table 1). The calcd λ_{abs} were in good agreement with the experimental data. The calcd absorption bands shifted to the red by 10−60 nm with respect to the measured spectra, but the relative position of the transition gave satisfactory results. In neutral compounds **1** and **2**, the π-orbitals of two imidazole units are in conjugate with that of the central ethynylanthracene unit. Under the assumption of the coplanar form of **3** obtained by constraining the dihedral angles of 0° between the anthracene and imidazolium units, the π-orbitals of two imidazolium units are in conjugate with that of the central ethynylanthracene unit. Consequently, the calcd λ_{abs} of **3** approached those of compound **1** and **2** in the most stable coplanar conformations. On the contrary, significant blue shifts are observed for compounds **1** and **2** when they are assumed to be in the unstable twisted conformation.[13] So the significant twist around the imidazolium units seems to be the origin of the spectral blue shift in the optical spectra of compound **3**. Yamamoto et al. have suggested that the repulsive interaction between the positively charged N−H unit in the imidazolium group and the partially polarized C−H unit would be responsible for the twisted geometry.[12a] The hyperconjugation between the N^+−H σ orbital and the p-orbitals of the neighboring ethynyl and aryl groups may stabilize the positive charges in the imidazolium groups in the twisted form of compound **3**.

In conclusion, the engineering control over the molecular conformation between a coplanar structure and a twisted structure was achieved by the introduction of cationic charge into the imidazole unit. These showed significantly high fluorescence emission quantum yields in both the protonated and deprotonated forms. The absorption and fluorescence spectra and DFT calculations revealed that the coplanar structures are more stable than the twisted one for neutral **1**. When cationic charges were introduced, the perpendicularly twisted structure became more stable than the coplanar one. This mechanism would open up a new design concept for controlling the molecular conformation in the alkyne−aryl bond of the conjugated molecules and polymers.

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Supporting Information Available: Experimental procedures and data for all new compounds, fluorescence decay data, NMR spectrum, optimized geometries, their relative enegies, and molecular orbitals. This material is available free of charge via the Internet at http://pubs.acs.org.

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