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Protonation-induced Cyclization of 1,8-Bis(arylethynyl)anthraquinones: Monopyrylium Salt Formation and Intensification of Donor–Acceptor Interaction

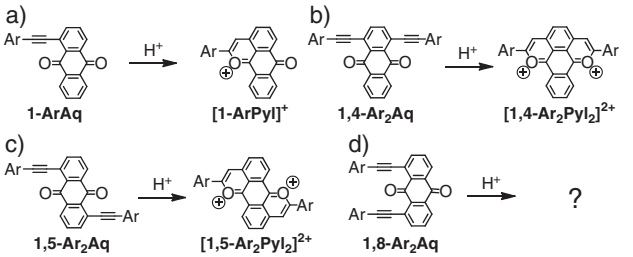
Koya Prabhakara Rao, Mio Kondo, Ryota Sakamoto, Tetsuro Kusamoto, Shoko Kume, and Hiroshi Nishihara*
Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033

(Received October 27, 2011; CL-111052; E-mail: nisihara@chem.s.u-tokyo.ac.jp)

We previously reported protonation-induced double cyclization reaction of **1,4-Ar$_2$Aq** and **1,5-Ar$_2$Aq** (**Ar$_2$Aq**: bis(arylethynyl)anthraquinone) with strong acid HX that generated the corresponding dipyrylium salts **[1,4-Ar$_2$Pyl$_2$]X$_2$** and **[1,5-Ar$_2$Pyl$_2$]X$_2$**. In this communication we disclose the protonation reactions of **1,8-Fc$_2$Aq** (**Fc**: ferrocenyl), **1,8-Am$_2$Aq** (**Am**: 4-*N*,*N*-bis(4-methoxyphenyl)aminophenyl), and **1,8-AmFcAq**, which is the first example of heterodonor molecules in the **Ar$_2$Aq** series, and synthesized by means of stepwise Sonogashira–Hagihara cross-coupling reactions. In contrast to the **1,4-Ar$_2$Aq** and **1,5-Ar$_2$Aq** series, **1,8-Ar$_2$Aq** undergoes protonation-induced single cyclization, so that it is converted into the corresponding monopyrylium salt **[1,8-Ar$_2$Pyl]X**. **[1,8-Ar$_2$Pyl]X** features an extremely small HOMO–LUMO gap (0.50–0.73 V), ascribable to the significant lowering of the LUMO level upon the pyrylium formation.

D–**A**, **D**–**A**–**D**, and **A**–**D**–**A** (**D**: donor; **A**: acceptor) types of compounds are exciting materials,[1] and have been intensively studied in terms of fundamental research as well as potential applications, such as nonlinear optics (NLOs) and organic electronics. The electronic structure of **D**–**A**, **D**–**A**–**D**, and **A**–**D**–**A** molecules can be systematically tuned by external stimuli,[2–4] such as protons, photons, electrons, and magnetic fields. Recently, these molecules have received unprecedented attention because of their peculiar physical and electronic properties, which can be employed to achieve switching behavior in molecular devices.[5,6]

Our recent studies have developed a new class of **D**–**A** and **D**–**A**–**D** molecules, **ArAq** and **Ar$_2$Aq**, where **Ar** represents an aryl group, such as ferrocenyl (**Fc**), 4-*N*,*N*-bis(4-methoxyphenyl)aminophenyl (**Am**), platinadithiolene, phenyl, *m*-tolyl, and *p*-tolyl, and **Aq** indicates ethynylanthraquinone or diethynylanthraquinone (Schemes 1a–1c).[7–12] This series of molecules underwent single and double intramolecular cyclization reactions to afford pyrylium and dipyrylium cations, respectively (Schemes 1a–1c). For example, **1-ArAq** gave rise to the pyrylium salt **[1-ArPyl]X** (**X**: counter anion) with a quadruply fused-ring structure, in which a cationic oxygen participated in the aromatic six-membered ring (Scheme 1a).[8] We have also described novel **D**–**A**–**D** molecules, **1,4-Ar$_2$Aq** and **1,5-Ar$_2$Aq**, which experienced unprecedented protonation-induced double cyclization reactions to yield the dipyrylium salts, **[1,4-Ar$_2$Pyl$_2$]X$_2$** and **[1,5-Ar$_2$Pyl$_2$]X$_2$** (Schemes 1b and 1c).[9,10] These compounds possessed new types of quintuply fused-ring structures, which were isoelectronic with benzo[*e*]pyrene and perylene-type skeletons with 20π electrons.[10] These doubly-condensed phases showed unique physical, chemical, and magnetic properties. Our successful studies on **D**–**A**–**D** **1,4-Ar$_2$Aq** and **1,5-Ar$_2$Aq** systems have prompted us to examine the **1,8-Ar$_2$Aq** system (Scheme 1d). We note that we previously disclosed the protonation behavior of **1,8-Fc$_2$Aq**,[7b] but we could not identify its chemical structure at that stage.



Scheme 1. (a)–(c) Proton-induced single and double cyclization in **1-ArAq**, **1,4-Ar$_2$Aq**, and **1,5-Ar$_2$Aq** that afford corresponding pyrylium and dipyrylium cations **[1-ArPyl]$^+$**, **[1,4-Ar$_2$Pyl$_2$]$^{2+}$**, and **[1,5-Ar$_2$Pyl$_2$]$^{2+}$**, respectively. d) The subject of the present work, the proton response of **1,8-Ar$_2$Aq** (**Ar** = **Fc** or **Am**).

In the present study, we report on the new **1,8-Ar$_2$Aq** type of molecules: a homodonor compound, **1,8-Am$_2$Aq**, and the first heterodonor one in the **Ar$_2$Aq** series, **1,8-AmFcAq**. We also address their protonation reactions, together with the exact structure of the protonated product of **1,8-Fc$_2$Aq**. All these **D**–**A**–**D** molecules undergo a protonation-induced single cyclization reaction with bis(trifluoromethanesulfon)imide (TFSIH) as a strong acid, so as to yield the corresponding pyrylium salts, **[1,8-Ar$_2$Pyl](TFSI)**. The synthesis, characterization, single-crystal X-ray diffraction (XRD) analysis, and physical properties of **1,8-Ar$_2$Aq** and **[1,8-Ar$_2$Pyl]X** (**Ar** = **Am** and **Fc**, **X** = **TFSI** and **BF$_4$**) are described in this paper.

1,8-Am$_2$Aq was synthesized by the Sonogashira–Hagihara cross-coupling of 4-ethynyl-*N*,*N*-bis(4-methoxyphenyl)aniline with 1,8-dibromoanthraquinone. **1,8-AmFcAq** was synthesized in two steps in order to introduce two different types of donor moieties. In the first step, intermediate **1,8-AmBrAq** was synthesized by the Sonogashira cross-coupling of 4-ethynyl-*N*,*N*-bis(4-methoxyphenyl)aniline with 1 equiv of 1,8-dibromoanthraquinone. In the second step, **1,8-AmFcAq** was obtained by a coupling of ethynylferrocene to the intermediate using a similar reaction condition. We note that **1,8-AmFcAq** could not be synthesized when the order of the reactions with the ethynyl derivatives of amine and ferrocene was reversed: In this condition, **1,8-Fc$_2$Aq** was preferentially obtained in the first step. This presumably stemmed from the bulkiness of **Am**, which decelerate the second Sonogashira–Hagihara reaction. **1,8-Am$_2$Aq** and **1,8-AmFcAq** were characterized by ^{1}H NMR and ESI-TOF-MS, as well as elemental analysis. Single crystals of **1,8-AmFcAq** was obtained by recrystallization from dichloromethane/hexane at 293 K, and its molecular structure were determined by single-crystal XRD analysis (Figure 1[13] and Table S1[14]).

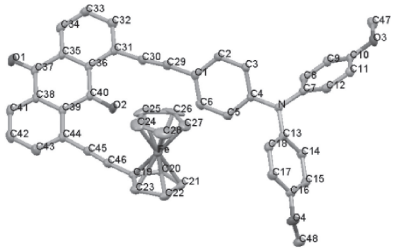
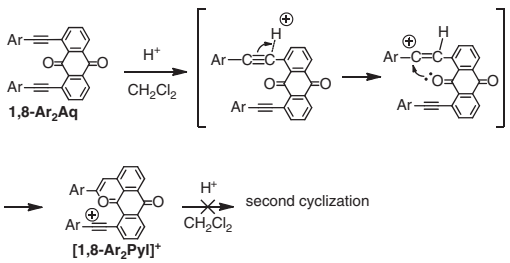


Figure 1. ORTEP drawing of **1,8-AmFcAq** with the thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted.



Scheme 2. Prausible reaction mechanism of proton-induced single cyclization in **1,8-Ar$_2$Aq**.

The protonation reaction of **1,8-Fc$_2$Aq** had been described in the previous paper, but the chemical structure had not been identified.[7b] On the other hand, in this study we succeeded in determining the crystal structure of the protonated product: A treatment of **1,8-Ar$_2$Aq** with TFSIH in dichloromethane afforded the singly-cyclized form **[1,8-Ar$_2$Pyl]$^+$** (Scheme 2). Figures S1[14] and 2 show the crystal structures of **[1,8-Fc$_2$Pyl]-(TFSI)** and its anion exchange product **[1,8-Fc$_2$Pyl](BF$_4$)**, respectively:[13] Their crystal data are collected in Table S1.[14] The C–C bond lengths in the tetracyclic moiety were in the range of 1.358(4)–1.481(5) Å, and the C–O bond lengths were in the range of 1.342(3)–1.378(4) Å, suggesting the formation of the π-conjugated and fused pyrylium skeleton. The C–O bond lengths of the carbonyl group that did not participate in the cyclization were in the range of 1.220(4)–1.233(3) Å. The cyclized products of the protonated salts **[1,8-Am$_2$Pyl](TFSI)** and **[1,8-AmFcPyl](TFSI)** were also isolated upon treatment with TFSIH in dichloromethane. Their identification relied on elemental analysis and ESI-TOF-MS. These materials were NMR silent, presumably because of valence tautomerism and resultant generation of paramagnetic species.[8c,8d,9,10] Unfortunately, their single crystals suitable for XRD analysis were not obtained due to poor crystallinity. Thus, **1,8-Ar$_2$Aq** is in sharp contrast to **1,4-Ar$_2$Aq** and **1,5-Ar$_2$Aq** that can form the pentacyclic dipyrylium structures. This difference comes from the fact that the the arylethynyl moieties at 1- and 8-positions are conjugated with the same carbonyl group so that second ring formation reaction is impossible for **1,8-Ar$_2$Aq**, whereas the arylethynyl moieties at 4- and 5-positions are conjugated with the other carbonyl group so that 1,4- and 1,5-derivatives can undergo two-step ring formation reactions. We note that **[1,8-AmFcPyl](TFSI)** has two possible structures where the pyrylium ring formed on **Fc** and **Am** sides, respectively. We already reported that **ArAq** and **Ar$_2$Aq** with the more strongly electron-donating **Ar** needed the shorter reaction time, less harsh acid,

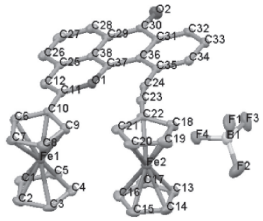


Figure 2. ORTEP drawing of **[1,8-Fc$_2$Pyl](BF$_4$)** with the thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted.

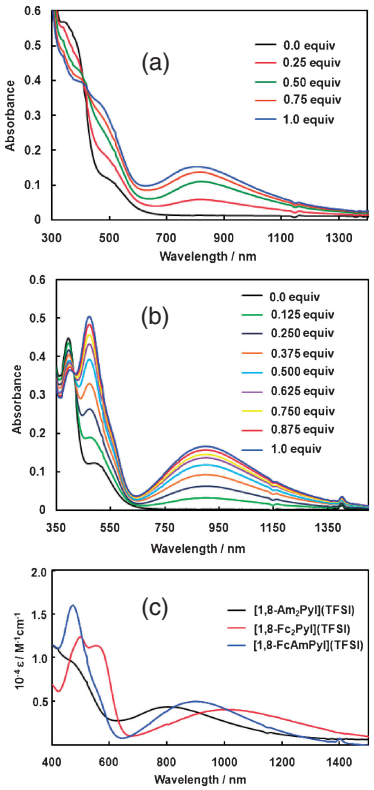


Figure 3. a) UV–vis–NIR spectral change of **1,8-Am$_2$Aq** in dichloromethane upon a stepwise addition of TFSIH; b) UV–vis–NIR spectral change of **1,8-AmFcAq** in dichloromethane upon a stepwise addition of TFSIH; (c) Overlay of the UV–vis–NIR spectra of **[1,8-Ar$_2$Pyl](TFSI)**.

and smaller equivalent of acid for the pyrylium formations, which we attributed to the stabilization of carbocationic intermediates by the **Ar** group.[12] **1,8-Ar$_2$Aq** is also expected to go through a similar carbocationic intermediate in the course of the cyclization (Scheme 2). With these backgrounds, we deduce that the cyclization preferentially occurs on the **Fc** side, because the donor ability of ferrocene is stronger than that of triarylamine by ca. 0.2 V.[15]

The protonation-induced cyclization reaction of **1,8-Am$_2$Aq** and **1,8-AmFcAq** with TFSIH in dichloromethane to generate **[1,8-Am$_2$Pyl](TFSI)** and **[1,8-AmFcPyl](TFSI)** was also monitored by UV–vis–NIR absorption spectroscopy. As shown in Figures 3a and 3b, each compound displayed a one-step spectral change with an isosbestic point, similar to **1-ArAq**,[8] indicating that only the single cyclization occurred. Figure 3c collects the spectra of **[1,8-Ar$_2$Pyl](TFSI)** in dichloromethane.

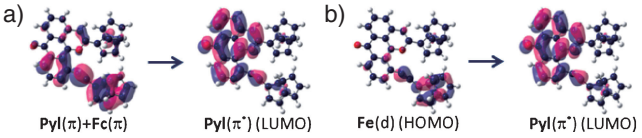


Figure 4. Main transitions of **[1,8-Fc$_2$Pyl]$^+$** estimated by TDDFT calculation: a) in the π–π^* band; b) in the CT band. See Figure S2 and Table S2[14] for the comprehensive transitions and molecular orbitals.

Table 1. Redox potentials of **1,8-Ar$_2$Aq** and **[1,8-Ar$_2$Pyl]$^+$** in 0.1 M *n*-Bu_4NClO_4–CH_2Cl_2

Compound	Oxidation		Reduction	HOMO–LUMO
	$E^{0\prime}$ (ox1)[a]	$E^{0\prime}$ (ox2)[a]	$E^{0\prime}$ (red)[a]	gap[c]
1,8-Am$_2$Aq	0.31[b]	—	−1.38	1.69
[1,8-Am$_2$Pyl]$^+$	0.40[b]	—	−0.33	0.73
1,8-AmFcAq	0.12	0.28	−1.41	1.53
[1,8-AmFcPyl]$^+$	0.26	0.48	−0.30	0.56
1,8-Fc$_2$Aq	0.07	0.14	−1.33	1.40
[1,8-Fc$_2$Pyl]$^+$	0.19	0.30	−0.31	0.50

[a]In V vs. ferrocenium/ferrocene. [b]A two-electron process. [c]Defined as $E^{0\prime}$(ox1) − $E^{0\prime}$(red), in V.

The common feature lies on the intense bands around 500–550 nm: According to a DFT calculation for **[1,8-Fc$_2$Pyl]$^+$**, these bands are ascribed to the π–π^* transtions of the pyrylium ring (Figure 4a). In addition, broad absorption bands spanning 600–1400 nm are also commonly observed, which stem from charge-transfer (CT) transitions from **Fc** or **Am** to **Pyl**(π^*) (Figure 4b). These kinds of absorption bands were also observed in other pyrylium and dipyrylium salts.[8–10] Upon addition of base (MeOH), **[1,8-Ar$_2$Pyl](TFSI)** underwent spectral changes (Figure S3)[14] similar to those of **[1-ArPyl](TFSI)**, which generated methoxide adducts **1-ArPyl-OMe**.[8b] Therefore, we deduce that **1,8-Ar$_2$Pyl-OMe** was also generated in this case.

The existence of the NIR CT bands infers that **[1,8-Ar$_2$Pyl]X** possesses quite a narrow HOMO–LUMO gap. Then **1,8-Ar$_2$Aq** and **[1,8-Ar$_2$Pyl](TFSI)** were subjected to electrochemical measurements in 0.1 M *n*-Bu_4NClO_4–CH_2Cl_2, and formal potentials ($E^{0\prime}$) were collected in Table 1. The cyclization significantly impacted the reduction: It positively shifted $E^{0\prime}$ for the first reduction by ca. 1.0 V, whereas the positive shifts of $E^{0\prime}$ for the first and second oxidations were no more than ca. 0.2 V. This series of results indicates that a significant lowering of the LUMO level is induced by the expansion of the π-conjugation upon the cyclization. As a result, **[1,8-Fc$_2$Pyl](TFSI)**, **[1,8-AmFcPyl](TFSI)**, and **[1,8-Am$_2$Pyl](TFSI)** featured extremely small HOMO–LUMO gaps (Table 1).

In conclusion, we described the protonation-induced cyclization reaction of new **D**–**A**–**D** conjugated molecules, **1,8-Ar$_2$Aq**, to yield the corresponding pyrylium salts **[1,8-Ar$_2$Pyl]X** with a tetracyclic structure. This single cyclization was in sharp contrast to **1,4-Ar$_2$Aq** and **1,5-Ar$_2$Aq** having two **Ar** groups and undergoing double cyclization. The pyrylium formation resulted in more intense **D**–**A** interaction, such as smaller HOMO–LUMO gaps and NIR CT transitions.

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