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Valence Tautomerism

Protonation-Induced Cyclocondensation of 1-Aryl Ethynylanthraquinones: Expanding the π Conjugation**

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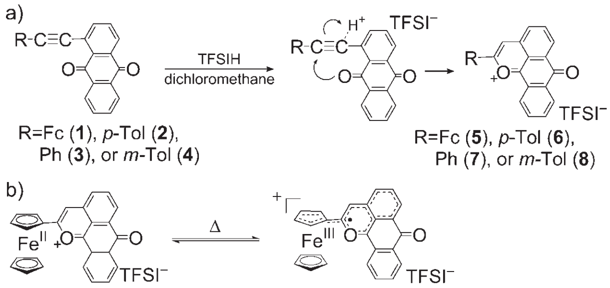
Functional molecules whose physical properties can be changed by external stimuli such as light, temperature, and magnetic fields have received considerable attention because of their potential use in the construction of molecular devices.[1] From this perspective, a number of molecules that exhibit bistability, which is a change in the distribution of two meta-stable states in response to an external stimulus, have been developed.[2] The utilization of valence tautomerization (VT) phenomena, which involve reversible intramolecular metal–ligand electron transfer, is one way of achieving molecular bistability.[3,4] In order to develop a new VT compound, and thereby develop a new method for designing bistable materials, we became interested in the chemistry of a new donor–acceptor conjugated system, namely ferrocenylethynylanthraquinones (FcAq's), which have been shown to exhibit a protonation-induced intramolecular electron-transfer reaction[5] both in solution and in the solid state.[6] The structures of protonated species have been proposed to have a "fulvene-cumulene"-type configuration by UV/Vis, IR, ^{1}H NMR, and ^{13}C NMR spectroscopy, although no crystal structures of these species are currently available.

Herein we report the crystal structure of the species **5** resulting from protonation of 1-ferrocenylethynylanthraquinone (**1**; Scheme 1 a). Cation **5** does not have the fulvene/cumulene-type configuration but rather exhibits an expanded π-conjugated system formed by a cyclocondensation reaction. We also show that the large π-conjugated system of **5** promotes intramolecular electron transfer from donor to acceptor in a valence tautomerism process and that the protonation-induced cyclocondensation reaction can be applied to aryl ethynylanthraquinones in general. We report a novel route to prepare new hetero-fused ring compounds of 2-substituted 7-oxo-7,11*b*-dihydrodibenzo[*de,h*]chromenylium cations and the molecular structures and VT properties of **5**, as determined by ^{57}Fe Mössbauer spectroscopy.



Scheme 1. Synthesis of compounds **5**–**8**. Fc = ferrocenyl; TFSIH = bis(trifluoromethanesulfone)imide.

Protonation of **1**–**4** was carried out by adding 1.4–1.7 equivalents of bis(trifluoromethanesulfone)imide (TFSIH) in dichloromethane to give the oxodihydrodibenzochromenylium cations **5**–**8** in yields of 82 %, 88 %, 83 %, and 97 %, respectively (Scheme 1 a). Compounds **5**–**8** are stable in air and were characterized by ^{1}H NMR (see Supporting Information), ^{13}C NMR, and HMQC spectroscopy and elemental analysis. Intramolecular cyclization of the ethynylquinone moiety probably proceeds by protonation of an ethynyl moiety followed by annulation of the carbonyl and ethylene groups (Scheme 1 a). The reactivities of compounds **1**–**4** with TFSIH are totally different. Thus, the ferrocenyl compound **1**, which possesses a more electron-donating group, reacts much faster than the aryl compounds **2**–**4**. Compound **1** reacts instantaneously with TFSIH (less than 10 s) even in 0.1 mM solution, which is a concentration 200 times lower than that of the synthetic conditions, whereas **2** did not react with the acid in 0.1 mM solution after 20 h (see Supporting Information). This difference in reactivity may be related to the proton affinity of the ethynylquinone moiety.[7]

Single crystals of **5** were grown by slow evaporation of the solvent from a dichloromethane solution at 293 K and the molecular structure of **5** was determined by single-crystal X-ray analysis (Figure 1 a). The structure shows that the plane of the pyrylium moiety (C11-C12-C13-C26-C25-O1) is parallel to the cyclopentadienyl ring (C6-C7-C8-C9-C10) of ferrocene (dihedral angle: 6.63(12)° for **5**). The high planarity of the molecules is due to an expansion of the π-conjugated system upon cyclization. Selected bond lengths and crystallographic

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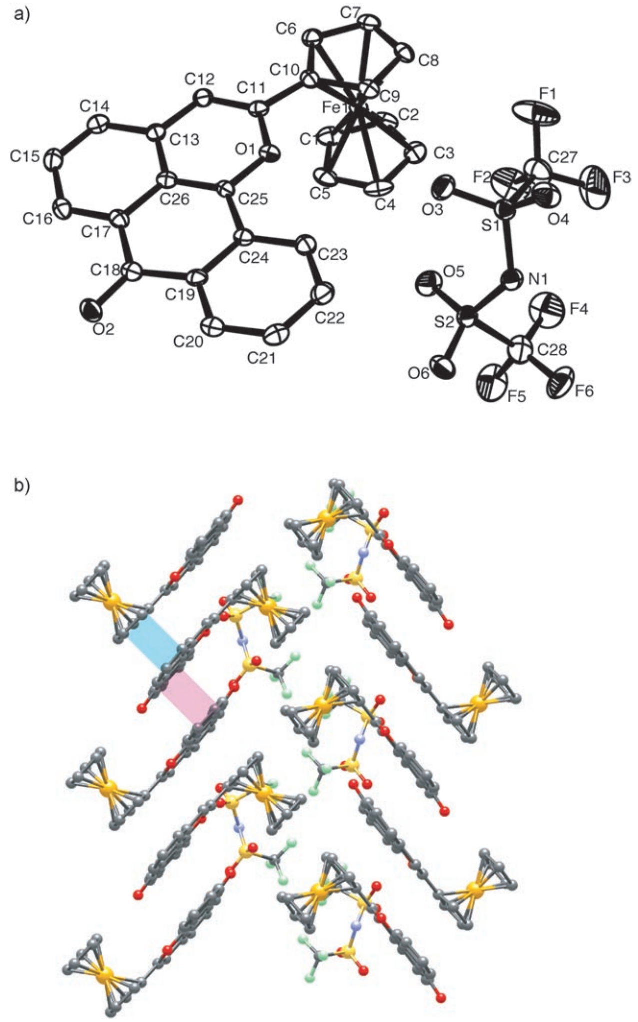

Figure 1. a) ORTEP plot and b) overall structure along the *a* axis of **5**. Hydrogen atoms have been omitted for clarity; gray C, red O, green F, blue N, yellow S, gold Fe.

data of **5** are compared with the values for **1** in the Supporting Information.[8] The C−C bond lengths in the pyrylium moiety are in the range 1.366(4)–1.415(4) Å, thus indicating the formation of an aromatic ring structure. The C24−C25, C25−C26, and C25−O1 bond lengths are 1.447(4), 1.389(4), and 1.347(4) Å, respectively, in **5**, while they are 1.494(4), 1.491(4), and 1.223(3) Å, respectively, in **1**. This increase in the C24−C25 and C25−C26 bond lengths and the decrease in the C25−O1 bond length on going from **5** to **1** suggest an expansion of the π-conjugated system upon cyclization. Figure 1b shows the packing structure of **5**. The average plane-to-plane distance between C6-C7-C8-C9-C10 and C11-C12-C13-C26-C25-O1 is 3.287(4) Å, which indicates the existence of intermolecular donor–acceptor interactions.[9]

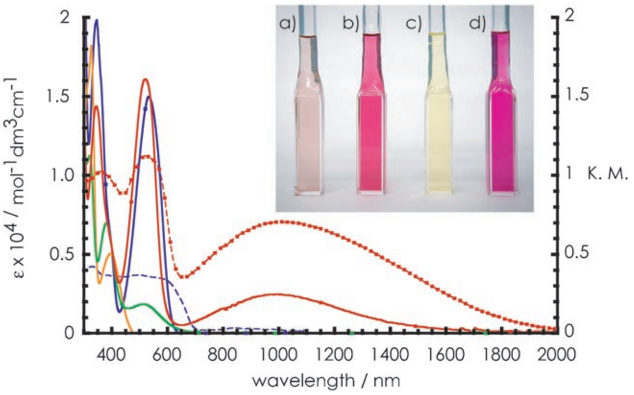

Figure 2. UV/Vis/NIR absorption spectra of **1** (green line), **2** (orange line), **5** (red line), and **6** (blue line) in dichloromethane (0.5 mM), and diffuse reflectance spectra of **5** (red dotted line) and **6** (blue dotted line) in the solid state (1% in KBr). K.M. = Kubelka–Munk value. Inset: Photo showing solutions of **1** (a), **5** (b), **2** (c), and **6** (d) in dichloromethane (0.1 mM).

The UV/Vis/NIR spectra of **1**, **2**, **5**, and **6** are shown in Figure 2. The protonated products **5** and **6** show an increase in intensity at around 500 nm relative to the respective starting compounds **1** and **2**. TD-DFT calculations with the B3LYP/LanL2DZ basis set for **5** and the B3LYP/6-31G (p,d) basis set for **6** indicate that the band around 500 nm can be assigned mainly to the transition from the π orbital consisting of a cyclopentadienyl ring or a *p*-tolyl moiety to the π* orbital consisting of a dibenzochromenylium moiety ($\lambda_{calcd} = 608$ nm, $f = 0.0981$, HOMO−2 (100) → LUMO (103) for **5**, and $\lambda_{calcd} = 590$ nm, $f = 0.1654$, HOMO (84) → LUMO (85) for **6**; see Figure 3 and Supporting Information). Compound **2** also shows a new band in the visible/near-IR region ($\lambda_{max} = 959$ nm) which is not observed for either **1** or **6**. TD-DFT calculations suggest that this band can be assigned to an intervalence charge transfer (IVCT) mainly from HOMO (102), which consists of the $d_{x^2-y^2}/\pi$ orbital of the ferrocene moiety, to LUMO (103), which consists of the π* orbital of a dibenzochromenylium moiety ($\lambda_{calcd} = 1065$ nm, $f = 0.0262$;

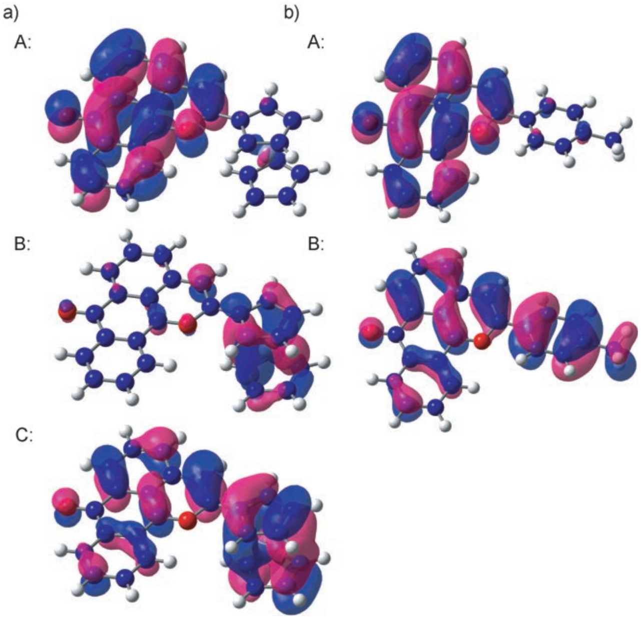

Figure 3. a) LUMO (103) (A), HOMO (102) (B) and HOMO−2 (100) (C) of **5** calculated at the B3LYP/LanL2DZ level. b) LUMO (85) (A) and HOMO (84) (B) of **6** calculated at the B3LYP/6-31G (p,d) level.

see Figure 3 and Supporting Information).[10] This low-energy band is also observed in the diffuse reflectance spectrum of **5** in the solid state (Figure 2). These results suggest a lowering of the π* (LUMO) level upon cyclization and that intramolecular electron transfer occurs more easily in **5** than in **1**. The crystallographic data of **1** and **5** indicate that **5** actually has a larger π-conjugated system, which contributes to a lowering of the LUMO level with respect to **1**.

^{57}Fe Mössbauer spectra were measured at 12, 100, 150, 200, 230, 260, and 290 K to confirm the VT behavior of **5** in the solid state (Figure 4 and Supporting Information). All spectra could be fitted satisfactorily by assuming that two kinds of species, namely F1 (red line) and F2 (blue line), are present. F1 shows a quadrupole doublet with a splitting of 2.11(1)–2.10(1) mm s^{-1} and an estimated isomer shift of 0.53(1) mm s^{-1} at 12 K (see Supporting Information). These values are typical for ferrocene derivatives.[11] F2 shows a quadrupole doublet splitting of 0.54(1) mm s^{-1} at 12 K, which is characteristic of a ferrocenium ion.[11] The isomer shift of this species is 0.30(2) mm s^{-1}, which is similar to that of a ferrocenium ion that has been linked covalently to an acceptor molecule to induce VT behavior.[4a] These data indicate that F1 and F2 can be assigned to Fe^{II} and Fe^{III} species, respectively. The molar ratios of Fe^{II} ($\varphi^{II} = (Fe^{II}/(Fe^{II}+Fe^{III}))$) and Fe^{III} ($\varphi^{III} = (Fe^{III}/(Fe^{II}+Fe^{III}))$) were estimated from the area fraction of F1 and F2 and are shown in Figure 4 d. The value of φ^{III} increases gradually with temperature. This change is fully reversible and is therefore indicative of electron transfer from the iron center of ferrocene to the dibenzochromenylium moiety induced by the change in temperature.

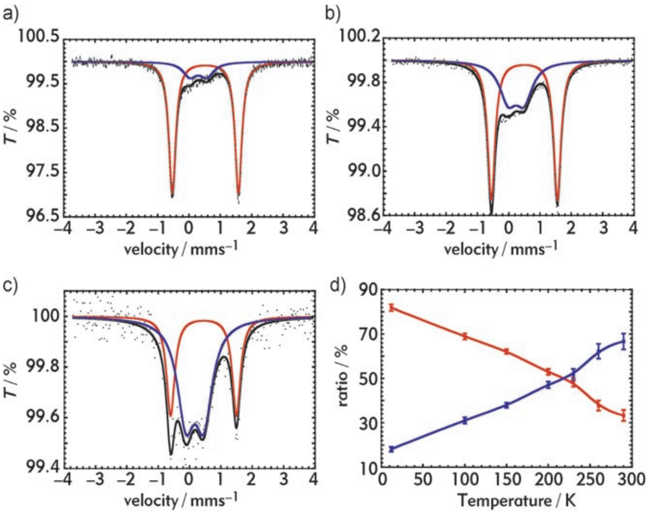

Figure 4. ^{57}Fe Mössbauer spectra of **5** at a) 12, b) 150, and c) 290 K (see text for explanation of colors), and d) the change in φ^{II} (red) and φ^{III} (blue) as a function of temperature.

The magnetic susceptibility of **5** is almost zero from 5 K to 400 K (see Supporting Information), where Fe^{III} species are present according to the results of Mössbauer spectroscopy. This result indicates that the presence of an organic radical is essential to offset the spin of Fe^{III} species as ferrocenium usually has an electronic spin, *S*, of 1/2. This organic radical could be located either on the cyclopentadienyl ring or the benzochromenylium ring and is strongly antiferromagnetically coupled with the ferrocenium radical. This means that **5** is likely to be in the equilibrium shown in Scheme 1 b in the solid state.

In conclusion, we have demonstrated a novel cyclocondensation reaction of 1-aryl ethynylanthraquinones in presence of a strong organic acid. This reaction proceeds almost quantitatively to give oxodihydrodibenzochromenylium compounds **5**–**8** in high yields. Expansion of the π-conjugated system in **5** and **6** with respect to that in **1** and **2** causes a lowering of the π* orbital (LUMO) level and promotes intramolecular electron transfer in **5**, which allows the valence tautomerism of **5** in the solid state.

Experimental Section

General synthesis of **5**–**8**: The 1-aryl ethynylanthraquinone (1 equiv) was dissolved in dichloromethane under argon to form a 0.025 M solution and stirred. Bis(trifluoromethanesulfone)imide (1.5 equiv) was added and the solution stirred for 60 min. The color gradually changed to dark red. Hexane was added and the mixture stirred overnight. Deep purple crystals were collected by filtration (see Supporting Information for further experimental details).

The crystals were mounted on a loop and data were collected with a Rigaku AFC8 diffractometer with the Rigaku Mercury CCD system equipped with a rotating-anode X-ray generator that emits graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.7107$ Å). An empirical absorption correction using equivalent reflections and Lorentzian polarization correction were performed with the program Crystal Clear 1.3.6 The structures were solved with the program SHELXS-97[12] and refined against F^2 using SHELXL-97.[13] Selected crystallographic data and experimental details are listed in the Supporting Information.

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