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# Synthesis and properties of 1,1'-bis[*p*-(*N*,*N*-dimethylaminophenyl)butadiynyl]ferrocene: a methodology for proton-mediated reversible conformation control of two function sites

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## ABSTRACT

An extended  $\pi$ -electronic conjugation system of the 1,1'-bis[p-(N,N-dimethylaminophenyl)butadiynyl]ferrocene derivative **1** has been synthesized, with our integrated cross-coupling reaction between the corresponding TMS-protected acetylenes in one-pot. Quantitative <sup>1</sup>H NMR and UV-vis spectral studies of **1** have been performed, providing a methodology for molecular functions transformable by a proton-mediated reversible conformation control.

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### Introduction

In recent years, a great deal of efforts have been taken for the construction of well-sophisticated  $\pi$ -electronic systems ( $\pi$ ES) reversibly transformable between well-defined molecular structures by means of various operations such as proton-base and metal-ligand interactions, to develop the new organic functional materials.<sup>1</sup> In relation with functional materials science aiming at such reversibly transformable  $\pi$ ES, we have been also engaged in the study of our original  $\pi$ ES reversibly transformable between its molecular functions with various outside stimuli.<sup>2</sup>

In the research processes, besides the promising functions, it is important as well that the structure-function relationships are readily and accurately evaluated. For these purposes, we have commonly introduced the 1,3-butadiyne linkage (diacetylene :  $-C \equiv C-C \equiv C-$ ) into our original  $\pi ES$ , which is useful not only for well-defining the constituents attached at both ends but also for the extension of conjugation with various  $\pi$ -electronic components, potentially leading to the new and curious molecular functions through one-, two, and/or three-dimensional interactions between them. As an example along this line, we previously reported the synthesis and properties of the 1,1'-bis (2-thienyldiacetylenyl)ferrocene derivative, described as Fc-Th<sub>2</sub>

(Chart 1).<sup>3</sup> Although each diacetylene-group connected Th constituent tightly combined with cyclopentadienyl ring (Cp) rotates along the Fc axis freely, the transformable functionality from the spectral changes would be brought purposively by control of the molecular motion and by manipulation of the spatial interactions between two Cp-Th constituents. In fact, Fc-Th<sub>2</sub> proved to be sensitive to Ag<sup>+</sup> and Hg<sup>2+</sup> ions selectively to change its electronic absorption spectra proportionally upon adding those metal ions and newly to afford the corresponding metal-ligand charge transfer (MLCT) transition bands, in striking contrast with the corresponding Fc derivative carrying one Cp-Th constituent (Fc-Th). This result suggests that two diacetylene-group connected Cp-Th constituents cooperatively react as ligands with these Ag<sup>+</sup> and  $Hg^{2+}$  ions, and then stop rotation along the Fc axis to face each other, like a pincette conformation, in a syn or synclinal conformation. The study of Fc-Th<sub>2</sub> which is further in progress can be regarded as a methodological research for the transformable functionality with conformation control by capturing Ag<sup>+</sup> or Hg<sup>2+</sup> ion as an outside stimulus, potentially leading to a new metal-ligand induced sensor.4

In our continuous investigations of the structure–function relationships of the 1,1'-bis(diacetylene-group)Fc system, the dimethylaminobenzene (DMAB) derivative **1** has been newly designed (Chart 2). There are two DMAB moieties in **1**, on which the protonation can be expected to proceed stepwise to produce one ammonium moiety at the first stage and two ammonium



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moieties at the second stage. In other words, the positive charge is introduced into 1 at each protonation stage one by one. The positive charge introduction, however, seems to bring in a different influence on the molecular motion between both protonation stages. At the first stage, the positive charge introduced by protonation on one DMAB as Lewis base could play an effective role for association with the other non-protonated DMAB in 1 for stabilization to stop rotation of two Cp-DMAB constituents along the Fc axis, resulting in a syn or synclinal conformation of those constituents preferably. Such an association between constituents of Cp-DMAB(H<sup>+</sup>) and Cp-DMAB in **1** likely arises from a hydrogenbonding, to form a proton sponge,<sup>5</sup> and/or from a CT interaction between them (Chart 2). To the contrary, at the second stage, the repulsive interaction between positive charges on both N/N atoms of DMABs in **1** should cause dissociation of the two Cp-DMAB(H<sup>+</sup>) constituents to restart rotation along the Fc axis, resulting in an anti or anticlinal conformation of those constituents preferably, similar to the conformation in neutral solutions due to the steric repulsion (vide infra). Based on the present speculative guideline, <sup>1</sup>H NMR, and electronic spectral changes of Fc-DMAB<sub>2</sub> between neutral and acidic solutions were examined and observed quantitatively. Taking  $pK_a$  values of 2.73–4.01 for conjugated acids p-(X)DMAB(H<sup>+</sup>) into consideration,<sup>6</sup> among a variety of acids, trifluoroacetic acid (TFA,  $pK_a = 0.23$ ) was employed in order to analyze the spectral changes in this experiment. In fact, TFA was found a good stimulus candidate to drive the purposive rotation of the Cp-DMAB constituents along the Fc axis in 1.

In this Letter, the synthesis of  $Fc-DMAB_2$  **1** and its spectral changes between neutral and acidic solutions will be reported together with a methodological concept for conformation control of the two Cp-DMAB constituents with TFA, as compared with those of the related compounds **2–4** (Chart 3).

The Fc-DMAB<sub>2</sub> and Fc-DMAB derivatives,  $\mathbf{1}$  and  $\mathbf{2}$ , were synthesized, as shown in Schemes 1 and 2. As conventional, the oxidative

cross-coupling reaction between terminal acetylenes of Fc (5,7 1.0 equiv) and DMAB ( $6^{8}$  1.1 equiv) under the Eglinton conditions<sup>9</sup> afforded Fc-DMAB **2**,<sup>10</sup> Fc<sub>2</sub> **3**,<sup>3,12</sup> and DMAB<sub>2</sub> **4**<sup>10</sup> in 65, 19, and 25% yields, respectively. On the other hand, Fc-DMAB<sub>2</sub> 1 cannot be obtained under the same reaction conditions as above, because the 1,1'-diethynyl Fc derivative 7 corresponding to 5 is extremely unstable to be employed as a convenient synthon.<sup>11</sup> Then. according to an integrated synthetic method for 1,1'-bis (diacetylene-group) connected Fc derivatives, just recently developed by us,<sup>12</sup> one-pot reaction between trimethylsilyl (TMS)protected Fc derivative  $\mathbf{8}^{13}$  and ethynyl-DMAB derivative  $\mathbf{6}$  under the TMS-deprotection and Eglinton-coupling conditions was applied to the synthesis of 1. As expected, the desired compound 1<sup>10</sup> could be obtained as a stable substance. But, its yield was 10% at most with very low reproducibility. Under the present reaction conditions, the DMAB dimer 4 formed in large quantity together with insoluble Fc polymer, indicating the much higher reactivity of the DMAB terminal acetylene 6 toward oxidative homo-coupling, as competed with deprotection reaction of the TMS group from  $\mathbf{8}^{12b}$ . Therefore, taking this fact into consideration, the TMS-deprotection and cross-coupling reaction between TMSprotected reactants 8 and 9 was carried out, consequently affording 1 in an acceptable yield of 45%. In the present tandem reaction conditions for Fc-TDMAB<sub>2</sub>, dimethoxyethane (DME) was found a better co-solvent than CHCl<sub>3</sub> somehow, similar to that for Fc-Th<sub>2</sub><sup>3</sup>.

The structures of new compounds including **1** were determined by Mass, IR, <sup>1</sup>H NMR, and UV–vis spectral measurements as well as their elemental analyses. In <sup>1</sup>H NMR spectra of **1–4**, even though the chemical shift differences between corresponding protons in respective compounds are fairly small, the structure-property analysis can be performed with confidence, because respective components are definitely combined with the rigid diacetylene linkage. In the case of **3** and **4**, it is shown that the diacetylene linkage induces low-field shift of aryl protons (Ar–H) by a maximum of





0.16 ppm from the corresponding ones of DMAB ( $\delta$  = 7.25 and 6.73 ppm), of methyl protons (Me–H) by 0.05 ppm from that of DMAB ( $\delta$  = 2.94 ppm), and of Cp-H by a maximum of 0.5 ppm from that of Fc ( $\delta$  = 4.15 ppm), respectively, apparently due to its inductive and anisotropic effects. In the case of 1 and 2, Cp-H of 1 ( $\delta$  = 4.54 and 4.33 ppm) appeared at the lower field than those of **2** ( $\delta$  = 4.49, 4.25, and 4.23 ppm), while Ar–H of **1** ( $\delta$  = 7.37 and 6.58 ppm) showed a small high-field shift than those of 2 ( $\delta$  = 7.40 and 6.62 ppm). The former can be explained by the same effects from the diacetylene linkage as above in consequence. On the other hand, the latter could be also attributed to an anisotropic effect from the increased diamagnetic ring current of Cp by connection with the diacetylene linkage, to affect Ar-H of an opposite DMAB. Otherwise, it suggests the more significance of a syn or synclinal conformation in **1** due to an attractive interaction between two extended Cp-DMAB conjugation constituents, where another small anisotropic effect has influence on the opposite Ar-H mutually more or less (Chart 2).<sup>14</sup> However, in practice, no chemical shift difference was observed in Me–H ( $\delta$  = 2.99 ppm) of DMAB between 1 and 2, clearly indicating a very low possibility of the



Figure 1. Electronic absorption spectra of 1 (green), 2 (red), 3 (purple), and 4 (blue) in CHCl<sub>3</sub> solution  $(1.3-1.5 \times 10^{-5} \text{ mol cm}^{-3})$ .

face-to-face conformation between two Cp-DMAB constituents in **1**. In other words, it can be concluded that under the neutral (non-protonated DMAB) conditions, as naturally deduced, Fc-DMAB<sub>2</sub> **1** exists in an anti or anticlinal conformation due to the steric repulsion (vide infra).





**Figure 2.** <sup>1</sup>H NMR spectral behavior of **2** ( $7.5 \times 10^{-3}$  M<sup>-1</sup> in CDCl<sub>3</sub>) by addition of TFA; (a) 0.0 equiv, (b) 0.2 equiv, (c) 0.4 equiv, (d) 0.6 equiv, (e) 0.8 equiv, (f) 1.0 equiv, (g) 3.0 equiv, (h) 5 equiv, and (i) 25 equiv.

The UV-vis spectra of **1**-**4** in CHCl<sub>3</sub> are shown in Figure 1. As is generally observed in Fc derivatives,<sup>15</sup> compounds 1, 2, and 3 characteristically exhibit very broad and weak bands at 400-550 nm due to the 3d-3d transition in Fe(II). The diacetylene-group connected DMAB dimer 4 afforded several vibration bands  $(\lambda_{\text{max}} = 327 \text{sh}, 351, \text{ and } 377 \text{ nm})$  together with a large bathochromic shift from DMAB ( $\lambda_{max} = 251 \text{ nm}$ ),<sup>16</sup> while the diacetylenegroup connected Fc dimer 3 showed almost one broad main band at  $\lambda_{max}$  = 290 nm similar to that of Fc ( $\lambda_{max}$  = 276 nm).<sup>15</sup> It simply concludes that the energy levels of HOMO and LUMO of the diacetylene linkage are much closer to those of DMAB to interact with each other efficiently. On the other hand, the derivatives 1 and 2 exhibited the electronic nature of both Fc and DMAB, indicating an electronic interaction between them through the diacetylene linkage. In particular, on the basis of Fc-DMAB 2, the Fc-DMAB<sub>2</sub> derivative **1** afforded a further combined spectrum between those of **3** and **4**, showing a fairly increased intensity in the main band at around 340 nm with two shoulders and a small bathochromic shift  $(\Delta \lambda = 18 \text{ nm})$  in the weak 3d–3d transition band.<sup>15</sup> These results conclude that the diacetylene linkage plays an important role as a transmission mediator to make an electronic communication between Cp and DMAB rings efficiently. Theoretical studies of 1 and 2 are in progress, for clarification of the absorption band origins between Cp and  $\pi$ -electronic components such as benzene, Th, and DMAB rings in this system.<sup>3,10</sup>

In order to examine the possibility of conformational control between two Cp-DMAB constituents in 1, the changes by TFA addition into chloroform solution were quantitatively observed by <sup>1</sup>H NMR spectral measurements (Figs. 2 and 3). From the sequential spectra of 1 and 2, it is apparently indicated that both Ar-H and Me-H are fairly sensitive to TFA to shift to the lower field more or less and thus the efficient protonation takes place rightly on DMAB to introduce the positive charge into these compounds. In the case of Fc-DMAB 2 (Fig. 2), Ar-H and Me-H as well as Cp-H simply shifted to the low field, almost proportionally upon adding TFA into CDCl<sub>3</sub> solution, respectively. The low-field shift changes with TFA contents for Ar-H and Me-H of Fc-DMAB<sub>2</sub> 1 (Fig. 3), however, proved not to be regular but rather of characteristic in behavior. In a range of 0.0–0.2 equiv addition of TFA, both Ar-H and Me-H swiftly moved down to 7.45 ppm for Ha, to 6.90 ppm for Hb, and to 3.05 ppm for Me–H (Fig. 3a and b). Unexpectedly, TFA addition beyond 0.2 equiv to 1 returned both Hb and Me-H shifting to the high field, with Ha almost remained at around 7.45 ppm similar to Cp-H at the original positions. This phenomenon was kept maintained successively up to 1.0 equiv TFA addition to 1 (Fig. 3c-f). Furthermore, TFA addition beyond 1.0 equiv to 1 again affected all protons to shift subtly and yet reversely to the low field toward 7.60 ppm for Ha, 7.44 ppm for Hb, and 3.31 ppm for Me-H (Fig. 3g-i) in a stationary spectrum, all of which are finally almost the same as those for corresponding



Figure 3. <sup>1</sup>H NMR spectral behavior of 1 ( $3.8 \times 10^{-3}$  M<sup>-1</sup> in CDCl<sub>3</sub>) by addition of TFA; (a) 0.0 equiv, (b) 0.2 equiv, (c) 0.4 equiv, (d) 0.6 equiv, (e) 0.8 equiv, (f) 1.0 equiv, (g) 3.0 equiv, (h) 5.0 equiv, and (i) 25 equiv.

protons of **2** in a CDCl<sub>3</sub> solution containing 25 equiv of TFA (Fig. 2i). From these spectral changes, it is apparently indicated that since TFA is stronger in acidity than DMAB(H<sup>+</sup>) by more than 300 times, the first-step protonation onto DMAB in 1 immediately and steadily takes place, similar to 2. On the other hand, the second-step protonation in 1 was found fairly slow, especially as made in a comparison between Figures 2f-i and 3f-i. These results clearly show that one DMAB(H<sup>+</sup>) site protonated in a range between 0.0 and 1.0 equiv of TFA interacts attractively for stabilization with the other non-protonated DMAB in **1** to stop rotation along Fc axis forming a closely connected conformation preferably, where the diamagnetic ring current effect of DMAB directly has influence on each other (Chart 2). To the contrary, two  $DMAB(H^{+})$  sites gradually formed in a range between 1.0 and 25 equiv of TFA interact repulsively with each other to restart rotation along Fc axis forming a far disconnected conformation preferably, where both  $DMAB(H^+)$  sites of **1** are free from such an anisotropic effect. independently behaving as the DMAB(H<sup>+</sup>) site of **2**. Also, it might be noted that in both cases, the peaks owing to Cp-H gradually broadened and completely disappeared in the baseline in a range of excessive amount of TFA somehow.<sup>10</sup>

Similarly, from sequences of UV-vis spectra of 1 and 2 in response to TFA contents in CHCl<sub>3</sub>, it is indicated that their changing behavior was characteristic (Figs. 4 and 5). In the case of 2, the spectra changed gradually but explicitly via two isosbestic points at 305 and 378 nm, accompanied by a simple hypochromic effect up to 600 equiv addition of TFA. Successively, in a region beyond 600 equiv of TFA, the spectral changes were fairly clear-cut to afford several vibration bands reaching the stationary spectrum at around 4000 equiv TFA addition. Nearly the same spectral changing behavior as **2** was observed in Fc-DMAB<sub>2</sub> **1** via isosbestic points at 294 and 395 nm, finally affording almost the same-shaped stationary spectrum as **2** at around 4000 equiv TFA addition. In the case of 1, distinct from 2, another set of isosbestic points was observed at 435 and 490 nm in the weak 3d-3d transition bands, which is almost overlapped so much as to be overlooked. These results apparently indicate that the stationary spectra of **1** and **2** at around 4000 equiv of TFA are both assigned to the completely protonated DMAB(H<sup>+</sup>) species. Both electronic absorption and <sup>1</sup>H NMR spectra of **1** and **2** changed by TFA addition recovered the original ones entirely by neutralization with triethylamine (NEt<sub>3</sub>), that is, these spectral changes are reversibly transformable with TFA and NEt<sub>3</sub> within a region under the applied conditions.

Even in such lower-concentration solutions for UV-vis spectral experiment, as compared with <sup>1</sup>H NMR spectral one, the monoprotonated Cp-DMAB(H<sup>+</sup>) constituent should evidently be produced in 1 somewhere in a range between 0 and 600 equiv TFA addition. And thus the Cp-DMAB(H<sup>+</sup>) constituent would interact with the other non-protonated Cp-DMAB constituent inductively to form a closely connected conformation, as already proved from the <sup>1</sup>H NMR spectral experiment. Further spectral changes in a range beyond 600 equiv of TFA presumably indicate the repulsive interaction between two Cp-DMAB(H<sup>+</sup>) constituents in 1 to recover a far disconnected conformation, reflecting a unique electronic structure owing to the completely protonated Cp-DMAB(H<sup>+</sup>) constituent. Unfortunately, beyond or according to expectation, it proved that no particularly new  $\pi$ -electronic interaction induces in the mono-protonated Cp-DMAB(H<sup>+</sup>) species of **1**. This is naturally because the two Cp-DMAB constituents in 1 are fixed and rotate along Fc axis so far at a distance of 4 Å as to be unable to make a transannular interaction electronically,<sup>17</sup> even though the Cp- $DMAB(H^+)$  species of **1** exists in a face-to-face conformation (Chart 2).

In conclusion, the 1,1'-bis(diacetylene-group) connected Fc-DMAB<sub>2</sub> derivative **1** has been synthesized in a moderate yield under the improved cross-coupling conditions between TMS-





**Figure 4.** UV–vis spectral changes of **2**  $(3.82 \times 10^{-5} \text{ M}^{-1} \text{ in CHCl}_3)$ . Arrows show the changing direction of respective spectra by addition of TFA from 0 equiv, 100 equiv, 200 equiv, 400 equiv, 600 equiv, 800 equiv, 1000 equiv, 2000 equiv, 4000 equiv, 4000 equiv, 8000 equiv, and to 10,000 equiv.

ε/10<sup>5</sup> M<sup>-1</sup>cm<sup>-1</sup>



**Figure 5.** UV–vis spectral changes of **1**  $(1.92 \times 10^{-5} \text{ M}^{-1} \text{ in CHCl}_3)$ . Arrows show the changing direction of respective spectra by addition of TFA from 0 equiv, 100 equiv, 200 equiv, 400 equiv, 600 equiv, 800 equiv, 1000 equiv, 2000 equiv, 4000 equiv, 6000 equiv, and to 10,000 equiv.

protected acetylenes **8** and **9**. <sup>1</sup>H NMR and UV–vis spectral studies of **1** and **2** indicated that the diacetylene linkage works as a mediator for communication with DMAB and Cp rings smoothly. It is also revealed that TFA–NEt<sub>3</sub> combination could drive a purposive rotation of two Cp-DMAB constituents along the Fc axis in **1**, potentially providing a methodology for reversibly transformable functions by the conformational control between them. Further investigations on the spectral changes of **1** by means of other outside stimuli such as metal-coordination and charge-transfer (CT) complexation are now in progress.<sup>18</sup>

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- 10. <sup>1</sup>H NMR (CDCl<sub>3</sub>) and UV-vis (CHCl<sub>3</sub>) spectral data are only just preliminarily shown. Other physical properties will be reported properly in a conclusive discussion on the structure-property relationship somewhere, in terms of solvent effect, temperature effect, theoretical interpretation, and so on. 1: <sup>1</sup>H NMR;  $\delta$  = 7.37 (d, *J* = 8.2 Hz, 4H, Ar-H), 6.58 (d, *J* = 8.2 Hz, 4H, Ar-H), 4.54 (d, *J* = 2.0 Hz, 4H, Cp-H), 4.33 (d, *J* = 2.0 Hz, 4H, Cp-H), and 2.98 ppm (s, 12H, Me-H). UV-vis;  $\lambda_{max}$  = 291 (log  $\epsilon$  4.46, sh), 341 (4.76), 364 (4.69, sh), and 457 nm (3.43). **2**: <sup>1</sup>H NMR;  $\delta$  = 7.40 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.62 (d, *J* = 8.4 Hz, 2H, Ar-H), 4.50 (dd, *J* = 2.0 and 2.0 Hz, 2H, Cp-H), and 2.99 ppm (s, 6H, Me-H). UV-vis;  $\lambda_{max}$  = 286 (4.22, sh), 334 (4.58), 355 (4.47, sh), and 439 nm (3.24). **4**: <sup>1</sup>H NMR;  $\delta$  = 7.39 (d, *J* = 8.9 Hz, 4H, Ar-H), 6.61 (d, *J* = 8.9 Hz, 4H, Cp-H), and 2.99 ppm (s, 12H, Me-H). UV-vis;  $\lambda_{max}$  = 327 (4.64, sh), 351 (4.71), and 377 nm (4.64).
- 11. As a few limited examples of 1,1'-bis(diacetylene-group) connected Fc derivatives, cyclophanes which are sterically hindered and multiply protected with bulky *tert*-butyl groups on both Cp rings were synthesized, using the corresponding 1,1'-diethynylferrocene derivatives under the Eglinton conditions. Fabian, K. H. H.; Lindner, H.-J.; Nimmerfroh, N.; Hafner, K. Angew. Chem., Int. Ed. 2001, 40, 3402–3405.
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- 16. DMAB which was purchased from Sigma-Aldrich (CAS No. 121-69-7) shows the absorption maxima at  $\lambda_{max} = 251 \text{ nm}$  (log  $\varepsilon$  4.05) for the main band and at  $\lambda_{max} = 298 \text{ nm}$  (3.35) for the transition-forbidden band in CHCl<sub>3</sub>.
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- 18. A synthetic method for the Fc derivatives with CT character, described as Fc-( $\pi$ -acceptor)( $\pi$ -donor), has been recently developed. From the viewpoint of the conformation control driven by CT interaction stimulus, the results will be reported in detail, through the comparative study between intra- and intermolecular complexation, together with their metal-coordination complexation.