

## 論文内容の要旨

### 論文題目

## Creation of Novel Donor-Acceptor-Donor-Type Molecules with Strong Photoabsorption and Intense Luminescence

(強い光吸収、発光を示す新規ドナー・アクセプター・ドナー型分子群の創製)

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### Chapter 1 : General introduction

In these days, much attention has been collected on molecules featuring photofunctionalities, conversion of light to signals such as luminescence and isomerization, because of their potential use in molecular optoelectronics, and ultimately, in molecular devices. One of well-known strategy of molecular design to harvest visible light is connecting electron donor and acceptor through  $\pi$ -conjugation in order to express intramolecular charge transfer (ICT) transition. Our laboratory has researched such molecules like donor-acceptor-donor (D-A-D) types, and one of good examples is those containing dimethyl diethynylfumarate (**DDF**) as an acceptor scaffold. For example, **E-1**, comprising **DDF** and triarylamine (**TAA**) as an electron donor site (Fig. 1) shows curious photochemical activities; strong absorption in the visible region and visible-light *E-Z* photoisomerization accompanied by switching of fluorescence and electronic communication in the mixed-valent (MV) state [1]. These properties would be suitable for molecule-based photofunctional devices; however, the efficiency of fluorescence and photoisomerization reaction of **E-1** is slightly low ( $\Phi_{\text{f}} = 0.15$  and  $\Phi_{\text{total}} = 0.075$ ), so that some efforts are required to improve these properties.

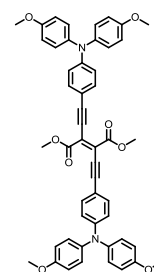


Fig. 1. **E-1**

My Ph.D work focuses on the creation of new photofunctional molecules based on **E-1**. In chapter 2, I focus on the improvement of photoisomerization property and adopt *N*-phenylcarbazole (**NPC**) group to new terminal donor moieties [2]. In chapter 3, I focus on the improvement of luminescent property, and attempt to convert the **DDF** framework into the Pechmann dye motifs as a central acceptor moiety by means of my original intramolecular double lactonization reaction. As a result, I found the missing structural isomer of Pechmann dye [3]. In chapter 4, I achieved the effective synthesis of the Pechmann dye's missing framework (**P<sub>56</sub>**-framework) and successfully introduced it into a new D-A-D system. As a result, I revealed that the **P<sub>56</sub>**-framework with two anisyl moieties shows efficient fluorescence ( $\Phi_{\text{f}} = 0.91$ ); in contrast, that with two **TAA** moieties displays slightly low luminescent property ( $\Phi_{\text{f}} = 0.20$ ).

### Chapter 2 : Introduction of NPC as the donor site focusing on improvement of photoisomerization property

**NPC**, a fused analogue of triarylamine, collects much attention because of its utility for the hole transport and luminescent materials in organic electronics. Their efficient fluorescent property mainly stems from the radiative process from locally excited (LE) state, but in case of the D-A shaped molecules consisting of **NPC** and acceptor moieties, they also show fluorescence from the intramolecular charge transfer (ICT) excited state stabilized with the mesomeric effect [4]. Thus, I introduced **NPC** and dimethoxy substituted **NPC** moieties as two donors into D-A-D shaped molecules containing **DDF** framework, and synthesized **E-2** and **E-3**. As a result, they show strong absorption in visible region assignable to the ICT transition from **NPC** to **DDF**. In particular, **E-3** shows reversible photoisomerization reaction by excitation of the ICT band

with high efficiency ( $\Phi_{\text{total}} = 0.40$ ) (Figs. 2 and 3). In addition, **E-3** is redox active because of preventing the electropolymerization reaction derived from carbazole moiety, so that its photochromism is accompanied by the modulation of electronic communication in the one-electron oxidized MV state; **E-3** features more intense interaction than **Z-3**. This behavior is a suitable property for photofunctional material of molecule-based devices.

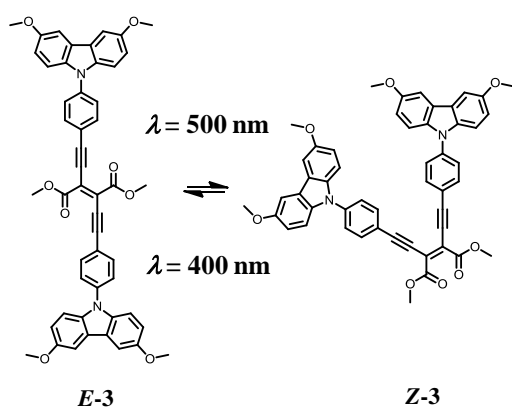


Fig. 2. Reversible **E/Z** photoisomerization in **E/Z-3**

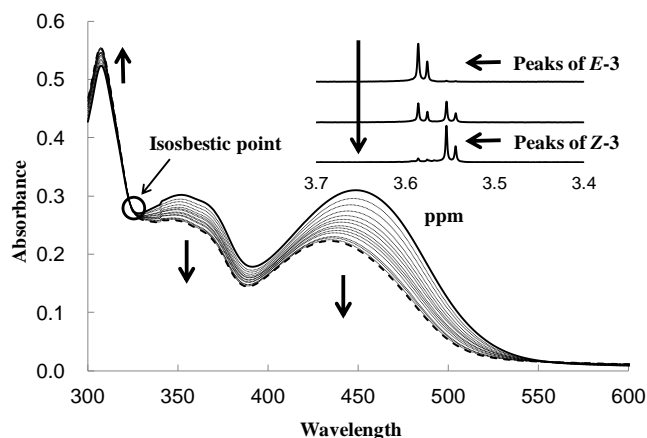


Fig. 3. Time-course UV/Vis spectral change of **E-3** in toluene upon irradiation with  $\lambda=500$  nm light. The inset shows a time-course  $^1\text{H}$  NMR spectral change in  $[\text{D}^8]$  toluene under the same condition.

### Chapter 3 : Conversion of DDF framework into Pechmann dyes focusing on improvement of luminescent property and discovery of a new structural isomer and an application in organic electronics

Pechmann dye ( $P_{55}$ -framework) and its known structural isomer ( $P_{66}$ -framework) are good pigments and acceptors, and feature rigid planar structures that stem from the cross-conjugated electron-withdrawing lactone rings [5]. These properties are optimal for the construction of D-A-D quadrupolar molecules with intense D-A interaction, and applications in organic electronics; however, the Pechmann dye frameworks have not been sufficiently appreciated in such studies. I regarded the **DDF** framework as an open form of Pechmann dyes protected by the methyl ester groups, and expected that with an appropriate ring closure reaction, it could open up a new route to the Pechmann dye family, and could provide access to their missing structural isomers (Fig. 4). Treatment of **E-1** in boiling acetic acid containing a catalytic amount of hydrochloric acid gave rise to  $P_{55}$ -**1**,  $P_{66}$ -**1**, and surprisingly,  $P_{56}$ -**1** comprising an unreported structural isomer of Pechmann dye (Fig. 5). The three compounds feature more intense and redshifted ICT bands in the visible and NIR region, and higher fluorescence quantum yields than those of **E-1** (Table 1 and Fig. 6). In particular, the value of fluorescent quantum yield of  $P_{66}$ -**1** is distinguished ( $\Phi_f = 0.81$ ) as displayed in Table 1. Moreover, the thin film of  $P_{66}$ -**1** fabricated by means of vacuum deposition on a silicon substrate works as stable P-type semiconductor with a hole mobility of  $5.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

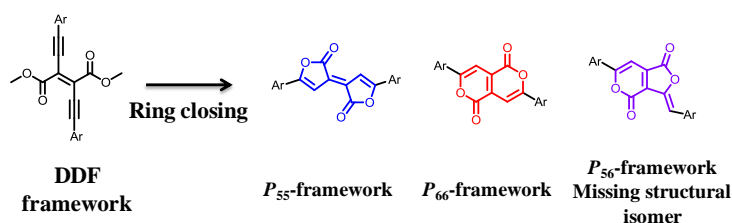


Fig. 4. My insight of the relationship between **DDF** framework and the frameworks of Pechmann dye family including a missing structural isomer.

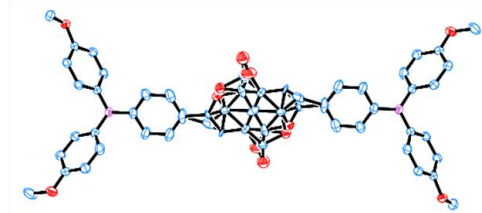


Fig. 5. ORTEP drawing of  $P_{56-1}$  in the crystal with thermal ellipsoids set at 50 % probability. Hydrogen atoms are omitted for clarity. ● = carbon, ● = oxygen and ● = nitrogen. Disordered atoms are remained in the center part.

Table 1. Photochemical properties of all D-A-D shaped molecules

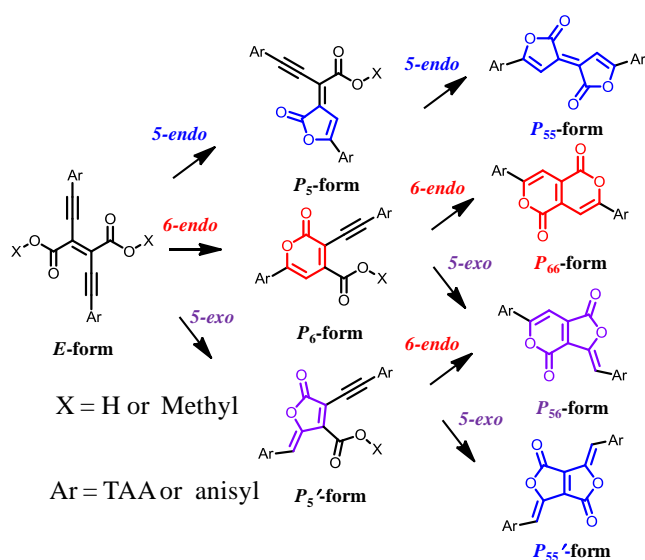
Compounds	Absorption		Fluorescence	
	$\lambda_{\max}/\text{nm}$	$\epsilon_{\max}/\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\max}/\text{nm}$	$\Phi_{\text{F}}$
$P_{55-1}$	674	65000	753	0.27
$P_{56-1}$	574	37000	692	0.20
$P_{66-1}$	538	50000	617	0.82
$E-1$	482	36000	660	0.15

#### Chapter 4 : The synthesis of a new molecule comprising $P_{56}$ -framework and its photochemical property

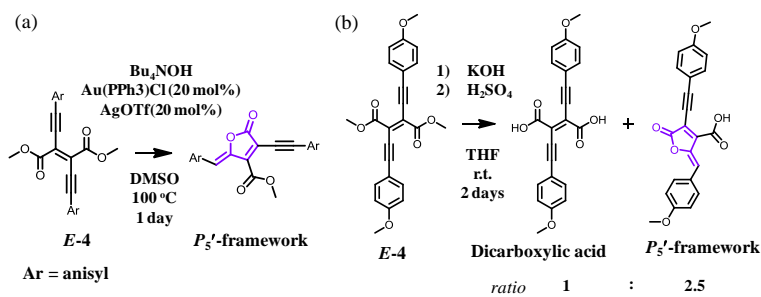
In Chapter 3,  $P_{56-1}$  does not show efficient fluorescence as seen in  $P_{66-1}$  although they consist of similar condensed lactone frameworks. To clarify this phenomenon, the creation of another molecules comprising  $P_{56}$ -framework is required, so that the next challenge is to achieve effective synthesis. A plausible reaction mechanism for  $P_{55}$ ,  $P_{66}$ , and  $P_{56}$ -frameworks is shown in Scheme 1. In case of  $E-1$  as a starting material, contiguous intramolecular double lactonization yields the products, where three types of cyclization, **5-endo**, **6-endo** and **5-exo** take part (Fig. 7). As seen in Scheme 1, there are two synthetic routes of  $P_{56}$ -framework in which the inversion of cyclization modes between **6-endo** and **5-exo** is required. I expected that this inversion could be achieved by varying the activator of an ethynyl moiety as a stepwise fashion. In particular, the following order, **5-exo** and **6-endo** is more attractive way because the  $P_5'$ -framework is a precursor to not only  $P_{56}$ -framework but also  $P_{55}'$ -framework which is another missing structural isomer of Pechmann dye as displayed in Scheme 1; in other words, the synthesis of the  $P_5'$ -framework will be a breakthrough to expand this research. Hereafter, I adopt this strategy to a new starting material,  $E-4$  which has **DDF** framework and two anisyl moieties as terminal donors.

I focused on three kinds of activator, proton, triphenylphosphinegold(I) chloride and silver powder. As a result, I found two ways to produce the  $P_5'$ -framework; one is the reaction of  $E-4$  with triphenylphosphinegold(I) chloride and tetrabutylammonium hydroxide ( $\text{Bu}_4\text{NOH}$ ), and the other is de-esterification reaction of  $E-4$  and following process to disengage the dicarboxylic acid moiety as seen in Scheme 2. Especially the latter structure is revealed to possess both the  $P_5'$ -framework and a carboxylic acid moiety by several measurement. This result indicates that its reaction with silver powder is expected to produce both  $P_{56}$ - and  $P_{55}'$ -frameworks because silver powder is a catalyst to mainly promote the cyclization in **5-exo** mode in case of a single lactonization reaction between carboxyl acid and ethynyl moieties. Unexpectedly, this reaction gave rise to only  $P_{56}$ -framework and I selectively synthesized  $P_{56-4}$  in the yield of 32%.

The crystal structure of  $P_{56-4}$  is shown in Fig. 8, and optical data for  $P_{55-4}$ ,  $P_{56-4}$ , and  $P_{66-4}$  are assembled in Table 2.  $P_{56-4}$  shows the highest fluorescence quantum yield ( $\Phi_{\text{F}} = 0.91$ ), which assures the usability of the  $P_{56}$  framework. From this result, the low  $\Phi_{\text{F}}$  of  $P_{56-1}$  would stem from the interaction between TAA moiety and  $P_{56}$ -framework in the ICT excited state; in other word,  $P_{66-1}$  would be a special case to show efficient fluorescence derived from the planar configuration of the ICT excited state [6].



Scheme 1. Plausible reaction mechanism of the intramolecular double lactonization



Scheme 2. Two way of reaction condition to produce  $P_5'$ -framework

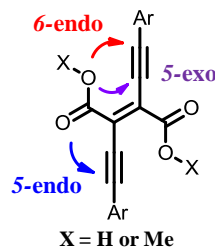


Fig. 7. The three modes of cyclization

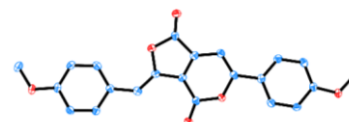


Fig. 8. ORTEP drawing of  $P_{56}$ -4 in the crystal with thermal ellipsoids set at 50 % probability. Hydrogen atoms are omitted for clarity. ● = carbon and ● = oxygen.

Table 2. Luminescent properties of  $P_{55}$ -4,  $P_{56}$ -4, and  $P_{66}$ -4

Compounds	Fluorescence	
	$\lambda_{\max}$ / nm	$\Phi_F$
$P_{55}$ -4	595	0.35 (577 nm)
$P_{56}$ -4	520	0.91 (500 nm)
$P_{66}$ -4	507	0.80 (500 nm)

## Conclusions

By substituting the TAA moiety of  $E$ -1 with NPC, I achieved the improvement of the photoisomerization quantum yield. Also, I for the first time observed MV communication in a NPC-based compound, the intensity of which is switched upon the photoisomerization. The DDF framework can be converted into the Pechmann dye families via intramolecular double lactonization reaction, including one of the missing structural isomers,  $P_{56}$ -framework. Donor-appended Pechmann dyes constitute D-A-D quadrupolar molecules, which show good photochemical properties and usability in organic electronics. The stepwise approach of this reaction leads the effective synthesis of a new molecule comprising  $P_{56}$ -framework. The comparison of luminescent properties with molecules consisting of  $P_{56}$ -or  $P_{66}$ -framework reveals that the nonradiative decay would be enhanced by the introduction of large donor moieties except for  $P_{66}$ -1 derived from the high planarity in the excited state.

## References

- [1] Sakamoto, R. *et al. Chem. Eur. J.* **2008**, *14*, 6978 – 6986. [2] Hayashi, M. *et al. Chem.-Eur. J.* **2012**, *18*, 8610-8613. [3] Hayashi, M. *et al. J. Am. Chem. Soc.* **2011**, *133*, 14518-14521. [4] Galievsky, V. A. *et al. J. Phys. Chem. A* **2010**, *114*, 12622–12638. [5] (a) Silver, J. *et al. J. Mater. Chem.*, **1994**, *4*, 1201-1204. (b) Bowden, K. *et al. J. Chem. Soc. Perkin Trans. 2* **1991** 743-746. [6] Kapturkiewicz, A. *et al. J. Phys. Chem. A* **1997**, *101*, 2332-2344.