Syntheses, Reactions, Absorption and Fluorescence Properties of Novel Anilines

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July 2010

Doctoral Thesis at Osaka Prefecture University

ACKNOWLEDGMENT

The author would like to express his deepest gratitude to Professor Kazuhiko Mizuno at Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, for his continuous and valuable guidance and encouragement throughout this study.

The author would like to express his gratitude to Professor Masamitsu Shirai and Professor Akiya Ogawa at Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University for their comments and suggestions by reading of the manuscript. The author would also like to express his deepest gratitude to Professor Hisaji Taniguchi at Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, for his continuous and valuable guidance and encouragement throughout this study.

The author is deeply indebted to Associate Professor Hiroshi Ikeda for his continuous and valuable guidance and encouragement along the course of the studies.

The author is sincerely express his gratitude to the presindent Yoshihisa Takeda at Wakayama Seika Kogyo Co., Ltd. for providing a chance to carry out this work and for his warm-hearted encouragement.

The author is sincerely grateful to Dr. Motonori Takeda (Senior Managing Director) and Dr. Akihiro Tamaki at Wakayama Seika Kogyo Co., Ltd. for their helpful discussions, continuous guidance and warm-hearted encouragement during the course of this work.

The author is deeply indebted to Mr. Toshitsugu Kobata, Dr. Asao Hosoda (present affiliation: the Wakayama prefectural government office), Dr. Hajime Mori, and Dr. Yoshie Tanaka at Industrial Technology Center of Wakayama Prefecture, for their helpful discussions. The author is also indebted to Dr. Yasuhito Miyake at Industrial Technology Center of Wakayama Prefecture, for X-ray crystallographic analysis and his helpful discussions.

Grateful acknowledgments are due to following contributors: Associate Professor Norimitsu Tonai at Osaka University and Mr. Issei Tsuji at Seika Corporation (for X-ray

crystallographic analysis and photographs of the crystals prepared in this research); Dr. Maki Ohashi (for X-ray crystallographic analysis), Mr. Takayuki Fujii (for optical measurements) and Mr. Yusuke Kano (for DFT calculations, and electric measurements) at Osaka Prefecture University.

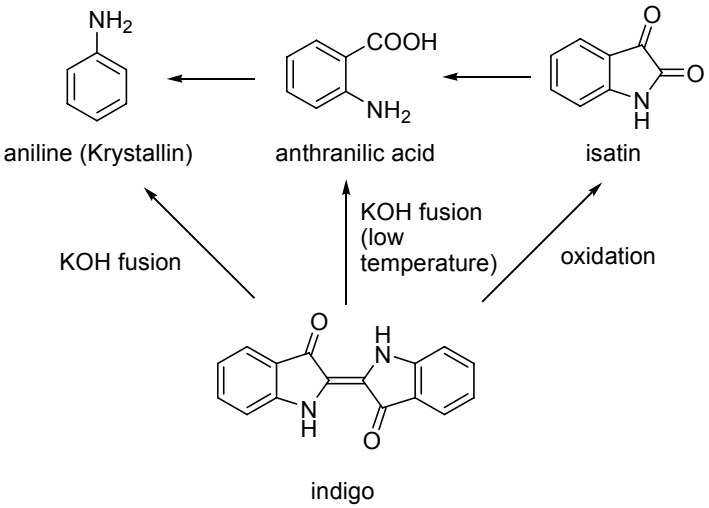
The author most sincerely thanks all members of Seika Group for everything and wish to dedicate this doctoral thesis to the late chairman of the Seika Corporation, Minoru Takeda.

Finally, the author would like to thank his wife Kayo Imoto, and his parents Sadafumi Imoto and Masami Imoto for their encouragement.

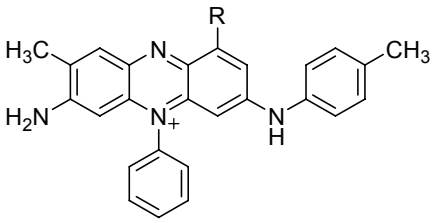
CONTENTS

GENERAL INTRODUCTION

Aniline was first isolated from the destructive distillation of indigo in 1826 by Unverdorben, who named it *Krystallin*.[1] In 1840, Fritzsche isolated the same oil when he distilled indigo in the presence of caustic potash, and called it *aniline* (Scheme 1).[2] In 1856, in an attempt to prepare quinine from coal tar, Perkin oxidized aniline using a strong oxidizing agent, potassium dichromate. He did not obtain quinine at all, but obtained a purple dye, and named it *mauveine*.[3] In order to manufacture his new synthetic dye, he built the world-first factory of the aniline dye industry. At the time of mauveine's discovery, aniline was an expensive laboratory compound, but it was soon prepared "by the ton" using a process previously developed by Béchamp (Scheme 2). From Perkin's serendipitous discovery, anilines went on to become a generic class of organic chemistry that made tremendous contributions to material well-being.

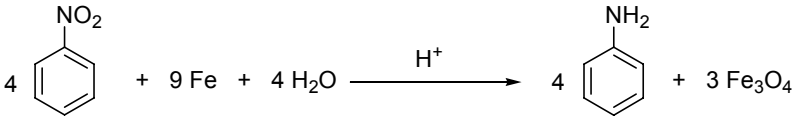


SCHEME 1. Formation of aniline (Krystallin) from indigo



mauveine

R = H
R = CH_3 (minor component)

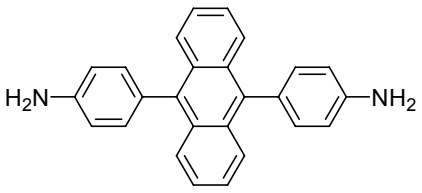


SCHEME 2. Béchamp reduction

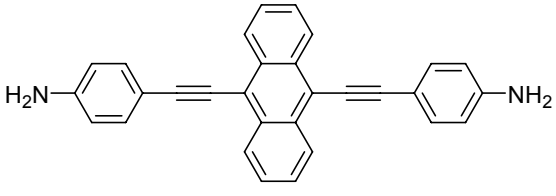
Initially, the chemistry of anilines started with synthetic dyestuffs.[4] In the 20th century, anilines were transformed into rubber,[5] sulfonamide drugs[6] and other therapeutic agents.[7] Anilines also contributed to the development of novel polymers. Melamine,[8] heterocyclic

triaminotriazine, became commercially available in 1939, followed in the 1950s by aniline- or toluidine-derived polyurethanes,[9] and aramids.[10] Photographic[11] and agricultural[12] products, vulcanizing agents,[13] antioxidants[14] and curing agents for epoxy resins[15] relied, and continue to rely, on the availability of a vast range of anilines. For a century, the manufacture of anilines for pigments was a leading industry,[16] giving stability and prosperity to a broad array of business activities. After the late 1970s, the industry reinvented itself, particularly through entry into the life sciences.[17] Further, newer uses of anilines include high performance engineering plastics,[18] organic semiconductors,[19] and traditional aniline pigments in the photorealistic ink jet printer.[20] Nowadays, quite apart from providing routes to synthetic pigments, pharmaceuticals and new polymers, anilines are revolutionizing the study of organic chemistry, and innovating technology of the chemical industry. Thus, novel anilines have strongly been attracting organic chemists because of their new performances.

For example, Hasegawa disclosed that polyimide film using 9,10-bis(4-aminophenyl)anthracene (**1**) is a excellent blue photoluminescent material.[21] Recently, Tohnai *et al.* studied solvatochromism and interesting crystalline-state fluorescence properties of the compound **1** through control of crystal structure.[22] They discovered that the compound **1** incorporates various solvent molecules that controled the crytal packing and fluorescence in the crystalline-state, when it was recrystalized from the solvents. In fact, the author and Seika Corporation that he works at provided the compound **1** for the study.[23] As the auther optimized Sonogashira coupling of 9,10-dibromoanthracene with 4-aminophenyl-acetylene to develop an efficient synthetic method for 9,10-bis(4-aminophenylethynyl)anthracene (**2**). Tohnai is continuing the study in detail and is finding more interesting optical properties in the



1

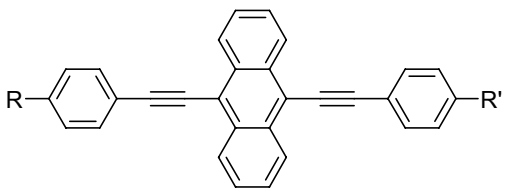


2

crystals of **2**.[24] Thus, anilines continue to be investigated in a broad range of fields such as functional optical materials.[25]

The amino groups of anilines have an electron-donating ability. All the anilines exhibit their performances as electron donors collaborating with electron acceptors. The auther has paid attention to effects of the *intra*- and *inter*molecular CT interactions between anilines and acceptors on optical properties of novel anilines. The presence of CT interactions between anilines and acceptors shows the optical properties of anilines different from anilines themselves.

Recently, the compound **3** and its derivatives have received attention as nonlinear optical materials.[26] Anilines also have been a main subject of research on two-photon absorption in the nonlinear optical science.[27] It is well known that introduction of CT interaction between acceptor and donor groups to the terminal positions of π conjugated systems, such as in *p*-nitroaniline, is one of the most effective means of improving nonlinear optical properties.[28] The heightened interest in the nonlinear optical characteristics of **3** has led to the synthesis and evaluation of derivatives with substituents at the *para*-positions (R and R', Fig. 1) of the ethynylphenyl groups.[29] So far, however, compounds that contain both *para*-acceptor and *para*-donor groups in the phenylethynyl moieties have not been thoroughly studied. In particular, the prototypical substance, 9-(4-aminophenylethynyl)-10-(4-nitro-phenylethynyl)anthracene (**4**), had never been prepared, though it is expected to exhibit interesting linear and nonlinear optical properties. As the compound **4** contains a strong electron donating group (NH_2) and a strong electron withdrawing group (NO_2) at the terminal positions of an extended π conjugated system, it should display strong CT characteristics. With its potentially interesting properties in mind, the auther has developed an efficient synthetic method of **4**.[30] In addition, the

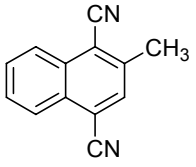


3: R , R' = H
4: R = NH_2, R' = NO_2

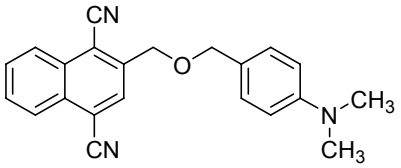
FIGURE 1. 9,10-Bis(phenylethynyl)anthracene derivatives

solvatochromism in the absorption and fluorescence spectra of **4** were measured and compared with those of **3**.

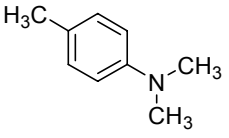
On the other hand, anilines also have been one of main subjects of researches on exciplexes in photophysics.[31] Exciplexes, which are photoinduced from donors with acceeptors and exhibit characteristic emissions, have been studied in solutions through evaluations of molecular structure and solvent effects. Most of them occur little CT interaction between donors and acceptors in the ground state, but occur CT interaction only in the excited state and emit the characteristic fluorescence. Although some pairs of donors and acceptors which already occur CT interaction in the groud state form exciplexes when photoexcited, they often transfer one electron from donors to acceptors because of the too strong CT interaction, instead of forming exciplexes. The important thing is how strong CT interaction is appropriate for formation of exciplexes in solution and in the crystalline state. However, effects of electron-donating substituents on exciplex formation are not clarified in solution and especially in crystals. To evaluate the function of anilines as donors in exciplexes, the author designed and synthesized a novel aniline derivative, 1,4-dicyano-2-(4'-*N,N*-dimethylaminobenzyloxy)-methylnaphthalene (**5**)[32] which would form an *intra*molecular exciplex between the 1,4-dicyano-2-methylnaphthalene (DCMN) acceptor and *N,N*-dimethyl-*p*-toluidine (DMT) donor moieties. The author investigated the substituent effects on the formation and properties of exciplexes. As the results, the crystals of this compound formed a unique *inter*molecular mixed-stack, one-to-one CT complex in the ground state. The observations clearly demonstrated that the *inter*molecular exciplex generated by excitation of the crystals of **5** arises directly from the ground state CT complex, in which the DCMN and DMT moieties are immobilized in a face-to-face manner by *inter*molecular CT interactions. The auther



DCMN



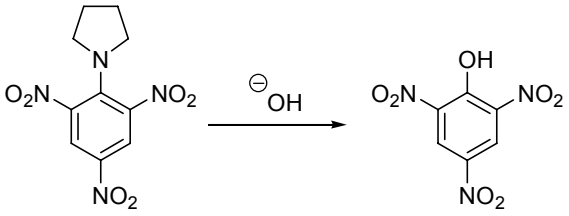
5



DMT

successfully has developed an effective methodology for preparing exciplex-emissive organic crystals through the investigation.

As a part of the continuing research program to investigate the CT interaction of anilines, the author was interested in the reactivity of nitrated anilines which could react with hydroxide ions in aqueous solutions directly providing the corresponding phenols,[33] naphtholes[34] and quinolinols.[35] However, amino groups generally have been known as poorer leaving groups compared with common ones such as halogens in aromatic necleophilic substitution reactions. Actually, it has been reported that only very highly activated anilines, for example 2,4,6-trinitro-1-pyrrolidinobenzene, react with hydroxide ions (Scheme 3).[36] The hydroxide ion is a much weaker base than the amide ion, NH_2^-. Besides, 4-nitroaniline has resonance forms (Fig. 2) which can contribute to stabilize the ground-state of 4-nitroaniline. The author thought, however, that an amino group would become a good leaving group in aqueous alkaline media, even when it was activated by only one nitro group. If the amino group interacts with H_2O in aqueous media (hydrogen bonding), the resonance stabilization of nitroanilines would be reduced. In fact, the author discovered that even mono-nitrated anilines are able to react with hydroxide ions under mild conditions. Surprisingly, the nitroanilines showed higher reactivity than nitrated chlorobenzenes that are common substrates for aromatic nucleophilic substitution reactions. Moreover, the author developed a methodology to synthesize bis(nitrophenol) derivatives, 4,4'-dihydroxy-3,3'-dinitrodiphenyl ether (**6**) and 1,3-bis(4-hydroxy-3-nitrophenoxy)benzene (**7**), as shown in Scheme 4.[37] The bis(nitrophenol) derivatives were easily hydrogenated



SCHEME 3. Reaction of nitrated aniline with hydroxide ion

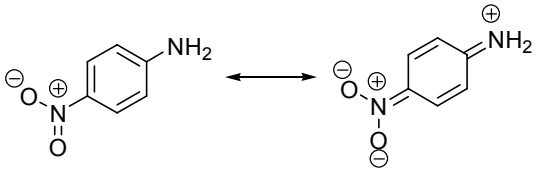
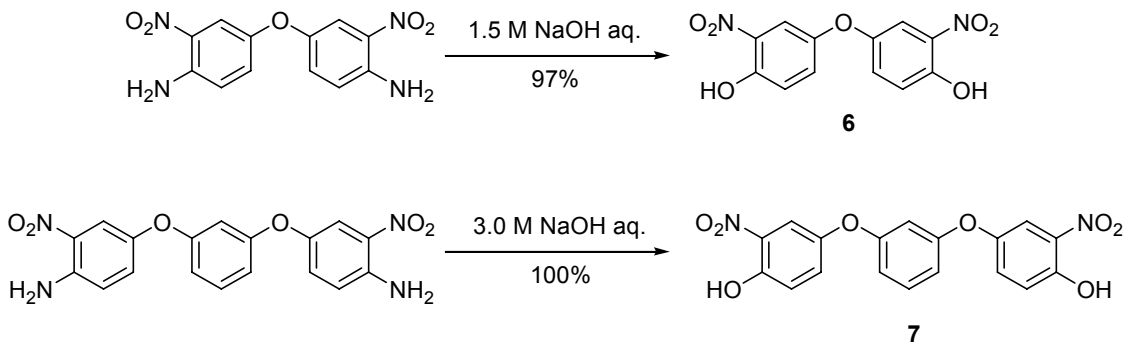


FIGURE 2. Resonance structure of 4-nitroaniline



SCHEME 4. Aromatic nucleophilic substitution reactions of bis(nitroaniline)s with hydroxide ions.

into 3,3'-diamino-4,4'-dihydroxydiphenyl ether and 1,3-bis(3-amino-4-hydroxyphenoxy) benzene, which are useful as positive-working photosensitive polymer precursor compositions for forming electric interlayer insulators and protective films for semiconductors.

In this thesis, the author has summarized these series of studies. The dissertation consists of general introduction, five chapters and conclusion.

Chapter 1 deals with optimized syntheses of new aniline derivatives **2**, **4** and **5.** These three novel aniline derivatives were efficiently synthesized. Their synthetic methods were optimized; the compounds **2** and **4** were synthesized in good yields by using Sonogashira cross coupling reactions, and the compound **5** was sucessfully obtained by Pd-catalyzed cyanation, though it could not be obtained in the classical method using CuCN in *N*-methylpyrrolidone.

Chapter 2 deals with comparison of *inter*molecular and *intra*molecular exciplex formation of a 1,4-dicyano-2-methylnaphthalene–*N,N*-dimethyl-*p*-toluidine dyad (**5**). The author have found that the dyad **5** in solution hardly form a CT complex in the ground state but that it produces an *intra*molecular exciplex between the DCMN and DMT moieties in cyclohexane in accord with the Hirayama rule (n = 3 rule). In contrast, the crystals of **5** form an *inter*molecular mixed-stack, one-to-one CT complex in the ground state. The observations made in this effort clearly demonstrate that the *inter*molecular exciplex generated by excitation of crystals of **5** arises directly from the ground state CT complex, in which the DCMN and DMT moieties are immobilized in a face-to-face manner by *inter*molecular CT interactions.

Chapter 3 deals with solvatochromatic properties of 9-(4-aminophenylethynyl)-10

-(4-nitrophenylethynyl)anthracene (**4**). The observations demonstrate that the absorption and emission properties of **4**, in contrast with **3**, display distinctive solvent effects (solvatochromism). The results suggest that the fluorescence of **4** arises from a singlet CT excited state that possesses an *intra*molecular charge transfer character. The observed strong dependence of the fluorescence quantum yield on solvent polarity shows that the CT character of its singlet excited state causes **4** to be more fluorescent in less polar solvents as compared with polar solvents.

Chapter 4 deals with the unexpectedly high reactivity of aniline derivatives with hydroxide ion in aromatic nucleophilic substitution reaction in aqueous alkaline media. It was revealed that the amino groups of aryl amines are unexpectedly more reactive than the chlorine atoms of aryl chlorides in aqueous NaOH solution. Aqueous media played a dominant role in the reaction of aryl amines with hydroxide ion, since the hydrogen bonding of amino groups with H_2O reduces adverse effect of the resonance, and eventually ammonia molecules are eliminated.

Chapter 5 deals with practical and efficient syntheses of **6** and **7** in aqueous alkaline media. The present method developed in Chapter 4 is environmentally friendly, because the reactions proceed in water without organic solvents and consume just one equivalent amount of H_2O to provide target compounds, releasing ammonia as the sole by-product.

In conclusion, the achievements of these series of studies were summarized.

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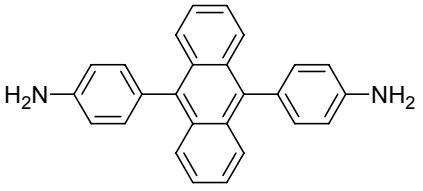
CHAPTER 1

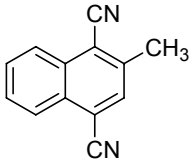
Optimized Syntheses of New Aniline Derivatives

1.1 INTRODUCTION

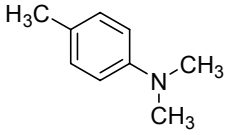
As described in General Introduction, novel anilines have strongly attracted organic chemists to their new performances. This chapter deals with optimized syntheses of novel aniline derivatives. The first of them is 9,10-bis(4-aminophenylethynyl)anthracene (**1**), which has been examining by Tohnai *et al.* on the study of modulation arrangements and photophysical properties of crystals of **1**. He has showed that the crystal forms of **1** depend on guest molecules.[1] The second is 9-(4-aminophenylethynyl)-10-(4-nitrophenylethynyl) anthracene (**2**), which is expected to exhibit interesting linear and nonlinear optical properties. As a preliminary study, solvatochromism in the absorption and fluorescence spectra of **2** will be described in Chapter 3. Efficient synthesis of the third aniline derivative, 1,4-dicyano-2-(4'-*N,N*-dimethylaminobenzyloxy)methylnaphthalene (**3**), is described. The compound **3** would form an *intra*molecular exciplex between the 1,4-dicyano-2-methyl-naphthalene (DCMN) acceptor and the *N,N*-dimethyl-*p*-toluidine (DMT) donor moieties. Contrasting *inter*- and *intra*molecular exciplex formation of **3** in cyclohexane and in the crystalline state will be discussed in Chapter 2.



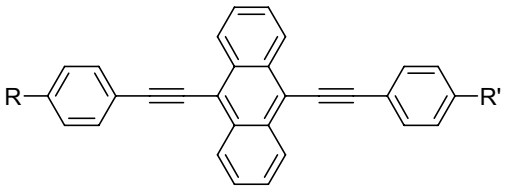
BAPA



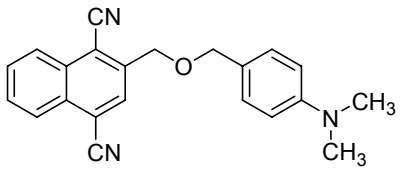
DCMN



DMT



1 R, R' = NH_2
2 R = NH_2, R' = NO_2



3

1.2 RESULTS & DISCUSSION

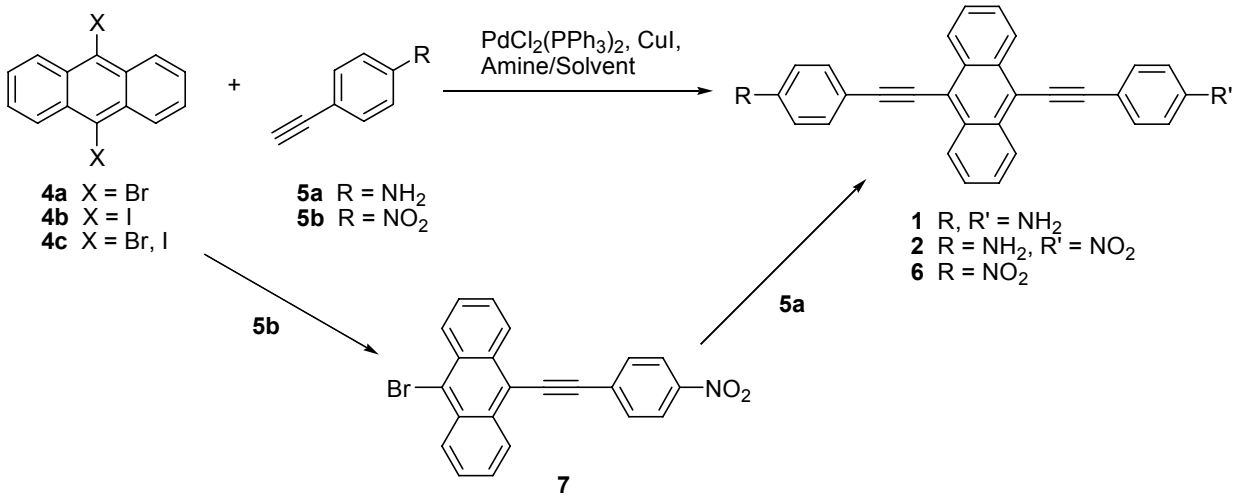
1.2.1 Syntheses of 9,10-Bis(4-aminophenylethynyl)anthracene and 9-(4-aminophenyl-ethynyl)-10-(4-nitrophenylethynyl)anthracene

Since Etienne *et al.* first synthesized 9,10-bis(4-aminophenyl)anthracene (BAPA),[2] BAPA have been a research subject in an area of photophysical materials.[3] In particular, Tohnai *et al.* have been studying solvatochromism and interesting crystalline-state fluorescence properties of BAPA through control of molecular arrangement.[4] They have discovered that BAPA incorporates various solvent molecules, when recrystallized, to control the molecular arrangement and the crystalline-state fluorescence. In the course of their research, the author was required to provide them with 9,10-bis(4-aminophenylethynyl)anthracene (**1**) in which the π conjugated system is extended.

As described in General Introduction, the author has paid attention to effects of the *intra*molecular CT interaction between anilino groups and electron-accepting groups on optical properties of novel anilines. 9-(4-Aminophenylethynyl)-10-(4-nitrophenylethynyl)anthracene (**2**) is expected to exhibit interesting linear and nonlinear optical properties. Since the compound **2** contains a strong electron donating group (NH_2) and a strong electron withdrawing group (NO_2) at the terminal positions of an extended π conjugated system, it is expected to display strong CT characteristics.

Sonogashira cross coupling reaction is the most promising for syntheses of **1** and **2**. The design of the synthetic pathway was aided by an analysis of the bond dissociation energies of Ar-I (272 kJ/mol) versus Ar-Br (335 kJ/mol)[5] and the difference between basicities of copper acetylides of 4-aminophenylacetylene (**5a**) and 4-nitrophenylacetylene (**5b**). In this section, efficient syntheses of **1** and **2** are described and discussed.

The results in this synthetic study are summarized in Table 1. The compound **1** was obtained in Et_3N only in a poor yield (Entry 1). In $^{i}Pr_2NH$, the reaction of 9,10-dibromoanthracene (**4a**) with **5a** was significantly accelerated, providing **1** in the presence



SCHEME 1. Syntheses of **1**, **2** and **6**.

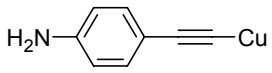
TABLE 1. Results of Sonogashira Cross Coupling for **1** and **2**.

Entry		X		R	Amine/Solvent	$PdCl_2(PPh_3)_2$	CuI	Temp.	Time		Yield
						mol%	mol%	°C	h		%
1	**4a**	Br	**5a**	NH_2	Et_3N	7	4	reflux	15	**1**	14
2	**4a**	Br	**5a**	NH_2	$^iPr_2NH$	2	2	Reflux	2	**1**	90
3	**4b**	I	**5a**	NH_2	$^iPr_2NH$	2	2	rt	2	**1**	76
4	**4a**	Br	**5b**	NO_2	$^iPr_2NH$	2	2	reflux	8	**6**	0
5	**4b**	I	**5b**	NO_2	$^iPr_2NH$	2	2	rt	12	**6**	64
6	**4c**	Br, I	**5b**	NO_2	$^iPr_2NH$	2	2	rt	3.5	**7**	59
7	**4c**	Br, I	**5b**	NO_2	$^iPr_2NH$	8	8	reflux	0.5	**7**	76
8	**7**	Br	**5a**	NH_2	$^iPr_2NH$	2	2	reflux	70	**2**	0
9	**7**	Br	**5a**	NH_2	$^iPr_2NH$/THF	5	5	reflux	24	**2**	3
10	**7**	Br	**5a**	NH_2	$^iPr_2NH$/DMF	50	10	85	0.5	**2**	91

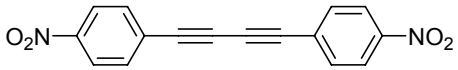
of a low loading amount of $PdCl_2(PPh_3)_2$ and CuI in 90% yield (Entry 2).

It indicates that the stronger basicity of $^iPr_2NH$ (pK_a = 11.5) than that of Et_3N (pK_a = 10.7) could contribute to formation of copper acetylide of **5a**. The diiodide **4b** provided **1** in a good

yield even at room temperature (Entry 3), suggesting acceleration of the oxidative addition of Pd (0) with the dihalide.



Copper acetylide of **5a**



1,4-Bis(4-nitrophenyl)butadiyne

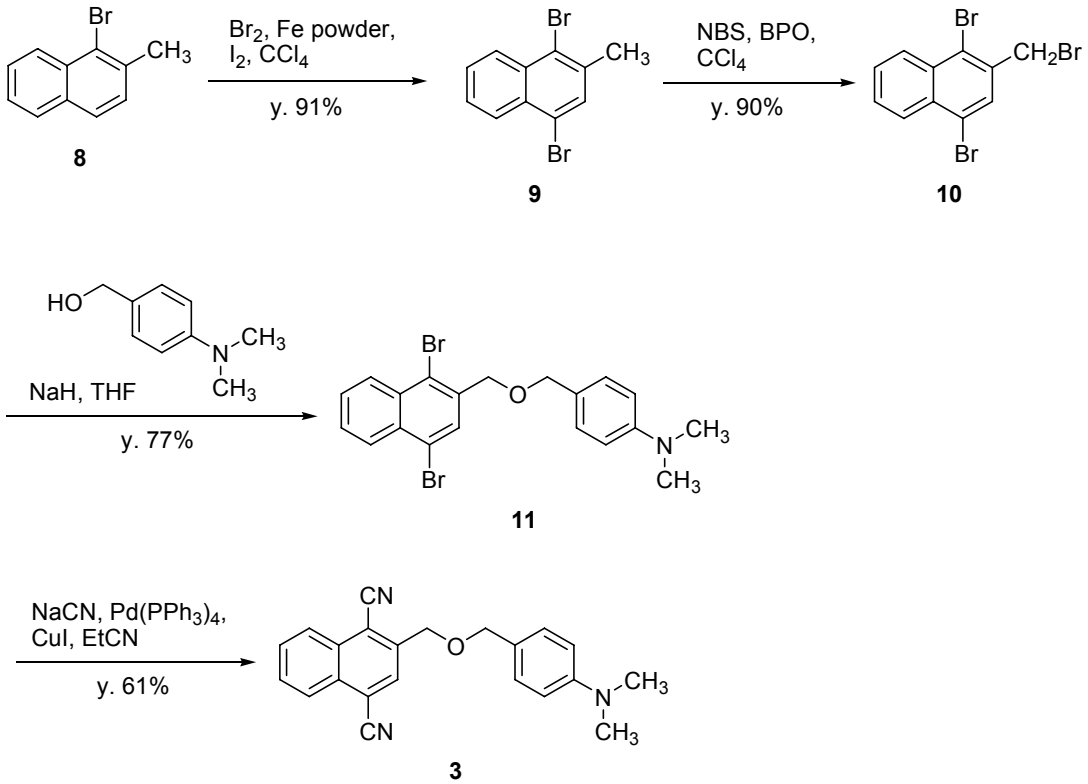
Whereas 9,10-bis(4-nitrophenylethynyl)anthracene (**6**) was not provided by the reaction of **4a** with **5b** at all (Entry 4), the diiodide **4b** readily reacted with **5b** even at room temperature (Entry 5). These differences in the reactivity of **4a** vs. **4b** and **5a** vs. **5b** strongly suggests that the compound **2** could be synthesized with high selectivity by using a route of stepwise Sonogashira cross coupling of 9-bromo-10-iodoanthracene (**4c**) with **5b** and followed with **5a**. Actually, the intermediate **7** was provided by the reaction of **4c** with **5b** in a moderate yield (Entry 6), though Glaser homocoupling occurred to form 1,4-bis(4-nitrophenyl)butadiyne as a by-product in 16% yield. The yield of **7** increased with increasing $PdCl_2(PPh_3)_2$ and CuI (Entry 7).

The intermediate **7** unfortunately does not react with **5a** at all (Entry 8). It is known that Sonogashira cross coupling reactions take place with enhanced rates in THF[6] and DMF[7] as compared with the case when common amines (e.g., triethylamine and diisopropylamine) are used as solvents. Fortunately, the compound **2** is obtained in an excellent yield (91%) by reaction of **7** with **5a** in DMF (Entry 10). Notably, this process in THF was attended by an extremely poor yield (3%, Entry 9).

1.2.2 Synthesis of 1,4-Dicyano-2-(4'-*N*,*N*-dimethyl-aminobenzyloxy)methylnaphthalene

Inter-[8] and *intra*molecular[9] exciplexes in solution have been studied from the viewpoint of the mechanism of their formation, and their photophysical and photochemical properties.[10] However, approaches to utilize exciplex emission have rarely been tried on luminescent organic single crystals, though luminescent organic crystals attract much attention

due to their potential applications to a variety of organic functional materials.[11] Hirayama found that linking a donor (D) and an acceptor (A) with a 3-carbon methylene chain, as represented by D–$(CH_2)_3$–A, results in a substance that effectively forms an intramolecular exciplex through conformational change that leads to charge-transfer (CT) processes.[12] This phenomenon has become known as the Hirayama rule. Although most exciplexes have been studied in the solution phases, exciplexes have also been observed in the crystalline states.[13] Becker *et al.* have uncovered evidence for an intramolecular anthracene–ethylene exciplex, generated by photoexcitation of a lepidopterene in the crystals.[14] However, many exciplexes in solution lose the property in the crystals. To the best knowledge, few studies have been conducted on molecules which form *inter*- and *intra*molecular exciplexes in both crystal and solution states.[15] In view of this situation, the author designed and synthesized a new dyad, 1,4-dicyano-2-(4'-*N,N*-dimethyl-aminobenzyloxy)methyl-naphthalene (**3**), which should form an *intra*molecular exciplex between the 1,4-dicyano-2-methylnaphthalene (DCMN) acceptor and *N,N*-dimethyl-*p*-toluidine (DMT) donor moieties according to the Hirayama rule.



SCHEME 2. Synthesis of **3**.

In this section, an optimized method for the synthesis of 1,4-dicyano-2-(4'-*N,N*-dimethyl-aminobenzyloxy)methylnaphthalene (**1**) from 1-bromo-2-methylnaphthalene (**3**) and some synthetic discussion are described. Contrasting *inter*molecular and *intra*molecular exciplex formation in solution and crystals of **3** will be described in detail in Chapter 2.

The compound **3** was synthesized from 1-bromo-2-methylnaphthalene (**8**) as a starting material (Scheme 2), which was brominated with Br_2, Fe powder and I_2 in CCl_4 to give 1,4-dibromo-2-methylnaphthalene (**9**) in 91% yield. 1,4-Dibromo-2-(bromomethyl)-naphthalene (**10**) was obtained by bromination of **9** (12.5 mM) with *N*-bromosuccinimide (NBS, 1 eq.) and benzoyl peroxide (BPO, 5 mol%) in CCl_4 in 90% yield. Higher concentration of **9** (200 mM) and smaller amounts of BPO (1 mol%) caused the yield of **10** to decrease to 29% because of by-product formation through dimerization of **9**. Then, **10** was etherified with 4-(*N,N*-dimethylamino)benzyl alcohol and NaH in dry THF to give 1,4-dibromo-2-(4'-*N,N*-dimethylaminobenzyloxy)methylnaphthalene (**11**) in 77% yield. The classical cyanation of **11** with CuCN in *N*-methylpyrrolidone failed to give **3**. Fortunately, **11** was cyanated with NaCN in the presence of $Pd(PPh_3)_4$ and CuI in EtCN to give **3** as a yellow powder in 61% yield. The powder was cooling-recrystallized from $CHCl_3$–CH_3OH (1/3) to yield yellow needles of **3** (mp. 160–161 ^oC). Interestingly, the yellow powder gave red prisms of **3** (mp. 165–166 ^oC) evaporatively recrystallized from CH_3OH.

1.3 CONCLUSION

The author developed an efficient method for syntheses of **1** and **2**. In particular, the compound **2** was synthesized in good yield by using a sequential Sonogashira cross coupling reactions of 9-bromo-10-iodoanthracene (**7**) with acetylenes **5a** and **5b**. The design of the synthetic pathway was aided by an analysis of the bond dissociation energies of Ar-I and Ar-Br,

and the difference between basicities of the conjugated bases of terminal acetylenes **5a** and **5b**. As predicted by using these information, a preliminary study showed that acetylene **5b** undergoes Sonogashira cross coupling with 9,10-diiodoanthracene but not with 9,10-dibromoanthracene. The reaction of **7** with **5a** does not take place in diisopropylamine. On the other hand, **2** is obtained in an excellent yield (91%) by the reaction of **9** with **8b** in DMF. Notably, this process in THF is attended by an extremely poor yield (3%).

The compound **3** was sucessfully obtained in 4 steps, In the final step, Pd-catalyzed cyanation provided **3** in a good yield, though it could not be obtained in the classical method using CuCN in *N*-methylpyrrolidone.

1.4 EXPERIMENTAL

General: Purchased 4-nitrophenylacetylene (**5b**) was recrystallized from 2-propanol. Diisopropylamine and DMF were dried over 4A molecular sieves and distilled. 9-Bromo-10-iodoanthracene (**4c**) was synthesized employing the literature method.[16] Other materials and solvents were also purchased and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively (Bruker Co. Ltd., Advance 400). All ^{13}C NMR resonances were assigned by using DEPT 45, HSQC and HMBC. Melting points were measured on a Yamato MP-21 melting point apparatus. UV-VIS spectra were recorded on a Hitachi U-2800A spectrophotometer, IR spectra on a Shimazdu IR prestige-21 spectrometer, and mass spectra on a ESI-TOF/MS Per Septive Biosystems Mariner using pentaethylene glycol and 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra(ethoxycarbonyl-methoxy) calix[4]arene[17] as internal standards. Elemental analysis was performed on a PerkinElmer 2400 II CHN elemental analyzer.

9,10-Bis(4-aminophenylethynyl)anthracene (1): To a round-bottom flask containing 9,10-dibromoanthracene (**4b**, 1.0 g, 3.0 mmol), $PdCl_2(PPh_3)_2$ (43 mg, 0.061 mmol), and CuI

(12 mg, 0.063 mmol) was added a solution of 4-aminophenylacetylene (**5a**, 0.82 g, 7.0 mmol) in diisopropylamine (300 mL) under a nitrogen atmosphere. The reaction mixture was stirred at reflux for 2 h, cooled to room temperature, and was filtered. The precipitate was dessolved in toluene and treated with charcoal, and the solution was concentrated and chilled for crystallization, yielding 1.1 g (90%) of **1** as red sticks; mp. 224–227 ^{o}C (decomp.); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 8.64–8.60 (m, 4H, anthracene), 7.75–7.71 (m, 4H, anthracene), 7.53 (d, J = 8 Hz, 4H, Ph), 6.68 (d, J = 8 Hz, 4H, Ph), 5.76 (br. s, 4H, NH_2).

9-Bromo-10-(4-nitrophenylethynyl)anthracene (7): To a round-bottom flask containing **4c** (1.15 g, 3.00 mmol), $PdCl_2(PPh_3)_2$ (172 mg, 0.245 mmol), and CuI (45 mg, 0.25 mmol) was added a solution of 4-nitrophenylacetylene (**5b**, 0.44 g, 3.0 mmol) in diisopropylamine (300 mL) under a nitrogen atmosphere. The reaction mixture was stirred at reflux for 30 min, cooled to room temperature, and was filtered. The precipitate was crystallized from chloroform after treatment with activated carbon yielding 0.92 g (76%) of **7** as red needles; mp. 255.0–255.5 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 8.76–8.74 (m, 2H, anthracene), 8.57–8.55 (m, 2H, anthracene), 8.38 (d, J = 8 Hz, 2H, Ph), 8.21 (d, J = 8 Hz, 2H, Ph), 7.57–7.83 (br d, J = 8 Hz, 4H, anthracene); IR (diamond ATR) 2191 cm^{-1} (alkyne).

9-(4-Aminophenylethynyl)-10-(4-nitrophenylethynyl)anthracene (2): To a round-bottom flask containing **7** (0.20 g, 0.50 mmol), 4-aminophenylacetylene (**5a**, 0.12 g, 1.0 mmol) and $PdCl_2(PPh_3)_2$ (172 mg, 0.245 mmol) was added a solution of diisopropylamine (1.4 mL, 9.9 mmol) in DMF (300 mL) under a nitrogen atmosphere. The mixture was stirred for 20 min at room temperature. CuI (12 mg, 0.063 mmol) was added quickly to the mixture and the resulting mixture was stirred at 85 ^{o}C for 30 min and concentrated in *vacuo*, giving dark-brownish solid residue. The solid was crystallized from toluene after treatment with activated carbon giving 0.20 g (91%) of **2** as dark red brownish needles; mp. 262 ^{o}C

(decomposition); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 8.66 (dd, J = 8 Hz, 4H, anthracene), 8.35 (d, J = 8 Hz, 2H, Ph), 8.13 (d, J = 8 Hz, 2H, Ph), 7.82–7.75 (m, 4H, anthracene), 7.57(d, J = 8 Hz, 2H, Ph), 6.70(d, J = 8 Hz, 2H, Ph), 5.84 (br s, 2H, NH_2); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 83.9 (ethynyl), 91.1 (ethynyl), 100.4 (ethynyl), 106.8 (ethynyl), 107.7 (Ph), 113.8 (Ph), 114.4 (anthracene), 120.7 (anthracene), 124.0 (Ph), 126.6 (anthracene), 127.1 (anthracene), 127.3 (anthracene), 128.1 (anthracene), 129.2 (Ph), 130.6 (anthracene), 131.8 (anthracene), 132.7 (Ph), 133.3 (Ph), 146.9 (C-NO_2), 150.5 (C-NH_2); m/z 439.13 (M + H); UV-VIS 478 nm (ε 40300 mol^{-1}Lcm^{-1}, toluene); IR (diamond ATR) 2180 cm^{-1} (alkyne).

Synthesis of 1,4-dicyano-2-(4'-*N*,*N*-dimethylamimobenzyloxy)methylnaphthalene (3):
The compound **3** were synthesized from 1-bromo-2-methylnaphthalene (**8**) in four steps, as shown in Scheme 1.

1,4-Dibromo-2-methylnaphthalene (9): To a mixture of **8** (10.1 g, 45.9 mmol), Fe powder (0.14 g, 2.5 mmol), I_2 (0.12 g, 0.47 mmol) and CCl_4 (18 mL) was titrated Br_2 (9.5 g, 59 mmol) for 4 h at room temperature. The mixture was refluxed for 6 h and cooled to room temperature. The reaction mixture was washed with 10% aqueous NaOH, and with brine until the aqueous layer became neutral. The combined organic layer was dried with Na_2SO_4 overnight, and then the solids were filtered out. The filtrate was evaporated in *vacuo*. The resulting dark brown oil was purified by silica-gel chromatography with hexane, giving 12.5 g of **9** as a pale yellow oil in 91% yield; bp. 148–150 ^{o}C, 1 mmHg (lit.[1] 146 ^{o}C, 0.4 mmHg); ^{1}H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 2.55 (s, 3H, CH_3), 7.68–7.76 (m, 2H), 7.89 (s, 1H), 8.12 (d, J = 8 Hz, 1H), 8.21 (d, J = 8 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 23.2 (CH_3), 121.3, 123.1, 126.9, 126.9, 127.7, 128.7, 130.4, 132.3, 132.5, 136.9.

1,4-Dibromo-2-(bromomethyl)naphthalene (10): A mixture of **9** (1.5 g, 5.0 mmol), NBS

(0.89 g, 5.0 mmol), BPO (0.085 g, 0.26 mmol) and CCl_4 (400 mL) was refluxed for 1 h and cooled to room temperature. After concentration in *vacuo*, a precipitated white solid of succinimide was filtered out. The filtrate was evaporated in *vacuo*. The resulting milky white residue was purified by silica-gel chromatography with hexane, giving 1.71 g of **10** as white powder in 90% yield; mp. 129–130 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 5.00 (s, 2H, CH_2), 7.78–7.83 (m, 2H), 8.16 (s, 1H), 8.17 (m, 1H), 8.30 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 34.4, 121.8, 124.3, 127.1, 127.7, 129.3, 129.3, 131.5 (2C), 132.5, 136.3.

1,4-Dibromo-2-(4'-*N,N*-dimethylaminobenzyloxy)methylnaphthalene (11): To a round-bottom flask containing *N,N*-dimethyl-4-aminobenzyl alcohol (0.82 g, 5.4 mmol) and NaH (0.66 g, 27 mmol) was added to dry THF (100 mL) at room temperature under nitrogen. The mixture was stirred for 1 h at room temperature. A solution of **10** (1.0 g, 2.7 mmol) in THF (10 mL) was added to the mixture. The reaction mixture was refluxed for 3 h and cooled to room temperature. The mixture was poured into ice water and extracted with $CHCl_3$. The combined organic layer was washed with brine, and evaporated in *vacuo*. The resulting brown residue was crystallized from methanol after treatment with activated carbon, giving 0.93 g of **11** as yellow powder in 77% yield; mp. 106–107 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 2.88 (s, 6H, CH_3), 4.53 (s, 2H, CH_2), 4.70 (s, 2H, CH_2), 6.71 (AA'BB', J = 12 Hz, 2H), 7.23 (AA'BB', J = 12 Hz, 2H), 7.74–7.79 (m, 2H), 7.94 (s, 1H), 8.16 (m, 1H), 8.27 (m. 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 40.1 (2C, CH_3), 70.2 (CH_2), 72.3 (CH_2), 112.0 (2C), 121.3, 121.8, 124.9, 126.9, 127.1, 128.5, 128.9, 129.3 (2C), 129.5, 131.3, 132.3, 137.2, 150.1.

1,4-Dicyano-2-(4'-*N,N*-dimethylamimobenzyloxy)methylnaphthalene (3): To a round-bottom flask containing **11** (1.3 g, 2.9 mmol), NaCN (0.57 g, 12 mmol), $Pd(PPh_3)_4$ (0.69 g, 0.60 mmol), CuI (0.23 g, 1.2 mmol) was added propionitrile (7.5 mL) at room temperature. The reaction mixture was refluxed for 30 min and cooled to room temperature. After addition

of EtOAc (60 mL), the reaction mixture was filtered through a celite pad, washed with water and brine, and the solvent was evaporated in *vacuo*. The resulting dark-brownish residue was purified by silica-gel chromatography with hexane–EtOAc (8/2), giving 0.61 g of **3** as yellow powder in 61% yield. The powder was cooling-crystallized from $CHCl_3$–CH_3OH (1/3), giving 0.44 g (44 % yield) of **1** as yellow needles; mp. 160–161 ^oC; ^1H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 2.86 (s, 6H, CH_3), 4.54 (s, 2H, CH_2), 4.85 (s, 2H, CH_2), 6.67 (AA'BB', J = 8 Hz, 2H), 7.21 (AA'BB', J = 8 Hz, 2H), 7.96–7.99 (m, 2H), 8.23–8.28 (m, 2H), 8.30 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 40.1 (2C, CH_3), 68.5 (CH_2), 72.6 (CH_2), 112.0 (2C), 112.6, 113.7, 114.9 (CN), 116.4 (CN), 124.7, 125.3, 125.4, 129.5 (2C), 130.3, 130.4, 130.8, 131.4, 132.5, 142.9, 150.2; ESI-MS *m/z* 342.1 ($M+H^+$); UV-VIS (cyclohexane) λ_{max} = 315 nm (ε 8165 $mol^{-1}Lcm^{-1}$); IR (diamond ATR) ν 2216 cm^{-1} (CN); Anal. Calcd for $C_{22}H_{19}N_3O$: C, 77.40; H, 5.61; N, 12.31. Found: C, 77.10; H, 5.52; N, 12.28. The yellow powder was evaporatively recrystallized from CH_3OH to give red prisms of **1**; mp. 165–166 ^oC.

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CHAPTER 2

Contrasting *Inter*molecular and *Intra*molecular Exciplex Formation of a 1,4-Dicyano-2-methylnaphthalene–4-substituted-toluene Dyad

2.1 INTRODUCTION

Inter-[1] and *intra*-molecular[2] exciplexes which are excited complexes formed between electron donors and acceptors have been studied in solution from the viewpoint of the mechanism of their formation, and their photophysical and photochemical properties[3] through evaluations of molecular structure[4] and solvent effects.[5] Hirayama originally found that 1,3-diphenylpropane and 1,3,5-triphenylpentane, where the phenyl groups are interlinked with 3-carbon methylene chains, effectively form *intra*molecular excimers (excited dimers) to emit excimer fluorescence through conformational change.[6] This phenomenon was applied to a variety of two chromophoric molecules including electron-donor (**D**) and acceptor (**A**) systems which form *intra*molecular exciplex to emit exciplex fluorescence. It is often called Hirayama rule or n = 3 rule. Very recently, exciplex formation is becoming the focus of attention in organic EL devices, where exciplexes result from charge recombination of electoron-hole.[7] However, approaches to utilize exciplex emission have rarely been tried on luminescent organic single crystals which began to attract much attention due to their potential applications to a variety of organic functional materials.[8]

Although most exciplexes have been studied in solution, some of them have also been observed in the crystalline states.[9] Becker *et al.* have uncovered evidence for an *intra*molecular anthracene–ethylene exciplex, generated by photoexcitation of a lepidopterene in the crystalline state.[10] However, many exciplexes in solution lose the property in crystals. To the best of the author's knowledge, a very few studies have been conducted on molecules which form *inter*molecular and *intra*molecular exciplexes in solution and the crystallin states, respectively.[11] On the other hand, crystal engineering of charge transfer (CT) complexes is one

of the most extensive research fields, in which exquisite packing of **D** and **A** has been prepared in crystalline state.[12] The author invented to apply the concept of CT-complex crystal design to prepare a new compound which efficiently forms an exciplex nicely aligned face to face in the crystalline state. He has studied the **D**–**A** preorientation in crystalline states to create exciplex-emissive organic crystals derived from **D**–**A** systems, which would tremendously have a novel impact on the area of luminescent organic crystals.

Most of pairs of **D** and **A** molecules to form exciplexes in solution hardly have CT interaction between **D** and **A** in the ground state. Barely in the excited state, there arises the CT interaction between them. Some pairs of **D** and **A** which already have CT interaction in the ground state could also form exciplexes in the excited state. However, many of them do not emit exciplex fluorescence, because they form radical ion pairs through single electron transfer (SET) process.

On the other hand, in the case of crystals of a dyad compound in which **D** and **A** are chained with each other, when there is little CT interaction between the **D** and **A** moieties, exciplex is hardly formed but formation of excimer mostly ocurres in the excited state because of *inter*molecular **D**–**D** or **A**–**A** stacking. The author conceived that strong CT interaction between **D** and **A** is required for preorientation of the **D** and **A** moieties in the ground-state crystals to form exciplexes. However, too strong CT interaction would cause SET as well as in the solution. In order to avoid that situation, if appropriate CT interaction operates between **D** and **A** moieties, not only the **D** and **A** moieties should be able to successfully preorientate to form exciplexes, but also SET should be avoided, when photoexcited.

In view of these situations, the author designed and synthesized a new dyad, 1,4-dicyano-2-(4'-*N,N*-dimethylaminobenzyloxy)methylnaphthalene (**1**, Fig. 1), which could form an *intra*molecular exciplex as a consequence of CT interaction between the 1,4-dicyano-2-methylnaphthalene (DCMN) and *N,N*-dimethyl-*p*-toluidine (DMT) moieties according to the n = 3 rule. In order to control the electron-donating ability of the donor

moieties, dyads **2**–**4** which possesses OCH_3, CH_3 and H substituents at R position were also synthesized.

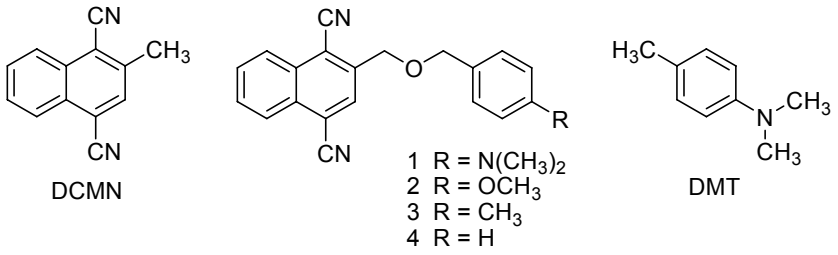


FIGURE 1. DCMN, DMT and Dyad **1**–**4**.

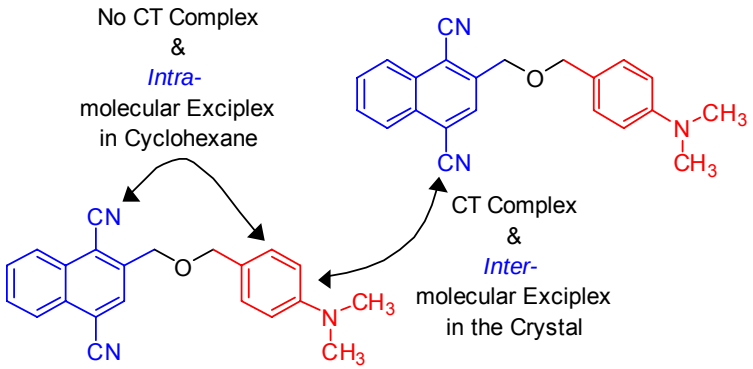


FIGURE 2. Schematic formation of CT complexes, and *inter*molecular and *intra*molecular exciplexes of **1**.

In this chapter, the author presents that *intra*molecular CT complexes of **1**–**4** hardly exist in the ground states in solution. The dyads **1**–**3** form *intra*molecular exciplexes in cyclohexane as expected, though dyad **4** does not. To the contrary, the **D** and **A** moieties of dyad **1** and **2** are *inter*molecularly preorientated face to face to form *inter*molecular CT complexes in the crystals. As desired, *inter*molecular exciplexes are successfully formed through the ground state CT complexes in the crystals of **1** and **2** against the Hirayama rule, while dyads **3** and **4** do not form *inter*molecular exiplexes but excimers in the crystals. Thus, nobel exciplex-emissive organic crystals of **1** and **2** have been created to fluoresce with the quantum yields of 0.09 and 0.39, respectively. It is demonstrated that the appropriate CT interaction between the **D** and **A** moieties in the crystals of **1** and **2** operates to prepare the

exciplex-emissive organic crystals. The more appropriate CT interaction ocurrs in the crystals of **2** preventing SET process, while the exciplex emission of the crystals of **1** is weak as a consequence of SET due to a little too strong CT interaction between the DMT and DCMN moieties.

2.2 RESULTS & DISCUSSION

As shown in Fig. 3a and 3b, a cyclohexane solution of **1** as well as DCMN is colorless under natural light. The absorption spectrum of **1** in cyclohexane (Fig. 4, black and bold) is virtually the sum of the spectra of DCMN (blue and broken) and DMT (red and broken), exhibiting intense bands in the 250–350 nm region and feeble CT absorptions between 350–400 nm. These findings indicate that an *intra*molecular CT complex of **1** is hardly formed in cyclohexane, even though the strong acceptor DCMN is interlinked with the strong donor DMT. The CT properties of the DCMN and DMT moieties could not overcome the stabilization of solvation with cyclohexane only to keep the most stable extended conformation which was supported by density function theory calculation B3LYP/6-31G(d,p) (Fig. 5). Actually, the absorption spectra of **1** and **2**–**4** closely resemble with each other, as shown in Fig. 6.

When a cyclohexane solution of DCMN (5.0×10^{-5} mol/L) was excited with 320-nm light, strong blue fluorescence was observed at *ca.* 350 nm (Fig. 3a, bottom and Fig. 4, blue bold line) with a quantum yield (Φ_f) of 0.29 and a fluorescence lifetime (τ_f^{MONO}) of 3.7 ns. On the other hand, excitation of a dilute cyclohexane solution of dyad **1** (5.0×10^{-5} mol/L) at 320 nm leads to significantly decreased emission from the DCMN moiety (λ_{em}^{MONO} = 354 nm, τ_f^{MONO} = 3.7 ns) and orange fluorescence (λ_{em}^{EX} = 550 nm, Φ_f = 0.05, τ_f^{EX} = 13.7 ns; Fig. 3b, bottom and Fig. 4, red), which is assigned to an *intra*molecular exciplex involving the DCMN and DMT moieties of **1**. In addition, excitation spectrum of **1** at 550 nm was virtually tha same as the absorption spectrum of **1** in the 250–540 nm region.

FIGURE 3. Photographs of DCMN (a) and **1**–**4** (b–e) in cyclohexane under natural light (top) and under light with 365 nm (bottom).

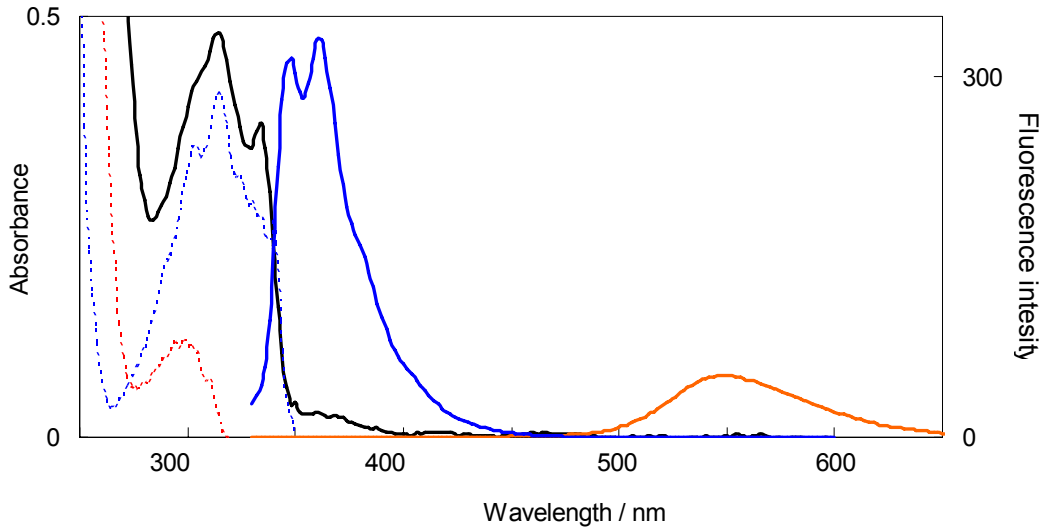


FIGURE 4. Absorption spectra of **1** (black, bold), DCMN (blue, broken) and DMT (red, broken) and fluorescence spectra (λ_{ex} = 320 nm) of **1** (red, bold) and DCMN (blue, bold) in cyclohexane (5.0×10^{-5} mol/L).

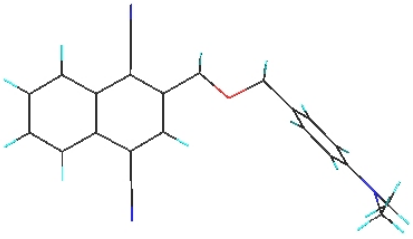


FIGURE 5. Molecular geometry of

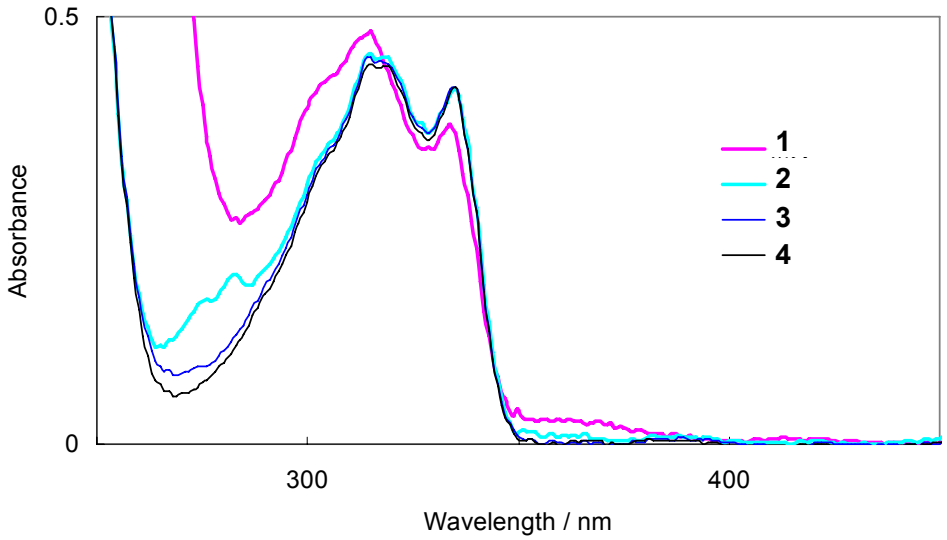


FIGURE 6. Absorption spectra of **1–4** in cyclohexane (5.0 × 10^{-5} mol/L). **1** (red, bold), **2** (aquablue, bold), **3** (blue, thin), **4** (black, thin).

The fluorescence spectra, the absorption and fluorescence data of dyads **1**–**4** and DCMN are shown in Fig. 7 and Table 1. Dyads **1**–**3** clearly displayed *intra*molecular exciplex emission bands (Fig. 7). The stronger the donor properties of substituents of **1**–**3** are, the weaker monomer emission bands of DCMN moieties were. Then the bands of *intra*molecular exciplexes were more bathochromicly shifted. On the other hand, the fluorescence spectrum of **4** was almost the same as that of DCMN and did not exhibit an exciplex emission band (Fig. 7). Indeed, only the fluorescence components of monomer emission from the DCMN moiety were detected but any exciplex components were not in fluorescence lifetime measurements for **4** (Table 1). It was found that the formation of *intra*molecular exciplexes of the dyads requires stronger donor property than that of hydrogen atom. In addition, the fluorescence quamtum yields Φ_f of **1**–**3** decreased with increasing donor property of the substituents. In particular, Φ_f of **1** with dimethylamino group was the lowest among them. It may indicate that strong donor property of the DMT moiety of **1** occurs complete ET from the DMT moiety to the DCMN

moiety of **1**, followed by back electron transfer (the $DCMN^{-\cdot}$ moiety → the $DMT^{+\cdot}$ moiety), which deactivates the excited state of **1**. Actually, τ_f^{EX} (33.7 ns) of dyad **2** substituted with the anisole moiety, that is a weaker donor than the DMT, is longer than that of **1** (13.7 ns).

The solvent effect on fluorescence of **1** is shown using cyclohexane, CCl_4, Et_2O and CH_3CN as solvents of which the dielectric constant ε are 2.02, 2.30, 4.42 and 36.0, respectively (red for cyclohexane, green for CCl_4, blue for Et_2O, and black bold for CH_3CN) in Fig. 8, where the intensity of a longer region than 500 nm are 4-times magnified. As ε values of the solvents became higher, the exciplex emission bands of **1** decayed towards longer wavelengths and the emission bands from the DCMN moiety drastically increased. Even the monomer emission decreased to almost zero in acetonitrile (ε = 36.0, Fig. 8, black bold). A change in Gibbs free energy ΔG_{PET} of photo-induced electron transfer (PET) of **1** in acetonitrile is –1.56 eV[13] determined with a cyclic voltammetry measurement.[14] This indicates that when dyad **1** is excited in acetonitrile, PET is an exergonic reaction.[15] In fact, absorption bands of $DMT^{+\cdot}$ moiety of **1** is observed at *ca.* 480 nm[16] with a transition absorption spectra measurement on laser flash photolysis in acetonitrile.[17]

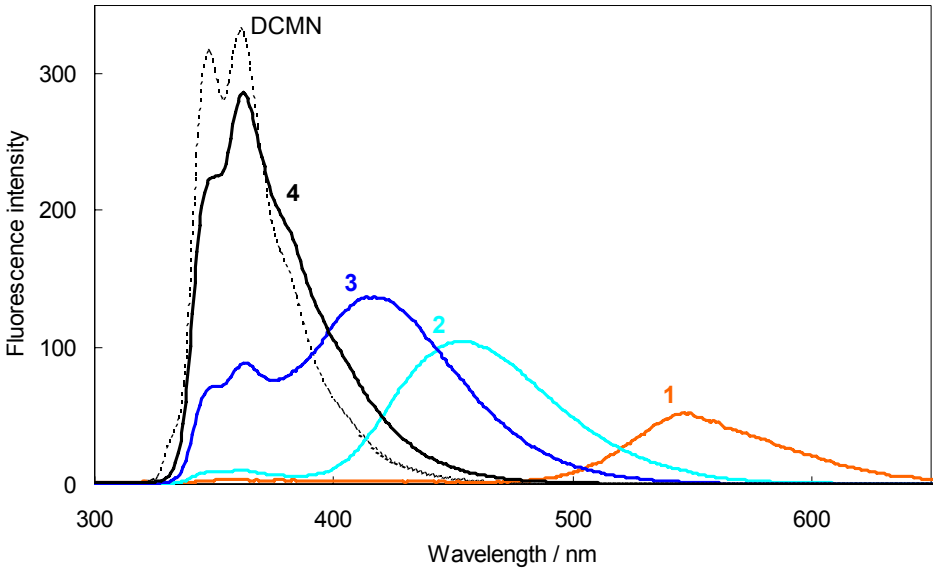


FIGURE 7. Fluorescence spectra of DCMN and **1**–**4** in cyclohexane (5.0×10^{-5} mol/L, λ_{ex} = 320 nm).

TABLE 1. Absorption and Fluorescence Data of DCMN and **1–6**

Compound	R	σ_p^{+a}	λ_{abs} (nm)	λ_{em}^{MONO} (nm)[b]	λ_{em}^{EX} (nm)[c]	Φ_f[d]	τ_f^{MONO} (ns)[e]	τ_f^{EX} (ns)[f]
1	$N(CH_3)_2$	-1.73	315, 334	347, 353	550	0.05	3.7	13.7
2	OCH_3	-0.80	315, 335	350, 361	546	0.22	6.5	33.7
3	CH_3	-0.31	314, 335	351, 363	417	0.25	1.4	12.1
4	H	0	315, 335	350, 362	nd[g]	0.27	4.9	nd[g]
DCMN	——	——	315, 340	347, 361	——	0.29	3.7	——

[a]Hammett constant. [b]Maximum fluorescence wavelength of monomer emission. [c]Maximum fluorescence wavelength of exciplex emission. [d]Fluorescence quantum yield. [e]Fluorescence lifetime of monomer emission. [f]Fluorescence lifetime of exciplex emission. [g]Not detected.

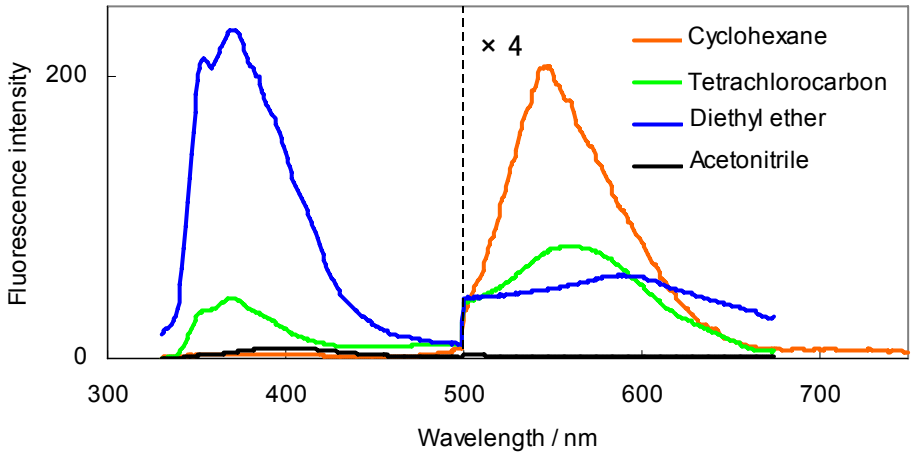


FIGURE 8. Effect of solvent on fluorescence of **1** (5.0×10^{-5} mol/L, λ_{ex} = 320 nm). The scale of intensity over 500 nm is 4-times magnified.

Based on the solvent effects on bathochromic shifts of exciplex emission bands of **1**–**3**, the transition dipole moments μ_{trans} of **1**–**3** were estimated as 13.7, 12.1, and 10.5 D, respectively, according to Mataga–Lippert formula[18];

$$\nu_f = \nu_0 - 2\mu_{trans}^2 f(\varepsilon, n)/4\pi\varepsilon_0 hca^3 \qquad \text{(eq. 1)}$$

$$f(\varepsilon, n) = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(4n^2 + 2)$$

where ν_f is the wavenumber of emission maximum, ν_0 corresponds to the emission maximum in the gas phase, ε_0 is the vacuum permittivity, h is the Plank constant, c is the velocity of the light, a is the radius of a spherical solute, μ_{ex} is the dipole moment of the solute in the excited state, ε is the dielectric constant of the solvent, and n is the refractive index of the solvent. Mataga–Lippert plots of **1** is shown in Fig. 9.

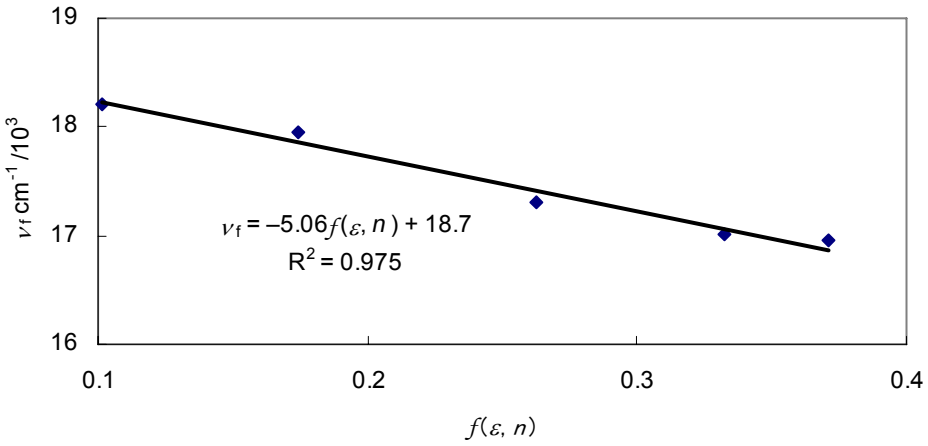


FIGURE 9. Mataga–Lippert plots of **1** in cyclohexane/diethyl ether.

Although a cyclohexane solution of **1** was colorless under natural light as described above (see Fig. 3b top), needle crystals of **1** (recrystallized from 1:3 $CHCl_3$–CH_3OH, mp. 160–161 °C) were yellow under natural light (Fig. 10c top). Interestingly, prisms of **1** (recrystallized from CH_3OH, mp. 165–166 °C) were red (Fig. 10b top). For comparison purposes, crystals of DCMN (Fig. 10a top) and **2**–**4** (Fig. 10d–f top, respectively) were essentially colorless. These observations suggest that the significant CT interaction epecifically takes place between the DCMN and DMT moieties in both yellow needles and red prisms of **1**.

Actually, when the diffuse reflection spectra of the yellow needles and the red prisms of **1** were measured in a KBr pellet, broad and structureless bands appeared in the 350–550 nm region after Kubelka–Munk transformation (Fig. 11, yellow bold and red bold). No band similar to them was observed for DCMN and **2**–**4** (Fig. 11). This finding clearly demonstates that CT complex between the DCMN and DMT moieties is formed in both yellow needles and red prisms of **1**.

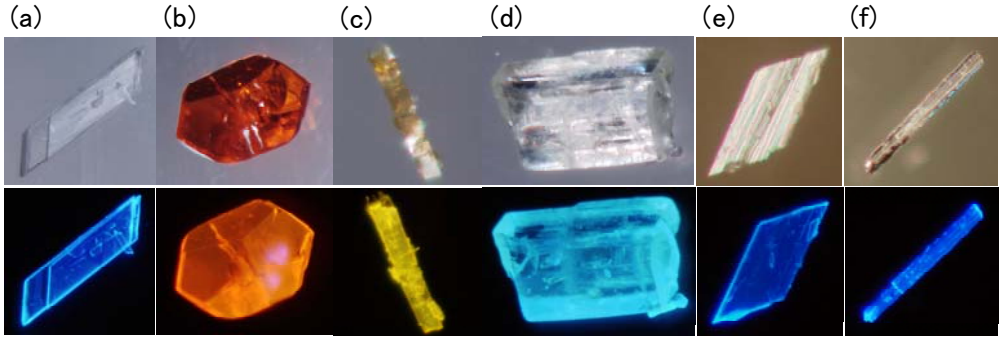


FIGURE 10. Photographs of **2** (a and d), **3** (b and e) and **4** (c and f) in crystals under natural light (top) and under light with 365 nm (bottom).

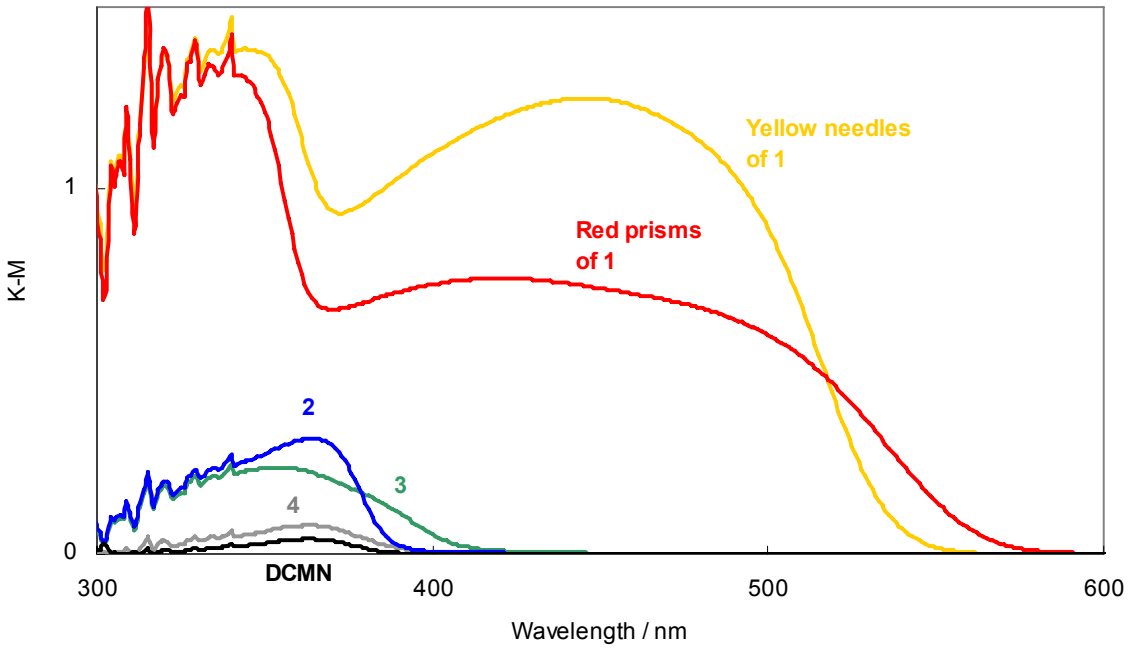


FIGURE 11. Diffuse reflection spectra of yellow needles and red prisms of **1**–**4** and DCMN in KBr.

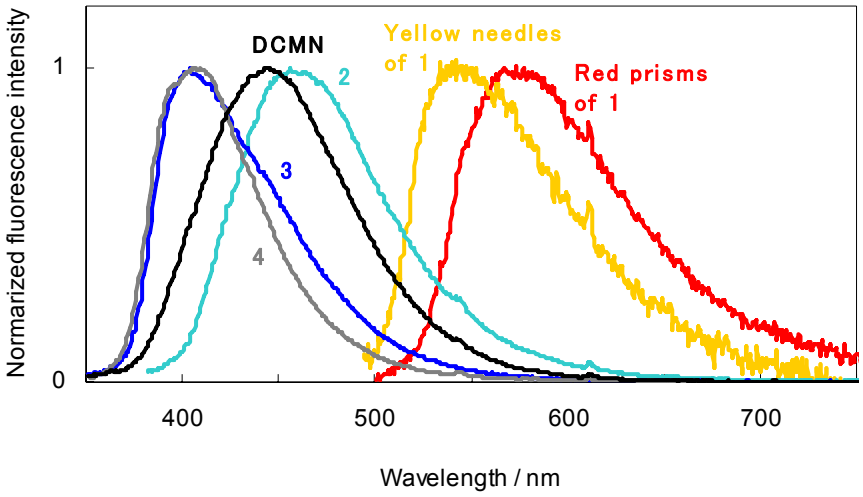


FIGURE 12. Fluorescence spectra of crystals of DCMN and **1**–**3**.

TABLE 2. Fluorescence Data of Crystals of 1–6 and DCMN.

Compound	R	λ_{em} (nm)[a]	Φ_f[b]
1	$N(CH_3)_2$	550,[c] 567[d]	0.10,[c] 0.09[d]
2	OCH_3	456	0.39
3	CH_3	404	0.29
4	H	407	0.55
DCMN		445	0.49

[a]Maximum fluorescence wavelength. [b]Fluorescence quantum yield.

[c]For yellow needles of **1**. [d]For red prisms of **1**.

Fluorescence spectra and data were summarized in Fig. 12 and Table 2. Columnar crystals of DCMN display typical blue fluorescence upon excitation at 365 nm (Fig. 10a bottom). Also, a broad emission band at 445 nm is produced by excitation of the colomnar crystals of DCMN (Φ_f = 0.49; Fig. 12, black bold line), which is referred to aggregation of DCMN in the crystals. In contrast, the yellow needles of **1** emitted yellow fluorescence (Φ_f =

0.10; Fig. 10c bottom) and the corresponding red prisms emitted orange fluorescence (Φ_f = 0.09; Fig. 10b bottom). The red prisms and yellow needles of **1** fluoresced in the 500–750 nm region (Fig. 12, red line for the red prisms; yellow line for the yellow needles), which are associated with exciplex fluorescence. The colorless crystals of **2** emitted aquablue fluorescence (Fig. 8a, bottom) upon excitation at 365 nm. The crystals of **2** fluoresced at 456 nm (Φ_f = 0.39; Fig. 12, aquablue line), that is identical with the exciplex fluorescence of **2** in cyclohexane. Dyad **3** showed the exciplex emission band at 417 nm when photoexcited in cyclohexane (see Fig. 5 and Table 1). However, in the crystals of **3** a fluorescence band was unexpectedly observed at 404 nm (Fig. 8b) which was more hypsochromic than that in cyclohexane by 13 nm (Fig. 12, blue, Table 2). Moreover, the fluorescence band was more more hypsochromic than that of DCMN itself (Fig. 12, blue and black lines). These results indicate that dyad **3** can form exciplex in cyclohexane but not do in the crystals. Evidently, it was found that the formation of exciplexes of the dyads requires stronger donor property than that of methyl group.

Actually, the X-ray crystallographic analysis of the crystals of **3** showed dimer formation in the crystals (Fig. 13). The 1- or 4-cyano group in one molecule of the dimer is overlapping with the aromatic ring of the adjacent DCMN moiety in the dimer. This fact suggests that the dyad **3** crystallizes with *inter*molecular CT interaction between the DCMN–DCMN moieties in the dimer of **3** and forms an *inter*molecular excimer in the crystals, when photoexcited. Itoh *et al.*[19] and Hutten *et al.*[20] reported that conjugated cyano compounds *inter*molecularly π-stacked in the crystals and formed excimer when photoexcited. Thus, the fluorescence of **3** in the crystals is identified as an *inter*molecular excimer emission. Evidently, CT interaction between the DCMN and toluene moieties of **3** is not superior to the DCMN–DCMN interaction. Similarly, the X-ray crystallographic analysis of the crystals of **4** showed that dimers of **4** are formed in the corresponding crystals, and 1- or 4-cyano group in the DCMN moieties of **4** is overlapping with the other aromatic rings of the adjacent DCMN

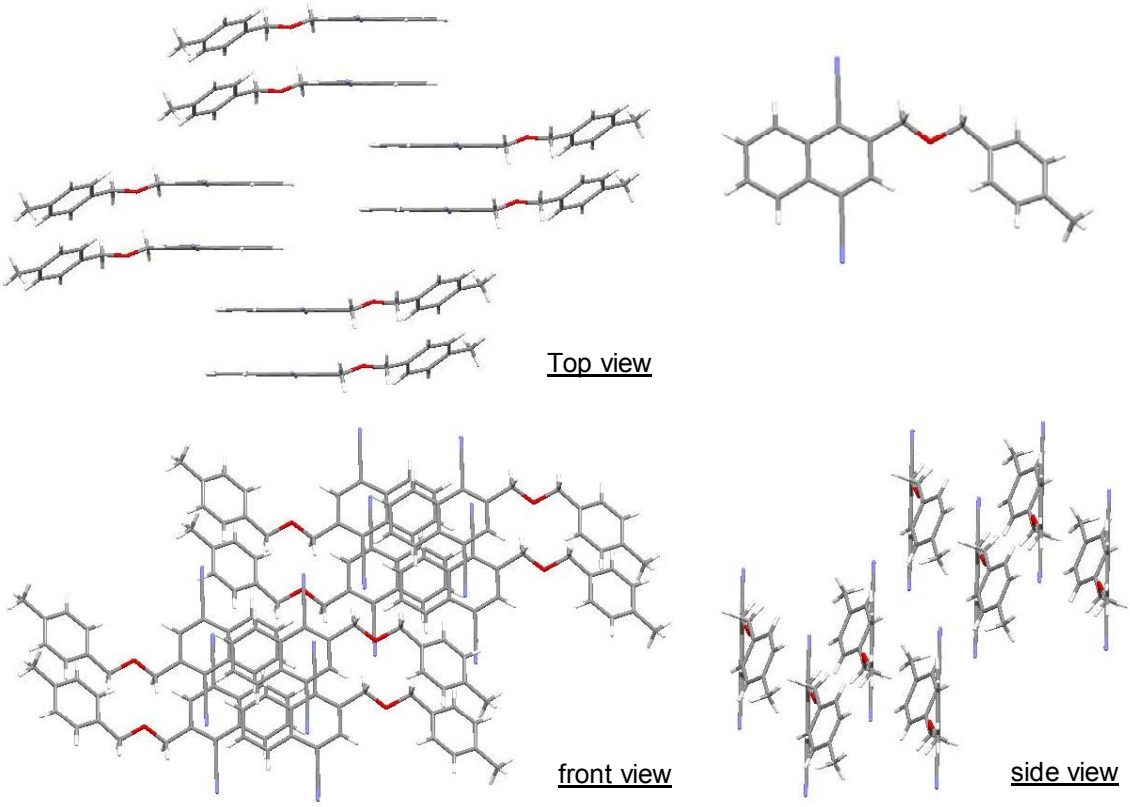


FIGURE 13. Molecular geometry and crystal structure of the crystals of **3**.

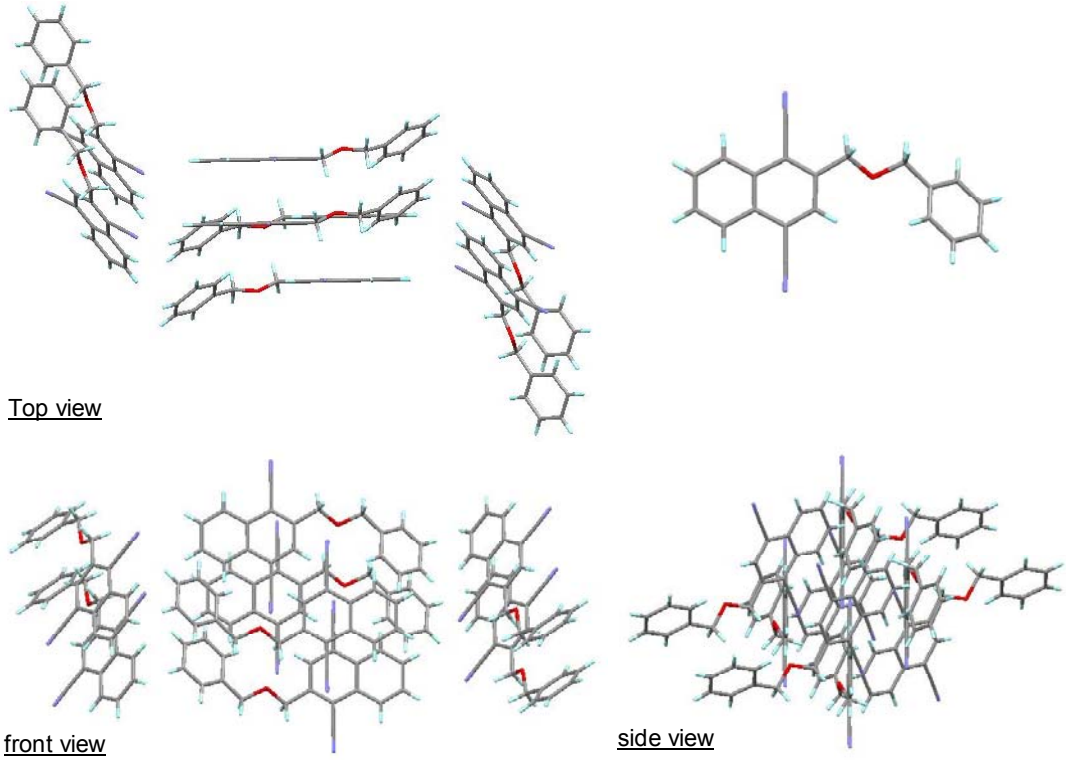


FIGURE 14. Molecular geometry and crystal structure of the crystals of **4**.

moieties in the dimer (Fig. 14). The fluorescence of **4** is also attributed to *inter*molecular excimer emission of dimers of the DCMN moieties.

The X-ray crystallographic analysis of these red prisms[21] of **1** showed that the torsion angle between the DCMN and DMT moieties in **1** is 106º (Fig. 10)[22] and the DCMN moiety is stacked with the DMT moiety of an adjacent molecule of **1**. The DCMN moiety of this "adjacent molecule" is further stacked with the DMT moiety of another molecule of **1**, as shown in Fig. 15. Thus, the *inter*molecular face-to-face overlap between the DCMN and DMT moieties of **1** in red prisms results in formation of an *inter*molecular one-to-one mixed-stack ground state CT complex that has a transition dipole moment oriented continuously in a zigzag manner. That is the reason why CT complex between the DCMN and DMT moieties is formed only in yellow needles and red prisms of **1**. As the results, the DCMN and DMT moieties of **1** could be superior to the DCMN–DCMN interaction and be preorientated to form *inter*molecular exciplex.

On the other hand, the X-ray crystallographic analysis of the crystals of **2** showed that the relationship between the DCMN and anisole moieties in **2** is coplanar (Fig. 16). The DCMN moiety of dyad **2** is successfully stacked with the anisole moiety of an adjacent molecule of **2** face to face in the same manner as in the case of dyad **1**, forming an *inter*molecular mixed-stack ground state CT complex. It was found that the DCMN and anisole moieties of **2** could be superior to the DCMN–DCMN interaction and be preorientated to form *inter*molecular exciplex. In addition, the transition dipole moment of a pair of DCMN and anisole moieties cancels each other in the crystals of **2**, as shown in Fig. 16. Since the absorbance of a compound depends on its transition dipole moment and it is known that exciton interaction in a crystalline state propagates throughout a whole crystal through resonance interaction between excited molecules,[23] the CT transition dipole moment in a whole crystal of **2** is almost zero, while dyad **2** forms the CT complex between the DCMN and anisole moieties in the crystalline state. Thus, it was found that the excitation of the CT

complex is a forbidden transition. Consequently, the crystals of dyad **2** do not show CT absorption bands and is colorless (Fig. 8a, Fig. 9, green).

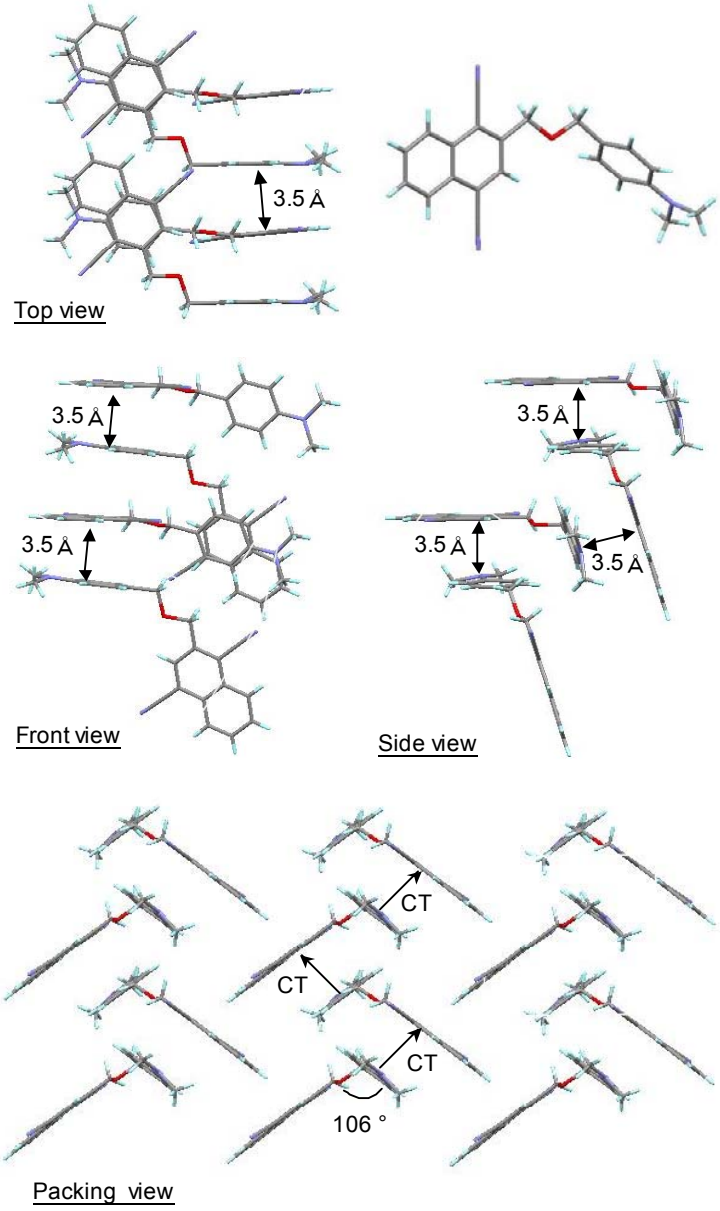


FIGURE 15. Molecular geometry and crystal structure of the red prisms of **1**.

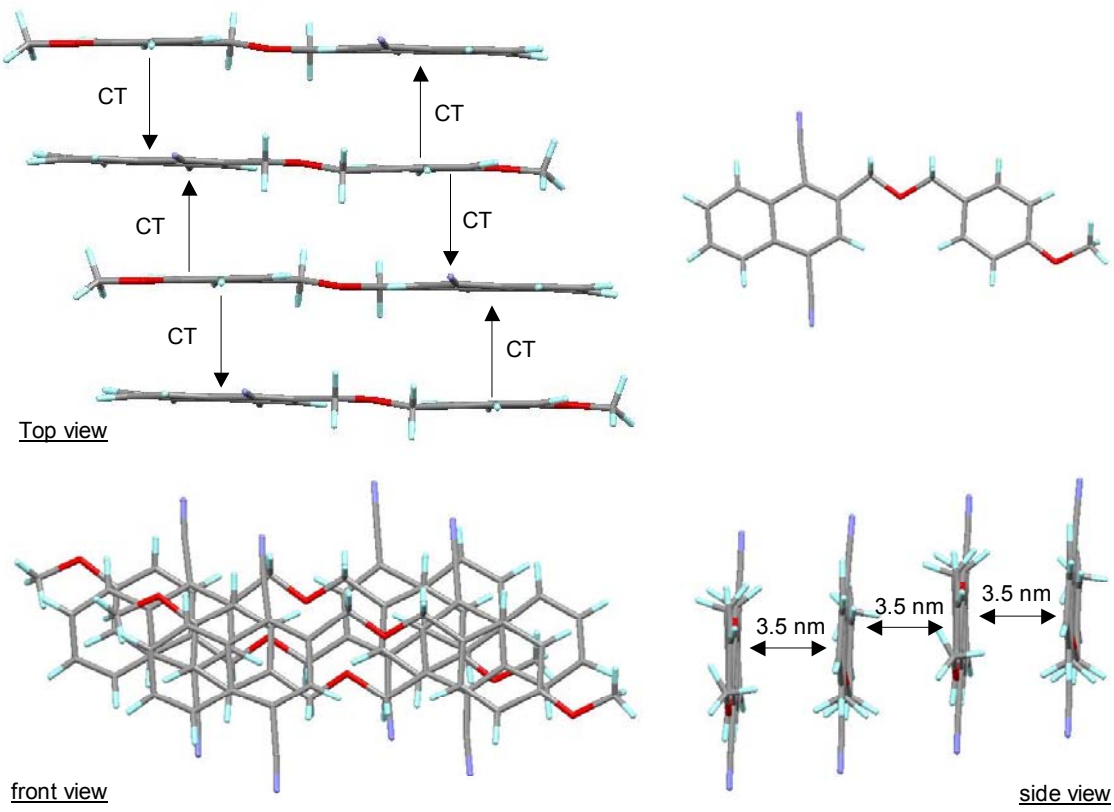
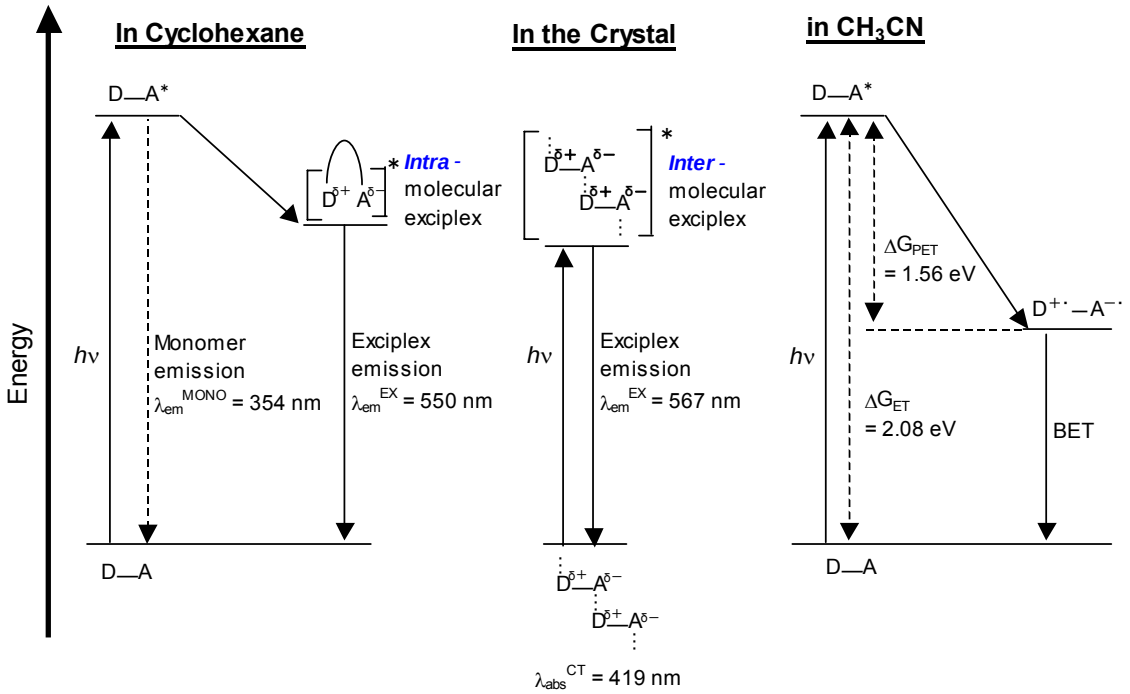


FIGURE 16. Molecular geometry and crystal structure of the crystals of **2**.

The dimers described above are not formed in the crystals of **1** and **2** and there is no overlapping between DCMN moieties (see Fig. 15, 16). *Inter*molecular mixed-stack CT complexes are efficiently formed with face-to-face CT interaction of the DCMN moieties with the DMT or anisole donor moieties in the crystals of **1** and **2**. As a consequence, *inter*molecular exciplexes of **1** and **2** are formed between the DCMN moiety and the respective donor moieties alligned in a face-to-face orientation through CT interactions. These results demonstrately indicate that stronger donor ability than toluene is required to preorientate the DCMN moieties with the donor moieties of the dyads.



SCHEME 2. Simplified energy diagrams of *intra*- and *inter*-molecular exciplex formation of **1** in cyclohexane and the crystals, and electron transfer, respectively. **A**, DCMN moiety; **D**, DMT moiety.

In Scheme 2 are shown the simplified energy diagrams for *intra*- and *inter*-molecular exciplex formation for **1** in a cyclohexane solution and the crystalline state, and *intra*molecular electron transfer in acetonitrile. The photoexcitation of a cyclohexane solution of dyad **1**, which does not have strong CT interactions in the ground state, results in production of an exciton that forms an *intra*molecular exciplex through a pathway involving a conformational change and charge transfer prior to monomer emission from the DCMN moiety. On the other hand, in acetonitrile, which is a strong polar solvent, photo-induced electron transfer (PET) occurs exergonicly and an extended radical ion pair is formed without conformational change, and followed by back electron transfer (BET), which deactivates the excited state of **1**. In contrast, in the crystalline state the dyad **1** exists in the state of continuous *inter*molecular CT ground state complex that is capable of directly forming an *inter*molecular exciplex when photoexcited.

2.3 CONCLUSION

In this chapter, the author presents that *intra*molecular CT complexes of **1**–**4** hardly exist in the ground states of these substance in solution, and dyads **1**–**3** form *intra*molecular exciplexes in cyclohexane as expected, though dyad **4** does not. To the contrary, the donor and acceptor moieties of dyad **1** and **2** are *inter*molecularly preorientated face to face to form *inter*molecular CT complexes in the crystals. As desired, *inter*molecular exciplexes are successfully formed through the ground state CT complexes in the crystals of **1** and **2** against the Hirayama rule, while dyads **3** and **4** do not form *inter*molecular exiplexes but excimers in the crystals. Thus, nobel exciplex-emissive organic crystals of **1** and **2** have been created to fluoresce with the quantum yields of 0.09 and 0.39, respectively. It is demonstrated that the appropriate CT interaction between the donor and acceptor moieties in the crystals of **1** and **2** operates to prepare the exciplex-emissive organic crystals. The more appropriate CT interaction ocurrs in the crystals of **2** preventing ET process, while the exciplex emission of the crystals of **1** is weak as a consequence of ET due to a little too strong CT interaction between the DMT and DCMN moieties.

2.4 EXPERIMENTAL

General. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively (Bruker Co. Ltd., Advance 400). Melting points were measured on a Yamato MP-21 melting point apparatus and uncorrected. UV-VIS spectra were recorded on a Hitachi U-2800A spectrophotometer, IR spectra were recorded on a Shimadzu IR prestige-21 spectrometer. Mass spectra were recorded on a ESI-TOF/MS Per Septive Biosystems. Fluorescence spectra were

recorded on a Jasco FP-6500 spectrofluorometer. Fluorescence quantum yields were determined on a Hamamatsu absolute PL quantum yield measurement system C9920-02. X-ray crystallographic analysis was measured on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite monochromated Cu(*K*a) radiation. Elemental analysis was performed on a PerkinElmer 2400 II CHN elemental analyzer.

1,4-Dibromo-2-(bromomethyl)naphthalene (9): A mixture of 1,4-dibromo-2-methylnaphthalene (**8**, 1.5 g, 5.0 mmol), *N*-bromosuccinimide (NBS, 0.89 g, 5.0 mmol) and benzoyl peroxide (BPO, 0.085 g, 0.26 mmol) was dissolved in CCl_4 (400 mL). The solution was refluxed for 1 h and cooled to room temperature. After concentration in vacuo, a white precipitate of succinimide was filtered out. The filtrate was evaporated in *vacuo*. The resulting milky white residue was purified by silica-gel chromatography with hexane, giving 1.71 g of **3** as a white powder in 90% yield; mp. 129–130 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 5.00 (s, 2H, CH_2), 7.78–7.83 (m, 2H), 8.16 (s, 1H), 8.17 (m, 1H), 8.30 (m, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 34.4, 121.8, 124.3, 127.1, 127.7, 129.3, 129.3, 131.5 (2C), 132.5, 136.3.

1,4-Dibromo-2-(4'-*N,N*-dimethylaminobenzyloxy)methylnaphthalene: To a round-bottom flask containing *N,N*-dimethyl-4-aminobenzyl alcohol (0.82 g, 5.4 mmol) and NaH (0.66 g, 27 mmol) was added dry THF (100 mL) at room temperature under nitrogen. The mixture was stirred for 1 h at room temperature. A solution of **3** (1.0 g, 2.7 mmol) in THF (10 mL) was added to the mixture. The reaction mixture was refluxed for 3 h and cooled to room temperature. The mixture was poured into ice water and extracted with $CHCl_3$. The combined organic layer was washed with brine, and evaporated in *vacuo*. The resulting brown residue was recrystallized from methanol after treatment with activated carbon, giving 0.93 g of **4** as a yellow powder in 77% yield; mp. 106–107 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 2.88 (s, 6H, CH_3), 4.53 (s, 2H, CH_2), 4.70 (s, 2H, CH_2), 6.71 (AA'BB', J = 12 Hz, 2H), 7.23 (AA'BB', J = 12 Hz, 2H), 7.74–7.79 (m, 2H), 7.94 (s, 1H), 8.16 (m, 1H), 8.27 (m. 1H); ^{13}C NMR

(DMSO-d_6, 100 MHz) δ_{ppm} 40.1 (2C, CH_3), 70.2 (CH_2), 72.3 (CH_2), 112.0 (2C), 121.3, 121.8, 124.9, 126.9, 127.1, 128.5, 128.9, 129.3 (2C), 129.5, 131.3, 132.3, 137.2, 150.1.

1,4-Dicyano-2-(4'-*N*,*N*-dimethylamimobenzyloxy)methylnaphthalene (1): To a round-bottom flask containing **4** (1.3 g, 2.9 mmol), NaCN (0.57 g, 12 mmol), $Pd(PPh_3)_4$ (0.69 g, 0.60 mmol), CuI (0.23 g, 1.2 mmol) was added propionitrile (7.5 mL) at room temperature. The reaction mixture was refluxed for 30 min and cooled to room temperature. After addition of EtOAc (60 mL), the reaction mixture was filtered through a celite pad, washed with water and brine, and the solvent was evaporated in *vacuo*. The resulting dark-brownish residue was purified by silica-gel chromatography with hexane–EtOAc (8/2), giving 0.61 g of **1** as a yellow powder in 61% yield. The powder was recrystallized from $CHCl_3$–CH_3OH (1/3), giving 0.44 g (44 % yield) of **1** as yellow needles; mp. 160–161 ^oC; ^1H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 2.86 (s, 6H, CH_3), 4.54 (s, 2H, CH_2), 4.85 (s, 2H, CH_2), 6.67 (AA'BB', *J* =8 Hz, 2H), 7.21 (AA'BB', *J* =8 Hz, 2H), 7.96–7.99 (m, 2H), 8.23–8.28 (m, 2H), 8.30 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 40.1 (2C, CH_3), 68.5 (CH_2), 72.6 (CH_2), 112.0 (2C), 112.6, 113.7, 114.9 (CN), 116.4 (CN), 124.7, 125.3, 125.4, 129.5 (2C), 130.3, 130.4, 130.8, 131.4, 132.5, 142.9, 150.2; ESI-MS *m/z* 342.1 ($M+H^+$); UV-VIS 315 nm (ε 9658 $mol^{-1}Lcm^{-1}$, cyclohexane); IR (diamond ATR) ν 2216 cm^{-1} (CN); Anal. Calcd for $C_{22}H_{19}N_3O$: C, 77.40; H, 5.61; N, 12.31. Found: C, 77.10; H, 5.52; N, 12.28.

The yellow needles was recrystallized from CH_3OH to give red prisms of **1**; mp. 165–166 ^oC.

1,4-Dicyano-2-(4'-methoxybenzyloxy)methylnaphthalene (2): mp. 110–111 ^oC; ^1H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 3.74 (s, 3H, OCH_3), 4.60 (s, 2H, CH_2), 4.88 (s, 2H, CH_2), 6.92 (AA'BB', *J* =8 Hz, 2H), 7.35 (AA'BB', *J* =8 Hz, 2H), 7.94–8.00 (m, 2H), 8.22–8.27 (m, 2H), 8.34 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 55.1 (OCH_3), 68.8 (CH_2), 72.1 (CH_2), 112.7, 113.7 (2C), 113.7, 114.8 (CN), 116.3 (CN), 125.3, 125.4, 129.5, 129.6 (2C), 130.4, 130.4, 130.8, 131.3, 132.4, 142.6, 158.9; UV-VIS 315 nm (ε 9123 $mol^{-1}Lcm^{-1}$, cyclohexane);

IR (diamond ATR) ν 2216 cm^{-1} (CN); Anal. Calcd for $C_{22}H_{19}N_3O$: C, 76.81; H, 4.91; N, 8.53. Found: C, 76.70; H, 4.79; N, 8.53.

1,4-Dicyano-2-(4'-methylbenzyloxy)methylnaphthalene (3): mp. 124–125 ^oC; ^1H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 2.29 (s, 3H, CH_3), 4.63 (s, 2H, CH_2), 4.89 (s, 2H, CH_2), 7.17 (AA'BB', *J* =8 Hz, 2H), 7.30 (AA'BB', *J* =8 Hz, 2H), 7.94–8.00 (m, 2H), 8.21–8.27 (m, 2H), 8.35 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 20.8 (CH_3), 69.0 (CH_2), 72.3 (CH_2), 112.7, 113.7, 114.8 (CN), 116.3 (CN), 125.3, 125.4, 128.0 (2C), 128.9 (2C), 130.4, 130.4, 130.8, 131.3, 132.4, 134.6, 137.0, 142.5; UV-VIS 314 nm (ε 9038 $mol^{-1}Lcm^{-1}$, cyclohexane); IR (diamond ATR) ν 2218 cm^{-1} (CN); Anal. Calcd for $C_{22}H_{19}N_3O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.61; H, 5.05; N, 8.93.

2-(Benzyloxy)methyl-1,4-Dicyanonaphthalene (4): mp. 96–97 ^oC; ^1H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 4.69 (s, 2H, CH_2), 4.92 (s, 2H, CH_2), 7.32 (t, 1H), 7.38 (t, 2H), 7.43 (AA'BB', *J* =8 Hz, 2H), 7.93–8.00 (m, 2H), 8.22–8.26 (m, 2H), 8.37 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 69.1 (CH_2), 72.4 (CH_2), 112.8, 113.8, 114.8 (CN), 116.3 (CN), 125.3, 125.4, 127.4, 127.8 (2C), 128.3 (2C), 130.4, 130.5, 130.8, 131.3, 132.4, 137.6, 142.4; ESI-MS *m/z* 321.2 ($M+Na^+$); UV-VIS 315 nm (ε 8893 $mol^{-1}Lcm^{-1}$, cyclohexane); IR (diamond ATR) ν 2216 cm^{-1} (CN); Anal. Calcd for $C_{22}H_{19}N_3O$: C, 80.52; H, 4.73; N, 9.39. Found: C, 80.09; H, 4.62; N, 9.35.

2-(4'-Chlorobenzyloxy)methyl-1,4-Dicyanonaphthalene (5): mp. 128–129 ^oC; ^1H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 4.68 (s, 2H, CH_2), 4.92 (s, 2H, CH_2), 7.44 (AA'BB', *J* =8 Hz, 2H), 7.44 (AA'BB', *J* =8 Hz, 2H), 7.95–8.01 (m, 2H), 8.23–8.27 (m, 2H), 8.39 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 69.2 (CH_2), 71.5 (CH_2), 112.8, 113.8, 114.8 (CN), 116.3 (CN), 125.3, 125.4, 128.3 (2C), 129.6 (2C), 130.4, 130.5, 130.8, 131.3, 132.3, 134.5, 136.7, 142.2; UV-VIS 317 nm (ε 8734 $mol^{-1}Lcm^{-1}$, cyclohexane); IR (diamond ATR) ν 2220 cm^{-1} (CN); Anal. Calcd for $C_{22}H_{19}N_3O$: C, 72.18; H, 3.94; N, 8.42. Found: C, 72.16; H, 3.83; N, 8.40.

1,4-Dicyano-2-(4'-trifluoromethylbenzyloxy)methylnaphthalene (6): mp. 135–136 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ_{ppm} 4.80 (s, 2H, CH_2), 4.97 (s, 2H, CH_2), 7.65 (AA'BB', J =8 Hz, 2H), 7.73 (AA'BB', J =8 Hz, 2H), 7.95–8.01 (m, 2H), 8.23–8.28 (m, 2H), 8.42 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ_{ppm} 69.5 (CH_2), 71.5 (CH_2), 112.9, 113.8, 114.8 (CN), 116.3 (CN), 125.2 (3C), 125.3, 125.4, 128.1 (2C), 130.4, 130.5, 130.8, 131.3, 132.5, 142.1, 142.6; UV-VIS 319 nm (ε 8891 $mol^{-1}Lcm^{-1}$, cyclohexane); IR (diamond ATR) ν 2224 cm^{-1} (CN); Anal. Calcd for $C_{22}H_{19}N_3O$: C, 68.85; H, 3.58; N, 7.65. Found: C, 68.71; H, 3.42; N, 7.62.

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13. $\Delta G_{PET} = E^{ox}_{1/2}$ ($D/D^{+\cdot}$) – $E^{red}_{1/2}$ ($A^{-\cdot}/A$) – E_{00} – ω_p; where $E^{ox}_{1/2}$ ($D/D^{+\cdot}$) is half wave potential of electron donor, + 0.81 V for DMT moiety of **1**, $E^{red}_{1/2}$ ($A^{-\cdot}/A$) is half wave potential of electron acceptor, –1.28 V for DCMN moiety of **1**, E_{00} is 0–0 transition energy, and ω_p is energy reqired to separate cation and anion outside coulombic force sphere ($\omega_p \approx$ 0 in acetonitrile).

14. Solvent, acetonitrile; electrolyte, tetraethylammonium perchlorate (0.1 mol/L); scan rate, 0.1 V/s; RE, SCE; WE and CE, Pt; under Ar.

15. There are some examples that when dyads consisting of donor and acceptor moieties, which are tethered with methylene chains, are photoexcited in strong polar solvents such as acetonitrile, very rapid electon transfer occurs in extended conformation of the molecules on a time scale of a few ps to hundreds ps, producing solvated ion pairs without passing through the exciplex state. See ref. 2e, 2h, 4f, 5b, 13b, and 13d.

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17. $h\nu_{pulse}$, 355 nm; concentration of **1**, 2.0×10^{-3} mol/L; in acetonitrile added $Mg(ClO_4)_2$ (0.1 mol/L); under Ar.

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22. The molecular geometry determined with X-ray crystallographic analysis was also supported by density function theory calculation B3LYP/6-31G(d,p).
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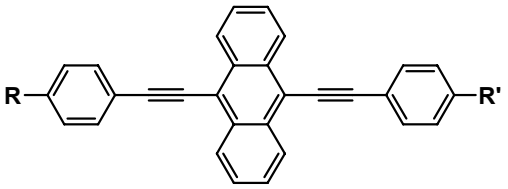
CHAPTER 3

Solvatochromatic Properties of 9-(4-Aminophenylethynyl)-10 -(4-nitrophenylethynyl)anthracene

3.1 INTRODUCTION

Among numerous fluorescent organic compounds, 9,10-bis(phenylethynyl)anthracene (**1**) and its derivatives have been studied intensely. Owing to their high fluorescence quantum yields in the green region, these substances have been probed for applications in OLEDs (organic light emitting diode),[1] PLEDs (polymer light emitting diode),[2, 3] luminescent liquid crystals,[4] chemiluminescence[5–9] and molecular probes.[10]



1: R, R' = H
2: R = NH_2, R' = NO_2

Recently, the compound **1** and its derivatives have received attention as nonlinear optical materials.[11, 12] It is well known that introduction of acceptor and donor groups at the terminal positions of π conjugated systems, such as *p*-nitroaniline, is one of the most effective means of improving nonlinear optical properties.[13] The heightened interest in the nonlinear optical characteristics of **1** has led to the synthesis and evaluation of derivatives with substituents at the *para*-positions of the phenylethynyl groups.[14] However, until now compounds that contain both electron accepting and electron donating groups in the phenylethynyl moieties have not been thoroughly studied.[4, 8, 11, 12] In particular, the prototypical substance, 9-(4-aminophenylethynyl)-10-(4-nitrophenylethynyl)anthracene **2**, has not been prepared even though it is expected to exhibit interesting linear and nonlinear optical properties. Since **2** contains a strong electron donating group (NH_2) and a strong electron withdrawing group (NO_2) at the terminal positions of an extended π conjugated system, it should display strong charge transfer characteristics.

As a consequence of its potentially interesting properties, we have developed an

efficient synthesis of **2** that relies on the use of the sequential Sonogashira cross coupling reactions. In addition, the solvatochromism in the absorption and fluorescence spectra of **2** were measured and compared with those of **1**.

3.2 RESULTS & DISCUSSION

In Fig. 1 are shown the absorption spectra of **1** and **2** in hexane and DMF and a summary of the absorption spectroscopic data for **1** and **2** in various solvents is given in Table 1. The absorption maxima (λ_{abs}) of **2** occur at longer wavelengths than those of **1**[4, 8] and, in contrast to **1**, the spectra of **2** are sensitive to solvent polarity (469 nm in hexane *vs.* 503 nm in DMF). The bathochromic shift observed in the absorption spectra of **2** is a consequence of the presence of the nitro and amino groups at the terminii of the highly conjugated system. This

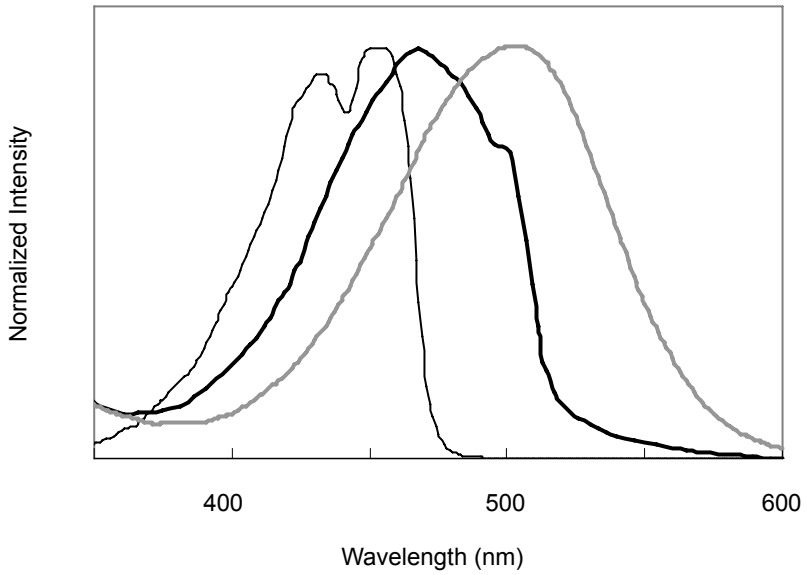
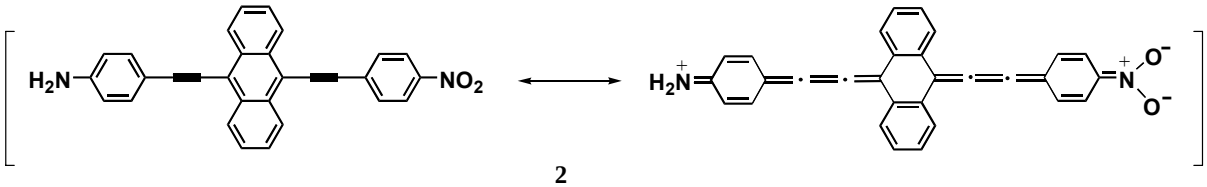


FIGURE 1. Absorption spectra of **1** in hexane (thin line), **2** in hexane (bold line) and DMF (bold gray line).

finding suggests that the excited state of **2** has intramolecular charge transfer character and a large dipole moment. However, the shoulders seen in the absorption spectra of **2** (Fig. 1 and Table 1) might indicate that an intramolecular charge-transfer state exists in the ground state also (vide infra).



2

TABLE 1. Absorption Maxima λ_{abs} of **1** and **2** in Various Solvents

Solvent	Dielectric constant	λ_{abs} / nm ($\varepsilon \times 10^{-4}$)[a]	
		1	**2**
Hexane	1.89	309 (2.65), 432 (2.02), 454 (2.15)	469 (0.09) + sh[b]
Cyclohexane	2.02	310 (2.65), 434 (2.10), 451 (2.31)	473 (0.11) + sh
Benzene	2.40	312 (3.25), 447 (3.09), 456 (3.28)	479 (4.05) + sh
Toluene	2.43	312 (2.95), 439 (2.85), 458 (3.00)	478 (3.66) + sh
m-Xylene	2.37		479 (4.14) + sh
Anisole	4.33		484 (4.23) + sh
Et_2O	4.42	309 (4.22), 433 (3.51), 456 (3.75)	478 (5.21) + sh
$CHCl_3$	4.89	313 (2.89), 439 (2.69), 461 (2.85)	480 (4.70) + sh
Chlorobenzene	5.74	314 (3.38), 442 (3.19), 464 (3.39)	486 (2.00) + sh
EtOAc	6.03	309 (4.00), 435 (3.41), 459 (3.68)	483 (4.30)
THF	7.47	311 (3.71), 437.5 (3.26), 461 (3.49)	490 (4.32)
Methanol	32.35	308 (1.38), 433 (1.05), 458 (1.14)	483 (1.39)
Acetonitrile	36.00	309 (4.46), 435 (3.84), 461 (4.35)	483 (4.67)
DMF	37.06	312 (4.15), 440 (3.74), 466 (4.20)	503 (4.11)

[a] L mol^{-1} cm^{-1}.

[b] sh ; shoulder.

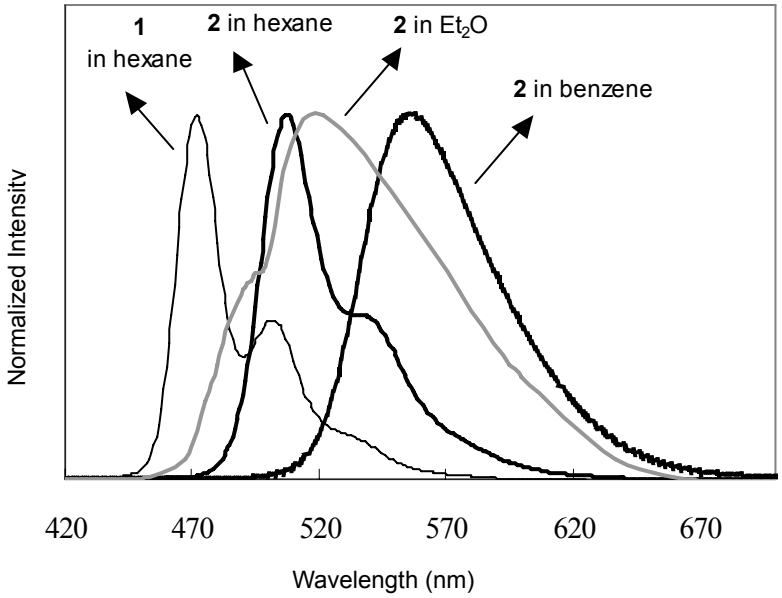


FIGURE 2. Fluorescence spectra of **1** and **2**. [**1**] = [**2**] = 1.1 × 10^{-5} mol/L

TABLE 2 Fluorescence Properties of **1** and **2** in Various Solvents[a]

Solvent	**1**			**2**		
	λ_{em} / nm[b]	Φ_F[c]	τ / ns[d]	λ_{em} / nm[b]	Φ_F[c]	τ / ns[d]
Hexane	468, 498	0.85		513	0.210	
Cyclohexane	471, 502	0.67	3.1	519	0.408	2.3
Benzene	477, 508	0.64	2.9	557	0.131	2.4
Toluene	476, 508	0.65		553	0.162	
m-Xylene				551	0.159	
Anisole				589	0.003	
Et_2O	469, 499	0.70		522	0.068	
$CHCl_3$	476, 507	0.71[e]		nd[f]		
Chlorobenzene	479, 510	0.50		592	0.003	
EtOAc	471, 501	0.68		547	0.001	
THF	474, 504	0.42	3.2	547	0.001	2.5
Methanol	469, 499	0.75		nd		
Acetonitrile	471, 501	0.65		nd		
DMF	476, 508	0.69		nd		

[a] [**1**] = [**2**] = 1.1 × 10^{-5} mol/L.

[b] Emission maxima, excited at 440 nm.

[c] Fluorescence quantum yield.

[d] Fluorescence lifetime in aerated conditions.

[e] Ref. 3.

[f] nd ; not detected.

In Fig. 2 and Table 2 are shown the respective fluorescence spectra and data for **1** and **2** in selected solvents.[4, 8] The fluorescence maxima (λ_{em} = 513 nm) of **2** in hexane occurs at a longer wavelength than that of **1** (468, 496 nm) and undergoes a solvatochromatic shift to 592 nm in chlorobenzene. Importantly, **1** does not show fluorescence solvatochromism. The fluorescence quantum yield (Φ_F) of **2** is markedly lower than that of **1**, even in less polar solvents. The fluorescence lifetimes (τ) of **2** were slightly shorter than those of **1** (Table 2). This observation suggests that the intramolecular charge transfer character of the excited state of **2** causes an increase in the rates nonradiative decay and/or intersystem crossing. In fact, the fluorescence quantum yield of **2** decreases with increasing solvent polarity. This observation suggests that the fluorescence of **2** arises from an excited state having intramolecular charge transfer character and that the excited state quinoid structure of **2** is non-emissive in polar solvents such as DMF and acetonitrile.

TABLE 3. Stokes Shifts (λ_{em} - λ_{ex}) of **1** and **2**

Solvent	**1**		**2**	
	λ_{ex} / nm[a]	λ_{em} - λ_{ex}	λ_{ex} / nm[a]	λ_{em} - λ_{ex}
Hexane	309, 434, 455	13	497	16
Cyclohexane	310, 435, 453	18	502	17
Benzene	312, 442, 457	20	514	43
Toluene	312, 441, 458	18	508	45
m-Xylene			513	38
Et_2O	308, 434, 456	13	511	11

[a] Excitation maxima.

The emission maximum (λ_{em}) of **2** in aromatic solvents, such as benzene and toluene, shifts to longer wavelengths (λ_{em} 557 nm in benzene) than those in nonaromatic solvents, such as cyclohexane (λ_{em} 519 nm). In addition, large Stokes shifts take place in the emission band of **2** in aromatic solvents as compared to nonaromatic solvents. This finding suggests that the singlet excited state of **2** strongly interacts with the aromatic solvents and that the interaction

promotes a change in its structure (Table 3). There may be π-π interaction of the planar quinoid structure in the excited state of **2** with aromatic solvents. In contrast, the Stokes shifts observed in the emission spectrum of **1** are small in both aromatic and nonaromatic solvents.

TABLE 4. Excitation-wavelength Dependence of Fluorescence Quantum Yields Φ_F of **2** in Toluene

Exciting wavelength/nm	Φ_F of **1**	Φ_F of **2**
400	0.66	0.066
440	0.65	0.162
478	0.66	0.168
520		0.322

In addition, Φ_F of **2** is found to depend on the excitation wavelength (Table 4). For example, Φ_F of **2** excited at 520 nm is much larger than when **2** is excited at 400 nm. This result indicates that the fluorescence of **2** corresponds to emission from a charge transfer (CT) excited state produced by absorption of light by a charge-transfer ground state (see above). In contrast, the Φ_F of **1** does not depend on the excitation wavelength.

3.3 CONCLUSION

The observation described in this chapter demonstrates that the absorption and emission properties of **2**, in contrast to **1**, display distinctive solvent effects (solvatochromism). The results suggest that the fluorescence of **2** arises from a singlet CT excited state that possesses intramolecular charge transfer character. The observed strong dependence of the fluorescence quantum yield on solvent polarity shows that the CT character of its singlet excited state causes **2** to be more fluorescent in less polar solvents as compared to polar solvents.

3.4 EXPERIMENTAL

UV-VIS spectra were recorded on a Hitachi U-2800A spectrophotometer. Fluorescence spectra were recorded on a Jasco FP-6500 spectrofluorometer. Fluorescence quantum yields were determined using **1** as an actinometer (Φ_f = 0.71 in chloroform) [3]. Fluorescence quantum yields were calculated by using the equation $\Phi_{f(spl)} = \Phi_{f(std)} \times [A_{std}/A_{spl}] \times [I_{spl}/I_{std}] \times [n_{spl}/n_{std}]^2$. where, $\Phi_{f(spl)}$ and $\Phi_{f(std)}$ are the quantum yields of the sample and standard, respectively, A_{spl}, I_{spl} and n_{spl} and A_{std}, I_{std} and n_{std} are the optical densities, the integrated emission intensities at the excitation wavelengths, and the refractive indexes of the solvent, for the sample and standard, respectively.

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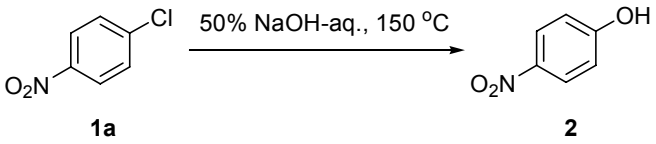
CHAPTER 4

Unexpectedly High Reactivity of Aniline Derivatives toward Hydroxide Ion in Aromatic Nucleophilic Substitution Reaction in Aqueous Alkaline Media

4.1 INTRODUCTION

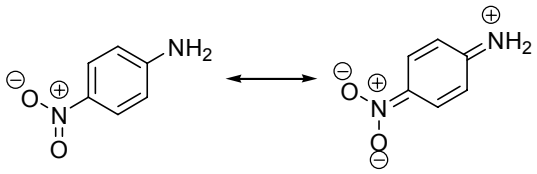
The decomposition of aryl diazonium salts derived from anilines in aqueous acid media gives the corresponding phenols. However, the yields of the phenols are often unreliable due to many undesired by-products. Consequently, the reactions require complicated purification processes. Meanwhile, aryl chlorides are used to obtain phenols in many cases because of the high reactivity and availability. For example, 4-nitrophenol (**2**) is obtained by the aromatic nucleophilic substitution reaction[1] of 1-chloro-4-nitrobenzene (**1a**) with hydroxide ion in 50 % aqueous sodium hydroxide at 150 ^{o}C in an autoclave (Scheme 1).[2]



1a **2**

SCHEME 1. The reaction of 1-chloro-4-nitrobenzene with hydroxide ion

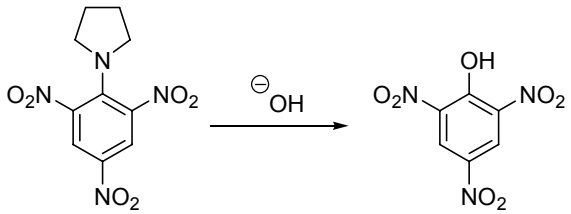
As a part of the continuing research program to investigate the *intra*molecular CT interaction of anilines as descibed in Chapter 3, the author was interested in the reaction in which aniline derivatives activated by one or more electron withdrawing groups such as nitro or trifluoroacetyl groups[3] reacted with hydroxide ion in alkaline aqueous solutions or organic solvents. Those reactions directly provide corresponding phenols,[4] naphthols[5] or quinolinols,[6] even though amino groups of aromatic amines generally are poor leaving groups in aromatic nucleophilic substitution reactions.[7] Hydroxide ion OH^- is a weaker base than amide ion, NH_2^-. Moreover, 4-nitroaniline (**1b**) has resonance forms as shown in Fig. 1 and the resonance form **1b'** can contribute to stabilization of 4-nitroaniline. It is also shown that the resonance stabilization strongly contributes to lowering the rate of attack of nucleophiles such as



1b **1b'**

FIGURE 1. Resonance structures of 4-nitroaniline

hydroxide ion at the C-1 position of 2,4,6-trinitroanisole.[8] In contrast, a hydroxide ion is a stronger base than a chloride ion. Moreover, little contribution of the resonance stabilization like in the case of **1b** would not be expected for the aryl chloride **1a**.[9] That is the reason why the amino group is much poorer leaving group in the aromatic nucleophilic substitution reaction than the chlorine atom. Actually, it has been reported that 2,4,6-trinitro-1-pyrrolidinobenzene, which is a very highly activated aniline because it has three nitro groups, reacts with hydroxide ions (Scheme 2).[10] Owing to the poor leaving ability of amino groups, there has been few studies to compare amino groups with chlorine atom as the leaving groups in the aromatic nuecleophilic substitution reactions.[10h]



SCHEME 2. Reaction of nitrated aniline with hydroxide ion

The author thought, however, that the amino groups of nitrated anilines might become good leaving groups in aqueous alkaline media, because the amino group of the resonance form **1b** (not **1b'**) would form hydrogen bonding with water molecules in the aqueous alkaline media to reduce the resonance stabilization of the nitrated aniline.

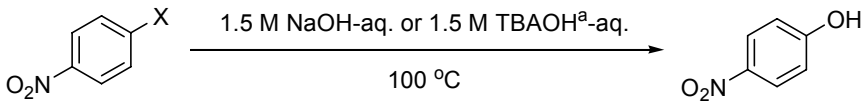
From the standpoint described above, the direct conversion of anilines into phenols under mild conditions would be prospective as an efficient synthetic method. The idea strongly prompted us to study in detail the aromatic nucleophilic substitution reactions of aromatic amines with nucleophiles in aqueous alkaline media. The important subject is how reactive the

anilines are toward hydroxide ions compared with the corresponding aryl chlorides. The author revealed that *p*- or *o*-mononitrated anilines are surprisingly more reactive than *p*- or *o*-mononitrated aryl chlorides in aqueous alkaline media. Those anilines quantitatively provided the corresponding phenols under mild conditions. In this chapter, the author describes the findings concerning the unexpectedly high reactivity of anilines toward hydroxide ion in aqueous alkaline media and the significance of hydrogen bonding with H_2O for the reaction.

4.2 RESULTS & DISCUSSION

The reactions of **1a** and **1b** with hydroxide ions were examined in aqueous alkaline media and the results were summarized in Table 1. When 1.5 M aqueous tetrabutylammonium hydroxide (TBAOH) was used as the alkaline medium, both the ary chloride **1a** and the aniline derivative **1b** reacted with hydroxide ions, and **1b** was less reactive than **1a** as expected (Entries 1 and 2). In thse reactions, cumbersome purification processes were required to remove a large amount of tar that was generated by the decomposition of quaternary ammonium ions with hydroxide ions, known as the Hofmann elimination. When NaOH was used in place of TBAOH, the aryl chloride **1a** could not react because of its low solubility (4 mmol/L) in 1.5 M aqueous NaOH (Entry 3). A longer reaction time (Entry 4) and addition of tetrabutylammonium chloride (Entry 5) slightly promoted the reaction. Interestingly, the aniline derivative **1b** easily reacted with hydroxide ion to provide **2** quantitatively (Entries 6 and 7), even though **1b** also shows low solubility in 1.5 M aqueous NaOH (24 mmol/L). Furthermore, the reaction of **1b** was very fast at 150 ^{o}C (Entry 8). In contrast, the aryl chloride **1a** was much less reactive than **1b** even at 150 ^{o}C (Entry 9). Those results seem to be attributable to difference in solubilities of the substrates, but the pseudo-first-order reaction rate constants were roughly estimated as 0.4×10^{-4} s^{-1} for **1a** and 4×10^{-4} s^{-1} for **1b** in 1.5 M aqueous NaOH at 100 ^{o}C . These facts indicate that the amino group would be intrinsically more reactive than the chlorine atom in aqueous NaOH media, though the order of reactivity

TABLE 1. The Aromatic Nucleophilic Substitution of 4-Nitroaniline and 1-Chloro-4-nitrobenzene by Use of Hydroxide Ion



1a X = Cl
1b X = NH_2

2

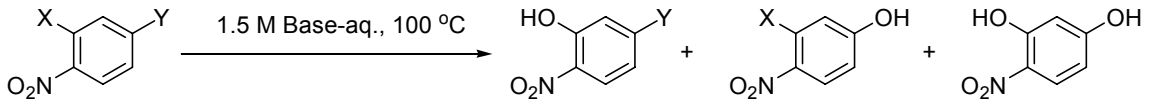
Entry	Substrate	X	Base	Solubility of **1** (mmol/L)	Temp. (°C)	Time (h)	Recovery of **1** (%)	Isolated Yield (%)
1	**1a**	Cl	TBAOH	soluble	100	4	0	96
2	**1b**	NH_2	TBAOH	soluble	100	4	60	32
3	**1a**	Cl	NaOH	4	100	4	100	0
4	**1a**	Cl	NaOH	4	100	16	97	2
5[b]	**1a**	Cl	NaOH	8	100	4	93	5
6	**1b**	NH_2	NaOH	24	100	4	60	40
7	**1b**	NH_2	NaOH	24	100	16	0	100
8	**1b**	NH_2	NaOH	—	150[c]	0.1	0	100
9	**1a**	Cl	NaOH	—	150[c]	0.1	78	18

[a] Tetrabutylammonium hydroxide. [b] Tetrabutylammonium chloride (10 mol%) was added. [c] Carried out in an autoclave.

was opposite when TBAOH was used.

To ascertain this finding, the reactions of 5-chloro-2-nitroaniline (**1c**) and 3-chloro-4-nitroaniline (**1d**) were examined and the results were summarized in Table 2. As deduced, the compound **1c** reacted with hydroxide ion at the amino position rather than the chloride position in aqueous NaOH, preferentially providing 5-chloro-2-nitrophenol (**3**) (Entry 1). In contrast, when TBAOH was used instead of NaOH as the base, **1c** preferentially reacted with hydroxide ion at the chloride position rather than the amino position, providing 3-amino-4-nitrophenol (**4**) as the main product (Entry 2). Also the compound **1d** was examined

TABLE 2. The Reaction of 5-Chloro-2-nitroaniline and 3-Chloro-4-nitroaniline



1c: X = NH_2, Y = Cl
1d: X = Cl, Y = NH_2

3: Y = Cl
6: Y = NH_2

4: X = NH_2
7: X = Cl

5

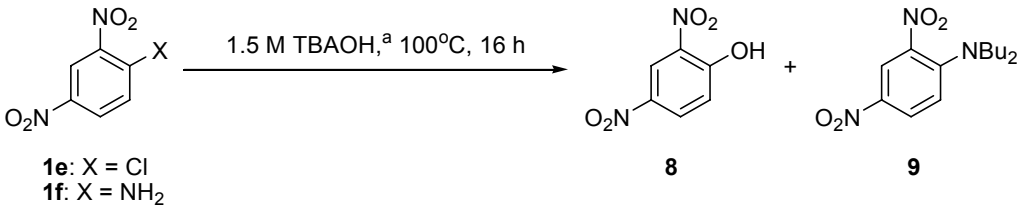
Entry	Substrate	X	Y	Base	Time (h)	Yield[a] (%)	Yield[a] (%)	Yield[a] of **5** (%)
1	**1c**	NH_2	Cl	NaOH	50	**3**; 68	**4**; 25	7
2	**1c**	NH_2	Cl	TBAOH	16	**3**; 32	**4**; 57	trace
3	**1d**	Cl	NH_2	NaOH	50	**6**; 22	**7**; 72	5

[a] Isolated yield.

in aqueous NaOH. The reaction of **1d** with hydroxide ion at the amino position preferred to that at the chloride position, providing 3-chloro-4-nitrophenol (**7**) rather than 5-amino-2-nitrophenol (**6**) (Entry 3).

In order to preclude the influence of hydrogen bonding of the amino groups with water, the reactivity of 1-chloro-2,4-dinitrobenzene (**1e**) and 2,4-dinitroaniline (**1f**) toward hydroxide ion was compared in 1.5 M TBAOH sulfolane solution and the results were summarized in Table 3. The aryl chloride **1e** was completely consumed to provide 2,4-dinitrophenol (**8**) and *N,N*-dibutyl-2,4-dinitroaniline (**9**), the latter resulted from the reaction of **1e** with tributylamine that was generated by the Hofmann elimination of the tetrabutylammonium ion (Entry 1). Interestingly, the aniline derivative **1f** hardly reacted with hydroxide ion in 1.5 M TBAOH solution in sulfolane, not providing **8** at all (Entry 2). It should be noted that even when 10 equivalents of water were added to the reaction, the phenol **8** was not obtained (Entry 3). In contrast, **1f** easily reacted with hydroxide ion in an aqueous TBAOH solution, providing **8** in 95% yield. These facts strongly demonstrate that aqueous media is necessary for the reaction of **1f** with hydroxide ion.

TABLE 3. The Reactions of 1-Chloro-2,4-dinitrobenzene and 2,4-Dinitroaniline in 1.5M Tetrabutylammonium Hydroxide Solution



1e: X = Cl
1f: X = NH_2

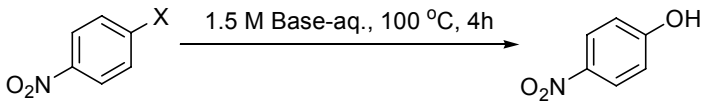
8 **9**

Entry	Substrate	X	Solvent	Recovery of Substrate (%)	Yield[b] of **8** (%)	Yield[b] of **9** (%)
1	**1e**	Cl	Sulfolane	0	39	25
2	**1f**	NH_2	Sulfolane	93	0	0
3[c]	**1f**	NH_2	Sulfolane	95	0	0
4[d]	**1f**	NH_2	H_2O	0	95	0

[a] Sulfolane (65 mL), 40 wt% aqueous tetrabutylammonium hydroxide (109 g, 168 mmol) and toluene (60 mL) were charged and distilled under atmospheric pressure to remove 66 mL of water and 60 mL of toluene before adding the substrate (32 mmol). [b] Isolated yield. [c] 10 eq. of water were added. [d] Carried out in 1.5 M aqueous TBAOH solution for 2 h.

Thus, it has been revealed that the amino groups of nitrated anilines are unexpectedly more reactive than the chlorine atoms of nitrated chlorobenzenes in aqueous NaOH. The aqueous media would play a dominant role in the aromatic nucleophilic substitution reactions of the anilines with hydroxide ion. It is speculated that the interaction of the amino groups of anilines with the aqueous media enhances their reactivity toward hydroxide ions. The reactivity of *N*-methyl-4-nitroaniline (**1g**) and *N,N*-dimethyl-4-nitroaniline (**1h**) toward hydroxide ions was compared with that of **1b** and the results were summarized in Table 4. The reactivity at 100 °C decreased with increasing number of methyl groups: $NH_2 > NHCH_3 > N(CH_3)_2$ (Entries 1–3). The *N,N*-dimethylaniline derivative **1h** easily reacted with hydroxide ion to provide **2** at higher temperature (150 °C, Entry 4). These results suggest that the hydrogen bonding of the

TABLE 4 Comparison of the Reactivity between Primary, Secondary and Tertiary Amino Groups



1b: X = NH_2
1g: X = $NHCH_3$
1h: X = $N(CH_3)_2$

2

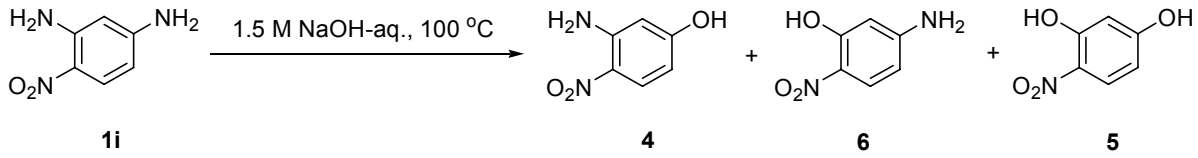
Entry	Substrate	X	Recovery of substrate (%)	Yield[a] of **2** (%)
1	**1b**	NH_2	60	40
2	**1g**	$NHCH_3$	82	13
3	**1h**	$N(CH_3)_2$	100	0
4[b]	**1h**	$N(CH_3)_2$	0	79

[a] Isolated yield. [b] Reaction temperature: 150 °C (in an autoclave), reaction time: 1 h.

amino groups with H_2O was sterically-inhibited by the methyl group.

It should be noted that the hydrogen atom of the aromatic amino group in 2-nitroaniline is known to form intramolecular hydrogen bonding with the *ortho*-nitro group.[11] In this respect, the selectivity of the reaction of 4-nitro-1,3-phenylene diamine (**1i**) with hydroxide ion was examined in aqueous NaOH and the results were summarized in Table 5. The *ortho* substituted product **6** was preferentially obtained in a yield almost three times as high as that of the *para* substituted product **4** (Entry 1). The temperature effect on the selectivity of **4** and **6** was examined at 100 and 150 °C (Entry 1 and 2). The reaction was very fast at 150 °C and the product **6** was obtained by almost five times in amount as much as **4**. These facts would indicate that the intramolecular hydrogen bonding between the *ortho*-amino group and the nitro group reduced the resonance stability to promote the substitution of the *ortho* amino group of **1i** with hydroxide ion.

TABLE 5 The Selectivity of the Reaction of 4-Nitro-1,3-phenylenediamine



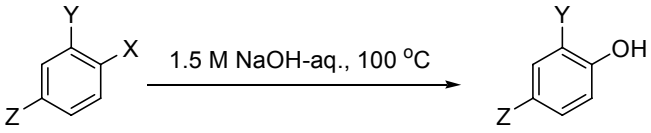
1i **4** **6** **5**

Entry	Temp. (°C)	Time (h)	Recovery of **1i** (%)	Yield[a] of **4** (%)	Yield[a] of **6** (%)	Yield of **5** (%)
1	100	40	23	18	55	trace
2	150	0.1	33	11	54	trace

[a] Determined by ^{1}H-NMR.

In addition, substituent effects on the reactivities of 4- or 2-nitrated aniline derivatives were examined in 1.5 M aqueous NaOH at 100 °C in comparison with those of the aryl chlorides. The results were summarized in Table 6, where X is chlorine atom or amino group as leaving groups, and Y, Z are nitro groups or other substituents. For all the examined substrates, the anilines were more reactive than the corresponding aryl chlorides in aqueous NaOH, except **1f** (Entries 1 – 10). Comparing with the reactivity of the mononitrated derivatives **1a** and **1b** toward hydroxide ions (see Table 1), the reactions of the dinitrated derivatives **1e** and **1f** (Y and Z = NO_2) with hydroxide ions were very fast to provide **8** quantitatively because of the very strong activation, (Entries 1 and 2). In the case of the *p*-hydroxy derivatives **10a** and **10b** (Y = OH, Z = NO_2), the aryl chloride **10a** did not react in spite of the good solubility in aqueous NaOH only to be recovered (Entry 3). In contrast, the aniline derivative **10b** readily reacted with hydroxide ion to provide **10c** in 95% yield (Entry 4). When Y was CH_3 (2-methyl-4-nitroaniline **11b**), the reactivity was somewhat deteriorated, presumably due to the steric hindrance by the CH_3 group (Entry 6). Interestingly, when Y was OCH_3 or NH_2 (2-methoxy-4-nitroaniline **12b**, 4-nitro-1,2-phenylene diamine **13b**), the reactivity of amino groups at X position in **12b** and **13b** were enhanced though electron-donating groups were

TABLE 6 The Reactions of 4- or 2-Nitrated Aniline Derivatives and Corresponding Chloride Derivatives in 1.5 M NaOH Aqueous Media



1e: X = Cl, Y, Z = NO_2
1f: X = NH_2, Y, Z = NO_2
10a: X = Cl, Y = OH, Z = NO_2
10b: X = NH_2, Y = OH, Z = NO_2
11a: X = Cl, Y = CH_3, Z = NO_2
11b: X = NH_2, Y = CH_3, Z = NO_2
12a: X = Cl, Y = OCH_3, Z = NO_2
12b: X = NH_2, Y = OCH_3, Z = NO_2
13a: X = Cl, Y = NH_2, Z = NO_2
13b: X = NH_2, Y = NH_2, Z = NO_2
14: X = NH_2, Y = NO_2, Z = H
16: X = NH_2, Y = NO_2, Z = OCH_3
18: X = NH_2, Y = NO_2, Z = NH_2

8: Y = NO_2, Z = NO_2
10c: Y = OH, Z = NO_2
11c: Y = CH_3, Z = NO_2
12c: Y = OCH_3, Z = NO_2
13c: Y = NH_2, Z = NO_2
15: Y = NO_2, Z = H
17: Y = NO_2, Z = OCH_3
19: Y = NO_2, Z = NH_2

Entry	Substrate	X	Y	Z	Solubility of substrate (mmol/L)	Time (h)	Recovery of substrate (%)	Isolated yield (%)
1	**1e**	Cl	NO_2	NO_2		1.5	0	**8**; 100
2	**1f**	NH_2	NO_2	NO_2	2.2	1.5	0	**8**; 98
3	**10a**	Cl	OH	NO_2	soluble	4	93	**10c**; 0
4	**10b**	NH_2	OH	NO_2	soluble	4	0	**10c**; 95
5	**11a**	Cl	CH_3	NO_2		4	96	**11c**; 0
6	**11b**	NH_2	CH_3	NO_2	11	4	70	**11c**; 29
7	**12a**	Cl	OCH_3	NO_2		4	92	**12c**; 5
8	**12b**	NH_2	OCH_3	NO_2	7.1	4	33	**12c**; 64
9	**13a**	Cl	NH_2	NO_2		4	95	**13c**; 0
10	**13b**	NH_2	NH_2	NO_2	7.2	4	25	**13c**; 65
11	**14**	NH_2	NO_2	H	52	4	86	**15**; 14
12	**16**	NH_2	NO_2	OCH_3	10	4	31	**17**; 63
13	**18**	NH_2	NO_2	NH_2	60	4	5	**19**; 79

expected to deteriorate the aromatic nucleophlic substitution reactions. This tendency was remarkable when 4-methoxy-2-nitroaniline (**16**) and 2-nitro-1,4-phenylene diamine (**18**) were compared with 2-nitroaniline (**14**), probably due to stabilization of the Meisenheimer complexes (Fig. 2). It should be noted that the transformation from **4** and **6** into **5** were very slow as shown in Table 5, probably because the amino groups and the hydroxy groups deteriorate the electron-withdrawing ability of the nitro groups of **4** and **6**.

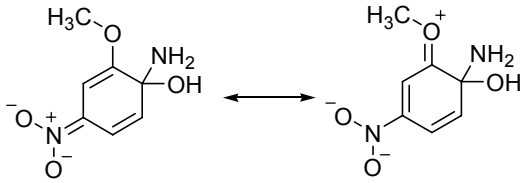
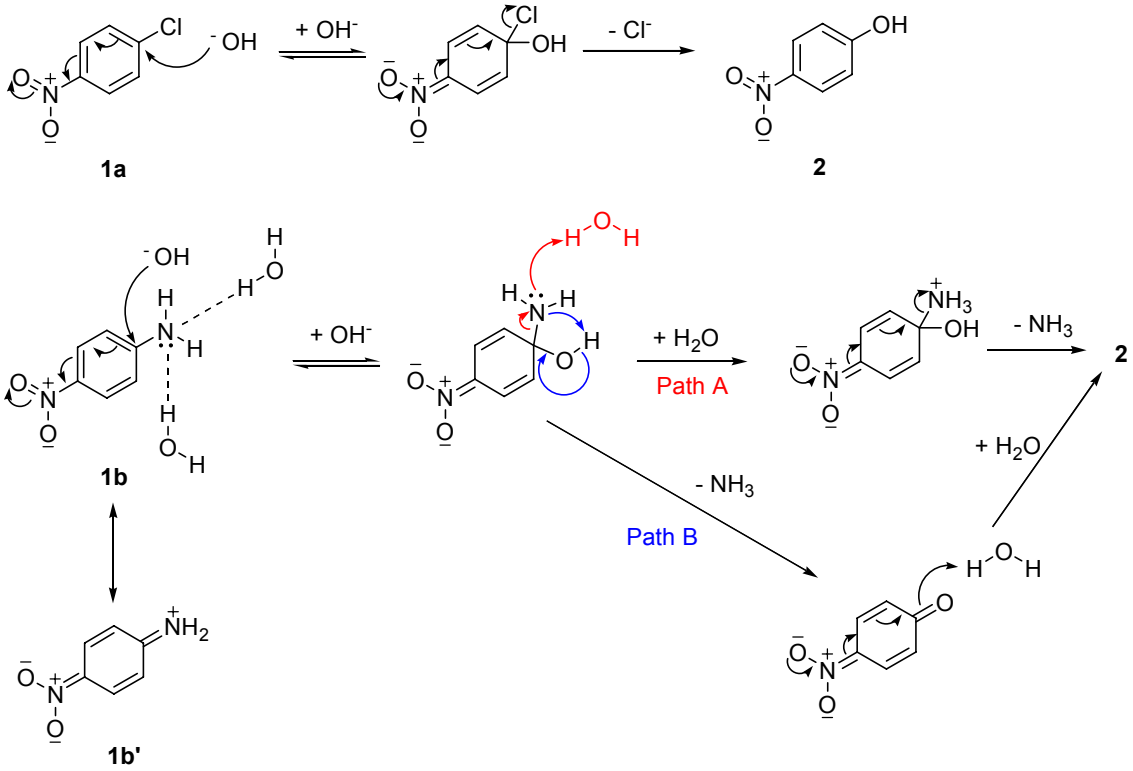


FIGURE 2. Resonance forms of Meisenheimer complex of **12b**

Finally, the proposed reaction mechanism was shown in Scheme 3. As well known, the aryl chloride **1a** reacts with a hydroxide ion and forms a Meisenheimer complex, and eliminates the chloride ion directly to provide **2**. Although the aniline **1b** is normally less reactive than **1a** due to the resonance contribution of **1b'**. The contribution of **1b'** would be reduced by the hydrogen bonding with water in aqueous media and **1b** would become more reactive toward a hydroxide ion collaborating with water to form the Meisenheimer complex. When **1b** is solvated by sulfolane or tetrabutylammonium ions, the hydrogen bonding would be ineffective. Accordingly, **1b** was less reactive than **1a** in aqueous tetrabutylammonium hydroxide or sulfolane. In consequence, the Meisenheimer complex is presumed to provide **2** through Path A or Path B. Here, Path A: the amino group in the Meisenheimer complex might subtract a proton of surrounding water and eliminate an ammonia molecule to provide **2**; Path B: the hydrogen atom of hydroxyl group in the Meisenheimer complex might undergo intramolecular proton migration to the amino group to eliminate an ammonia molecule, and then a quinoid intermediate formed might be hydrolyzed to give **2**. Additionally, the formation of the Meisenheimer complex would be the rate-determining process as well as normal aromatic nucleophilic substitution reactions rather than the protonation of amino group and

elimination of ammonia, because the isotope effect was not observed in the reaction in D_2O used instead of H_2O.



SCHEME 3 The proposed reaction mechanism

4.3 CONCLUSION

It was revealed that the amino groups of nitrated anilines are unexpectedly more reactive than the chlorine atom of nitrated aryl chlorides in aqueous NaOH, even though the amino groups are normally much less reactive than the chlorine atoms in organic solvents in aromatic nucleophilic substitution reactions. Aqueous media played a dominant role in the reaction of the anilines with hydroxide ions, since the hydrogen bonding of the amino groups with water reduces an adverse effect of the resonance stabilization so that the amino groups become more reactive toward hydroxide ions to form the Meisenheimer complexes, and eventually ammonia molecules eliminate. The solvation of organic solvents or

tetraalkylammonium ions surrounding the anilines would hinder the hydrogen bonding with water and the aromatic amino group turns back to just a poor leaving group in the reactions. The present reactions are not only synthetically prospective but also are environmentally friendly, because the reactions proceed in water without any organic solvents to provide the phenols and ammonia gas.

4.4 EXPERIMENTAL

General Procedure: A mixture of 4-nitroaniline (**1b**) (4.4 g, 32 mmol) and 1.5 M NaOH aqueous solution (113 g, 165 mmol) was stirred for 4 h at 100 ^{o}C. The smell of ammonia showed progress of the reaction. The reaction mixture was cooled down to room temperature and 200 mL of water was added. Then, the mixture was extracted twice with EtOAc and the combined organic layer was washed with dilute aqueous sodium hydroxide and water, and dried over Na_2SO_4, and the solvent was removed under reduced pressure to recover 2.7 g of yellow-colored solid of 4-nitroaniline after drying in *vacuo* (recovery; 60 %). On the other hand, the combined alkali solution was neutralized with 17 g of acetic acid and extracted twice with EtOAc. The combined organic layer was washed with brine and dried over Na_2SO_4, and the solvent was removed under reduced pressure to give 1.7 g of yellowish solid of 4-nitrophenol (**2**) after drying in *vacuo*. yield; 40 %. The solid was pure enough for confirmation of the purity of **2** with NMR, while recrystallization from toluene gave slightly yellowish needles. mp. 113-114 ^{o}C (lit. 114 ^{o}C[12]); ^{1}H-NMR (400 MHz, DMSO-d6): δ_{ppm} 6.96 (d, J = 8 Hz, 2H, Ph), 8.14 (d, J = 8 Hz, 2H, Ph), 11.10 (br s, 1H, OH).

The reaction at 150 ^{o}C was performed as described above, except as carried out in a 300 mL stainless-steel autoclave eqiupped with a mechanical agitator and a thermometer.

5-Chloro-2-nitrophenol (3): ^{1}H-NMR (400 MHz, DMSO-d6): δ_{ppm} 7.05 (dd, J = 8 Hz, J' = 2 Hz, 1H, Ph), 7.19 (d, J = 2 Hz, 1H, Ph), 7.94 (d, J = 8 Hz, 1H, Ph), 11.50 (br s, 1H, OH); ^{13}C-NMR (100 MHz, DMSO-d6): δ_{ppm}, 118.6, 119.4, 127.0, 135.9, 139.1, 153.0; ESI-MS: *m/z*

172 (M - H).

3-Amino-4-nitrophenol (4): mp. 183–184 °C (lit. 185–186 °C[13]); ^{1}H-NMR (400 MHz, DMSO-d6): δ_{ppm} 6.13 (dd, *J* = 8 Hz, *J'* = 2 Hz, 1H, Ph), 6.29 (d, *J* = 2 Hz, 1H, Ph), 7.40 (br s, 2H, NH_2), 7.88 (d, *J* = 8 Hz, 1H, Ph), 11.60 (br s, 1H, OH); ^{13}C-NMR (100 MHz, DMSO-d6): δ_{ppm}, 100.8, 107.1, 124.6, 128.0, 148.8, 164.0; ESI-MS: *m/z* 153 (M - H).

4-Nitroresorcinol (5): mp. 121–122 °C (lit. 121–122 °C[14]); ^{1}H-NMR (400 MHz, DMSO-d6): δ_{ppm} 3.51 (br s, 1H, OH), 6.43 (dd, *J* = 8 Hz, *J'* = 2 Hz, 1H, Ph), 6.46 (d, *J* = 2 Hz, 1H, Ph), 7.92 (d, *J* = 8 Hz, 1H, Ph), 10.88 (br s, 1H, OH); ^{13}C-NMR (100 MHz, DMSO-d6): δ_{ppm}, 103.6, 108.8, 127.7, 128.0, 156.0, 165.0; ESI-MS: *m/z* 154 (M - H).

5-Amino-2-nitrophenol (6): ^{1}H-NMR (400 MHz, DMSO-d6): δ_{ppm} 6.11 (dd, *J* = 8 Hz, *J'* = 2 Hz, 1H, Ph), 6.27 (d, *J* = 2 Hz, 1H, Ph), 7.38 (br s, 2H, NH_2), 7.86 (d, *J* = 8 Hz, 1H, Ph), 10.62 (br s, 1H, OH); ^{13}C-NMR (100 MHz, DMSO-d6): δ_{ppm}, 100.8, 107.1, 124.5, 128.0, 148.8, 164.0; ESI-MS: *m/z* 153 (M - H).

3-Chloro-4-nitrophenol (7): ^{1}H-NMR (400 MHz, DMSO-d6): δ_{ppm} 7.05 (dd, *J* = 8 Hz, *J'* = 2 Hz, 1H, Ph), 7.18 (d, *J* = 2 Hz, 1H, Ph), 7.94 (d, *J* = 8 Hz, 1H, Ph), 11.50 (br s, 1H, OH); ^{13}C-NMR (100 MHz, DMSO-d6): δ_{ppm}, 118.5, 119.3, 127.0, 135.9, 139.0, 152.9; ESI-MS: *m/z* 173 (M - H).

2,4-Dinitrophenol (8): mp. 112–113 °C (lit. 108–112 °C[15]); ^{1}H-NMR (400 MHz, DMSO-d6): δ_{ppm} 7.35 (d, *J* = 8 Hz, 1H, Ph), 8.48 (dd, *J* = 8 Hz, *J'* = 2 Hz, 1H, Ph), 9.08 (d, *J* = 2 Hz, 1H, Ph), 10.97 (br s, 1H, OH); ^{13}C-NMR (100 MHz, DMSO-d6): δ_{ppm}, 121.3, 121.9, 131.7, 132.6, 140.3, 159.1; ESI-MS: *m/z* 183 (M - H).

***N,N*-Dibutyl-2,4-dinitroaniline (9):** ^{1}H-NMR (400 MHz, $CDCl_3$): δ_{ppm} 0.90 (t, 6H, CH_3), 1.27 (sex, 4H, CH_2), 1.59 (f, 4H, CH_2), 3.28 (t, 4H, CH_2), 7.07 (d, *J* = 8 Hz, 1H, Ph), 8.19 (dd, *J* = 8 Hz, *J'* = 2 Hz, 1H, Ph), 8.64 (d, *J* = 2 Hz, 1H, Ph); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_{ppm}, 13.7, 20.0, 29.4, 52.0, 118.8, 124.0, 127.6, 136.7, 137.6, 148.7; EI-MS: *m/z* 295.

4-Nitrocatechol (10c): ^{1}H-NMR (400 MHz, DMSO-d6): δ_{ppm} 6.93 (d, *J* = 8 Hz, 1H, Ph), 7.64

(s, 1H, Ph), 7.67 (d, *J* = 8 Hz, 1H, Ph), 10.30 (br. s, 2H, OH); ^{13}C-NMR (100 MHz, DMSO-d6): δ_{ppm}, 110.5, 115.0, 116.5, 139.6, 145.5, 152.9; EI-MS: *m/z* 155.

4-Nitro-*o*-cresol (11c): mp. 96–97 ^{o}C (lit. 93–98 ^{o}C[15]).

2-Methoxy-4-nitrophenol (12c): mp. 103–104 ^{o}C (lit. 103–104 ^{o}C[16]).

2-Amino-4-nitrophenol (13c): mp. 141–142 ^{o}C (lit. 140–143 ^{o}C[15]).

2-Nitrophenol (15): ^{1}H-NMR (400 MHz, $CDCl_3$): δ_{ppm} 7.00 (t, 1H, Ph), 7.16 (d, *J* = 8 Hz, 1H, Ph), 7.58 (t, 1H, Ph), 8.10 (d, *J* = 8 Hz, 1H, Ph), 10.57 (br. s, 2H, OH); ^{13}C-NMR (100 MHz, $CDCl_3$): δ_{ppm}, 120.0, 120.2, 125.1, 133.8, 137.6, 155.2; EI-MS: *m/z* 139.

4-Methoxy-2-nitrophenol (17): mp. 79–80 ^{o}C (lit. 78–80 ^{o}C[15]).

4-Amino-2-nitrophenol (19): mp. 125–126 ^{o}C (lit. 125–127 ^{o}C[15]).

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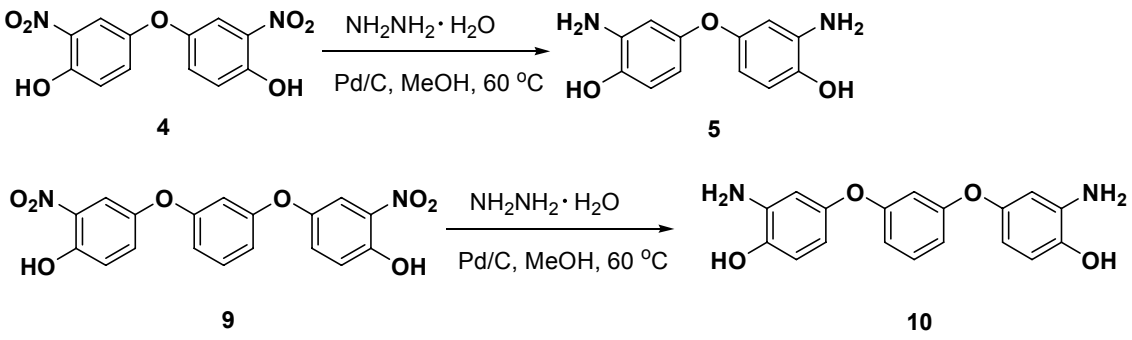
CHAPTER 5

Practical and Efficient Syntheses of 4,4'-Dihydroxy-3,3'-dinitrodiphenyl Ether and 1,3-Bis(4-hydroxy-3-nitrophenoxy)benzene in Aqueous Alkaline Media

5.1 INTRODUCTION

4,4'-Dihydroxy-3,3'-dinitrodiphenyl ether (**4**) and 1,3-bis(4-hydroxy-3-nitrophenoxy)-benzene (**9**) are highly valuable precursors of 3,3'-diamino-4,4'-dihydroxydiphenyl ether[1] (**5**) and 1,3-bis(3-amino-4-hydroxyphenoxy)benzene[2] (**10**), respectively. They are not only interesting because of their amphoteric properties in acid-base behavior[3] and as precursors of symmetrical bis-phenolic Mannich derivatives of biological interest,[4] but also they are important starting materials for thermally stable plastics such as polyamides, polyarylates, polyimides and polybenzoxazoles, which are especially useful as positive-working photosensitive polymer precursor compositions to form electric interlayer insulators and protective films for semiconductors.[5-11]



SCHEME 1 Reduction of **4** and **9** into **5** and **10**.

The critical problem is the synthesis of **4** and **9** as precursors of **5** and **10**. So far, their synthesis has involved nitration of 4,4'-dihydroxydiphenyl ether[4,7] and 1,3-bis(4-hydroxy-phenoxy)benzene.[2] Preparation of these compounds[12-33] suffers from very serious problems

such as low yields due to low conversion, formation of many undesired by-products, the use of high reaction temperatures and of environmentally harmful reagents.

In contrast, 4,4'-diaminodiphenyl ether (**1**) and 1,3-bis(4-aminophenoxy)benzene (**6**) are commercially available and can be selectively nitrated, providing 4,4'-diamino-3,3'-dinitrodiphenyl ether (**3**) and 1,3-bis(4-amino-3-nitrophenoxy)benzene (**8**) quantitatively.[34-35] Although the compound **4** could be obtained by decomposition of the diazonium salt derived from **3** using the Sandmeyer reaction, the yield was very low due to many undesired by-products which required complicated purification.

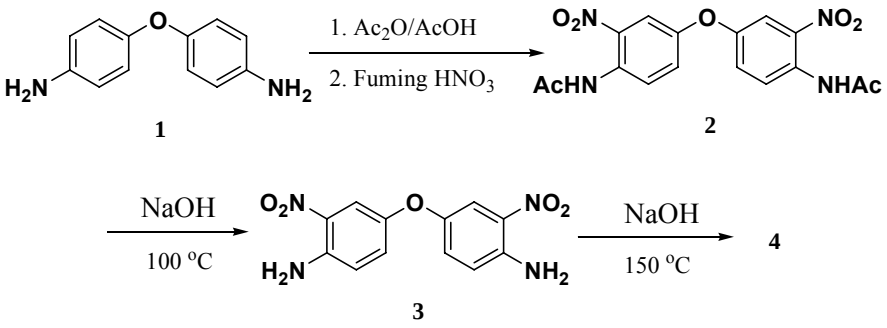
So far, there has been no study on reactions to convert dianilines directly into corresponding diphenols. Although the amino group is generally considered a much poorer leaving group than halide ions in aromatic nucleophilic substitution reactions, there are examples of replacement of aromatic amino groups activated by one or more nitro groups in aqueous alkaline solutions or aqueous organic solvents, providing corresponding phenols,[36-42] naphthols[43] and quinolinols.[44] However, most applications of these reactions are limited to very activated substrates such as derivatives of 2,4,6-trinitroaniline and 2,4-dinitroaniline.

Thus, the investigations on the reactions of **3** and **8** with hydroxide ion have been neglected for a long time. It was thought, however, that amino groups of **3** and **8**, which have only one nitro group *ortho* to the amino group, might become good leaving groups, if the amino groups are protonated and turned into $ArNH_3^+$ in water. From these considerations, the direct conversion of the amino groups might prove to be a practical synthetic methods of **4** and **9**. This consideration prompted us to investigate the direct conversion of **3**, **8** and of their acetylated derivatives (**2** and **7**) into **4** and **9** in aqueous alkaline media.

5.2 RESULTS & DISCUSSION

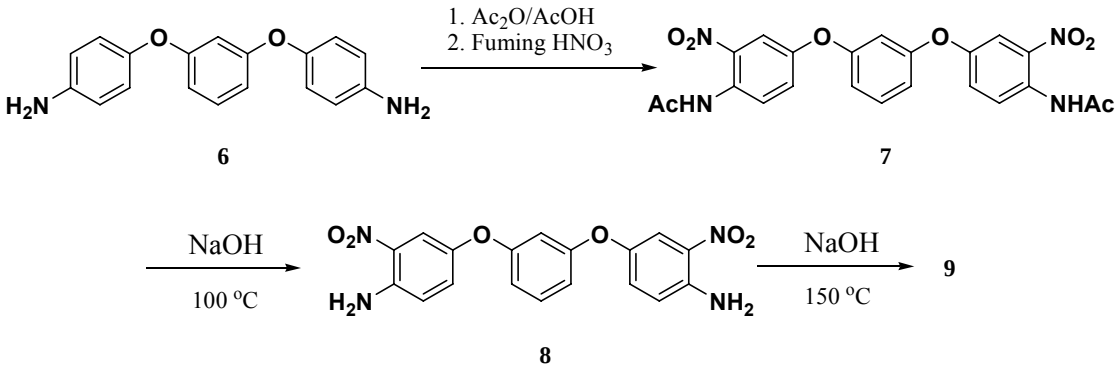
Commercially available **1** and **6** were used without further purification. 4,4'-*bis*(*N*-Acetylamino)-3,3'-dinitrodiphenyl ether (**2**) was obtained form **1** in an excellent

yield. Deacetylation of **2** provided **3** quantitatively. 1,3-bis(4-*N*-Acetylamino-3-nitrophenoxy)benzene (**7**) was obtained in the same manner.



1 **2** **3** **4**

Scheme 2



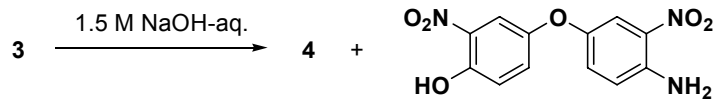
6 **7** **8** **9**

SCHEME 3. Syntheses of **4** and **9**.

Substitution of **3** in aqueous alkaline media was examined and the results are summarized in Table 1. The reaction was very slow at 100 °C (Entries 1 and 2), but was very rapid at 150 °C (Entry 3) and provided **4** in an excellent yield after neutralization. Higher concentration of sodium hydroxide (Entry 4) or addition of tetrabutylammonium chloride (Entry 5) accelerated the reaction only slightly. Use of tetrabutylammonium hydroxide in place of sodium hydroxide at 100 °C (Entry 6) showed somewhat more acceleration albeit the yield of **4** was only 23% due to the high solubility of **9** in 1.5 M aqueous tetrabutylammonium hydroxide solution. However, cumbersome purification processes were required to remove a large amount of tar generated through the decomposition of quaternary ammonium ions with

hydroxide ions (Hofmann elimination). Under these conditions, the main product was 4-amino-4'-hydroxy-3,3'-dinitrodiphenyl ether (**11**) formed in 50% yield.

TABLE 1. Hydrolysis of **3** into **4** in 1.5 M Aqueous Sodium Hydroxide



11

Entry	Temp. (°C)	Time (h)	Recovery of **3** (%)	Yield of **4** (%)	Yield of **11** (%)
1	100	1	100	0	0
2	100	10	93	2	0
3	150[a]	1	0	97	0
4[b]	100	1	91	2	5
5[c]	100	1	90	2	6
6[d]	100	1	21	23	50

[a] Carried out in an autoclave. [b] 6.0 M Sodium hydroxide was used. [c] Tetrabutylammonium chloride (10 mol %) was added. [d] 1.5 M Aqueous tetrabutylammonium hydroxide was used instead of sodium hydroxide.

The reaction of **2** and **7** in aqueous sodium hydroxide was examined at 150 °C in an autoclave and the results are shown in Table 2. Even when the acetylated derivative **2** was used, the deacetylation and the hydroxylation proceeded simultaneously to give **4** in excellent yields. Similarly, the hydroxylation of diacetylated derivative **7** provided **9** quantitatively, though higher concentration of sodium hydroxide and longer reaction time were required.

TABLE 2. Hydrolysis in 1.5 M Aqueous NaOH at 150 °C[a]

Entry	Substrate	Product	Time (h)	Yield (%)
1	**2**	**4**	1	98
2[b]	**7**	**9**	5	100

[a] Carried out in an autoclave. [b] 3.0 M aqueous sodium hydroxide was used.

The Pd-charcoal-catalyzed hydrogenation of **4** and **9** with aqueous hydrazine hydrate in methanol provided **5** and **10** in excellent yields, respectively.

5.3 CONCLUSION

We have developed an efficient synthesis of 3,3'-diamino-4,4'-dihydroxydiphenyl ether (**5**) and of 1,3-bis(3-amino-4-hydroxyphenoxy)benzene (**10**) by the facile and direct conversion of 4,4'-diamino-3,3'-dinitrodiphenyl ether (**3**) and 1,3-bis(4-amino-3-nitro-phenoxy)benzene (**8**) into 4,4'-dihydroxy-2,2'-dinitrodiphenyl ether (**4**) and 1,3-bis(4-hydroxy-3-nitrophenoxy)benzene (**9**), respectively. The present method is environmentally friendly, because the reactions proceed in water without organic solvents to provide target compounds, releasing ammonia as the sole by-product.

5.4 EXPERIMENATAL

General: Melting points were determined on a Yamato MP-21 melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively (Bruker Co. Ltd., Avance 400) and mass spectra were recorded on an ESI-TOF/MS Per Septive Biosystems Mariner. A stainless-steel autoclave made by Nac-autoclave Co. Ltd. (SIF-2 type, SUS316) was used for the reactions.

4,4'-Dihydroxy-3,3'-dinitrodiphenyl Ether (4): In a 300 mL stainless-steel autoclave were placed 4,4'-diamino-3,3'-dinitrodiphenyl ether (9.3 g, 32.0 mmol) and 1.5 M sodium hydroxide aqueous solution (224 g, 336 mmol) and the mixture was heated and kept at 150 ^{o}C for 1 h. TLC (silica gel 60, EtOAc/hexane = 1/1) showed that the spot of the starting compound (Rf: 0.50) had disappeared and only the spot of 4,4'-dihydroxy-3,3'-dinitrodiphenyl ether (Rf: 0.85) appeared. The smell of ammonia indicated the satisfactry progress of the reaction. Upon cooling the solution and addition of 28.5 g (276 mmol) of 95% sulfuric acid, the red solution turned to an orange-colored slurry. Then the slurry was cooled to 5 ℃ and the precipitated orange-colored solid was collected. The solid was extracted with EtOAc (100 mL) and washed with water. The combined organic layer was dried over Na_2SO_4, and the solvent was removed

under reduced pressure to give 9.0g (97%) of 4,4'-dihydroxy-3,3'-dinitrodiphenyl ether (**4**) as an orange-colored solid, mp. 156－157 ℃ (*lit*.[20] 156－157 ℃). The solid was pure enough to confirm the purity of **4** with NMR, though recrystallization from methanol gave orange colored needles (91%, mp. 157－158 ℃). ^{1}H-NMR (400 MHz, DMSO): δ_{ppm} 7.17 (d, J = 8 Hz, 2H, Ph), 7.35 (dd, J = 8 Hz, J' = 4 Hz, 2H, Ph), 7.55 (d, J = 4 Hz, 2H, Ph). ^{13}C-NMR (100 MHz, DMSO): δ_{ppm}, 114.42, 120.55, 126.27, 136.50, 148.10, 148.46. ESI-MS: *m/z* 291 (M - H).

1,3-Bis(4-hydroxy-3-nitrophenoxy)benzene (9):

1,3-bis(4-N-Acetylamino-3-nitrophenoxy)benzene (14.9 g, 32.0 mmol) was transformed into **9** as described above [3.0 M NaOH aqueous solution was used instead of 1.5 M NaOH aqueous solution. The reaction time was 5 h at 150 ^{o}C] to yield 12.3 g (100%) of 1,3-bis(4-hydroxy-3-nitrophenoxy)benzene as an orange-colored solid, mp. 128-130 ^{o}C (lit.[2] 128.5-130 ^{o}C). The solid was pure enough to confirm the purity of **9** with NMR. ^{1}H-NMR (400 MHz, DMSO): δ_{ppm} 6.67 (s, 1H, Ph), 6.73 (d, J = 8 Hz, 2H, Ph), 7.17 (d, J = 8 Hz, 2H, Ph), 7.36 (d, J = 8 Hz, 2H, Ph), 7.39 (t, J = 8 Hz, 1H, Ph), 7.58 (s, 2H, Ph), 10.88 (br s, 2H, OH). ^{13}C-NMR (100 MHz, DMSO): δ_{ppm} 107.51, 112.37, 115.54, 120.60, 127.23, 131.28, 136.59, 147.00, 148.89, 158.48.ESI-MS: *m/z* 383 (M - H).

The melting point, ^{1}H NMR and ^{13}C NMR are agreement with data given in the literature.[2]

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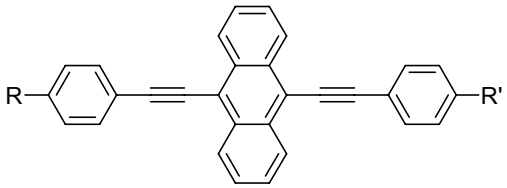
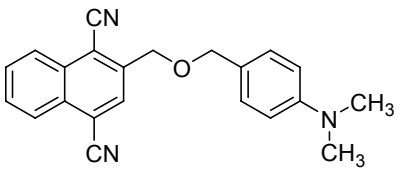
CONCLUSION

This thesis dealt with the studies on syntheses, reactions and optical properties via charge transfer (CT) interaction of novel anilines. The author focused on the performances of the anilines exhibited as electron donors collaborating with electron acceptors. The following are the results obtained in the respective studies.

In Chapter 1, three novel aniline derivatives were efficiently synthesized. Their synthetic methods were optimized; 9,10-bis(4-aminophenylethynyl)anthracene **1** and 9-(4-aminophenylethynyl)-10-(4-nitrophenylethynyl)anthracene **2** were synthesized in good yields by using Sonogashira cross coupling reactions. In particular, the compound **2** was produced through a sequential Sonogashira cross coupling reactions of 9-bromo-10-iodoanthracene with 4-nitro- and 4-aminophenylacetylene. The yield of the second coupling was significantly sensitive to the solvents used. The coupling did not proceed in typical amine solvents. In THF, the coupling gave **2** in an extremely poor yield. On the other hand, in DMF, the compound **2** was obtained in an excellent yield. 1,4-Dicyano-2-(4'-*N,N*-dimethylaminobenzyloxy)methylnaphthalene **3** was successfully obtained in 4 steps, In the final step, Pd-catalyzed cyanation provided **3** in a good yield, though it could not be obtained in the classical method using CuCN in *N*-methylpyrrolidone.



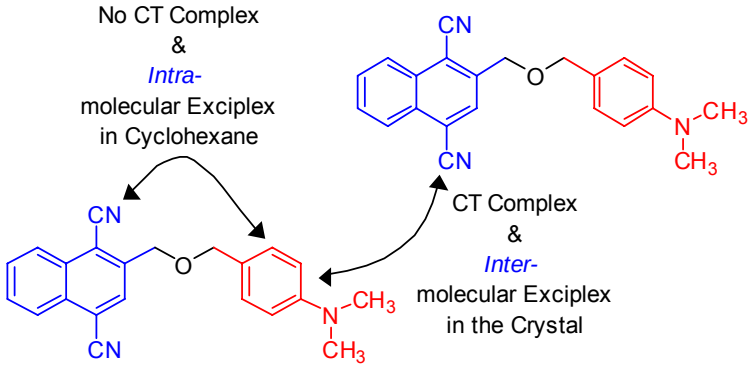
1 R, R' = NH_2
2 R = NH_2, R' = NO_2



3

In Chapter 2, the author has found that the dyad **1** does not form a strong CT complex in the ground state, but that it shows a typical *intra*molecular exciplex fluorescence between

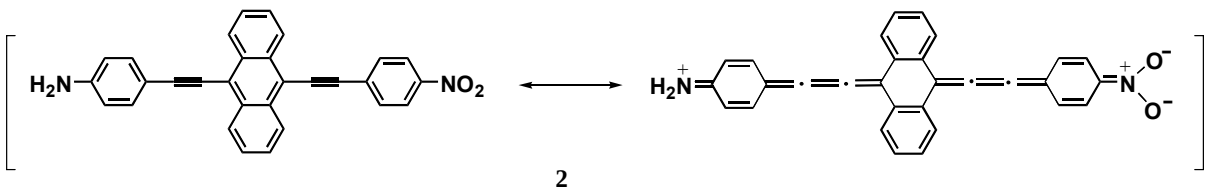
1,4-dicyano-2-methylnaphthalene (DCMN) and *N,N*-dimethyl-*p*-toluidine (DMT) moieties in cyclohexane in accord with the Hirayama rule. In contrast, the crystals of the dyad **1** form an *inter*molecular mixed-stack, one-to-one CT complex in the ground state. It's color is yellow to orange. The observations made in this study clearly demonstrate that the *inter*molecular exciplex generated by excitation of crystals of **1** arises directly from the ground state CT complex, in which the DCMN and DMT moieties are immobilized in a face-to-face manner by *inter*molecular CT interactions.



The author presented that *intra*molecular CT complexes of **1**–**4** hardly exist in the ground states of these substance in solution, and dyads **1**–**3** form *intra*molecular exciplexes in cyclohexane as expected, though dyad **4** does not. To the contrary, the donor and acceptor moieties of dyad **1** and **2** are *inter*molecularly preorientated face to face to form *inter*molecular CT complexes in the crystals. As desired, *inter*molecular exciplexes are successfully formed through the ground state CT complexes in the crystals of **1** and **2** against the Hirayama rule, while dyads **3** and **4** do not form *inter*molecular exiplexes but excimers in the crystals. Thus, novel exciplex-emissive organic crystals of **1** and **2** have been created to fluoresce with the quantum yields of 0.09 and 0.39, respectively. It is demonstrated that the appropriate CT interaction between the donor and acceptor moieties in the crystals of **1** and **2** operates to prepare the exciplex-emissive organic crystals. The more appropriate CT interaction occurs in the crystals of **2** preventing ET process, while the exciplex emission of the crystals of **1** is weak

as a consequence of ET due to a little too strong CT interaction between the DMT and DCMN moieties.

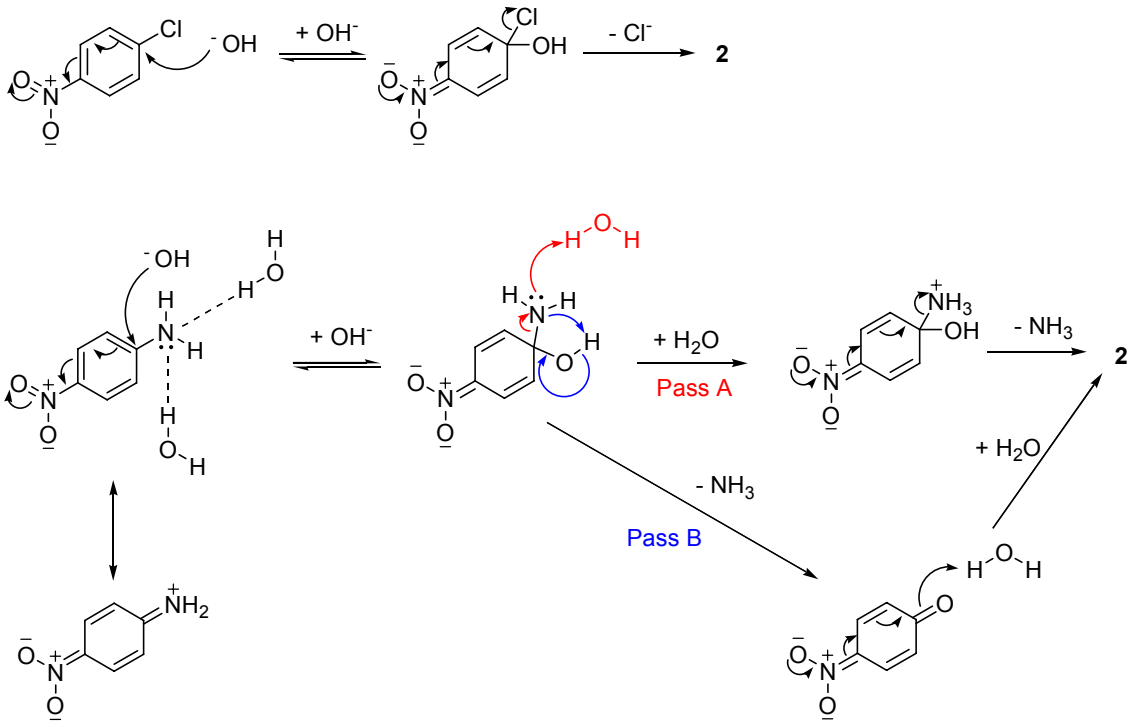
In Chapter 3, the observation made in this study demonstrates that the absorption and emission properties of **2** display distinctive solvent effects (solvatochromism) compared with 9,10-bis(phenylethynyl)anthracene. The results suggest that the fluorescence of **2** arises from a singlet CT excited state that possesses intramolecular charge transfer character. The observed strong dependence of the fluorescence quantum yield on solvent polarity shows that the CT character of its singlet excited state causes **2** to be more fluorescent in less polar solvents than that in more polar solvents.



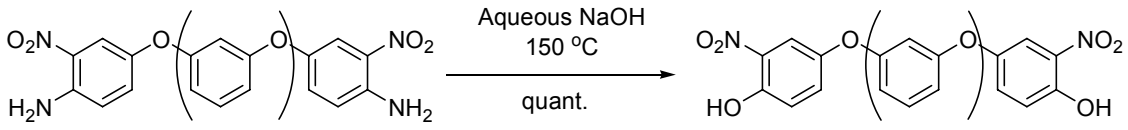
2

In Chapter 4, it was revealed that the amino groups of nitrated anilines are unexpectedly more reactive than the chlorine atoms of nitrated aryl chlorides in aqueous NaOH, even though the amino groups are normally much less reactive than the chlorine atoms in organic solvents in aromatic nucleophilic substitution reactions. Aqueous media played a dominant role in the reaction of the anilines with hydroxide ions, since the hydrogen bonding of the amino groups with water reduces an adverse effect of the resonance stabilization so that the amino groups become more reactive with hydroxide ions to form the Meisenheimer complexes, and eventually ammonia molecules are eliminated. Solvation of the anilines with organic solvents or tetraalkylammonium ions would hinder the hydrogen bonding with water and turn the aromatic amino group back to just a poor leaving group in the reactions. The present reactions are not only synthetically prospective but also are environmentally friendly, because the reactions proceed in water without any organic solvents and consume just one

equivalent of H_2O to provide the aryl hydroxides releasing ammonia gas as the sole by-product.



In Chapter 5, 4,4'-diamino-3,3'-dinitrodiphenyl ether (**4a**) and 1,3-bis(4-amino-3-nitrophenoxy)benzene (**4b**) were successfully converted by using the method developed in Chapter 4 into 4,4'-dihydroxy-2,2'-dinitrodiphenyl ether (**5a**) and 1,3-bis(4-hydroxy-3-nitrophenoxy)benzene (**5b**) which are highly valuable precursors for electric interlayer insulators and protective films for semiconductors.



4a n = 0
4b n = 1

5a n = 0
5b n = 1

LIST OF PUBLICATIONS

1. "Contrasting Intermolecular and Intramolecular Exciplex Formation of a 1,4-Dicyano-2-methylnaphthalene–*N,N*-Dimethyl-p-toluidine Dyad"

   Mitsutaka Imoto; Hiroshi Ikeda; Takayuki Fujii; Hisaji Taniguchi; Akihiro Tamaki; Motonori Takeda; Kazuhiko Mizuno, *Org. Lett.* **2010**, *12*, 1940–1943.

2. "Selective Formation of Intermolecular Exciplex of a 1,4-Dicyanonaphthalene–Anisole Dyad in Crystalline State"

   Mitsutaka Imoto; Hiroshi Ikeda; Maki Ohashi; Motonori Takeda; Akihiro Tamaki; Hisaji Tniguchi; Kazuhiko Mizuno, *Tetrahedron Lett.* Submitted for publication.

3. "Intra- and Intermolecular Exciplex Formation of a 1,4-Dicyanonaphthalene–4-Substituted Toluene Dyad"

   Mitsutaka Imoto; Hiroshi Ikeda; Maki Ohashi; Yusuke Kano; Motonori Takeda; Akihiro Tamaki; Hisaji Taniguchi; Kazuhiko Mizuno, *J. Org. Chem.* Submitted for publication.

4. "Synthesis and Solvatochromatic Properties of 9-(4-Aminophenylethynyl)-10-(4-nitrophenylethynyl)anthracene"

   Mitsutaka Imoto; Motonori Takeda; Akihiro Tamaki; Hisaji Tniguchi; Kazuhiko Mizuno, *Res. Chem. Intermed.* **2009**, *35*, 957.

5. "Unexpectedly High Reactivity of Aniline Derivatives toward Hydroxide Ion in Aromatic Nucleophilic Substitution Reaction in Aqueous Alkaline Media"

   Mitsutaka Imoto; Hiroshi Ikeda; Motonori Takeda; Akihiro Tamaki; Hisaji Taniguchi; Kazuhiko Mizuno, *Org. Prep. Proced. Int.* Submitted for publication.

6. “Practical and Efficient Synthesis of 4,4’-Dihydroxy-3,3’-dinitrodiphenyl Ether and 1,3-Bis(4-hydroxy-3-nitrophenoxy)benzene in Aqueous Alkaline Medium”

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