# Photoresponsive Molecules

# Photoinduced Color Change and Photomechanical Effect of Naphthalene Diimides Bearing Alkylamine Moieties in the Solid State

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**Abstract:** Photoinduced color change of naphthalene diimides (NDIs) bearing alkylamine moieties has been observed in the solid state. The color change is attributed to the generation of a NDI radical-anion species, which may be formed through a photoinduced electron-transfer process from the alkylamine moiety to the NDI. The photosensitivity of NDIs is highly dependent on the structures of the alkylamine moieties. Crystallographic analysis, kinetic analysis, UV/ Vis/NIR spectroscopic measurements, and analysis of the photoproduct suggested that a radical anion was formed

# Introduction

Molecules that possess the ability to change their structural and electronic properties in response to light have attracted much interest.<sup>[1]</sup> Photochromic molecules represented by diarylethenes and azobenzenes are recognized as typical light-responsive molecules, which undergo a reversible color change accompanied by a photochemical structural isomerization, and their properties provide applications of these molecules to not only optoelectronic devices, such as memories and switches, but also to mechanical materials.<sup>[2,3]</sup> Besides the photochromic molecules, molecules that can form persistent radicals or radical ions in response to light are fascinating because of the unique optical, electrical, and magnetic properties based on the unpaired spins of the radical species. The photoinduced

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through an irreversible process initiated by proton abstraction between an amine radical cation and the neutral amine moiety. The radical anions formed stacks including mixed-valence stacks and radical-anion stacks, as shown by the broad absorption bands in near-IR spectra. These photosensitive NDIs also showed crystal bending upon photoirradiation, which may be associated with a change in the intermolecular distance of the NDI stacks by the formation of monomeric radical anions, mixed-valence stacks, and radical-anion stacks.

formation of persistent radical species has been demonstrated by various molecules, such as viologens,<sup>[4–6]</sup> tetrathiafulvalenes,<sup>[7]</sup> biindenylidenediones,<sup>[8]</sup> dibenzobarrelenes,<sup>[9]</sup> and a pyridine/carboxylic acid complex,<sup>[10]</sup> in solution, as polymers, and in the crystalline state, and the formed radical species induce color changes, conductivity enhancement, and magnetism.

The aromatic diimide moiety is recognized as one of the most promising n-type semiconductors and has been intensively investigated for applications to optoelectronic devices.<sup>[11]</sup> The aromatic diimide species undergoes two reversible chemical and electrochemical one-electron reductions to give relatively stable radical anions and dianions,<sup>[12]</sup> and the radical anions have a tendency to aggregate to form stacks.<sup>[13, 14]</sup>

Besides chemical and electrochemical reductions, the aromatic diimide moiety also undergoes a photochemical oneelectron reduction to form a persistent radical anion through a photoinduced electron transfer (PET) from electron donors, such as triethylamines<sup>[15]</sup> and anions.<sup>[16]</sup> We have been interested in the intramolecular version of the photoinduced radicalanion formation of aromatic diimides bearing electron-donating moieties and want to study their intramolecular PET phenomena.<sup>[17]</sup>

During the course of this study, we unexpectedly observed a photoinduced color change by simple naphthalene diimides (NDIs)<sup>[18]</sup> bearing alkylamine moieties in the solid state (Figures 1, 2, and 5), which is due to the formation of the NDI radical anion. Furthermore, these photosensitive NDIs showed crystal bending on photoirradiation. Herein, we report our investigation into the mechanism of color change and crystal bending of these photosensitive NDIs.

In our continuing study of the properties of the radical anion of the aromatic diimide moiety, we previously demon-

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Figure 1. Structures of NDIs 1–11 and the magnitude of the color change by photoirradiation in the solid state. "Clear" and "Weak" denote clear and weak color changes, respectively, whereas "No" indicates no color change.



**Figure 2.** Photoinduced color change of **1** in the solid state. Upon photoirradiation, the yellow microcrystalline solid turned black ( $\lambda_{max} = 370$  nm, 3 min), which reverted to yellow after being stored in the dark at room temperature in air (48 h).

strated the generation of radical anions of the self-assembled aggregate of pyromellitic diimide-based macrocycles<sup>[19]</sup> by means of a chemical reaction in the solid state (this will be reported elsewhere).<sup>[20]</sup>

#### **Results and Discussion**

#### Photoinduced color change of NDI 1 in the solid state

When a microcrystalline solid of *N*,*N*'-bis[2-(dimethylamino)ethyl]-1,4,5,8-naphthalenetetracarboxylic 1,8:4,5-diimide (1)<sup>[21,22]</sup> was irradiated with UV light ( $\lambda_{max}$ =370 nm, 3 min) at room temperature in air, 1 changed from yellow to black (Figure 2). This color change of 1 was also observed even under room light within 5–10 minutes. After discontinuation of the irradiation of 1, the resultant black solid was stored in the dark and reverted to yellow after 48 hours. The change from yellow to black and black to yellow was repeatedly observed more than 20 times without any significant deterioration, whereas no color change was observed when a degassed solution of 1 in MeCN was irradiated (1×10<sup>-3</sup> m;  $\lambda$  > 300 nm, 10 min).

To characterize the chemical species formed by the photoirradiation of **1**, UV/Vis/near-infrared (NIR) diffuse reflectance spectra were measured (Figure 3 a). New absorption bands appeared in the region of  $\lambda = 400-800$  nm upon photoirradiation ( $\lambda_{max} = 370$  nm, 5 min) due to the monomeric NDI radical anion.<sup>[23]</sup> In addition, significantly broad absorption bands appeared in the region of  $\lambda = 800-2600$  nm, which were more clearly observed in the spin-coated film of **1** upon photoirra-



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**Figure 3.** a) UV/Vis/NIR diffuse reflectance spectra of 1 in air (dashed line) and after irradiation (solid line;  $\lambda_{max} = 370$  nm, 5 min). b) UV/Vis/NIR absorption spectra of 1 as the spin-coated film under vacuum before (dashed line) and after (solid line) irradiation ( $\lambda_{max} = 370$  nm, 3 min). Inset: spectra in the region of  $\lambda = 300-900$  nm.

diation under vacuum (Figure 3b), and these bands were ascribed to the formation of two different species, in which the band at approximately  $\lambda = 1300$  nm closely resembled the absorption of the NDI radical-anion stacks, whereas the other band at approximately  $\lambda = 2300$  nm was ascribed to the species of the mixed-valence stacks between the NDI radical anions and the neutral NDIs.<sup>[13]</sup> The formation of the NDI radical anion was also supported by electron-spin resonance (ESR) spectrometric analysis. The broad and anisotropic ESR spectrum with *g* values of 2.0042–2.0023 was observed after photoirradiation of 1 in the solid state in air (Figure 4) in contrast to the symmetric spectrum with a hyperfine structure in solution.<sup>[23]</sup> A similar ESR spectrum was reported for the NDIs con-



**Figure 4.** ESR spectra of 1 before (dashed line) and after irradiation (solid line) in the crystalline state in air. Irradiation:  $\lambda_{max} = 370$  nm, 5 min.

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taining the stacked NDI radical anions,<sup>[13]</sup> thus supporting the formation of the radical-anion stacks in this system. The formation of the NDI radical anion was also confirmed by the IR spectrum of **1** in a KBr pellet, which showed characteristic absorption bands of the NDI radical anion at  $\tilde{\nu} = 1627$  and  $1525 \text{ cm}^{-1}$  upon photoirradiation (see Figure S1 in the Supporting Information).<sup>[13]</sup> In contrast to the photochemical formation of the NDI radical anion in **1**, NDI **11** without alkylamine moieties showed no color change upon photoirradiation. Therefore, the formation of the NDI radical anion in **1** is ascribed to a PET process from the dimethylamine moiety to the NDI moiety. The conversion of neutral NDI **1** to a radical anion was estimated to be approximately 4% after irradiation for 2 hours in the solid state on the basis of magnetic-susceptibility measurements (see the Supporting Information).

### Effect of the structure of alkylamine moieties on the photosensitivity of the NDIs

The dependence of the photoinduced color change of the NDIs on the structure of the amine moieties was examined (Figure 5). When NDI **2** bearing *N*,*N*-dimethylaminopropyl groups was irradiated in the solid state, a color change similar

to that of **1** was observed. NDI **3** bearing *N*,*N*-diethylaminoethyl groups also showed a similar clear color change, whereas NDI **4** bearing a bulkier *N*,*N*-diisopropylaminoethyl groups exhibited a weak color change, even after prolonged irradiation (30 min) under vacuum. In the case of NDIs **5** and **6** with pyrrolidylethyl and pyrrolidylpropyl groups, respectively, **6** showed a clear color change and **5** exhibited a weak color change, even after prolonged irradiation (30 min) under vacuum.

Cyclic voltammograms of 1-6 in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M $n\text{Bu}_4\text{NPF}_6$  showed no significant difference in the redox potentials of these NDIs (see Figure S2 and Table S1 in the Supporting Information), thus suggesting that the difference in the photosensitivity does not arise from the difference in the electronic properties of these NDIs. In the cases of NDIs **7–10** bearing either *N*-methylphenylamine or diphenylamine moieties, no color change was observed, even during spectroscopic measurements under vacuum.

#### Insight into the mechanism of the radical-anion formation

To obtain insight into the dependence of the photosensitivity on the crystal structure of the NDIs, X-ray crystallographic studies of 1-6 were carried out (Figure 6).<sup>[24]</sup> The NDIs with clear



**Figure 5.** Photographs and diffuse reflectance UV/Vis/NIR spectra of NDIs with various substituents before (left side in photographs and dashed line in spectra) and after (right side in photographs and solid line in spectra) photoirradiation in air ( $\lambda_{max}$  = 370 nm, 5 min): a) **2**, b) **3**, c) **4**, d) **5**, and e) **6**.

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Figure 6. Crystal structures of a) 1, b) 2, c) 3, d) 6, e) 4, and f) 5. Dashed lines in (a)-(e) show the distances between the stacked NDIs, the imide carbon and oxygen atoms, and the nitrogen atoms and the nearest methyl or methylene carbon atoms of neighboring alkylamine moieties. Another conformation observed as disorder in the amine moieties of 2 and the solvent molecules in 5 are omitted for clarity.

color changes (i.e., 1-3 and 6) adopt similar  $\pi$ -stacked geometries with interplanar distances of 3.28-3.34 Å (Figure 6a-d), which are shorter than that of graphite (3.35 Å),<sup>[25]</sup> and the imide carbonyl carbon and oxygen atoms of the stacked NDIs are closely located each other (3.19-3.28 Å). This close stacking suggests significant  $\pi$ -electron delocalization over the continuously stacked NDIs in the solid state (Figure 6a-d), which is consistent with the observation of the broad and asymmetric ESR spectrum (Figure 4) and the broad NIR absorption bands (Figure 3) in 1 after irradiation.

It is well known that alkylamines, such as triethylamine and triethanolamine, serve as sacrificial reagents in photocatalytic reactions.<sup>[26]</sup> These reagents donate one electron to a photocatalyst through a PET process and the resultant radical cations undergo irreversible reactions initiated by proton abstraction by neutral amines around the radical cations.<sup>[27]</sup> A nitrogen atom of an alkylamine moiety is located near the methyl or methylene carbon atoms of the alkylamine moiety of the neighboring molecule with distances of 3.73-4.43 Å (Figure 6a-d). There is some void space around the alkylamine moieties, which allows thermal rotation and/or vibration of the amine moieties required for the reaction between the amine moieties. In contrast, NDI 4 with a weak color change adopts a more of a slipped-stack geometry along the long axis of the molecule than those of 1-3 and 6, and amino nitrogen atoms are surrounded by bulky isopropyl groups (Figure 6e). In the case of 5 with a weak color change, the molecules are stacked in columnar fashion, and the pyrrolidine moieties are located far from each other (Figure 6 f). Crystal-structural analyses suggest that proton abstraction from the amine radical cation by the neighboring neutral amine moiety of the facing NDI may be feasible in 1-3 and 6, but difficult in 4 and 5. Thus, the importance of the proper arrangements of the alkylamine moieties in the solid state for the radical anion formation was elucidated.

The possibility of the proton abstraction between the amine radical cation and the neutral amine moiety, namely, an irreversible mechanism of radical-anion formation, was also supported by kinetic analysis of the formation of the NDI radical anion. The generation of the NDI radical anion upon photoirradiation was evaluated by the following second-order Equation (1):

$$kt = 1/(A_{\infty} - A_{t}) - 1/(A_{\infty} - A_{0})$$
(1)

where  $A_0$ ,  $A_{\infty}$ , and  $A_t$  are the observed absorption data that correspond to  $\lambda =$  765 nm at time zero, infinite time, and time t of the reaction, respectively. The time-dependent change of the UV/Vis/NIR spectrum of 1 upon photoirradiation and the second-order plot are shown in Figure 7 a, b, respectively. The second-order plot showed a linear correlation. Evaluation of the spin-coated film also showed linearity in the second-order plot (see Figure S3 in the Supporting Information). These results indicate that the rate-determining step in the radicalanion formation is bimolecular process, which does not conflict with the hypothesis that proton abstraction occurs between the amine radical cation and the neutral amine moiety.



Figure 7. a) Time-dependent change of the UV/Vis/NIR diffuse-reflectance spectra of **1** upon photoirradiation ( $\lambda_{max}$  = 370 nm). b) Second-order kinetic plot for change in absorbance at  $\lambda = 765$  nm.

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Figure 8. <sup>1</sup>H NMR spectra of 3 after photoirradiation (400 MHz, CDCl<sub>3</sub>).

Furthermore, the irreversibility of the generation of the radical anion was supported by analysis of the photoproducts. The decomposition pathway of the alkylamines in a photocatalytic reaction is dealkylation.<sup>[26]</sup> Dealkylation of the alkylamine was reported during electrochemical oxidation, in which proton abstraction from the resultant amine radical cation by the neutral amine and subsequent irreversible reactions afford the dealkylated amine and aldehyde.<sup>[27]</sup> When NDI **3** was repeatedly irradiated in the solid state, the formation of NDIs bearing dealkylated amine moieties, namely, *N*-ethylaminoethyl groups, and acetaldehyde were observed as major products by <sup>1</sup>H NMR spectroscopic analysis (see Figure 8 and Scheme S2 for the dealkylation mechanism of **3**). In addition, when NDI **1** was irradiated at low temperature (in liquid N<sub>2</sub>), the color change was drastically suppressed (see Figure S4 in the Supporting Information), probably due to the frozen thermal motions of the alkylamine moieties.

Based on the results described above, we propose a plausible mechanism for the photoinduced color change of the NDI radical anion in the solid state (Scheme 1). When NDI absorbs a photon, a charge-separated state may be formed through a PET process from the alkylamine moiety to the NDI. The proton abstraction from the resultant amine radical cation by a neighboring neutral amine moiety followed by decomposition of the resultant amine radical cation may lead to accumulation of the NDI radical anion, which induces a color change in the solid state. Sensitivity to photoirradiation is affected by the ease of proton abstraction, which is related to the arrange-

ment of the reacting amine moieties in the solid state. The reversion of the color may be caused by the one-electron oxidation of the NDI radical anion by atmospheric oxygen to form the neutral NDI. Although the possible existence of the longlived charge-separated species still cannot be completely excluded, the results presented herein support the irreversible process for the generation of the NDI radical anion.

#### Formation of $\pi$ -stacked radical anions

Time-dependent UV/Vis/NIR spectra of the spin-coated film of 1 were measured under vacuum (Figure 9). After irradiation for 30 seconds, new absorption bands due to the radical-anion stacks and the mixed-valence stacks appeared at approximate-ly  $\lambda = 1190$  and 2300 nm, respectively (Figure 9a). As the irradi-



Scheme 1. A plausible mechanism for the radical-anion formation by photoirradiation.

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**Figure 9.** a, b) Time-dependent change in the UV/Vis/NIR spectra for spin-coated 1 under vacuum upon irradiation at a)  $\lambda_{max} = 370$  nm and b)  $\lambda_{max} = 370$  nm (5 min). c) Schematic representation of the formation and the interconversion of the NDI radical anion, the mixed-valence stacks, and the radical-anion stacks. Conversion of the mixed-valence stacks into monomeric radical anions by oxygen is likely to occur, but not confirmed, therefore, it is depicted as (O<sub>2</sub>).

ation time increased, the intensity of the absorption band due to the mixed-valence stacks decreased, whereas the intensity of the band due to the radical-anion stacks increased with the isosbestic point at approximately  $\lambda = 1800$  nm. In sharp contrast, the intensity of the absorption band of the radical-anion stacks gradually decreased after discontinuation of the photoirradiation (Figure 9b). Along with this behavior, the intensity of the band due to mixed-valence stacks increased with the isosbestic point at approximately  $\lambda = 1800$  nm. These observations indicate an interconversion between radical-anion stacks and mixed-valence stacks. Oxygen, which enters the evacuated cell, may be responsible for the conversion of radical-anion stacks into mixed-valance stacks.

#### Photomechanical bending of NDI crystals

When a rodlike crystal of 1 was irradiated, the crystal bent away from the light accompanied by a change in the crystal from yellow to dark brown (Figure 10a, b). When the darkbrown crystal was kept in the dark, the crystal became almost straight after 48 hours along with a change from dark brown to yellow (Figure 10 c). This photoinduced crystal bending was observed more than three times. When the crystal of 1 was irradiated with red light ( $\lambda_{max}$  = 580 nm), no change in the crystal shape was observed due to the weak absorption of the light at approximately  $\lambda = 580$  nm. This observation eliminates any thermal effect on the crystal bending. Therefore, the crystal bending may be attributed to the behavior of the NDI radical anions. Similar crystal bending was observed in NDIs 2, 3, and 6 with clear color changes (see Figure S5 in the Supporting Information). A photomechanical effect in crystals has been reported for several photochromic molecules, such as diarylethenes,<sup>[28]</sup> azobenzene,<sup>[29]</sup> salicylideneaniline,<sup>[30]</sup> fulgide,<sup>[31]</sup> and anthracenecarboxylic acid and its derivatives.<sup>[32]</sup> In these systems, changes in the shape and size of the molecules by photoisomerization cause stress in the crystal, which leads to deformation.<sup>[28d]</sup> For the crystal bending of **1**, in contrast, drastic changes in the molecular shape and size is not expected between the neutral NDI and NDI radical anion according to theoretical calculations (see Figure S6 in the Supporting Information).

One possible reason for this crystal bending is the change in the intermolecular distance caused by attractive or repulsive interactions among the NDI radical anions. As described above, the neutral NDIs are converted into monomeric radical anions, mixed-valence stacks, and radical-anion stacks upon photoirra-

diation. Considering the bending direction of the crystal, the irradiated crystal surface is expected to be elongated along the long axis of the crystal because of an increase in the intermolecular distance of the NDIs relative to the neutral NDI species. The monomeric radical anions are expected to show electrostatic repulsion among themselves, which may cause elongation of the irradiated crystal surface due to an increase in the intermolecular distance of the NDI  $\pi$  planes relative to the neutral NDI species. On the other hand, according to reports on the mixed-valence  $\text{dimer}^{\scriptscriptstyle[33]}$  and the  $\pi\,\text{dimer}^{\scriptscriptstyle[34]}$  of the radical anions, the intermolecular distances in the mixed-valence stacks and the radical-anion stacks is expected to be shorter than in the stacks of the neutral species, which may induce the contraction of the irradiated crystal surface. In these electronic interactions, the repulsive interaction among the monomeric radical anions may be predominant for the observed crystal bending. However, more detailed investigation is necessary to elucidate the mechanism of the crystal bending observed here.

### Conclusion

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A photoinduced color change of NDIs bearing alkylamine moieties has been observed in the solid state. This color change was attributed to NDI radical-anion formation through a PET process, and the photosensitivity of the NDIs was highly dependent on the structure of the alkylamine moieties. Crystallographic analysis, kinetic analysis, and analysis of the photoproducts suggest that a NDI radical anion was formed by decomposition of the amine moiety, which was initiated by proton abstraction between an amine radical cation and the neutral amine moiety in the solid state. The generated monomeric radical anions may form stacks including mixed-valence

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**Figure 10.** Bending of a rodlike crystal (1.4 mm × 20 µm × 10 µm) of 1 upon photoirradiation before irradiation (a), immediately after irradiation (b;  $\lambda_{max}$  = 370 nm, 30 s), and after being kept in the dark at room temperature in air for 48 h (c).

stacks and radical-anion stacks, as shown by broad absorption bands in NIR spectra. Crystal bending of these photosensitive NDIs upon photoirradiation may be associated with a change in the intermolecular distance of the NDI stacks by the formation of monomeric radical anions, mixed-valence stacks, and radical-anion stacks. Further investigation into the mechanism of this crystal bending and the synthesis of other NDIs bearing amine moieties, which stabilize the radical-cation species, are currently in progress, and the results will be reported elsewhere.

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# **Experimental Section**

#### **ESR** measurement

A small amount of crystalline powder 1 was put into an ESR tube (O.D.: 5 mm, I.D.: 4 mm). The tube was set in the cavity of the ESR machine, and the machine was covered with a black-out curtain. Photoirradiation was carried out through the window in the cavity.

### X-ray crystallographic analysis

Crystals of **1–6** were obtained by recrystallization from solvents (EtOH for **1**, MeCN for **2–4**, CHCl<sub>3</sub>/octane for **5** and **6**). The structures were solved by using direct methods with SHELXS-97,<sup>[35]</sup> SIR92,<sup>[36]</sup> or SIR2004<sup>[37]</sup> and refined by full-matrix least-squares procedures on  $F^2$  for all reflections with SHELXL-97.<sup>[35]</sup> The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically.

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# **FULL PAPER**

**Drastic change** in the color of naphthalene diimides (NDIs) bearing alkylamine moieties in the solid state upon photoirradiation (see picture) is observed, and the mechanism of this color change has been elucidated. These photosensitive NDIs also show crystal bending upon photoirradiation.



### Photoresponsive Molecules

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Photoinduced Color Change and Photomechanical Effect of Naphthalene Diimides Bearing Alkylamine Moieties in the Solid State