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Control of the intermolecular photodimerization of anthracene derivatives by hydrogen bonding of urea groups in dilute solution[†]

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The photodimerization reaction of anthracene derivatives was performed by capitalizing on intermolecular hydrogen bonds. Anthracene derivatives that can control the dimerization reaction depending on the substitution site were designed by using two anthryl moieties and one urea group, referred to as N,N'-dianthracen-n-ylurea, nDAU (n = 1, 2 and 9), which are symmetrically substituted by 1-anthryl, 2-anthryl and 9-anthryl groups, respectively. We investigated the excimer emission and photodimerization reaction of these anthracene-urea derivatives using absorption, emission, and ¹H NMR spectroscopy along with fluorescence decay measurements. All derivatives showed a concentration dependence of their fluorescence spectra and multiple fluorescence lifetime components even at 10^{-6} M. Significantly, **9DAU** resulted in an intermolecular photodimerization reaction. These differences in photoreactivity of nDAU may depend on variations in the overlap of the intermolecularly associated anthracene rings of nDAU by hydrogen bonding between intermolecular urea moieties. Furthermore, the dimerization quantum yield of **9DAU** was reduced by the addition of tetrabutylammonium acetate (TBAAc). Consequently, we revealed that the substitution site and the addition of TBAAc affected the dimerization reaction of anthracene-urea derivatives.

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Introduction

Control of photochemical reactions by reactive conditions would be an important advancement with respect to various photoactive organic materials.^{1–3} For example, anthracene is well known to undergo an intermolecular $[4\pi + 4\pi]$ photocycloaddition reaction upon irradiation at around 350 nm,^{4–10} and the generated photoproduct is reversibly photodissociated by irradiation at less than 300 nm.¹¹ This reversible reaction has been widely studied for photochemical cross-linking of DNA,¹² in polymers containing anthracene moieties,¹³ and as photoresistive materials^{14–16} and recording materials.¹⁷

Furthermore, anthracene derivatives play an important role in the design of a wide range of applications as fluorescent substances, *e.g.*, laser dyes,¹⁸ organic light emitting displays,^{19–22} fluorescence sensors,^{23–26} and solid-state emission.^{27,28} One of the characteristic emissions of anthracene is its excimer fluorescence emission under certain specific conditions, *e.g.*, at extremely low temperature or in spatially restricted circumstances. An excimer is defined as a dimer that is stabilized in the excited state and dissociated in the ground state. Since an excimer is more stable than the monomer in the excited state and deactivates to the dissociative potential surface in the ground state, excimer emission appears in a longer wavelength region than the monomer emission.²⁹ At the low temperature of 77 K, a concentrated solution of anthracene exhibits excimer fluorescence.^{4,7} It is worthwhile to achieve photodimerization and excimer emission under ambient conditions, especially at low concentrations. With regard to the photochemical and photophysical properties of excimers, several studies have been reported in restricted environments such as cyclodextrin,³⁰ phospholipids,²⁶ and duplexes of DNA.³¹ We have also investigated photodimerization with molecular assemblies.^{32,33}

Much attention has been focused on the hydrogen bonding interactions in urea derivatives.^{25,34–40} We previously studied the photochemistry of urea derivatives bearing pyrene fluorophores.⁴¹ While the urea derivative 1-pyren-1-yl-3-phenylurea, containing one pyrenyl group, shows only monomer emission, the urea derivative N,N'-1-dipyrenylurea, containing two pyrenyl groups, forms an excimer due to the intermolecular interaction of the pyrenyl groups. We revealed that N,N'-1-dipyrenylurea forms an excimer *via* an intermolecular hydrogen bonding interaction through the urea moiety at extremely



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Scheme 1 Structures of symmetrical anthracene-urea derivatives.

low concentrations. Consequently, we found that this intermolecular interaction of the pyrenyl moiety is promoted by the introduction of double pyrene rings to a urea group. In this sense, the photodimerization reaction of anthracene through intermolecular interactions between aromatic rings even at quite low concentrations could be expected.

We synthesized three types of anthracene-urea derivatives, *N*,*N*'-dianthracen-*n*-ylurea, *n*DAU (n = 1, 2 and 9), bearing the n-anthryl group at both sides of the urea (Scheme 1), and investigated excimer formation and photodimerization resulting from intermolecular hydrogen bonding between urea moieties. In addition, we examined the differences in photoreactivity such as photodimerization and excimer formation relative to the substitution position on the anthracene ring. By the irradiation at 365 nm, 9DAU showed significant excimer emission and photodimerization compared with 1DAU and 2DAU, indicating remarkable dependence on the substitution site of the anthracene moiety. Furthermore, we succeeded in controlling the dimerization reaction by the addition of tetrabutylammonium acetate (TBAAc) due to the dissociation of 9DAU aggregates, indicating that intermolecular hydrogen bonding interactions are necessary for the intermolecular dimerization reaction.

Experimental

Synthesis

1DAU. Into a 100 mL two-necked round-bottom flask were added 1-anthracene carboxylic acid (161 mg, 0.724 mmol), toluene (20 mL), triethylamine (200 μL, 1.44 mmol), and diphenylphosphoryl azide (300 μL, 1.2 mmol). After the mixture had been stirred for 30 min at 80 °C, 1-aminoanthracene (160 mg, 0.745 mmol) in THF (10 mL) was added, and the mixture was refluxed for 15 hours. The solvent was removed by suction filtration and the residue was washed with methanol several times. The product was a light yellow solid (260 mg, 87%). ¹H NMR (DMSO-*d*₆, 400 MHz): δ 7.51–7.60 (6*H*, m), 7.86 (2*H*, d, *J* = 8.08 Hz), 8.11 (2*H*, d, *J* = 8.08 Hz), 8.14 (6*H*, m), 8.22 (2*H*, d, *J* = 9.36 Hz), 8.65 (2*H*, s), 8.92 (2*H*, s), 9.47 (2*H*, s). Anal. calcd for C₂₉H₂₀N₂O: C, 84.44; H, 4.89; N, 6.79; O, 3.88; found: C, 84.15; H, 5.05; N 6.64; O, 4.16.

2DAU. Into a 100 mL two-necked round-bottom flask were added 2-anthracene carboxylic acid (185 mg, 0.832 mmol), toluene (20 mL), triethylamine (250 μ L, 1.80 mmol), and diphenylphosphoryl azide (450 μ L, 1.8 mmol). After the mixture had been stirred for 30 min at 80 °C, 2-aminoanthracene (145 mg, 0.751 mmol) in THF (10 mL) was added, and the mixture was refluxed for 17 hours. The solvent was removed by suction filtration and the residue was washed with methanol several times. The product was a light yellow solid (285 mg, 92%). ¹H NMR (DMSO-*d*₆, 400 MHz): δ 7.45–7.56 (6*H*, m), 8.03–8.08 (6*H*, m), 8.36 (2*H*, s), 8.44 (2*H*, s), 8.51 (2*H*, s), 9.11 (2*H*, s). Anal. calcd for C₂₉H₂₀N₂O: C, 84.44; H, 4.89; N, 6.79; O, 3.88; found: C, 84.62; H, 5.01; N 6.76; O, 3.61.

9DAU. Into a 100 mL two-necked round-bottom flask were added 9-anthracene carboxylic acid (555 mg, 2.50 mmol), THF (25 mL), triethylamine (250 µL, 1.80 mmol), and diphenylphosphoryl azide (300 µL, 1.2 mmol). The mixture was refluxed for 15 hours. The solvent was removed by suction filtration and the residue was washed with methanol several times. The product was a light yellow solid (206 mg, 40%). ¹H NMR (DMSO-*d*₆, 400 MHz): δ 7.56 (4*H*, t, *J* = 6.96 Hz), 7.62–7.70 4*H*, m), 8.13 (4*H*, d, *J* = 7.4 Hz), 8.40–8.44 (4*H*, m), 8.58 (2*H*, s). Anal. calcd for C₂₉H₂₀N₂O: C, 84.44; H, 4.89; N, 6.79; O, 3.88; found: C, 84.32; H, 5.07; N 6.45; O, 4.16.

Method

¹H NMR spectra were recorded on a JEOL EX-270 (270 MHz for ¹H NMR) or a Bruker ARX-400 (400 MHz for ¹H NMR) spectrometer using DMSO- d_6 as a solvent and tetramethylsilane as an internal standard. Absorption and fluorescence spectra were recorded on a Shimadzu UV-1600 and a Hitachi F-4500 fluorescence spectrometer, respectively. JASCO F-777 was used as an irradiation source. Fluorescence decay measurements were performed using a time-correlated single-photon counting method. Laser excitation at 375 nm was performed using a diode laser (PicoQuant, LDH-P-C-375) with a power control unit (PicoQuant, PDL 800-B) with a repetition rate of 2.5 MHz. The temporal profiles of the fluorescence decays were detected using a microchannel plate photomultiplier (Hamamatsu, R3809U) equipped with a TCSPC computer board module (Becker and Hickl, SPC630). The full width at half maximum (FWHM) value of the instrument response function was 51 ps.⁴² The values of χ^2 and the Durbin–Watson parameters were used to determine the quality of the fit obtained by nonlinear regression.43 DMSO (spectroscopic grade, Wako Pure Chemical Industries, Japan) was used as a solvent without further purification. Acetate anions were in the form of tetrabutylammonium acetate (TBAAc), which contains a tetrabutylammonium cation (Sigma-Aldrich, Japan). All measurements were carried out at room temperature under an Ar atmosphere. The concentrations were adjusted so that the absorption maximum of the excitation wavelength was about 0.1 for each sample. DFT calculations were performed using the Spartan '04 program (Wavefunction, Inc., Irvine, CA).

Determination of the dimerization quantum yield

The light quantity, *I*, was determined to be $I = 4.70 \times 10^{-7}$ mol min⁻¹ according to the literature.⁴⁴ Using the light quantity, the photodimerization quantum yield was calculated using eqn (1):

$$\Phi_{\rm dim} = \frac{AV}{I(1-10^{-A_{365}})\varepsilon} \tag{1}$$

where *A* is the slope of the change in absorbance against time, *V* is the volume of the photoirradiated sample (3.0×10^{-3} L), ε is the molar extinction coefficient of the derivative and A_{365} is the absorbance at 365 nm.

Results and discussion

Absorption spectra

To investigate the electronic interaction of anthryl moieties of nDAU via the urea group in the ground state, the absorption spectra were recorded (Fig. 1). The spectral profiles of nDAU were very similar to those of previously reported urea–anthryl derivatives, nPUA, having a single anthryl moiety. The nDAU derivatives showed about 2-fold higher molar extinction coefficients compared with the corresponding nPUA as shown in Scheme S1 and Fig. S1† and listed in Table 1.^{25,38} These results indicate that the electronic interaction between anthryl moieties through the urea unit is relatively weak in the ground state.



Fig. 1 Absorption spectra of 1DAU, 2DAU and 9DAU in DMSO under Ar.

	$\lambda_{ m Abs}/ m nm$	$\varepsilon/10^4 \mathrm{M^{-1} cm^{-1}}$	$\lambda_{ m Fl}/ m nm$
1DAU	366, 388, 405	1.0, 1.5, 1.3	450
2DAU	340, 358, 384, 403	1.4, 1.0, 0.99, 0.76	450
9DAU	353, 368, 392	0.88, 1.4, 1.5	426
1PUA	384	0.79	462
2PUA	340, 359, 384, 403	0.46, 0.43, 0.43, 0.35	447
9PUA	353, 370, 389	0.46, 0.69, 0.65	435

Fig. S2[†] illustrates the concentration dependence of the absorption spectra of **1DAU**, **2DAU** and **9DAU**. Although the absorption spectra of **1DAU** and **2DAU** did not change with the concentration, that of **9DAU** increased in absorbance ranging from 290 nm to 380 nm with increasing the concentration. This indicates that **9DAU** molecules interact with each other in the ground state depending on the concentration, in contrast to **1DAU** and **2DAU**.

Fluorescence spectra

Fluorescence spectra of *n*DAU and *n*PUA were recorded at various concentrations ranging from 1.0×10^{-7} to 5.5×10^{-6} M. The fluorescence spectrum of **1DAU** at 3.3×10^{-7} M showed a broad profile having a maximum at 445 nm along with a shoulder at 415 nm, in contrast to its absorption spectrum with vibronic bands (Fig. 2), indicating that the emissive



Fig. 2 Concentration dependence of fluorescence spectra: (a) 1DAU, (b) 2DAU and (c) 9DAU in DMSO under Ar.

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state of 1DAU is electronically delocalized, while the concentration dependence was not observed in the spectra of nPUA (Fig. S3[†]). The fluorescence spectrum was red-shifted to 455 nm at 3.4 \times 10⁻⁶ M and showed an increase in fluorescence intensity around 500 nm relative to the peak intensity following the disappearance of the shoulder. A similar concentration dependence was observed in the spectra of 9DAU accompanying a negligible peak shift and a relatively slight increase of fluorescence intensity around 550 nm. In contrast to 1DAU and 9DAU, the fluorescence spectrum of 2DAU showed no increase in the 550 nm region with a change in the concentration. Intermolecular interactions in the excited state are the main cause of the concentration dependence of the fluorescence spectra. As previously reported, 1DAU molecules bearing a pyrenyl group at both sides of the urea moiety are allowed to interact with each other by hydrogen bonding interactions with a urea unit.⁴¹ The same situation may apply to nDAU.

Differences in the photoreaction depending on the substitution site of the anthracene ring

Photoirradiation experiments of nDAU were performed to investigate their photoreactive properties. Fig. 3 shows the changes in the absorption spectra of nDAU upon photoirradiation. The irradiation wavelength was set at 365 nm for all derivatives. The spectra of 1DAU and 9DAU showed a decrease in the absorbance under irradiation. The absorbance of 1DAU decreased from 350 nm to 425 nm, showing isosbestic points at 350 nm and 425 nm, while an increment of absorbance was observed at shorter and longer wavelength regions, indicating that the photoproduct has a different electronic structure than the parent 1DAU. In contrast to 1DAU, the absorption spectrum of 9DAU almost disappeared after 250 min of irradiation. Although isosbestic points were confirmed at 290 nm and 425 nm, photoproducts seem to be produced through a different pathway from 1DAU. On the other hand, 2DAU gave no remarkable spectral changes in the course of photoirradiation. It is noteworthy that *n*PUA, which have only a single anthracene moiety, exhibited fewer changes upon photoirradiation than nDAU (Fig. S4[†]). This suggests that intermolecular interactions may be involved in the photoreaction. With respect to 1DAU and 9DAU, we investigated the changes in fluorescence spectra by photoirradiation. The fluorescence spectrum of 1DAU having a maximum at 445 nm gradually red-shifted and this was accompanied by a new fluorescence band with a 498 nm maximum along with a shoulder at 520 nm (Fig. S5a[†]). Although the isoemissive point was less remarkable than the isosbestic point, the fluorescence changes of 1DAU were consistent with the absorption spectrum. The photoirradiation of 9DAU yielded an increase in the intensity of the fluorescence spectrum along with the disappearance of the long tail, which may be ascribed to an intermolecular excimer emission analogous to 1DAU.⁴¹ ESI-MS measurements were performed to examine the photoproduct after photoirradiation and a new peak was observed at m/z845.25 for 9DAU. Since the calculated ESI-MS value of the



Fig. 3 Changes in absorption spectra of (a) 1DAU, (b) 2DAU and (c) 9DAU with irradiation at 365 nm in DMSO under Ar.

intermolecular dimer $C_{58}H_{40}NaO_2$ was m/z 847.30 for $[M + Na]^+$, the calculated and the measured values were consistent with each other. To elucidate the photodimerization mechanism of 9DAU, the absorption spectra of 9DAU were recorded, as shown in Fig. S5b.† The absorbance of 9DAU gradually decreased with irradiation time, with isosbestic points at 290 nm and 425 nm. Similar phenomena were obtained for 1DAU. In order to identify the structure of 9DAU after photoirradiation, we recorded the ¹H NMR spectrum. After 150 minutes of photoirradiation, the anthracene proton signals vanished completely, and new signals appeared (Fig. S6[†]). These peaks were assigned as follows. Signals at 7.65 ppm, 7.14-6.85 ppm and 4.72 ppm were attributed to the N-H of urea groups, C-H of the benzene ring and C-H of the cross-linking site of the methyl protons, respectively. These symmetric peaks and the observation of the intermolecular

dimer in the ESI-MS revealed the structure of the photoreaction product as shown in Fig. S6.† The photodimerization quantum yield of 9DAU was determined to be 0.0093. Except for absorption and fluorescence spectra, there is little information on photoproducts of 1DAU due to a lack of successful analyses of ¹H NMR and ESI-MS spectra. However, it is noteworthy that the photoreaction of 1DAU yields unknown products (Fig. S7[†]) in contrast to the remarkable photostability of 2DAU (Fig. 3b). There have been previously reported photodimerization reactions that depend on hydrogen bonding, e.g., thymine-adenine interaction,⁴⁶ dimerization of *trans*-cinnamamide,⁴⁷ transformation of one coordination polymer to another,48 alkene photodimerization in the solid state,49 and [2 + 2] photodimerization in the solid state.⁵⁰ However, to the best of our knowledge, this is the first example of an anthracene photodimerization reaction under low concentration that depends on urea hydrogen bonding.

The origin of photodimerization in the ground state examined by the addition of acetate

Among the three urea derivatives, **9DAU** showed the most significant photodimerization reaction. *n*DAU derivatives form intermolecular aggregates by hydrogen bonding between intermolecular N–H and C=O in the ground state,⁵¹ and these aggregates may promote photodimerization due to the close proximity of the anthracene rings. Thus, it is anticipated that dissociation of the aggregates by hindering intermolecular hydrogen bonding inhibits the photodimerization reaction. We attempted to inhibit intermolecular hydrogen bonding between intermolecular anthryl moieties of **9DAUs** by the addition of tetrabutylammonium acetate (TBAAc) to cleave intermolecular hydrogen bonding in the presence of TBAAc was revealed by research in the disappearance of excimer emission in the case of N,N'-1-dipyrenylurea.⁴¹

To examine the interaction between **9DAU** and TBAAc, absorption and ¹H NMR spectra were recorded. Fig. S8† shows the absorption spectra of **9DAU** in DMSO with various concentrations of TBAAc. In the presence of TBAAc, the spectral shape at the red-edge region (wavelengths longer than 350 nm) was broad compared to that in the absence of TBAAc due to the interaction with **9DAU**.

To confirm the complex formation of **9DAU** with TBAAc, ¹H NMR spectra were recorded in the absence and presence of TBAAc. This revealed the existence of hydrogen bonding between **9DAU** and TBAAc through the urea moiety, since downfield shifts of the urea N–H protons in **9DAU** from 9.01 ppm to 12.39 ppm were observed in the presence of 5 equiv. TBAAc (Fig. S9†). The association constant of **9DAU** with TBAAc was determined according to eqn (2) to be $7.7 \times 10^2 \text{ M}^{-1}$:

$$\frac{1}{A - A_0} = \frac{1}{A_{\max} - A_0} \left(\frac{1}{K_a[A]} + 1 \right)$$
(2)

where A_0 and A are the absorbances of the host monitored at 370 nm in the absence and presence of TBAAc, respectively, [A] is the total TBAAc concentration, and A_{max} is the absorbance of **9DAU** under full association with TBAAc. Using the association constant of **9DAU**, we examined the dimerization reaction in the presence of 0, 1.37×10^{-3} and 1.37×10^{-2} M TBAAc. The ratio of free **9DAU** was derived from the following equations:

$$[9DAU-AcO^{-}] = \frac{a - \sqrt{a^2 - 4b}}{2}$$

$$a = [TBAAc] + [9DAU]_0 + 1/K_a, \quad b = [TBAAc][9DAU]_0$$
(3)

$$[\text{free 9DAU}]/[\text{9DAU}]_0 = -[\text{9DAU}] - [\text{9DAU}-\text{AcO}^-]/[\text{9DAU}] \quad (4)$$

where [9DAU–AcO⁻], [TBAAc], [9DAU]₀ and [free 9DAU] are the concentrations of the complex of 9DAU with TBAAc, total TBAAc, initial 9DAU, and 9DAU without interaction with TBAAc, respectively. From eqn (4), the ratios of free 9DAU were calculated to be 1, 0.51 and 0.09, and dimerization yields were determined to be 9.32×10^{-3} , 5.04×10^{-3} and 1.52×10^{-3} for 0, 1.37×10^{-3} and 1.37×10^{-2} M TBAAc, respectively (Fig. 3c, 4a and b). Plotting the dimerization yield against the concentration of free 9DAU gave a good linear relationship (Fig. S10†), indicating that the dimerization yield was directly related to the concentration of 9DAU associated with no acetate anion. This implies that the dimerization reaction of



Wavelength / nm

Fig. 4 Changes in absorption spectra of 9DAU in the presence of (a) 1.37 \times 10⁻² M TBAAc and (b) 1.37 \times 10⁻³ M TBAAc with irradiation at 365 nm in DMSO under Ar.

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9DAU proceeds not from the **9DAU**...TBAAc complex in the presence of TBAAc, but from the aggregates between **9DAU**s without interaction with TBAAc (Scheme 2). Aggregate formation in the ground state by intermolecular hydrogen bonding interactions promotes the photodimerization reaction even in dilute solution.

Excimer formation examined by fluorescence lifetime analysis

Only **9DAU** underwent the photodimerization reaction in contrast to **1DAU** and **2DAU**. These differences in photoreactivity of *n*DAU may result from the excimer formation since the photodimer is related to the excimer intermediate in anthracene derivatives according to the fluorescence measurements. Usually, the attribution of excimer fluorescence should be performed on the basis of the fluorescence spectra. However, since fluorescence spectral separation was difficult in the present case due to a lack of characteristic spectra of various excimers, we measured fluorescence decay curves to examine fluorescence lifetimes of *n*DAU, as listed in Table 2. Those of **1DAU** and **2DAU** consisted of a biexponential decay and that of



Scheme 2 Photodimerization reaction of 9DAU.

Table 2 Fluorescence lifetimes of nDA	J
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Sample	λ/nm	$\tau_{\rm s}/{ m ns}$
1DAU	450	13.7 (0.07), 0.62 (0.93)
	560	14.3 (0.07), 0.65 (0.93)
2DAU	450	14.2 (0.01), 2.19 (0.99)
	560	16.0 (0.01), 2.24 (0.99)
9DAU	450	9.62 (0.01), 1.78 (0.05), 0.34 (0.94)
	560	10.8 (0.04), 2.12 (0.16), 0.13 (0.80)

The values in parentheses are the normalized amplitudes for the respective lifetimes.

9DAU had a triexponential decay (Fig. S11[†]). The observed lifetimes of 14.3, 16.0 and 2.12 ns at 560 nm for 1DAU, 2DAU and 9DAU, respectively, seemed to agree with those of nPUA, implying that these are attributed to monomer emission.^{25,38} In general, two types of anthracene excimers are known: a 55° dimer and a sandwich dimer.^{5,52,53} The 55° dimer is defined as having the long molecular axes of two anthracene monomers nearly parallel, while the short molecular axes are at an angle of about 55°. Since this dimer is relatively unstable, the lifetime of the excimer emission becomes shorter than that of the monomer. On the other hand, the sandwich dimer has two anthracene moieties arranged by parallel stacking. This excimer emits a red-shifted wavelength region and has a longer lifetime than the stable excimer.52-54 Thus, the lifetimes of 0.65 and 2.24 ns observed at 560 nm for 1DAU and 2DAU, respectively, are attributed to the 55° dimer. With respect to 9DAU, the fluorescence lifetime of 0.13 ns is ascribed to the 55° dimer and 10.8 ns is ascribed to the sandwich dimer. All DAU derivatives emit both monomer and excimer emissions. Since a significant concentration dependence of the fluorescence spectrum was observed, this excimer originates from intermolecular stacking of anthryl moieties. The above attribution is also supported by a pyrenyl-urea derivative that emits intermolecular excimer emission.41 Accordingly, anthracene-urea derivatives promote intermolecular interactions followed by excimer emission in the excited state in dilute solution. Since the anthracene molecules must be in close proximity to generate excimers, a relatively concentrated anthracene solution is required for intermolecular excimer formation, unless restricted environments such as cyclodextrin and micelles are used.45,54 Similar to our previous work, we found that nDAU can generate hydrogen bonding assemblies even at extremely low concentrations, by introducing anthracene instead of pyrene.41

DFT calculations were performed to investigate the stacking conformation of two *n*DAU molecules by intermolecular hydrogen bonding through the urea groups. Since intermolecular anthracene rings of **9DAU** are overlapped in a face-to-face fashion, **9DAU** is allowed to form the sandwich dimer, which may undergo photodimerization (Fig. S12e and f^{\dagger}).²⁹ On the other hand, although **1DAU** and **2DAU** may form the 55° dimer, it seems that no dimerization reaction proceeds due to the dihedral angle of 55° between anthracene rings (Fig. S12a–d[†]).

Consequently, we revealed that the intermolecular hydrogen bonding interactions with a urea unit in the ground state play a significant role in the dimerization reaction of *n*DAU in the excited state resulting from the dependence of the substitution site of an anthracene ring as well as the inhibition of the photodimerization by the addition of TBAAc.

Conclusions

We synthesized three types of symmetric anthracene-urea derivatives, **1DAU**, **2DAU** and **9DAU**, to investigate the differ-

ences in photoreactivity. In dilute solution, all derivatives formed aggregates by hydrogen bonding between intermolecular urea moieties in the ground state. These aggregates were confirmed by the addition of TBAAc. The photodimerization reaction occurred in the case of 9DAU photoirradiation at 365 nm, but no photoreaction of 2DAU was observed. This observation indicates that the substitution position plays an important role in the photodimerization reaction of anthracene. nDAU exhibited multi-component fluorescence lifetimes. The excimer fluorescence was assigned to the intermolecular excimer due to intermolecular stacking of anthracene rings through hydrogen bonding. Furthermore, under photoirradiation with 365 nm light, photodimerization was confirmed only in the case of 9DAU. DFT calculations revealed that the most important factor is the orientation of the anthracene rings induced by the intermolecular hydrogen bonding between urea derivatives. Consequently, we successfully controlled the photodimerization of anthracene rings by the substitution position of the urea moiety as well as by intermolecular hydrogen bonding interactions through the C=O and N-H of the urea moiety, even though anthracene rings have a repulsive potential surface in the ground state. This may provide new insight into the molecular design of desirable photoreactive molecules. While 1DAU and 9DAU are photoreactive, 2DAU has excellent photostability. Therefore, changing the substitution site of the anthracene derivatives can remarkably modify the properties of anthracene. 9DAU undergoes the intermolecular photodimerization reaction even in dilute solution. Furthermore, its applications can be extended by using intermolecular cross-linking based on the inhibition of the dimerization reaction of 9DAU by the addition of TBAAc.

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