

Exciplex Formation of Intermolecularly Hydrogen-Bonded System between Anthracene and *N*,*N*-Dimethylaniline Derivatives

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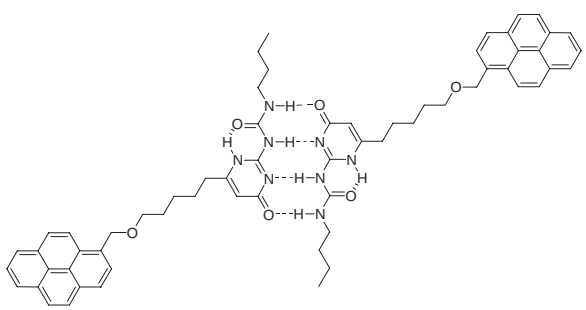
We prepared 2-ureido-4(1*H*)-pyrimidinone (UPy) derivatives bearing anthracene (AN) and *N*,*N*-dimethylaniline (DMA) connected by various lengths (n) of methylene chains (UPyAN, UPyDMA$_n$) to examine the electron-transfer dynamics between the excited state of UPyAN and the ground state of UPyDMA$_n$ by spectroscopy. UPyAN and UPyDMA$_n$ formed quadruple hydrogen bonds and exhibited exciplex emission between AN and DMA chromophores. From the fluorescence lifetime measurement, the lifetime of exciplex emission increased from 38 to 64 ns with increasing n. The quenching process of singlet excited UPyAN by UPyDMA$_n$ is proposed to be different from that of methylene-linked dimethylaniline and anthracene. Furthermore, the results indicate that both AN and DMA keep almost constant distance regardless of n of UPyDMA$_n$. DMA was considered to be located near a quadruple hydrogen-bonding region in the excited state, while deactivation process of exciplex was independent of n, which may be characteristic of a hydrogen-bonded system.

Studies on properties of higher-ordered aggregates, rather than each individual molecule, are important for the construction of functional materials.[1–6] Weak interactions, such as hydrogen-bonding interactions and electrostatic interactions, can be used to construct molecular assemblies or aggregates. Hydrogen bonding is the most important to humans, because it works in the amide parts of peptide chains and forms double-helix structure of DNA.[7] Therefore, control of the structure to build ordered assemblies is possible by using hydrogen bonding, i.e., one can obtain higher-ordered gels and polymers by arranging plural hydrogen-bonding parts in a molecule.[8–11] The aim of the present study is to develop new compounds exhibiting excimer or exciplex emission by way of connecting the functional chromophores with intermolecular hydrogen bonds. Especially, we are interested in using quadruple hydrogen-bonding systems, such as 2-ureido-4(1*H*)-pyrimidinone (UPy) to connect aromatic molecules.[12–14]

Upon the excitation of pyrene moiety of a UPy derivative bearing pyrene connected by methylene chain (Scheme 1),[15] monomer and excimer emissions were observed even in dilute solution. In this work, we have prepared UPy derivatives bearing AN or DMA connected by methylene chains, UPyDMA$_n$, as shown in Scheme 2. Note that n means the sum of the number of methylene groups and oxygen atoms in the bridge, i.e., this definition is considered to reflect the distance between AN and DMA. It was confirmed by ^{1}H NMR spectroscopy that UPyAN and UPyDMA$_n$ form hydrogen bonds in the aprotic solvents, such as chloroform. By forming quadruple hydrogen bonds at UPy moieties, fluorescent assemblies exhibiting exciplex emission were expected to be formed even in dilute solution. Actually, exciplex emission between AN and DMA was observed even in highly diluted solutions of UPy derivatives (10^{-5} M) (1 M = 1 mol dm^{-3}); however, a concentration of 10^{-2} M was necessary to detect the formation of the exciplex in the quenching with the parent DMA.[16,17]



Scheme 1.

We wish to report, here, the effect of n on exciplex formation between anthracene group and *N*,*N*-dimethylaniline group connected by quadruple hydrogen bonding. In this respect, nine kinds of UPyDMA$_n$ with different n were synthesized, and the exciplex formation was examined in the mixture of UPyAN and UPyDMA$_n$ (Scheme 2). Consequently, the lifetime of exciplex emission was found to range from 38 to 64 ns with increasing n. This result indicates that the exciplex becomes stable with increasing n.

Results and Discussion

^{1}H NMR Experiment. ^{1}H NMR peaks of UPyAN with a quadruple hydrogen bond were observed at 13.18, 11.88, and 10.15 ppm in $CDCl_3$, which are characteristic of a dimer, even at dilute concentration of 1×10^{-5} M. This is consistent with the fact that UPy derivatives form dimers by quadruple hydrogen bonding in chloroform and toluene with an association constant $>10^6$ M^{-1}, reported by Meijer et al.[18]

Absorption and Fluorescence Experiment. The absorption and fluorescence spectra of UPyAN were measured in chloroform. The absorption maxima of UPyAN (333, 350, 368, and 387 nm) appeared at similar wavelengths to those of anthracene, as shown in Fig. 1, indicating that the intra-

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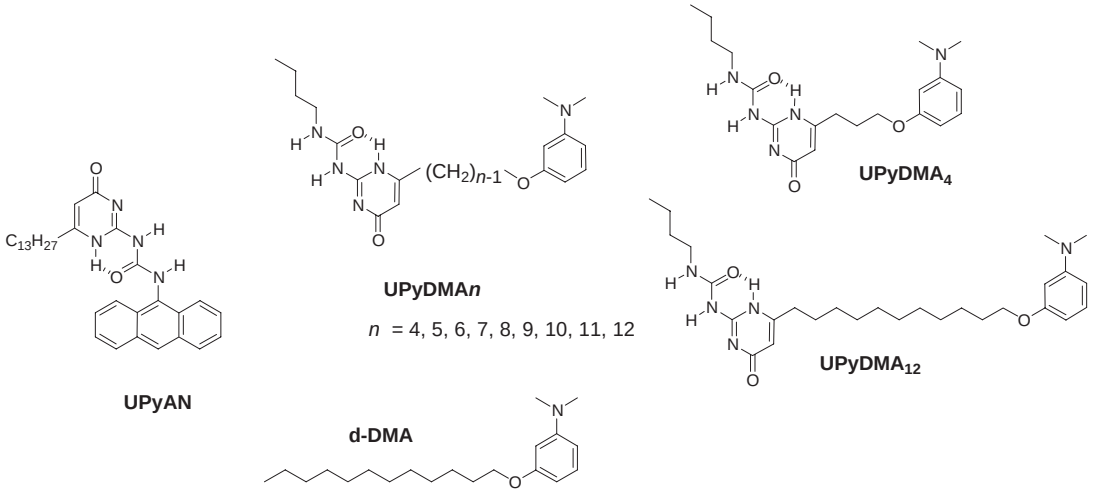

Scheme 2.

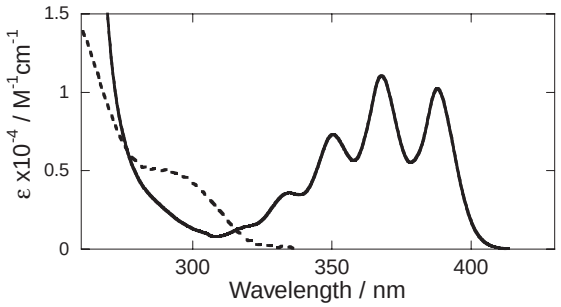

Fig. 1. Absorption spectra of UPyAN (solid line) and $UPyDMA_5$ (dashed line) in chloroform.

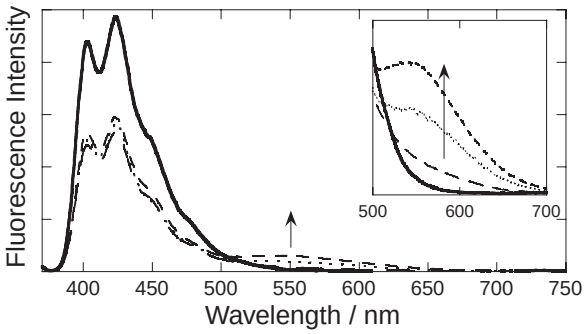

Fig. 2. Change in fluorescence spectra of UPyAN (solid line, 1.0×10^{-5} M) upon the addition of $UPyDMA_4$ (5.0×10^{-4} M, broken line), $UPyDMA_7$ (5.0×10^{-4} M, dotted line), and $UPyDMA_{12}$ (5.0×10^{-4} M, dashed line) excited at 368 nm in chloroform. The inset shows emission spectra ranging from 500 to 700 nm.

molecular electronic interaction between AN and UPy is very small in the ground state.

The absorption spectrum of $UPyDMA_n$ showed broad absorption maxima at 300 nm with a red-edge at 330 nm. A series of $UPyDMA_n$ ($n = 4$–12) showed no differences in absorption spectrum, indicating that the electronic interaction between DMA and UPy is negligible. The absorption spectra of UPyAN in the presence of $UPyDMA_n$ are basically the sum of their spectra. This fact suggests that there is no significant intramolecular electronic interaction between UPyAN and $UPyDMA_n$ in the ground state. AN has an absorption band in the region of 350–400 nm where neither DMA nor UPy absorbs light. Hence, AN can be selectively excited by the light at these wavelengths.

After excitation of AN at 368 nm in a UPyAN solution, fluorescence was observed from 400 to 500 nm, which is attributed to the locally excited (LE) AN. The vibrational progression of the fluorescence at 400–500 nm is a roughly mirror image of that of the absorption spectrum of AN. The fluorescence spectrum of UPyAN was broad and red-shifted compared with that of the parent anthracene. The quantum yield (Φ_f) and lifetime (τ_s) of fluorescence of UPyAN in chloroform were determined to be 0.60 and 6.5 ns, respectively, while those of the parent anthracene were 0.15 and 2.5 ns, respectively. The k_f value ($k_f = \Phi_f/\tau_s$) of UPyAN was calculated to be $9.2 \times 10^7\ s^{-1}$, which is slightly larger than that of the parent anthracene ($6.0 \times 10^7\ s^{-1}$). These results suggest that the urea group affects the fluorescence properties of AN.

The fluorescence spectra of UPyAN in the presence of $UPyDMA_n$ at room temperature are shown in Fig. 2. After excitation of AN in the mixture of UPyAN and $UPyDMA_n$, a new fluorescence band appeared from 500 to 700 nm in addition to normal fluorescence band of 400–500 nm. From these results, the broad fluorescence shown in Fig. 2 is attributed to an intermolecular exciplex formation between the excited state AN and the ground state DMA.

Exciplex Formation. The fluorescence spectra of UPyAN in the presence of $UPyDMA_n$, which can form an intermolecularly hydrogen-bonded dimer with UPyAN, were measured as a function of $UPyDMA_n$ concentration. Figure 3a shows that the change in the fluorescence spectra of UPyAN after the addition of $UPyDMA_{12}$. In the fluorescence measurements of the mixed solution of UPyAN and $UPyDMA_{12}$, exciplex fluorescence was observed in the long wavelength region around 550 nm following decrease of about 40% in the LE fluorescence, as shown in Fig. 3a.

The emission of UPyAN was quenched by the addition of 3-dodecyl-*N*,*N*-dimethylaniline (d-DMA), as shown in Fig. 3b. The fluorescence peak at 400 nm decreased when the concen-

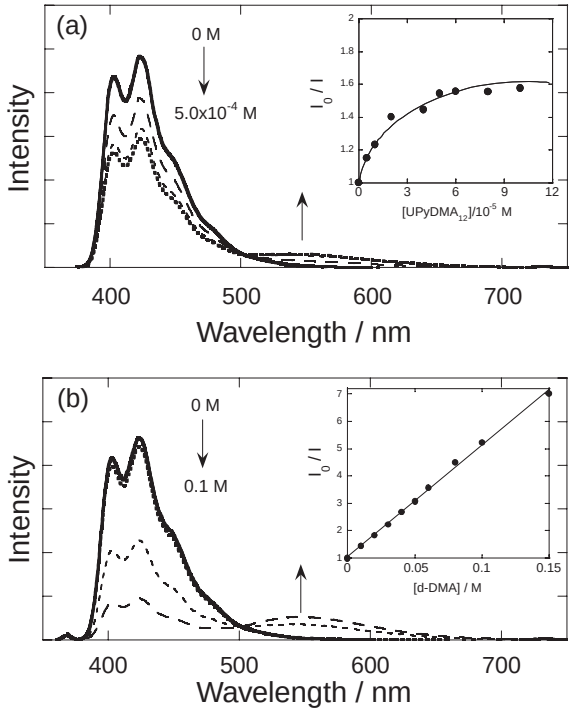

Fig. 3. Change in fluorescence spectra of UPyAN (1.0×10^{-5} M) by the addition of (a) UPyDMA$_{12}$ (0, 1.0×10^{-5}, 1.0×10^{-4}, 5.0×10^{-4} M) and (b) d-DMA (0, 5.0×10^{-4}, 3.0×10^{-2}, 0.1 M) in chloroform. The inset shows Stern–Volmer plot for fluorescence quenching.

tration of d-DMA was increased with concomitant increase in the fluorescence intensity at around 480 nm, which is assigned to the exciplex emission between AN and d-DMA. I_0 and I stand for the fluorescence intensity at 400 nm in the absence and presence of d-DMA, respectively. The Stern–Volmer plot of the I_0/I vs the concentration of d-DMA gave a Stern–Volmer constant $k_q\tau_s$ of 41 M^{-1}, and therefore, the rate constant of fluorescence quenching was determined to be 6.3×10^9 M^{-1} s^{-1} by using τ_s of 6.5 ns. The quenching rate constant seems to be of the same order as the diffusion-controlled rate constant,[19] indicating that the electron-transfer process is exothermic process. The peak wavelength of the exciplex emission in the presence of d-DMA was 550 nm, and the quantum yield of exciplex emission (Φ_{ex}) was calculated to be 0.098 by subtraction of the normalized fluorescence spectrum in the absence of d-DMA from that in the presence of d-DMA.

Chain-Length Dependence. The peak wavelength of exciplex emission depends on n of UPyDMA$_n$ and shifted to longer wavelength from 525 to 550 nm with increasing from $n = 4$ to 7, Fig. 4, and then remained constant at 550 nm from $n = 7$ to 12.

Figure 5 shows changes in fluorescence lifetimes of LE and exciplex between UPyAN and UPyDMA$_n$ as a function of n. The lifetime of LE, which reflects a change in quenching rate constant by DMA, was found to be independent of n. This indicates that the distance between AN and DMA in the hydrogen-bonding formation between UPyAN and UPyDMA$_n$ is also independent on n. On the other hand, the lifetime of exciplex emission was dependent of n, varying from 38 to 64 ns. This result suggests that the exciplex becomes stable with increasing n.

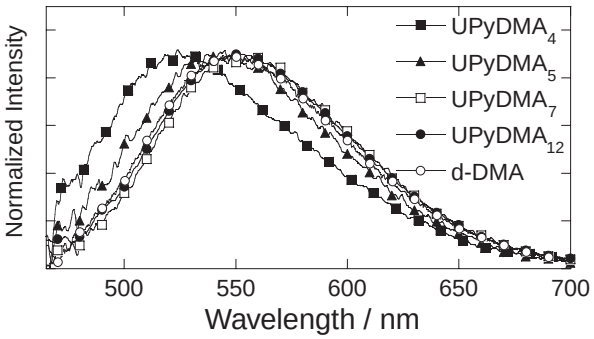

Fig. 4. Exciplex emission spectra of UPyAN in the presence of UPyDMA$_n$ ($n = 4$, 5, 7, and 12) and d-DMA. The spectra were normalized by their maximum intensity.

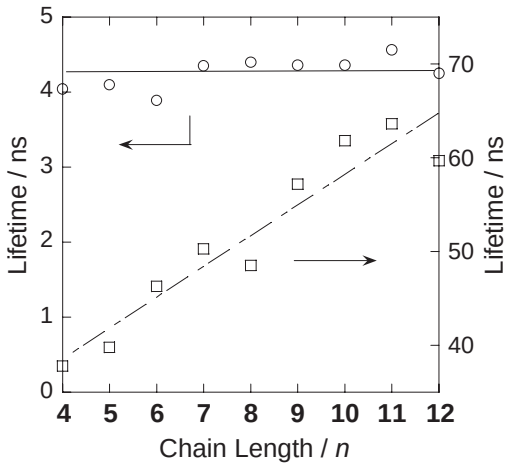

Fig. 5. Chain-length dependence of fluorescence lifetime in the presence of UPyAN. LE (circle) and exciplex (square).

Mechanism of Exciplex Formation Promoted by Hydrogen Bonding. A mixed solution of UPyAN and UPyDMA$_n$ gave both LE and exciplex fluorescence around 420 and 560 nm, respectively. Exciplex fluorescence was even observed with a low concentration of UPyDMA$_{12}$ (5×10^{-4} M), while no exciplex formed with the same concentration of d-DMA, as shown in Fig. 3. In other words, the ability to hydrogen bond is required, since higher concentrations of d-DMA are needed to form an exciplex.[19] In the case of UPyDMA$_n$, the intensity of the exciplex fluorescence increased with n. The exciplex lifetime of the mixed solution became longer as the chain length increased from 38 ns for $n = 4$ to 63 ns for $n = 11$. In contrast, the fluorescence lifetime of AN was almost constant concerning to n, that is, the quenching rate constant by DMA is independent of n. The possibility of a homodimer formation is negligible with an excess quantity of UPyDMA$_n$, since hydrogen-bonding part is common between AN and DMA. In this experiment, the concentration of UPyDMA$_n$ was 10 times higher than that of UPyAN resulting in more than 95% abundance of the heterodimer, and so, the contribution of homodimer can be ignored in the case of excess quantity of UPyDMA$_n$, hereafter.

From these results, it appears that DMA keeps a certain distance from AN in spite of changing n, because the fluorescence lifetime of LE part did not change when UPyDMA$_n$ was var-

ied. The interaction between DMA and hydrogen-bonding part of UPyDMA$_n$ may be the driving force that causes to come in close contact to each other. One possibility to explain the origin of this driving force is a nonbonding orbital interaction on the nitrogen atom of DMA, which seems to be able to form hydrogen bonds to some extent.[21] However, quadruple hydrogen-bonding formation is considered to be the dominant interaction between UPyAN and UPyDMA$_n$. It has been reported that exciplex is stable with increasing chain length in the case of methylene-linked anthracene and other aromatics.[22,23] Yamamoto et al. reported that intramolecular fluorescence quenching and exciplex formation of (carbazole)-$(CH_2)_n$-(terephthalic acid methyl ester), and the lifetime of exciplex with $n = 10$ was longer than $n = 5$.[24] They considered that the increase in the exciplex lifetime was ascribed to more stable conformation of $n = 10$ than $n = 5$ due to decrease of conformational strain. This explanation may be applicable to the present findings concerning exciplex behavior in UPy derivatives.

Conclusion

We investigated the electron-transfer dynamics between the excited state of UPyAN and the ground state of UPyDMA$_n$ by using time-resolved spectroscopy. Although the details of quenching mechanism have not been fully elucidated, the quenching process of singlet excited UPyAN by UPyDMA$_n$ is proposed to be different from that of methylene-linked *N*,*N*-dimethylaniline and anthracene, which may be due to hydrogen bonding in the system.

Experimental

Methods. Absorption and fluorescence spectra were measured on Shimadzu UV-1600 and on Hitachi F-4500 fluorescence spectrometer, respectively. Fluorescence lifetimes were determined with a time-resolved spectrofluorometer, Horiba NAES-1100. Chloroform for spectroscopy (Wako Chem. Japan) was used without further purification. All measurements were carried out at room temperature under Ar. The concentration was adjusted so that the absorption maximum of the excitation wavelength is 0.1 in each solution. ^{1}H NMR spectra were measured with 400 MHz NMR spectrometer, ARX-400.

Synthesis. 2-(*N*′-9-Anthrylureido)-6-tridecyl-4(1*H*)-pyrimidinone (UPyAN): 9-Anthracenecarboxylic acid (152 mg, 0.7 mmol), triethylamine (103 mL, 0.74 mmol), and DPPA in toluene (6 mL) were refluxed for 2 h. Dodecylpyrimidine derivative was added and then the solution was refluxed for 12 h. After cooling, the reaction mixture was washed with acetone and water. The residue was purified with silica-gel column chromatography (eluent: chloroform), followed by recrystallization from ethanol to give pure product.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.03 (s, 1H, N–H), 13.00 (s, 1H, N–H), 12.73 (s, 1H, N–H), 8.49 (s, 1H, anthracene), 8.28 (d, 2H, $J = 4.4$ Hz, anthracene), 8.05 (d, 2H, $J = 4.4$ Hz, anthracene), 7.57 (t, 2H, $J = 7.2$ Hz, anthracene), 7.49 (t, 2H, $J = 7.2$ Hz, anthracene), 5.81 (s, 1H, pyrimidyl), 2.33 (t, 2H, $J = 7.6$ Hz, –CH_2–Ar), 1.53–1.46 (m, 4H), 1.30–1.07 (m, 18H), 0.85 (t, 3H, $J = 7.2$ Hz, CH_3–CH_2–) ppm. ESI-MS cald. for $C_{32}H_{40}N_4O_2$ $[M + H]^+ = 513.32$ found: 513.19.

2-(*N*′-Butylureido)-6-[3-(3-dimethylaminophenoxy)propyl]-4(1*H*)-pyrimidinone (UPyDMA$_4$): A suspension of *N*,*N*-dimethylaniline, pyrimidine derivative (1.09 g, 3.44 mmol), and butyl isocyanate (1 mL) in dry pyridine (15 mL) was refluxed for 4 h. After cooling, the reaction mixture was poured into water to precipitate the product, which was then filtered off and was washed with water and acetone. The crude solid was purified with silica-gel column chromatography (eluent: chloroform), followed by recrystallization from ethanol to give pure product.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.28 (s, 1H, N–H), 11.88 (s, 1H, N–H), 10.13 (s, 1H, N–H), 7.13 (t, 1H, $J = 8.4$ Hz, dimethylaniline), 6.365 (d, 1H, $J = 4.0$ Hz, dimethylaniline), 6.25 (m, 2H, dimethylaniline), 5.88 (s, 1H, pyrimidyl), 4.02 (t, 2H, $J = 6.0$ Hz, O–CH_2–), 3.24 (m, 2H, –N–CH_2–), 2.93 (s, 6H, –N(CH_3)$_2$), 2.70 (t, 2H, $J = 8.0$ Hz, –CH_2–Ar), 2.12 (m, 2H, O–CH_2–CH_2–), 1.59 (m, 2H, –CH_2–C_2H_5), 1.38 (m, 2H, –CH_2–CH_3), 0.93 (t, 3H, $J = 8.0$ Hz, CH_3–CH_2–) ppm. ESI-MS cald. for $C_{20}H_{29}N_5O_3$ $[M + H]^+ = 388.23$ found: 388.24.

2-(*N*′-Butylureido)-6-[4-(3-dimethylaminophenoxy)butyl]-4(1*H*)-pyrimidinone (UPyDMA$_5$): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.25 (s, 1H, N–H), 11.87 (s, 1H, N–H), 10.14 (s, 1H, N–H), 7.13 (t, 1H, $J = 8.4$ Hz, dimethylaniline), 6.36 (d, 1H, $J = 4.0$ Hz, dimethylaniline), 6.25 (m, 2H, dimethylaniline), 5.86 (s, 1H, pyrimidyl), 3.985 (t, 2H, $J = 5.6$ Hz, O–CH_2–), 3.25 (q, 2H, –N–CH_2–), 2.93 (s, 6H, –N(CH_3)$_2$), 2.55 (t, 2H, $J = 6.0$ Hz, –CH_2–Ar), 1.87–1.84 (m, 4H), 1.60 (m, 2H), 1.38 (sextet, 2H, –CH_2–CH_3), 0.93 (t, 3H, $J = 8.0$ Hz, CH_3–CH_2–) ppm. ESI-MS cald. for $C_{21}H_{31}N_5O_3$ $[M + H]^+ = 402.24$ found: 402.24.

2-(*N*′-Butylureido)-6-[5-(3-dimethylaminophenoxy)pentyl]-4(1*H*)-pyrimidinone (UPyDMA$_6$): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.22 (s, 1H, N–H), 11.88 (s, 1H, N–H), 10.13 (s, 1H, N–H), 7.13 (t, 1H, $J = 8.0$ Hz, dimethylaniline), 6.35 (d, 1H, $J = 4.0$ Hz, dimethylaniline), 6.26 (m, 2H, dimethylaniline), 5.83 (s, 1H, pyrimidyl), 3.96 (t, 2H, $J = 6.4$ Hz, O–CH_2–), 3.28–3.22 (m, 2H, –N–CH_2–), 2.93 (s, 6H, –N(CH_3)$_2$), 2.50 (t, 2H, $J = 8.0$ Hz, –CH_2–Ar), 1.85–1.77 (m, 2H, O–CH_2–CH_2–), 1.77–1.69 (m, 2H), 1.64–1.55 (m, 4H), 1.38 (sextent, 2H, –CH_2–CH_3), 0.93 (t, 3H, $J = 8.0$ Hz, CH_3–CH_2–) ppm. ESI-MS cald. for $C_{22}H_{33}N_5O_3$ $[M + H]^+ = 416.26$ found: 416.24.

2-(*N*′-Butylureido)-6-[6-(3-dimethylaminophenoxy)hexyl]-4(1*H*)-pyrimidinone (UPyDMA$_7$): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.20 (s, 1H, N–H), 11.88 (s, 1H, N–H), 10.15 (s, 1H, N–H), 7.13 (t, 1H, $J = 8.4$ Hz, dimethylaniline), 6.35 (d, 1H, $J = 4.0$ Hz, dimethylaniline), 6.26 (m, 2H, dimethylaniline), 5.83 (s, 1H, pyrimidyl), 3.95 (t, 2H, $J = 6.4$ Hz, O–CH_2–), 3.28–3.22 (m, 2H, –N–CH_2–), 2.93 (s, 6H, –N(CH_3)$_2$), 2.475 (t, 2H, $J = 8.0$ Hz, –CH_2–Ar), 1.82–1.74 (m, 2H), 1.72–1.63 (m, 2H), 1.63–1.56 (m, 2H), 1.55–1.44 (m, 4H), 1.38 (sextent, 2H, –CH_2–CH_3), 0.93 (t, 3H, $J = 8.0$ Hz, CH_3–CH_2–) ppm. ESI-MS cald. for $C_{23}H_{35}N_5O_3$ $[M + H]^+ = 430.27$ found: 430.24.

2-(*N*′-Butylureido)-6-[7-(3-dimethylaminophenoxy)heptyl]-4(1*H*)-pyrimidinone (UPyDMA$_8$): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.18 (s, 1H, N–H), 11.88 (s, 1H, N–H), 10.15 (s, 1H, N–H), 7.12 (t, 1H, $J = 8.4$ Hz, dimethylaniline), 6.36 (d, 1H, $J = 4.0$ Hz, dimethylaniline), 6.28 (m, 2H, dimethylaniline), 5.82 (s, 1H, pyrimidyl), 3.94 (t, 2H, $J = 6.4$ Hz, O–CH_2–), 3.28–3.22 (m, 2H, –N–CH_2–), 2.92 (s, 6H, –N(CH_3)$_2$), 2.45 (t, 2H, $J = 8.0$ Hz, –CH_2–Ar), 1.81–1.72 (m, 2H), 1.72–1.28 (m, 12H), 0.94 (t, 3H, $J = 8.0$ Hz, CH_3–CH_2–) ppm. ESI-MS cald. for $C_{24}H_{37}N_5O_3$ $[M + H]^+ = 444.29$ found: 444.30.

2-(*N*′-Butylureido)-6-[8-(3-dimethylaminophenoxy)octyl]-4(1*H*)-pyrimidinone (UPyDMA$_9$): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.18 (s, 1H, N–H), 11.88 (s, 1H, N–H), 10.16 (s, 1H, N–H), 7.12 (t, 1H, $J = 8.4$ Hz, dimethylaniline), 6.36 (d, 1H, $J = 4.0$ Hz, dimethylaniline), 6.28 (m, 2H, dimethylaniline), 5.82 (s, 1H, pyrimidyl), 3.94 (t, 2H, $J = 6.4$ Hz, O–CH_2–), 3.28–3.22 (m, 2H,

–N–CH_2–), 2.92 (s, 6H, –$N(CH_3)_2$), 2.45 (t, 2H, $J = 8.0$ Hz, –CH_2–Ar), 1.81–1.72 (m, 2H), 1.72–1.25 (m, 14H), 0.93 (t, 3H, $J = 8.0$ Hz, CH_3–CH_2–) ppm. ESI-MS cald. for $C_{25}H_{39}N_5O_3$ $[M + H]^+ = 458.31$ found: 458.32.

2-(*N*′-Butylureido)-6-[9-(3-dimethylaminophenoxy)nonyl]-4(1*H*)-pyrimidinone (UPyDMA$_{10}$): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.18 (s, 1H, N–H), 11.87 (s, 1H, N–H), 10.15 (s, 1H, N–H), 7.12 (t, 1H, $J = 8.4$ Hz, dimethylaniline), 6.36 (d, 1H, $J = 4.0$ Hz, dimethylaniline), 6.28 (m, 2H, dimethylaniline), 5.82 (s, 1H, pyrimidyl), 3.94 (t, 2H, $J = 6.4$ Hz, O–CH_2–), 3.28–3.22 (m, 2H, –N–CH_2–), 2.92 (s, 6H, –$N(CH_3)_2$), 2.45 (t, 2H, $J = 8.0$ Hz, –CH_2–Ar), 1.81–1.72 (m, 2H), 1.72–1.24 (m, 16H), 0.93 (t, 3H, $J = 8.0$ Hz, CH_3–CH_2–) ppm. ESI-MS cald. for $C_{26}H_{41}N_5O_3$ $[M + H]^+ = 472.32$ found: 472.34.

2-(*N*′-Butylureido)-6-[10-(3-dimethylaminophenoxy)decyl]-4(1*H*)-pyrimidinone (UPyDMA$_{11}$): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.18 (s, 1H, N–H), 11.88 (s, 1H, N–H), 10.15 (s, 1H, N–H), 7.12 (t, 1H, $J = 8.4$ Hz, dimethylaniline), 6.36 (d, 1H, $J = 4.0$ Hz, dimethylaniline), 6.28 (m, 2H, dimethylaniline), 5.82 (s, 1H, pyrimidyl), 3.94 (t, 2H, $J = 6.4$ Hz, O–CH_2–), 3.28–3.22 (m, 2H, –N–CH_2–), 2.92 (s, 6H, –$N(CH_3)_2$), 2.45 (t, 2H, $J = 8.0$ Hz, –CH_2–Ar), 1.81–1.72 (m, 2H), 1.72–1.24 (m, 18H), 0.94 (t, 3H, $J = 8.0$ Hz, CH_3–CH_2–) ppm. ESI-MS cald. for $C_{27}H_{43}N_5O_3$ $[M + H]^+ = 486.34$ found: 486.34.

2-(*N*′-Butylureido)-6-[11-(3-dimethylaminophenoxy)undecyl]-4(1*H*)-pyrimidinone (UPyDMA$_{12}$): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.18 (s, 1H, N–H), 11.88 (s, 1H, N–H), 10.16 (m, 1H, N–H), 7.12 (t, 1H, $J = 8.4$ Hz, dimethylaniline), 6.35 (d, 1H, $J = 4.0$ Hz, dimethylaniline), 6.28 (m, 2H, dimethylaniline), 5.83 (s, 1H, pyrimidyl), 3.94 (t, 2H, $J = 6.4$ Hz, O–CH_2–), 3.28–3.22 (m, 2H, –N–CH_2–), 2.93 (s, 6H, –$N(CH_3)_2$), 2.45 (t, 2H, $J = 8.0$ Hz, –CH_2–Ar), 1.82–1.74 (m, 2H), 1.72–1.28 (m, 20H), 0.93 (t, 3H, $J = 8.0$ Hz, CH_3–CH_2–) ppm. ESI-MS cald. for $C_{28}H_{45}N_5O_3$ $[M + H]^+ = 500.35$ found: 500.36.

3-Dodecyloxy-*N*,*N*-dimethylaniline (d-DMA). A mixture of *N*,*N*-3-dimethylaminophenol (5.00 g, 36.4 mmol), dodecyl bromide (9.36 g, 37.5 mmol), and K_2CO_3 (5.06 g, 36.6 mmol) in 2-butanone (100 mL) was refluxed for 12 h. After cooling, the reaction mixture was filtered, and the solvent was evaporated. The residue was purified by silica-gel column chromatography (eluent: hexane:ethyl acetate = 9:1), followed by recrystallization from hexane to give pure product. (Yield 30%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.13 (t, 1H, $J = 8.4$ Hz, dimethylaniline), 6.37 (d, 1H, $J = 4.0$ Hz, dimethylaniline), 6.28 (m, 2H, dimethylaniline), 3.95 (t, 2H, $J = 6.0$ Hz, O–CH_2–), 2.93 (s, 6H, –$N(CH_3)_2$), 1.78 (m, 2H, O–CH_2–CH_2–), 1.43–1.27 (m, 20H), 0.89 (t, 3H, $J = 8.0$ Hz, CH_3–CH_2–) ppm.

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References

1 P. S. Corbin, S. C. Zimmerman, *J. Am. Chem. Soc.* **1998**, *120*, 9710.
2 T. Hayashi, H. Ogoshi, *Chem. Soc. Rev.* **1997**, *26*, 355.
3 P. Piotrowiak, *Chem. Soc. Rev.* **1999**, *28*, 143.
4 M. D. Ward, *Chem. Soc. Rev.* **1997**, *26*, 365.
5 A. J. Myles, N. R. Branda, *J. Am. Chem. Soc.* **2001**, *123*, 177.
6 J. L. Sessler, M. Sathiosatham, C. T. Brown, T. A. Rhodes, G. Wiederrecht, *J. Am. Chem. Soc.* **2001**, *123*, 3655.
7 G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, **1997**.
8 H. Kihara, T. Kato, T. Uryu, J. M. J. Fréchet, *Chem. Mater.* **1996**, *8*, 961.
9 J. M. Lehn, *Makromol. Chem. Makromol. Symp.* **1993**, *69*, 1.
10 P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133.
11 L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071.
12 R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. Ky Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, *Science* **1997**, *278*, 1601.
13 H. K. Ky Hirschberg, L. Brunsveld, A. Ramzi, J. A. J. M. Vekemans, R. P. Sijbesma, E. W. Meijer, *Nature* **2000**, *407*, 167.
14 E. H. A. Beckers, v. P. A. Hal, A. P. H. J. Schenning, A. El-Ghayoury, E. Peeters, M. T. Rispens, J. C. Hummelen, E. W. Meijer, *J. Mater. Chem.* **2002**, *12*, 2054.
15 M. Ikegami, T. Arai, *Chem. Lett.* **2001**, 694.
16 W. R. Ware, J. D. Holmes, D. R. Arnold, *J. Am. Chem. Soc.* **1974**, *96*, 7861.
17 J. Saltiel, D. E. Townsend, B. D. Watson, P. Shannon, S. L. Finson, *J. Am. Chem. Soc.* **1977**, *99*, 884.
18 F. H. Beijer, R. P. Sijbesma, H. Kooijman, A. L. Spek, E. W. Meijer, *J. Am. Chem. Soc.* **1998**, *120*, 6761.
19 S. L. Murov, I. Carmichael, G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York, **1993**.
20 N. Mataga, T. Kubota, *Molecular Interactions and Electronic Spectra*, Marcel Dekker, New York, **1970**, p. 442.
21 G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond*, IUCr/Oxford, Oxford, **1999**.
22 S. Masaki, T. Okada, N. Mataga, Y. Sakata, S. Misumi, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1277.
23 T. Okada, T. Saito, N. Mataga, Y. Sakata, S. Misumi, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 331.
24 Y. Hatano, M. Yamamoto, Y. Nishijima, *J. Phys. Chem.* **1978**, *82*, 367.