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Photoinduced Triplet−Triplet Energy Transfer via the 2-Ureido-4[1*H*]-pyrimidinone Self-Complementary Quadruple Hydrogen-Bonded Module

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Phosphorescence quenching and flash photolysis experiments demonstrate that photoinduced intra-assembly triplet−triplet energy transfer can take place via a 2-ureido-4[1*H*]-pyrimidinone-bridged benzophenone−naphthalene assembly **I** with a rate constant of 3.0×10^6 s^{-1} and an efficiency of 95% in CH_2Cl_2. This new finding suggests that with high binding strength and directionality, the 2-ureido-4[1*H*]-pyrimidinone hydrogen-bonded module may serve as a new model to illustrate the fundamental principles governing the triplet−triplet energy-transfer process through hydrogen bonds.

1. Introduction

Photoinduced electronic energy transfer is an important process of the photosynthetic reaction center in nature and thus has been the subject of intense studies.[1,2] It is generally accepted that triplet−triplet energy transfer, namely, energy transfer from a triplet excited donor to the ground state of an acceptor, proceeds via the Dexter electron-exchange mechanism,[3] which requires a strong donor−acceptor orbital overlap either directly or mediated by a bridge, and decay is therefore dependent on the donor−acceptor distance. In principle, the rate constant of triplet−triplet energy transfer would be negligibly small as the donor−acceptor distance is beyond the sum of their van der Waals radii.[3] Nonetheless, long-range intramolecular triplet−triplet energy transfer has been observed in bichromophoric molecules separated by a covalent rigid or flexible saturated bridge.[4−7] For the covalent rigid-bridged donor−acceptor molecules, the "all-trans" arrangement of the σ bonds would facilitate orbital mixing of the donor and the acceptor with that of the bridge; thereby, a "through bond" mechanism operates, while in the covalent flexible-bridged molecules, rapid conformational equilibrium would make a fraction of the excited molecules experience conformations that allow the donor to associate with the acceptor "through space" mechanism. Therefore, determining the extent of intramolecular electronic interactions between the donor and acceptor that occur by the "through-bond" or the "through-space" mechanism has been a long-standing interest.

Hydrogen bonds are ideal noncovalent interactions to construct and characterize higher-order arrays of supramolecular architectures owing to their high directionality and selectivity.[8] Synthetic hydrogen-bonded donor−acceptor assemblies have also been used to unravel the factors that govern the triplet−triplet energy-transfer process, which is directly relevant to the energy transfer in biological systems and appears to be promising in applications in molecular photonic materials and devices. O'Donnell et al.,[9a] who prepared a single hydrogen-bonded carbazole−benzophenone assembly, and Sessler and Harriman et al.,[9b−d] who constructed donor−acceptor systems linked by triple hydrogen bonds, observed the intra-assembly triplet−triplet energy transfer. However, no further study that might elucidate the key mechanistic questions associated with the triplet−triplet energy transfer through hydrogen bonds has been reported so far. The lack of such model systems may be due to the fact that the fairly weak hydrogen-bonded interactions and low binding constants only allow a small fraction of the donor and acceptor to associate with each other, and the remaining molecules are free to diffuse in solution. The diffusion encounter, rather than the through-hydrogen-bond interaction between the triplet excited donor with relatively long lifetime and the ground state of the acceptor, has always been invoked to account for the observed triplet−triplet energy transfer.[9] Thus, developing new hydrogen-bonded donor−acceptor assemblies with higher binding strength is badly required.

The 2-ureido-4[1*H*]-pyrimidinone motif reported by Meijer and Sijbesma represents a fascinating self-complementary quadruple hydrogen-binding module.[10] Benefiting from its intermolecular and intramolecular hydrogen bonds, the dimerization constant of 2-ureido-4[1*H*]-pyrimidinones can exceed 10^7 M^{-1} in nonpolar solvents like chloroform and toluene.[10] With the great binding strength and directionality, the 2-ureido-4[1*H*]-pyrimidinone binding module has shown extensive applications in assembling and disassembling supramolecular systems.[10−12] Recently, the 2-ureido-4[1*H*]-pyrimidinone module has also been employed to create hydrogen-bonded donor−acceptor dyads, with only a singlet energy-transfer process operated by the Föster mechanism in several cases observed.[13]

To examine whether the 2-ureido-4[1*H*]-pyrimidinone hydrogen-bonded module could mediate the triplet−triplet energy transfer, 2-ureido-4[1*H*]-pyrimidinone-bridged assembly **I** (Chart 1) has been designed in this work. The benzophenone and naphthalene was used as the respective donor and acceptor because they are typically an exothermic triplet−triplet energy-transfer pair. It is anticipated that (1) the high binding strength of the 2-ureido-4[1*H*]-pyrimidinone quadruple hydrogen-binding unit would enhance the intra-assembly donor−acceptor interaction even at low concentration, (2) with the directionality and rigidity of the hydrogen-bonded module,[10−12] the naphthalene

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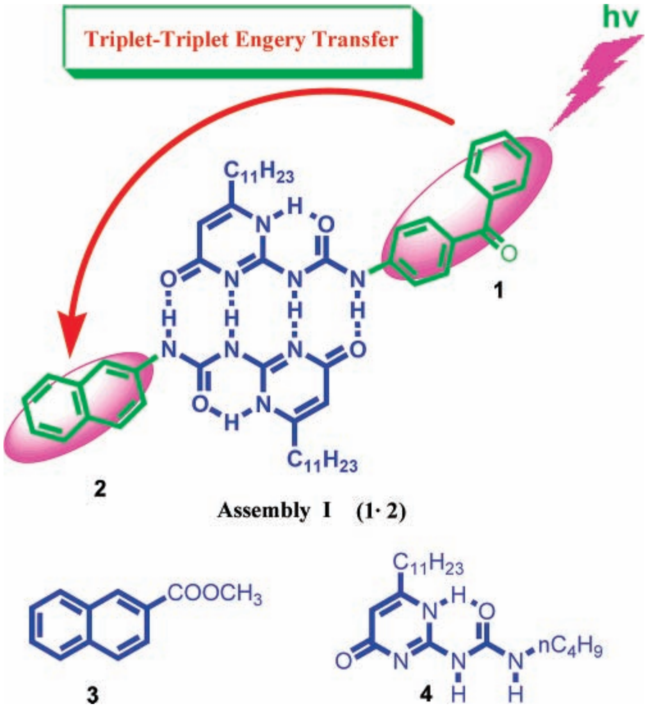
CHART 1: The 2-Ureido-4[1*H*]-pyrimidinone Hydrogen-Bonded Benzophenone−Naphthalene Assembly I (1·2) and the Model Compounds of 3 and 4

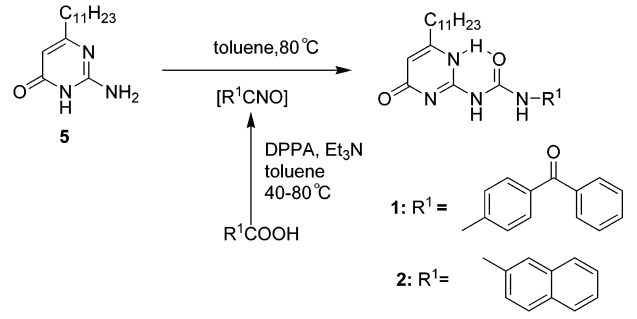


and benzophenone chromophores in assembly **I** would be extended to the opposite direction of the AADD array, as sketched in Chart 1, and (3) the direct attachment of the two typical small chromophores to the rigid 2-ureido-4[1*H*]-pyrimidinone quadruple hydrogen-binding unit would inhibit the collisions between the donor and acceptor via the through space mechanism. In the present work, we report that photoinduced intra-assembly triplet−triplet energy transfer can take place via the 2-ureido-4[1*H*]-pyrimidinone-bridged benzophenone−naphthalene assembly **I**. The naphthalene group quenches the phosphorescence of the benzophenone efficiently upon selective excitation of the benzophenone in assembly **I** at 77 K, while the same observation is absent in the mixture of **1** and **3** (or **4**) under the same conditions. A flash photolysis experiment at room temperature indicates that the intra-assembly triplet−triplet energy transfer occurs with a rate constant of 3.0×10^6 s^{-1} and an efficiency of 95% in CH_2Cl_2. 2-Ureido-4[1*H*]-pyrimidinone hydrogen bonds here not only act as rigid scaffolds that fix the well-defined relative separations and orientations of the chromophores but also play a crucial role in mediating the photoinduced intra-assembly triplet−triplet energy-transfer process.

2. Experimental Section

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance dpx 400 MHz instruments using TMS as the internal standard. ESI-MS was performed on a Bruker APEX II mass spectrometer. Elemental analyses were performed on a Carlo Erba1106 analyzer. The UV/vis spectrum was obtained using a Shimadzu 1601PC spectrophotometer. Phosphorescence spectral measurements were carried out on a Hitachi 4500 fluorescence spectrophotometer in 2-MTHF at 77 K. Nanosecond transient absorption spectra were performed on a LP-920 pump−probe spectroscopic setup (Edinburgh) in CH_2Cl_2 at room temperature. The excited source was the unfocused third-harmonic (355 nm, 7 ns fwhm) output of a Nd:YAG laser (Continuum Surelite II); the probe light source was a pulse xenon lamp. Electrochemical measurements were performed with a Princeton Applied Research potentiostat-galvanostat model 283 potentiostat in dry THF with a Pt wire auxiliary electrode, a $Ag/AgNO_3$ nonaqueous reference electrode, and a glass carbon working electrode.

SCHEME 1: Synthetic Routes for Compounds 1 and 2



NaH: 52% mineral oil dispersion. Anhydrous THF and toluene were obtained by distillation from sodium/benzophenone. Pyridine and Et_3N were heated under reflux with CaH_2 for 3 h and then distilled. Dichloromethane was washed with H_2SO_4 and H_2O, dried with $CaCl_2$, and distilled from CaH_2. Other reagents were of analytical grade and were used as received.

2-(*p*-Benzoylbenzo)uredio-6-(1-undecyl)-4[1*H*]-pyrimidinone (1): *p*-Benzoylbenzoic acid (403 mg, 1.783 mmol) and Et_3N (0.3 mL, 2.19 mmol) in dry toluene (10 mL) were stirred under an argon atmosphere to dissolve completely. Diphenylphosphoryl azide (DPPA) (0.49 mL, 2.29 mmol) was added into the mixture. Upon heating at 40 °C for 1 h and at then 80 °C for 4 h, **5**[11c] (530 mg, 2.0 mmol) was added into the mixture and subsequently stirred at 80 °C for 16 h. After evaporation of the solvent, the resultant residue was thoroughly washed with cold methanol and subjected to the purification by chromatography on silica gel (CH_2Cl_2/MeOH, 100:1). Recrystallization from $CH_3OH/CHCl_3$ afforded the product as a white solid in 73% yield. ^1H NMR ($CDCl_3$, δ ppm): 12.95 (s, 1H), 12.58 (s, 1H), 12.35 (s, 1H), 7.85 (m, 4H), 7.78 (d, $J = 7.2$, 2H), 7.60 (m, 1H), 7.48 (m, 2H), 5.95 (s, 1H) 2.48 (br, 2H), 1.66 (br,2H), 1.27 (m, 16H), 0.87 (t, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 195.8, 173.1, 154.8, 154.6, 153.1, 142.6, 138.2, 132.8, 132.3, 131.6, 130.1, 128.4, 119.7, 106.5, 32.7, 32.0, 29.7, 29.6, 29.5, 29.3, 29.0, 27.0, 22.8, 14.3. MS (ESI): *m/z* 489.4 $[M + H]^+$. Anal. Calcd (%) for $C_{29}H_{36}N_4O_3$: C 71.28, H 7.48, N 11.47. Found: C 71.01, H 7.45, N 11.39.

2-(2-Naphthalene)uredio-6-(1-undecyl)-4[1*H*]-pyrimidinone (2): The synthetic procedure is similar to that for compound **1**. ^1H NMR ($CDCl_3$, δ ppm): 13.00 (s, 1H), 12.42 (s, 1H), 12.28 (s, 1H), 8.30 (s, 1H), 7.81 (m, 4H), 7.45 (t, 1H), 7.38 (m, 1H), 5.82 (br, 1H), 2.15 (m, 2H), 1.26 (m, 18H), 0.87 (t, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 173.1, 154.8, 154.6, 153.0, 136.2, 134.1, 130.6, 128.7, 127.9, 127.6, 126.3, 124.9, 120.8, 116.9, 105.9, 32.5, 32.1, 29.7, 29.6, 29.5, 29.3, 29.0, 26.5, 22.9, 14.3. MS (ESI): *m/z* 435.4 $[M + H]^+$. Anal. Calcd (%) for $C_{26}H_{34}N_4O_2$: C 71.86, H 7.89, N 12.89. Found: C 71.66, H 7.91, N 12.79.

3. Results and Discussion

Synthesis and Characterization of Assembly I. The preparations of the key monomers for assembly **I** are summarized in Scheme 1. Briefly, the urediopyrimidinones of **1** and **2** were readily synthesized in good chemical yield in one pot by reacting compound **5** with isocyanate, which was generated via a Curtius rearrangement. Here, the undecyl groups were present for solubility purposes.

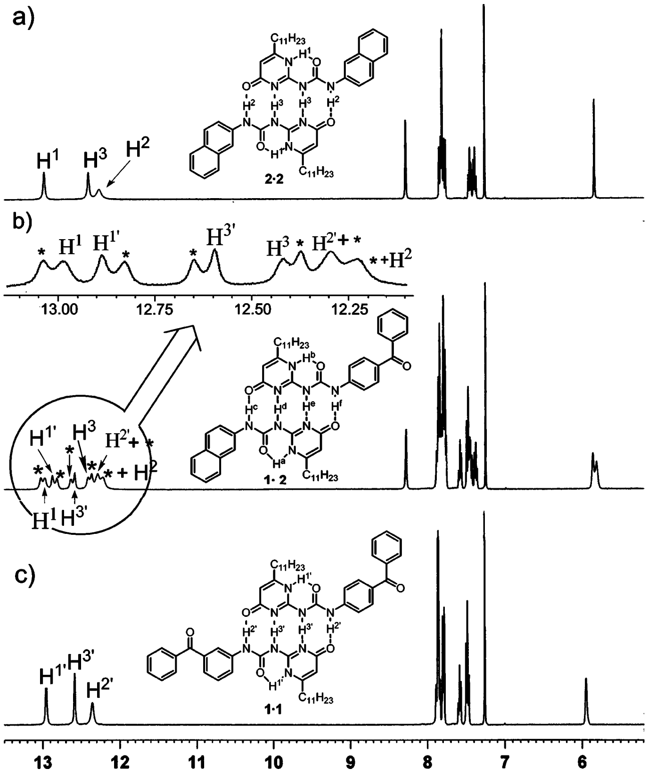


Figure 1. Partial 400 MHz ^{1}H NMR spectra of dimers in CDCl$_3$: (a) **2·2**; (b) 1:1 mixture of **1** and **2**; inset: enlarged ^{1}H NMR spectrum downfield in the range of 12.00−14.00 ppm; (c) **1·1**.

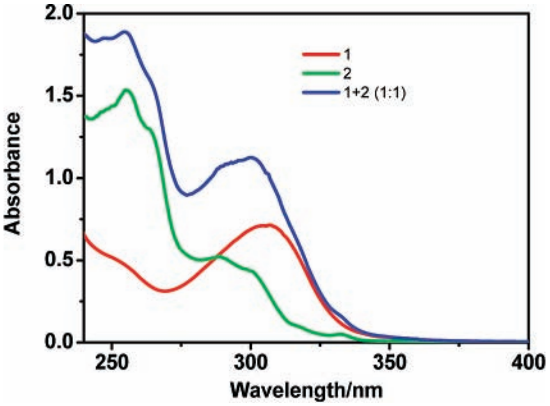


Figure 2. The absorption spectra of **1**, **2**, and a 1:1 mixture of **1** and **2** in CH$_2$Cl$_2$; [**1**] = [**2**] = 2 × 10^{-5} M.

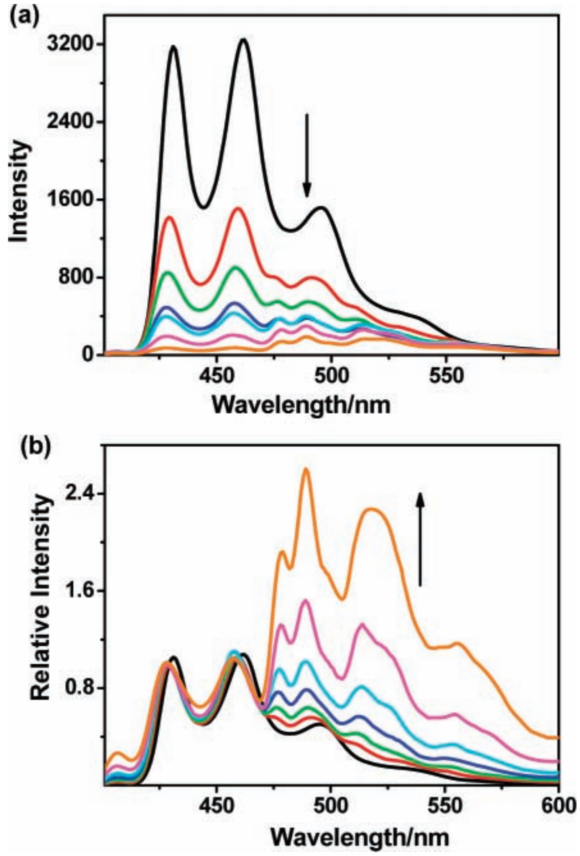


Figure 3. Phosphorescence spectra (a) and normalized phosphorescence spectra at 430 nm (b) of **1** in the absence and presence of **2** in 2-methyltetrahydrofuran at 77 K (excitation wavelength: 310 nm); [**1**] = 2 × 10^{-5} M; [**2**] = 0, 0.5, 1.0, 2.0, 4.0, 8.0, 20 × 10^{-5} M.

^{1}H NMR spectra reveal that **1** and **2** exist as homodimers **1·1** and **2·2** in the nonpolar solvents like CD$_2$Cl$_2$ and CDCl$_3$, respectively. Figure 1 gives the partial spectra of dimers of **1·1** and **2·2** and 1:1 mixture of **1** and **2** in CDCl$_3$. The large downfield shift in NH protons (>12 ppm) provides direct evidence for their involvement in strong hydrogen bonding. Dilution of **1** and **2** solutions in CDCl$_3$ to 1 × 10^{-5} M did not lead to an observable dissociation, indicating the low limit for the binding constant to be 10^5 M^{-1}, consistent with the value for similar compounds.[10a] Mixing 1 equiv of **1** with 1 equiv of **2** in CDCl$_3$ caused partial dissociation of homodimers **1·1** and **2·2** and led to the formation of assembly **I** (Figure 1a−c). The relative signal strengths of **1·1** and **2·2** in the 1:1 mixture solution were decreased, accompanied by a new set of signals at the downfield (H^a−H^f) labeled with an asterisk (Figure 1b). Considering the reversibility and the similar binding constants for the homo- and heteroassembly, we inferred that **1·1**, **1·2**, and **2·2** existed in a ratio of 1:2:1 in the 1:1 mixture of **1** and **2** by integration of the H^1−H^3 peaks for **2·2**, H^a−H^f for **1·2**, and H$^{1'}$−H$^{3'}$ for **1·1**.

Phosphorescence Quenching The absorption spectra of **1**, **2**, and a 1:1 mixture of the two compounds in CH$_2$Cl$_2$ are shown in Figure 2. The absorption spectrum of the 1:1 mixture resembles the superposition of the spectra of **1** and **2**, suggesting the absence of significant electronic interaction between the benzophenone and the naphthalene chromophores in assembly **I** (**1·2**) at the ground state. Importantly, the low-energy characteristic absorption of **1** allows for the selective excitation of the benzophenone at a spectral region where the naphthalene in **2** is almost transparent. Such a spectral behavior was also evidenced in their 2-methyltetrahydrofuran (2-MTHF) solution (Figure S1, Supporting Information).

An initial observation for the intra-assembly triplet−triplet energy-transfer process in assembly **I** (**1·2**) came from steady-state phosphorescence quenching measurements. The phosphorescence spectra were measured in glassy 2-MTHF at 77 K. The family spectra of **1** taken in the course of a titration are shown in Figure 3. In the absence of **2**, no fluorescence from **1** was observed with the excitation wavelength at 310 nm, while phosphorescence of the benzophenone with maxima at 431, 462, and 495 and a shoulder at 538 nm was detected. Progressive addition of **2** into a 2-MTHF solution of **1** led to a growth with maxima at 476, 488, 512, and 555 nm, typical for phosphorescence of the naphthoate,[14a−c] at the expense of the benzophenone phosphorescence. Apparently, the naphthalene group in **2** dramatically quenched the phosphorescence from the benzophenone chromophore in **1**, thus giving rise to its phosphorescence. In contrast, with the addition of model compounds of **3** or **4** under the same conditions (Figures S2 and S3, Supporting

Information), neither a change in the intensity nor in the shape of the phosphorescence characters of **1** was observed, thus excluding any possible inter-assembly interactions between the donor and the acceptor in the excited state. Upon increasing the concentration of **3** higher than 4×10^{-4} M, the phosphorescence of **1** (2×10^{-5} M) was also altered, with an intermolecular quenching constant of 5.2×10^{2} s^{-1} (Figure S4, Supporting Information). Evidently, the bimolecular quenching rate constant is too negligibly small to compete with the intra-assembly interactions between the donor and the acceptor in assembly **I**.

The anisotropic phosphorescence measurements have also been investigated. Since the relative orientations of the absorption dipole and emission dipole of a chromophore in a rigid matrix are fixed, when the chromophore absorbs polarized radiation, its emission will retain the memory of the excitation polarization.[15] The degree of polarization P is defined as

$$P(\lambda) = \frac{I_{||}(\lambda) - I_{\perp}(\lambda)}{I_{||}(\lambda) + I_{\perp}(\lambda)} \qquad (1)$$

where $I_{||}$ and $I_{\perp}$ denote the intensities of the emitted light polarized parallel and perpendicular to the polarization of the incident light, respectively. It has been well-known that the energy transfer from one chromophore to the other with different orientations leads to depolarization. Representative P values at $\lambda_{\mathrm{em}} = 432$ nm for **1·1** and a 1:1 mixture of **1** and **2** in 2-MTHF glassy solution at 77 K were found to be identical (0.33) (Figure S6, Supporting Information). The similar polarization suggests that the chromophores in assembly **I** have a preferred orientation despite the fact that many different orientations may be involved, especially at 77 K.

Since the energy of the singlet excited state of benzophenone (325 kJ/mol) is much lower than that of naphthalene (346 kJ/mol)[14d] (Figure 2), the singlet energy transfer from the excited benzophenone chromophore to the naphthalene group in assembly **I** is thermodynamically impossible. On the other hand, the triplet energy of benzophenone (289 kJ/mol) is much higher than that of naphthalene (251 kJ/mol), which indicates that the triplet−triplet energy transfer from the triplet excited benzophenone chromophore to the naphthalene group is exothermic. Thus, the phosphorescence quenching of the benzophenone phosphorescence by the naphthalene group in assembly **I** (**1·2**) might be attributed to the photoinduced intra-assembly triplet−triplet energy-transfer process.

One may suspect that the phosphorescence quenching may be a result of photoinduced intra-assembly electron-transfer processes. To rule out such a possibility, we calculated the free-energy change involved in an electron-transfer process by the Rehm−Weller equation[16]

$$\Delta G = e(E_{\mathrm{ox}}(\mathrm{D/D^{+\bullet}}) - E_{\mathrm{red}}(\mathrm{A/A^{-\bullet}})) - E_{00} - \frac{e^2}{4\pi\epsilon_0\epsilon_{\mathrm{s}}R} - \frac{e^2}{8\pi\epsilon_0}\left(\frac{1}{r^+} + \frac{1}{r^-}\right)\left(\frac{1}{\epsilon_{\mathrm{ref}}} - \frac{1}{\epsilon_{\mathrm{s}}}\right) \qquad (2)$$

$E_{\mathrm{ox}}(\mathrm{D/D^{+\bullet}})$ and $E_{\mathrm{red}}(\mathrm{A/A^{-\bullet}})$ represent the redox potentials of the donor and the acceptor, determined as −2.24 V (vs Ag/Ag^{+}) for **1** and +1.15 V (vs Ag/Ag^{+}) for **2** in tetrahydrofuran (THF), respectively. E_{00} is the excited-state energy and, in this study, represents the triplet-state energy of **1** (289 kJ/mol); ϵ_0, ϵ_{s}, and ϵ_{ref} refer to the vacuum permittivity and the dielectric constants of CH_2Cl_2 and THF, respectively. Evaluated by the Hyperchem 5.1 (CNDO) program, r^{+} and r^{-} were taken as 3 and 4 Å, respectively. With reference to the crystal structure of the 2-ureido-4[1*H*]-pyrimidinone motif,[10a,12a] the urea functionality is in a trans−trans conformation, and an intramolecular hydrogen bond is present from the pyrimidine N−H to the urea carbonyl group. A preorganized array of hydrogen-bonding sites forms a centrosymmetrical dimer that is almost coplanar. The chromophores are bridged by the building block and extended to the opposite direction, as shown in Chart 1. With the directionality and rigidity, the benzophenone and naphthalene in assembly **I** will retain the structural rigidity in solution and arrange side-by-side with the edge-to-edge separation being 10 Å, namely, R. Calculation according to eq 2 shows that $\Delta G = 14.5$ kJ/mol for the triplet electron-transfer process in CH_2Cl_2, suggesting that electron transfer from the naphthalene to the triplet state of the benzophenone group would be very inefficient. Considering the intersystem crossing efficiency from the singlet to the triplet excited state of the benzophenone chromophore equals unity, the singlet electron-transfer process should not be dominant if it occurs. Therefore, the triplet−triplet energy transfer should be responsible for the intra-assembly benzophenone phosphorescence quenching and the naphthalene phosphorescence enhancing in assembly **I**. The smaller phosphorescence quantum yield of the naphthalene group leads to the observed relatively weak phosphorescence as compared with that of the benzophenone chromophore.

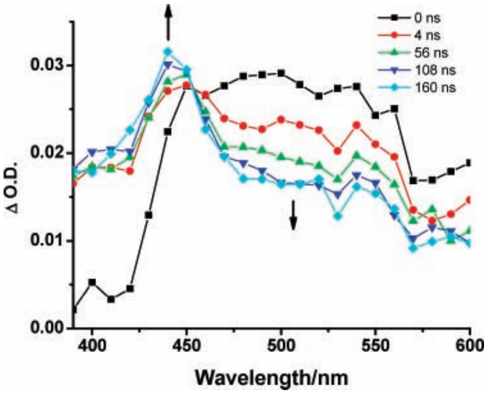


Figure 4. Transient absorption spectra of the mixture of **1** and **2** in CH_2Cl_2 at room temperature; $\lambda_{\mathrm{ex}} = 355$ nm; [**1**] = 1.5×10^{-4} M; [**2**] = 1.5×10^{-3} M.

Flash Photolysis. The intra-assembly triplet−triplet energy transfer in assembly **I** is further evidenced by a flash photolysis investigation at room temperature. Pulsed laser photolysis investigations were performed in degassed CH_2Cl_2 by using 355 nm excitation light, giving rise to a strong transient absorption spectrum of the lowest triplet state of the benzophenone[7d,14c] with a maximum at 530 nm for **1** immediately after the laser pulse, which is readily quenched by oxygen. Significantly, the triplet-state absorption at 530 nm for the mixture of **1** and **2** ([**1**] = 1.5×10^{-4} M, [**2**] = 1.5×10^{-3} M, in which 95% of **1** interacts with **2** to form assembly **I**) is progressively replaced by a new absorption in the region of 400−500 nm (Figure 4), which was ascribed to the lowest triplet state of the naphthalene chromophore.[14] Evidently, the transient absorption of assembly **I** displayed a growth of naphthalene absorption at the expense of the benzophenone, with an isobestic point at 450 nm. Moreover, the absorption decay at 530 nm and the growth at 440 nm occur on the same time scale (Figure S8, Supporting Information). In this case, only the benzophenone in assembly **I** was excited; the triplet−triplet energy transfer from the benzophenone chromophore to the naphthalene group in assembly **I** indeed takes place.

Analysis of the transient spectrum found that in the absence of **2**, the transient decay of **1** at 530 nm could be well-described by a monoexponential function with the lifetime of 6.0 μs (τ_1) in CH_2Cl_2 solution. While in the presence of **2** the feature of the transient absorption is identical to that of **1** in the beginning, it is gradually replaced by a new absorption at 400−500 nm. In the case of the ratio of **1** to **2** being 1:10, the lifetime of the benzophenone at 530 nm in assembly **I** was found to be 310 ns (τ_2) (Figure S9, Supporting Information), while that of the naphthalene at 440 nm was about 25.6 μs. The shorter lifetime of the benzophenone triplet state in assembly **I** (**1·2**) in comparison with that of **1** is consistent with the phosphorescence quenching experiment, indicating that the intra-assembly triplet−triplet energy transfer from the benzophenone chromophore to the naphthalene group in assembly **I** operates. According to eqs 3 and 4, the rate constant and efficiency for this energy transfer can be subsequently obtained as $k_{ET} = 3.0 \times 10^6\ s^{-1}$ and $\Phi_{ET} = 95\%$, respectively

$$k_{ET} = (1/\tau_2) - (1/\tau_1) \tag{3}$$

$$\Phi_{ET} = 1 - \tau_2/\tau_1 \tag{4}$$

4. Conclusions

In summary, steady-state phosphorescence quenching at 77 K and flash photolysis experiments at room temperature demonstrate that selective excitation of the benzophenone chromophore in assembly **I** leads to a long-range intra-assembly triplet−triplet energy transfer to the naphthalene group. The efficiency is up to 95%, and the rate constant is ~3.0 × 10^6 s^{-1} in CH_2Cl_2. As we know, triplet−triplet energy transfer occurs via the Dexter electron-exchange mechanism, and its rate constant decreases exponentially with donor−acceptor distance. When the donor−acceptor distance increases beyond the sum of their van der Waals radii, this kind of energy transfer process is generally negligible. In our case, the benzophenone and the naphthalene in assembly **I** arrange side-by-side with a much larger separation. Since the rigid structure prevents the donor and acceptor from any collisions through the solvent or space mechanism, the highly efficient intra-assembly triplet−triplet energy transfer in assembly **I** occurs through the hydrogen bonds. This new finding indicates that the 2-ureido-4[1*H*]-pyrimidinone hydrogen-bonding module with high binding strength and directionality may serve as a new model system to illustrate the fundamental principles governing the triplet−triplet energy-transfer process through the hydrogen-bond mechanism.

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Supporting Information Available: Absorption spectra of **1** and **2** in 2-methyltetrahydrofuran; phosphorescence spectra of **1** in the absence and presence of model compounds; calculation of the observed phosphorescence quenching rate constant; plot of $I_0/I - 1$ as a function of [**3**] and [**2**]; anisotropic phosphorescence spectra; transient absorption spectra of the mixture of **1** and **2**; the growth and decay of the transient absorption of the mixture of **1** and **2** at 440 and 530 nm; the decay of transient absorption at 530 nm. This material is available free of charge via the Internet at http://pubs.acs.org.

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