

# Inner-assembly singlet energy transfer in naphthalene–anthracene system linked by 2-ureido-4{1*H*}-pyrimidinone binding module

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**Abstract**—Naphthalene–naphthalene, anthracene–anthracene, and naphthalene–anthracene assemblies **1.1**, **2.2**, and **1.2** linked by 2-ureido-4{1*H*}-pyrimidinone binding module were synthesized. Fluorescence quenching and lifetime measurements demonstrate that the inner-assembly singlet energy transfer from naphthalene to anthracene in **1.2** occurs with the efficiency of ca. 89% and rate constant of ca.  $9.8 \times 10^8 \text{ s}^{-1}$ . Förster energy transfer mechanism operates in this energy transfer process.

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## 1. Introduction

Hydrogen bonding networks play an important role in biological energy- and electron-transfer processes.<sup>1,2</sup> Considerable research efforts have been devoted to the study of these processes that occur in hydrogen-bonded systems in order to understand the photosynthetic reaction center in plants and provide a base for designing molecular photonic devices and artificial solar-energy-conversion systems.<sup>1–5</sup> Early studies<sup>1–4</sup> have established that doubly hydrogen-bonded systems such as carboxylate–urea<sup>3a</sup> and amidinium–carboxylate,<sup>3b,c</sup> and triply hydrogen-bonded systems such as cyanuric acid–melamine and cytosine–guanine<sup>4</sup> motifs, could be used to construct various molecular assemblies, and the photo-induced energy- and (or) electron-transfer can be achieved over long distances along the predetermined directions in these systems. However, these hydrogen-bonded systems suffer from the weak interactions and low association constants.<sup>4b</sup> As a result, intermolecular diffusional encounter between the donor and acceptor is also invoked to account for the observed energy- or electron-transfer processes. Since 1998, self-complimen-

tary quadruply hydrogen-bonded homodimers have received increasing attention because of their great binding strength and directionality.<sup>6a</sup> Particularly, the 2-ureido-4{1*H*}-pyrimidinone AADD (A = hydrogen-bonding acceptor, D = hydrogen-bonding donor) binding module developed by Meijer and co-workers has shown extensive applications in assembling supramolecular oligomers and polymers.<sup>6</sup> Recently, the 2-ureido-4{1*H*}-pyrimidinone AADD module has also been utilized to create hydrogen-bonded donor–acceptor dyads. However, in most of such dyads, the donor and acceptor are linked to the AADD module via flexible chains, and the molecules may adopt many conformations.<sup>7</sup> Evidently, better-defined systems would be needed in order to interpret unambiguously the dynamics of energy- or electron-transfer process in this kind of AADD hydrogen-bonded assemblies. Here we report the synthesis and inner-assembly energy transfer process in a relatively rigid system (**1.2**), where naphthalene as the energy donor and anthracene as the energy acceptor, which are connected via only a methylene group to the 2-ureido-4{1*H*}-pyrimidinone AADD unit. Due to the rigidity, directionality, and specificity of the linker, naphthalene and anthracene are arranged in side-by-side with donor-to-acceptor edge-to-edge distance being 13 Å. Excitation of the naphthalene chromophore in assembly **1.2** resulted in the inner-assembly singlet energy transfer from naphthalene to anthracene with high efficiency and a large rate constant.

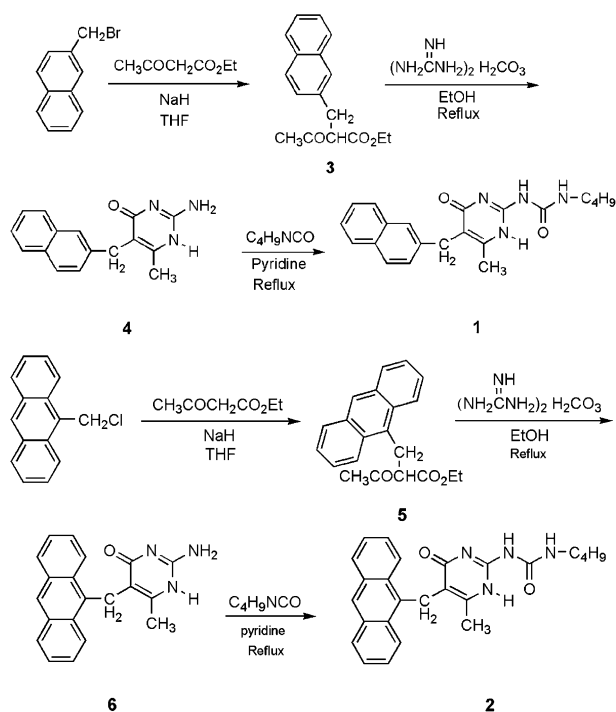
**Keywords:** Inner-assembly singlet energy transfer; Hydrogen bonding; Naphthalene; Anthracene.

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## 2. Synthesis of the quadruply hydrogen-bonded assemblies 1.1, 2.2, and 1.2

The synthesis<sup>11</sup> of **1** and **2** involved three steps, as shown in Scheme 1. Treatment of 2-bromomethyl-naphthalene with ethyl acetoacetate in the presence of NaH afforded intermediate **3**, which was then reacted with guanidinium carbonate in refluxing absolute ethanol. After separation, the crude product **4** was reacted with butylisocyanate in refluxing pyridine to give compound **1** in good chemical yield. Similar procedures were also followed in the preparation of compound **2**. Here the butyl groups were present for solubility purpose.

<sup>1</sup>H NMR spectra (Fig. 1) revealed that compounds **1** and **2** existed as assemblies **1.1** and **2.2** in CDCl<sub>3</sub>. The large downfield shift for N–H protons provided direct evidence for the involvement of strong hydrogen bonding. Their AADD hydrogen-binding motif was determined by NOESY spectra, given in the supporting information. No other binding modes were observed. Dilution of the solutions of the compounds in CDCl<sub>3</sub> to  $1 \times 10^{-5}$  M did not lead to observable dissociation, thus giving a lowest estimation of binding constant of  $1 \times 10^7$  M<sup>-1</sup>, which was in good agreement with the value for a similar compound.<sup>6</sup> Mixing equimolar of **1** and **2** in CDCl<sub>3</sub> resulted in a <sup>1</sup>H NMR spectrum which was almost identical with that of the sum of **1.1** and **2.2**. Since the spectrum of assembly **1.2** was not distinguishable from that of **1.1** + **2.2**, we did not have assurance of the formation of **1.2**. However, considering the reversibility of the assembly formation and similar binding constants for homo- and hetero-assemblies, we inferred that a mixture of **1.1**, **1.2**, and **2.2** existed in the solution in a ratio of 1:2:1 based on the statistical distribution.<sup>6h</sup>



Scheme 1. Synthesis of compounds **1** and **2**.

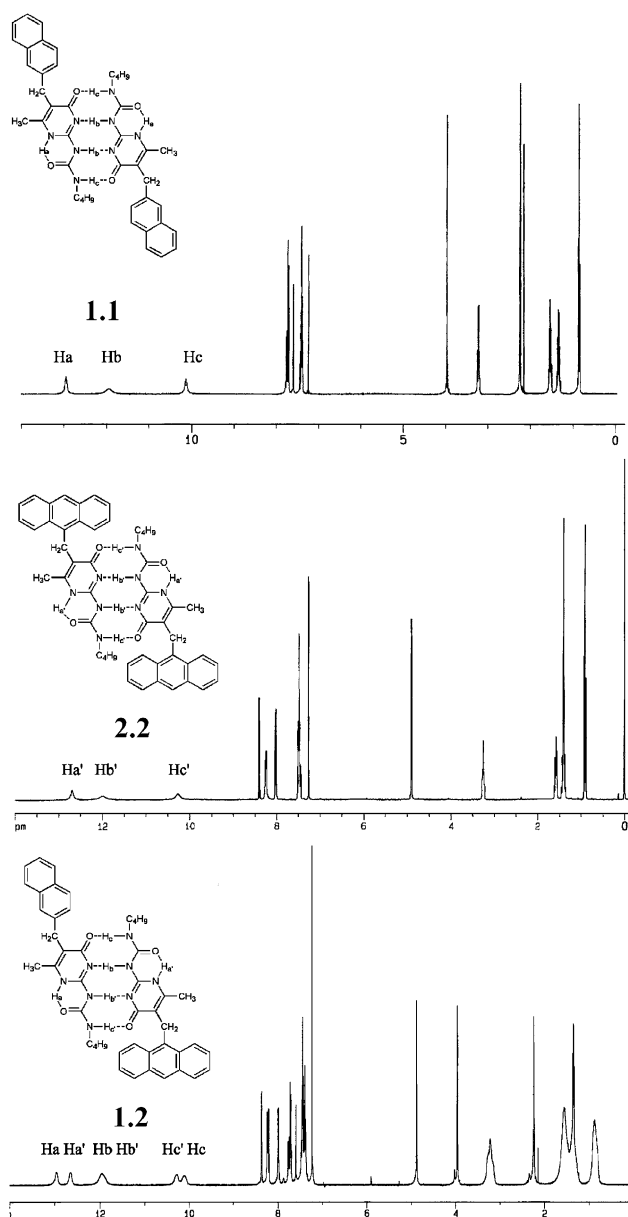
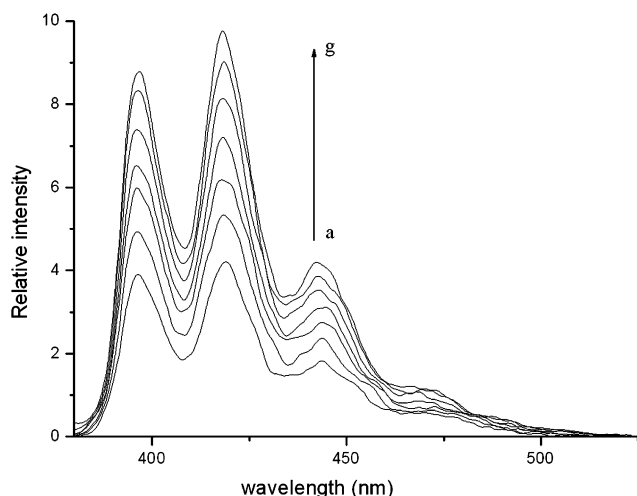


Figure 1. <sup>1</sup>H NMR spectra of the quadruply hydrogen-bonded assemblies **1.1**, **2.2**, and **1.2** in CDCl<sub>3</sub>.

This proposal was supported by the fluorescence lifetime measurements (see below).

### 3. Inner-assembly singlet energy transfer from naphthalene to anthracene in **1.2**

The absorption spectra of **1** and **2** as well as their equimolar mixture in dichloromethane were examined. The spectrum of the mixture was essentially identical to the sum of the spectra of **1** and **2**, indicating the absence of interactions between naphthalene and anthracene in their ground states. Notably, at 290 nm the molar extinction coefficient of **1** was much greater than that of **2**. Thus irradiation of the mixture of **1** and **2** with 290 nm mainly excited the naphthalene chromophore, and only a small fraction of light was absorbed by the anthracene chromophore.



**Figure 2.** Fluorescence spectra of **2** in dichloromethane in the absence and presence of **1**. [**2** =  $5 \times 10^{-6}$  M; [**1**] = 0, 1, 2, 3, 5, 8, and  $15 (\times 10^{-6})$  M.

Figure 2 showed the fluorescence spectra of **2** in dichloromethane in the absence and presence of **1**. In the absence of **1**, **2** exhibited a weak fluorescence characteristic of the anthracene chromophore with maxima at 397, 420, and 445 nm and a shoulder at 480 nm upon excitation at 290 nm. This weak fluorescence was obviously due to the direct absorption of the anthracene chromophore at the excitation wavelength. Upon addition of **1** into the solution of **2**, the fluorescence of **2** increased under the same excitation condition. A weak naphthalene fluorescence in the region of 310–375 nm was also observed. As mentioned above, at 290 nm the light was mainly absorbed by naphthalene chromophore. Evidently, the enhancement, rather than reduction of the anthracene fluorescence in the presence of **1** was due to the singlet energy transfer from the naphthalene to the anthracene chromophore. Since in the solution **1** and **2** existed in the forms of **1.1**, **1.2**, and **2.2**, both inter-assembly and inner-assembly energy transfer may occur. However, because the used concentrations of **1** and **2** were very low, the energy transfer should mainly occur in assembly **1.2**.<sup>8</sup>

The inner-assembly energy transfer in **1.2** was further evidenced by the fluorescence lifetime measurements. In the absence **2**, the naphthalene fluorescence of **1** in dichloromethane solution decayed monoexponentially and the lifetime ( $\tau_1$ ) was ca. 8.2 ns. However, in the presence of **2**, the fluorescence decay profile for the naphthalene was well described by a biexponential function:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

The longer lifetime ( $\tau_1$ ) was found to be identical with that in the absence of **2** (ca. 8.2 ns), and the shorter lifetime ( $\tau_2$ ) was ca. 0.9 ns. These fluorescence lifetimes were independent to the concentrations of **1** and **2**. Evidently, the longer lifetime fluorescence was attributed to the naphthalene in **1.1**, and the shorter lifetime fluorescence to the naphthalene in **1.2**. The preexponential coefficients  $A_1$  and  $A_2$  in Eq. 1 reflected the contributions of the longer and shorter lifetime fluorescence components

to the fluorescence intensity at the end of excitation pulse, respectively, and were related to the respective concentrations of **1.1** and **1.2**. The ratio of  $A_1$  to  $A_2$  was found to be dependent on the relative concentrations of **1** and **2** in the solution. For example, for the solution with equimolar of **1** and **2** ( $5 \times 10^{-6}$  M), the ratio of  $A_1$  to  $A_2$  was found to be 1.0. Considering that **1.1** involves two naphthalene chromophores, the concentration ratio of **1.1** to **1.2** should be 1:2.

The fluorescence lifetimes of the naphthalene in the solution of the mixture of **1** and **2** allowed the calculation of the rate constant ( $k_{ET}$ ) and efficiency ( $\phi_{ET}$ ) of the singlet energy transfer in **1.2**.

$$k_{ET} = 1/\tau_2 - 1/\tau_1 \quad (2)$$

$$\phi_{ET} = 1 - \tau_2/\tau_1 \quad (3)$$

$k_{ET}$  and  $\phi_{ET}$  were obtained to be ca.  $9.8 \times 10^8 \text{ s}^{-1}$  and 89%, respectively.

#### 4. Mechanism of the inner-assembly singlet energy transfer from naphthalene to anthracene in **1.2**

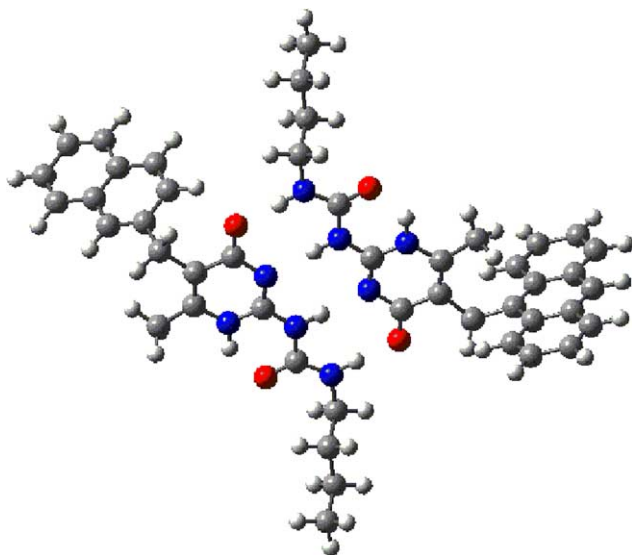
The highly efficient singlet energy transfer from the naphthalene to anthracene in **1.2** prompted us to rationalize the mechanism. It has been well established<sup>9</sup> that dipole–dipole interaction is possible for singlet–singlet energy transfer. To ascertain this mechanism we performed a calculation for  $k_{ET}$  and  $\phi_{ET}$ . According to Förster theory<sup>9</sup> the  $k_{ET}$  for dipole–dipole interaction is related to the geometric and spectroscopic factors of the donor and acceptor chromophores by Eq. 4

$$k_{ET} = R^{-6} J \chi^2 n^{-4} \tau_1^{-1} \phi_f \times 8.8 \times 10^{-25} \text{ s}^{-1} \quad (4)$$

where  $R$  is the distance (in Å) between the donor and the acceptor;  $\chi^2$  is the dipole–dipole orientation factor;  $n$  is the refractive index of the medium;  $\tau_1$  and  $\phi_f$  are the fluorescence lifetime and fluorescence quantum yield of the donor, respectively, in the absence of acceptor;  $J$  is the spectral overlap integral. To estimate  $R$  and  $\chi^2$ , we used GAUSSIAN 98 program<sup>10</sup> to calculate the energies of several conformations of assembly **1.2**, and found that the extended conformation (Fig. 3) had the lowest energy. In this conformation the naphthyl and anthryl chromophores were parallel and located on the different sides of the AADD plane. Thus,  $\chi^2$  was signed to be 1.0. The edge-to-edge distance between the two chromophores was ca. 13.0 Å.  $\tau_1$  and  $\phi_f$  were measured to be 8.2 ns and 0.028, respectively.  $J$  is given by Eq. 5.

$$J = \frac{\int F(\lambda) \varepsilon(\lambda) \lambda^4 d\lambda}{\int F(\lambda) d\lambda} \quad (5)$$

where  $F(\lambda)$  is the fluorescence intensity of the donor at the wavelength  $\lambda$  (in cm), and the  $\varepsilon(\lambda)$  is the molar extinction coefficient (in  $\text{cm}^{-1} \text{ M}^{-1}$ ) of the acceptor at wavelength  $\lambda$ . Calculation revealed that  $J$  for the naphthyl and anthryl chromophores in **1.2** had the value of  $5.36 \times 10^{-15} \text{ M cm}^6$ . This in turn gave  $k_{ET}$  to be  $8.1 \times 10^8 \text{ s}^{-1}$  according to Eq. 4. By using Eqs. 2 and



**Figure 3.** The structure of **1.2** in extended conformation calculated by GAUSSIAN 98 program.

3, and the calculated  $k_{ET}$  and  $\tau_1$ , we obtained  $\phi_{ET}$  to be 87%. Both the calculated rate and efficiency were consistent with the values obtained from the experiments. The excellent agreement between the calculated and observed data indicates that the singlet energy transfer indeed proceeds by Förster mechanism.

### Acknowledgements

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### Supplementary material

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2004.06.138](https://doi.org/10.1016/j.tetlet.2004.06.138). Contains the amplified  $^1\text{H}$  NMR spectra of **1.1**, **2.2**, and **1.1+2.2** with ratio of 1 as well as 2D NOESY spectra of **1.1** and **2.2**.

### References and notes

- (a) Pictrowiak, P. *Chem. Soc. Rev.* **1999**, *28*, 143–150; (b) Ward, M. D. *Chem. Soc. Rev.* **1997**, *26*, 365–375; (c) Sessler, J. L.; Wang, B.; Springs, S. L.; Brown, C. T. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Murakami, Y., Eds.; Pergamon: Oxford, 1996; Vol. 4, p 311; (d) Sessler, J. L.; Vrown, C. T.; Oconnor, D.; Springs, S. L.; Wang, R.; Sathiosatham, M.; Hirose, T. *J. Org. Chem.* **1998**, *63*, 7370–7374; (e) de Rege, P. J. F.; Williams, S. A.; Therein, M. J. *Science*. **1995**, *269*, 1409–1413; (f) Prasad, E.; Gopidas, K. R. *J. Am. Chem. Soc.* **2000**, *122*, 3191–3196.
- (a) Duun, A. R.; Dmochowski, I. J.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **2003**, *125*, 12450–12456; (b) Winkle, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369–379.
- (a) Myles, A. J.; Branda, N. R. *J. Am. Chem. Soc.* **2001**, *123*, 177–178; (b) Roberts, J. A.; Kirby, J. P.; Nocera, D. G. *J. Am. Chem. Soc.* **1995**, *117*, 8051–8052; (c) Derg, Y. Q.; Roberts, J. A.; Peng, S. M.; Chang, C. K.; Nocera, D. G. *Angew. Chem., Int. Ed.* **1997**, *36*, 2124–2127.
- (a) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704–714; (b) Zimmerman, S. C.; Corbin, P. S. *Struct. Bonding* **2000**, *96*, 63–94.
- (a) Zhang, L.-P.; Chen, B.; Wu, L.-Z.; Tung, C.-H.; Cao, H.; Tanimoto, Y. *Chem. Eur. J.* **2003**, *9*, 2763–2769; (b) Zhang, L.-P.; Chen, B.; Wu, L.-Z.; Tung, C.-H. *J. Phys. Chem. A* **2003**, *107*, 3438–3442; (c) Fu, X.-G.; Chen, B.; Wu, L.-Z.; Zhang, L.-P.; Tung, C.-H. *Res. Chem. Intermed.* (in press).
- (a) Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 6761–6769, and references cited therein; (b) Söntjens, S. H. M.; Sijbesma, R. P.; Van Genderen, M. H. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 7487–7493; (c) Wang, X.-Z.; Li, X.-Q.; Shao, X.-B.; Zhao, X.; Deng, P.; Jiang, X.-K.; Li, Z.-T.; Chen, Y.-Q. *Chem. Eur. J.* **2003**, *9*, 2904–2913; (d) Shao, X.-B.; Jiang, X.-K.; Zhao, X.; Chen, Y.; Li Z.-T. *J. Org. Chem.* **2004**, *69*, 899–907; (e) Rispens, M. T.; Sánchez, L.; Knol, J.; Hummelen, J. C. *Chem. Commun.* **2001**, 161–162; (f) El-ghayoury, A.; Peeters, E.; Schenning, A. P. H. J.; Meijer, E. W. *Chem. Commun.* **2000**, 1969–1970; (g) Sánchez, L.; Rispens, M. T.; Hummelen, J. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 838–840; (h) Söntjens, S. H. M.; van Genderen, M. H. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 7487–7493.
- Ikegam, M.; Arai, T. *Chem. Lett.* **2001**, 694–695.
- The concentration of **2** used in the present study was  $5 \times 10^{-6}$  M, and that of **1** less than  $1.5 \times 10^{-5}$  M. In such concentration the average separation between **1** and **2** is greater than 300 Å, and singlet energy transfer can not occur.<sup>9</sup>
- Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: London, 1978; p 319.
- GAUSSIAN 98, Revision A.9, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E., Jr.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1998.
- Notes:** Anhydrous THF was obtained by distillation from sodium/benzophenone. Absolute ethanol was obtained by distillation from sodium/diethyl phthalate. Pyridine was heated under reflux with  $\text{CaH}_2$  for 3 h then distilled. Spectral-grade dichloromethane was prepared by normal procedure. Other solvents were of analytical grade. UV/vis spectra were obtained on a SHIMADZU UV-1601PC

spectrophotometer. Steady-state emission spectra were recorded on a Perkin–Elmer LS50B spectrofluorometer.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectrum were recorded on a Bruker-400 FT-NMR spectrometer. NOESY spectram were recorded on a Bruker-400 FT-NMR spectrometer. Elemental analysis was performed on a Carlo Erba 1106 elemental analyzer. The quantum yields of the emission were obtained by the optical dilute method using a benzene solution of anthracene ( $\Phi_0 = 0.27$ ) as a reference.<sup>12</sup>

**Compound 3:** To a solution of ethyl acetoacetate (2.6 g, 0.02 mol) in dry THF (100 mL) was added NaH (0.93 g, 52%). The mixture was stirred for 30 min at room temperature, and to this was added  $\beta$ -bromomethylnaphthalene (4.44 g, 0.02 mol) in THF (50 mL) dropwise. The resulting mixture was stirred for 5 h at room temperature. The reaction was quenched by the addition of 5% HCl (ca. 50 mL) and extracted with ethyl acetate. The organic extracts were washed with 5%  $\text{NaHCO}_3$  and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated in vacuo. The residue was purified by chromatography to give 4.08 g (75%) of **3**.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.81–7.74 (m, 3H), 7.64 (s, 1H), 7.47–7.44 (m, 2H), 7.32 (d,  $J = 9.0$  Hz, 1H), 4.20–4.12 (m, 2H), 3.91–3.87 (m, 1H), 3.45 (d,  $J = 8.7$  Hz, 1H), 3.33 (d,  $J = 7.8$  Hz, 1H), 2.21 (s, 3H), 1.20 (t,  $J = 7.2$  Hz, 3H). MS:  $m/z = 270$ .

**Compound 1:** The compound **3** (1.496 g, 5.5 mmol) in absolute ethanol was heated under reflux with guanidinium carbonate (0.60 g, 3.33 mmol) overnight. The resulting solution was cooled, inducing precipitation of a white

powder, which was filtered off and washed thoroughly with water, acetone, and cooled ethanol. The crude product **4** was used for next step without further purification. A suspension of **4** (0.602 g, 2.27 mmol) and butylisocyanate (0.449 g, 4.54 mmol) in dry pyridine (30 mL) was heated under reflux for 4 h, after which it was cooled and acetone was added. The formed precipitate was filtered off and recrystallized from  $\text{CHCl}_3$  to give 0.752 g (91%) of **1**.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 12.94 (s, 1H), 11.94 (s, 1H), 10.12 (s, 1H), 7.77–7.70 (m, 3H), 7.59 (s, 1H), 7.43–7.36 (m, 3H), 3.96 (s, 2H), 3.24–3.19 (m, 2H), 2.23 (s, 3H), 1.56–1.49 (m, 2H), 1.37–1.29 (m, 2H), 0.84 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 172.5, 156.8, 153.5, 144.6, 137.4, 133.6, 132.2, 128.1, 127.7, 127.6, 127.2, 126.3, 126.0, 125.4, 117.2, 39.8, 31.4, 30.2, 20.2, 17.6, 13.8. Anal. Calcd for  $\text{C}_{21}\text{H}_{24}\text{N}_4\text{O}_2$ : C, 69.21; H, 6.64; N, 15.37. Found: C, 68.68; H, 6.65; N, 15.38.

**Compound 2:** The similar procedures were followed by the preparation of compound **2** with 70% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 12.69 (s, 1H), 11.99 (s, 1H), 10.27 (s, 1H), 8.40 (s, 1H), 8.24 (d,  $J = 7.2$  Hz, 2H), 8.01 (d,  $J = 7.2$  Hz, 2H), 7.50–7.45 (m, 4H), 4.90 (s, 2H), 3.28–3.23 (m, 2H), 1.60–1.55 (m, 2H), 1.44–1.35 (m, 5H), 0.90 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 172.5, 156.8, 153.3, 144.7, 132.4, 131.6, 130.6, 129.4, 126.7, 126.1, 125.1, 124.8, 118.3, 39.8, 31.5, 24.1, 20.2, 17.8, 13.9. Anal. Calcd for  $\text{C}_{25}\text{H}_{26}\text{N}_4\text{O}_2$ : C, 72.44; H, 6.32; N, 13.52. Found: C, 72.31; H, 6.30; N, 13.59.

12. Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024.