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Synthesis and luminescent properties of some novel naphthalimide dimers

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Abstract

The four kinds of novel naphthalimide dimers were synthesized and their fluorescent lifetimes were investigated. The ground-state/excited state interaction and photo-induced energy/electron transfer in these dimers, which would result in a serial of photochemical properties changes, has been discussed. Using MM2, the energy-minimized molecular modelings of the dimers were studied and confirmed cofacial conformation of chromophores in some dimers, and the pH sensitivity of the dimers has also been detected by fluorescent spectra.

Keywords: Fluorescence; Cofacial dimer; Synthesis; Naphthalimide

Molecular assembles or supramolecular systems which are forced to be cofacial conformation of chromophores with large planar structure, such as porphyrin, via the use of a rigid spacer may improve the efficiency of energy-transfer and could be potential models of the natural photosynthetic systems [1–6]. Cofacial π-stacked arrangements of chromophores are found in many biologically important molecules such as DNA and the primary electron donor within photosynthetic reaction center proteins. If the interchromophore distance of the well-defined dimer is appropriate, photochemical processes, such as ground-state/excited state interaction and photo-induced energy/electron transfer, may occur and would result in a serial of photochemical properties changes such as the formation of excimer or exciplex. Much effort has been devoted to regulating the orientation among the chromophores [7–9]. Wasielewski et al. [10,11] recently reported that some symmetric cofacial 1, 7-bis(pyrrolidin-1′-yl) perylene-3, 4:9, 10-bis (dicarboximide) dimer undergoes symmetry breaking following photoexcitation yielding complete charge separation between the two halves of the dimer in the relatively low polarity solvent toluene.

We report herein the synthesis of four novel naphthalimide dimers (Scheme 1), some of them are cofacial configuration, by taking advantage of

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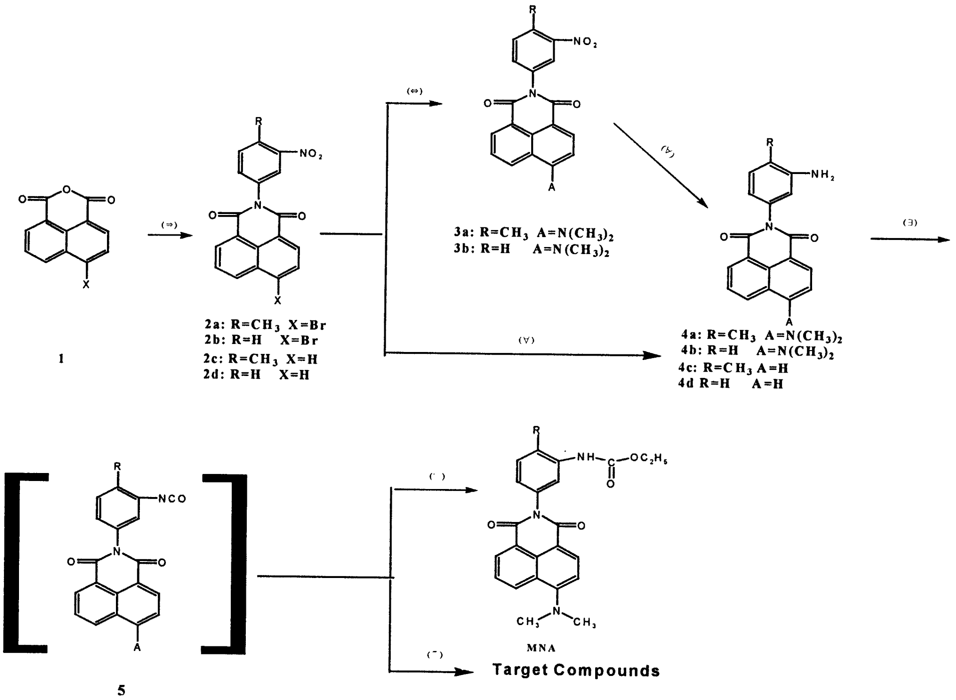
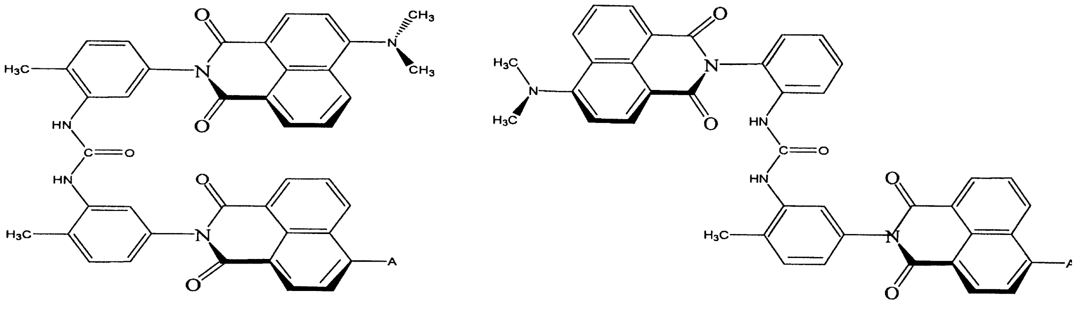


Scheme 1. Reagents and conditions: (i) 4-amino-2-nitro-toluene or *m*-dinitrobenzene, Acetic acid, reflux; (ii) Dimethylamine, DMF, $CuSO_4$, reflux; (iii) Fe, ethanol/H_2O, reflux; (iv) Triphosgene, dry $CHCl_3$, dry $N(CH_2CH_3)_3$, r. t.; (v) Ethanol, reflux; (vi) **4a** or **4b**–**4d**, reflux.

the steric repulsion between the methyl group and the carbonyl group [7], as shown in Fig. 1. A diarylurea linkage has been chosen for its easy obtainment by the reaction of the corresponding amine and isocynate in good yield. In generally, the charge separation or transfer in dimer systems would quench the fluorescence of the fluorophore. Therefore, the charge separation between identical chromophores in a π-stacked configuration in low polarity media has not been reported so many [10]. In order to understand what kind of influence on the emission by the intramolecular interaction between two identical chromophores with a cofacial configuration, and in an effort to develop more fluorescent materials in solid-state, we have synthesized novel dimers as model systems shown in Fig. 1. The influence on the fluorescence, especially on solid state fluorescence, by charge


cof-**NA**: A=$N(CH_3)_2$; *cof*-**NADA**: A=H

lin-**NA**: A=$N(CH_3)_2$; *lin*-**NADA**: A=H

Fig. 1. Cofacial naphthalimide dimers in this study.

separation or transfer between two chromophores would be discussed using these model systems. Fluorescence spectra including fluorescent lifetimes of the dimers have been investigated. Unlike other dimers, these dimers show strong fluorescence emission in the solid state and they will have potential application as laser dyes, fluorescence makers, etc.

1. Experimental

^{1}H NMR spectra were obtained using a Brücker AM 500 spectrometer. Mass spectra (MS) were carried out on a MA1212 instrument using standard conditions. UV–vis spectra were performed on a Varian Cary500 spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer. The fluorescence lifetime study was performed by an Edinburgh FL 900 single-photon counting system with a hydrogen-filled flash lamp/or a nitrogen lamp as the excitation source. Data were analyzed using a nonlinear least-squares fitting program with deconvolution method. The temporal resolution after deconvolution of the exciting pulse is ~200 ps [12].

*1.1. 6-Bromo-2-(4-methyl-3-nitro-phenyl)-benzo[*de*]iso- quinoline-1,3-dione (**2a**)*

1.5 g (5.4 mmol) 4-Bromo-1,8-naphthalic anhydride, 2.0 g (13.2 mmol) 4-amino- 2-nitro-toluene were refluxed with stirring for 6 h in 40 ml glacial acetic acid. The suspension was poured into 200 ml ice–water and filtered to give a brown solid (1.8 g, 82%). Recrystallization from chlorobenzene gave pale gray needles, m.p. > 300 °C. TLC revealed the presence of a single component and the needles were used directly for the next reaction.

*1.2. 6-Bromo-2-(3-nitro-phenyl)-benzo[*de*]isoquinoline-1,3-dione (**2b**)*

The similar procedure as **2a** is carried out with 4-Bromo-1,8-naphthalic anhydride (2.0 g, 7.2 mmol) and 3-nitroaniline (2.5 g, 18 mmol) to yield **2b**, 3.6 g (80%); m.p. > 300 °C.

*1.3. 2-(4-Methyl-3-nitro-phenyl)-benzo[*de*]isoquinoline-1,3-dione (**2c**)*

The same procedure as the preparation of **2a** was used for preparation of **2c** and **2d**. **2c**: m.p. 279–281 °C. ^{1}H NMR (DMSO-d_6) δ (ppm): 2.71 (s, –CH$_3$, 3H), 7.80 (m, 2H), 8.02 (t, J = 7.69 Hz, 7.86 Hz, 2H), 8.26 (d, J = 9.91 Hz, 1H), 8.62 (t, J = 7.75 Hz, 7.09 Hz, 4H). Anal. calcd. for $C_{19}H_{12}N_2O_4$: C 68.67, H 3.64, N 8.43. Found: C 68.79, H 3.71, N 8.39%.

*1.4. 2-(3-Nitro-phenyl)-benzo[*de*]isoquinoline-1,3-dione (**2d**)*

m.p. 278–282 °C. ^{1}H NMR (DMSO-d_6) δ(ppm): 7.60 (m, 1H), 7.85 (m, 2H), 8.10 (t, J = 7.75 Hz, 7.85 Hz, 2H), 8.30 (d, J = 9.87 Hz, 1H), 8.60 (m, 4H). Anal. calcd. for $C_{18}H_{10}N_2O_4$: C 67.92, H 3.17, N 8.80. Found: C 67.84, H 3.26, N 8.70%.

*1.5. 6-Dimethylamino-2-(4-methyl-3-nitro-phenyl)-benzo[*de*]isoquinoline-1,3-dione (**3a**)*

Compound **2a** (1.0 g, 2.4 mmol) was dissolved in 15 ml DMF. Then 3 ml of 33% dimethylamine aqueous solution (20.2 mmol) and 0.1 g $CuSO_4 \cdot 5H_2O$ were added. The resulting mixture was heated to reflux for 5 h with stirring. After cooling to room temperature, the solution was poured into 100 ml water, and the precipitate was collected by filtration, washed with water and dried to yield 0.8 g (87%) yellow powder. Recrystallization from chlorobenzene gave yellow needles. m.p. 262–264 °C. ^{1}H NMR (DMSO-d_6) δ(ppm): 2.30 (s, –CH$_3$, 3H), 3.28 (s, –N(CH$_3$)$_2$, 6H), 7.52 (d, J = 7.9 Hz, 1H), 7.85 (m, 2H), 8.20 (m, 3H), 8.39 (d, J = 7.51 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H). Anal. calcd. for $C_{21}H_{17}N_3O_4$: C 67.19, H 4.56, N 11.19. Found: C 67.05, H 4.58, N 11.26%.

*1.6. 6-Dimethylamino-2-(3-nitro-phenyl)-benzo[*de*]iso-quinoline-1,3-dione (**3b**)*

The above procedure is carried out with compound **2b** (3.2 g, 8.1 mmol) and 9 ml of 33% dimethylamine aqueous solution (60.6 mmol); yield: 2.4 g (86%); m.p. 261–262 °C. ^{1}H NMR

(DMSO-d_6) δ(ppm): 3.14 (s, –N(CH_3)$_2$, 6H), 7.27 (d, J = 8.33 Hz, 1H), 7.82 (m, 2H), 7.90 (d, J = 8.0 Hz, 1H), 8.35 (m, 3H), 8.49 (d, J = 7.17 Hz, 1H), 8.59 (d, J = 8.5 Hz, 1H). Anal. calcd. for $C_{20}H_{15}N_3O_4$: C 66.48, H 4.18, N 11.63. Found: C 66.54, H 4.08, N 11.79%.

*1.7. 2-(3-Amino-4-methyl-phenyl)-6-dimethylamino-benzo[de]isoquinoline-1,3-dione (**4a**)*

A mixture of compound **3a** (0.4 g, 1.1 mmol), 1.8 g (32.1 mmol) iron powder, 20 ml ethanol and 10 ml water were heated to refluxed. Three ml 10% HCl was added under N_2 and the mixture refluxed for another 1 h. Then the mixture was filtered with hot and the filtrated was subsided to cool to room temperature, orange needle crystal precipitated and collected by filtration, washed with ethanol and dried to give 0.3 g (82%) **4a**. m.p. 253–254 °C. TLC revealed the presence of a single component and the needles were used directly for the next reaction.

*1.8. 2-(3-Amino-phenyl)-6-dimethylamino-benzo[*de*]-isoquinoline-1,3-dione (**4b**)*

The above procedure is carried out with **3b** (0.4 g, 1.1 mmol) and 1.8 g (32.1 mmol) iron powder; yield 0.32 g (87%); m.p. 264–265 °C.

1.9. 2-(3-Amino-4-methyl-phenyl)-benzo[de]isoquinoline-1,3-dione (4c)

m.p. 275–277 °C. ^{1}H NMR (DMSO-d_6) δ(ppm): 2.04 (s, –CH_3, 3H), 4.92 (s, –NH_2, 2H), 6.34 (d, J = 7.39 Hz, 1H), 6.45 (s, 1H), 6.94 (d, J = 7.58 Hz, 1H), 7.82 (t, J = 7.59 Hz, 7.60 Hz, 2H), 8.41 (d, J = 4.47 Hz, 4H). Anal. calcd. for $C_{19}H_{14}N_2O_2$: C 75.48, H 4.67, N 9.27. Found: C 75.53, H 4.75, N 9.16%.

*1.10. 2-(3-Amino-phenyl)-benzo[de]isoquinoline-1,3-dione (**4d**)*

m.p. 273–275 °C. ^{1}H NMR (DMSO-d_6) δ (ppm): 5.18 (s, –NH_2, 2H), 6.21 (d, J = 7.51 Hz, 1H), 6.64 (s, 1H), 7.05 (m, 2H), 7.95 (t, J = 7.70 Hz, 7.85 Hz, 2H), 8.30 (d, J = 5.20 Hz, 4H). Anal. calcd. for $C_{18}H_{12}N_2O_2$: C 74.99, H 4.20, N 9.72. Found: C 74.86, H 4.31, N 9.77%.

*1.11. [5-(6-Dimethylamino-1,3-dioxo-1H,3H-benzo[*de*]isoquinolin-2-yl)-2-methyl-phenyl]-carbamic acid ethyl ester (MNA)*

To a stirred solution of **4a** (0.3 g, 0.87 mmol) and Et_3N (0.71 g, 6.96 mmol) in $CHCl_3$ (20 ml) was added triphosgene (0.3 g, 1.0 mmol) under N_2. The reaction mixture was stirred at room temperature for 1 h, after which time ethanol (0.34 g, 4.35 mmol) was added and refluxed for 12 h. The solvent was removed by rotary evaporator, and the residue was reflux in 40 ml ethanol for 1 h. After cooled to room temperature, the precipitated was collected by filtration, washed with ethanol and dried to give yellow powder (0.22 g, 60%). m.p. > 300 °C. ^{1}H NMR (DMSO-d_6) δ (ppm): 1.23 (m, 3H), 2.28 (s, 3H), 3.12 (s,-N(CH_3)$_2$, 6H), 4.10 (m, 2H), 7.01 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.34 (s, 1H), 7.25 (d, J = 8.30 Hz, 1H), 7.79 (t, J = 7.86 Hz, 7.45 Hz, 1H), 8.34 (d, J = 8.30 Hz, 1H), 8.46 (d, J = 6.90 Hz, 1H), 8.56 (d, J = 8.40 Hz, 1H). Anal. calcd. for $C_{24}H_{23}N_3O_4$: C 69.05, H 5.55, N 10.07. Found: C 69.18, H 5.58, N 10.11%.

*1.11.1. Naphthalimide dimer (**cof**-NA)*

The above procedure is carried out with **4a** to produce compound **5**, and then take **5** (0.3 g, 0.87 mmol) directly without separation and **4a** (0.3 g, 0.87 mmol) to produce ***cof*-NA** 0.4 g (64%); m.p. > 300 °C. ^{1}H NMR (DMSO-d_6) δ (ppm): 2.36 (s, 6H), 3.08 (s, 12H), 6.89 (d, J = 7.90 Hz, 2H), 7.20 (d, J = 8.30 Hz, 2H), 7.30 (d, J = 7.90 Hz, 2H), 7.74 (t, J = 7.90 Hz, 7.50 Hz, 2H), 7.81 (s, 2H), 8.30 (d, J = 8.30 Hz, 2H), 8.41 (d, J = 7.4 Hz, 2H), 8.52 (d, J = 8.20 Hz, 2H). Anal. calcd. for $C_{43}H_{36}N_6O_5$: C 72.05, H 5.06, N 11.72. Found: C 72.19, H 5.03, N 11.69%.

The above procedure is carried out with **5** (0.3 g, 0.87 mmol) and **4b** (0.3 g, 0.86 mmol) to produce ***lin*-NA** 0.42 g (67%); m.p. > 300 °C. ^{1}H NMR (DMSO-d_6) δ (ppm): 2.30 (s, 3H), 3.09 (s, 12H), 6.92 (t, J = 9.66 Hz, 9.52 Hz, 2H), 7.23 (d, J = 8.24 Hz, 2H), 7.30 (d, J = 7.94 Hz, 1H), 7.41 (m, 2H), 7.52 (s, 1H), 7.77 (t, J = 7.8 Hz, 7.60 Hz, 2H), 7.85 (s, 1H), 8.09 (s, 1H), 8.33 (d, J = 8.16 Hz, 2H), 8.44 (d, J = 7.05 Hz, 2H), 8.54 (d, J = 8.41 Hz, 2H), 9.28

(s, 1H). Anal. Calcd. for $C_{42}H_{34}N_6O_5$: C 71.78, H 4.88, N 11.96. Found: C 71.92, H 4.85, N 11.90%.

*1.11.2. Naphthalimide dimer (***cof-***NADA)*

m.p.>300 °C. ^1H NMR (DMSO-d_6) δ(ppm): 2.34 (s, 6H), 3.02 (s, 6H), 6.91 (t, J=9.52 Hz, 9.50 Hz, 2H), 7.23 (d, J=8.3 Hz, 1H), 7.30 (d, J=7.80 Hz, 2H), 7.79 (t, J=7.8 Hz, 7.50 Hz, 1H), 7.85 (s, 2H), 7.94 (t, J=7.85 Hz, 7.60 Hz, 2H), 8.38 (d, J=8.30 Hz, 1H), 8.55 (m, 6H). Anal. calcd. for $C_{41}H_{31}N_5O_5$: C 73.09, H 4.64, N 10.40. Found: C 73.25, H 4.65, N 10.48%.

*1.11.3. Naphthalimide dimer (***lin-***NADA)*

m.p.>300 °C. ^1H NMR (DMSO-d_6) δ(ppm): 2.33 (s, 3H), 3.08 (s, 6H), 6.95 (t, J=9.50 Hz, 9.45 Hz, 2H), 7.25 (d, J=8.25 Hz, 1H), 7.38 (m, 3H), 7.55 (s, 1H), 7.80 (t, J=7.9 Hz, 7.55 Hz, 1H), 7.88 (s, 1H), 7.91 (t, J=7.70 Hz, 7.55 Hz, 2H), 8.32 (d, J=8.30 Hz, 1H), 8.52 (m, 6H). Anal. calcd. for $C_{40}H_{29}N_5O_5$: C 72.83, H 4.43, N 10.62. Found: C 72.96, H 4.48, N 10.67%.

2. Results and discussion

2.1. Absorption and fluorescence spectra of dimers

The UV–vis absorption and fluorescence emission curves of dimers were shown in the Figs. 2–5. UV–vis spectra of the dimers and **MNA** were recorded. A comparison of the absorption spectra of ***cof-***

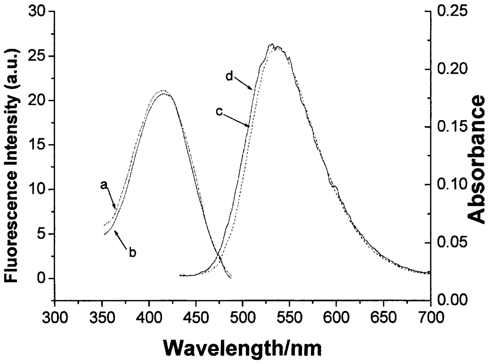


Fig. 2. Absorption and fluorescence spectra of ***cof*-NA** and **MNA** in methanol (10^{-5} M): (a) absorption of ***cof*-NA**; (b) absorption of **MNA**; (c) fluorescence of ***cof*-NA**; (d) fluorescence of **MNA**.

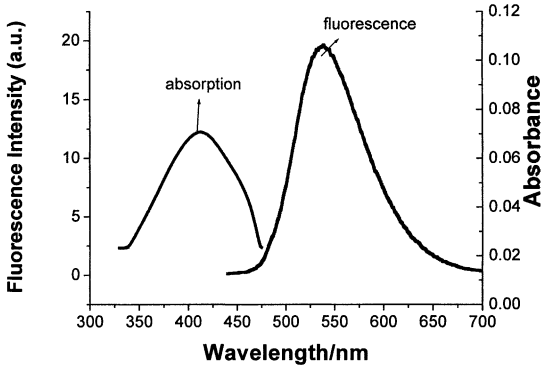


Fig. 3. Absorption and fluorescence spectra of ***lin*-NA** in methanol (10^{-5} M).

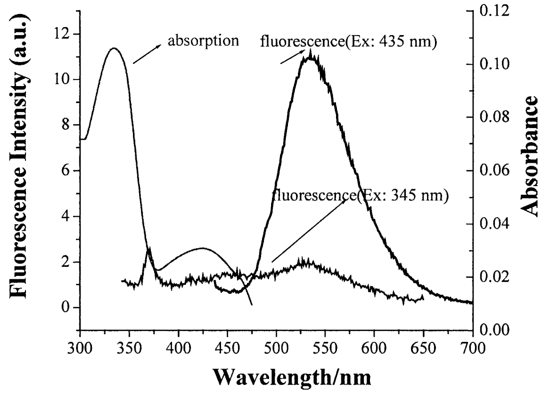


Fig. 4. Absorption and fluorescence spectra of ***cof*-NADA** in methanol (10^{-5} M).

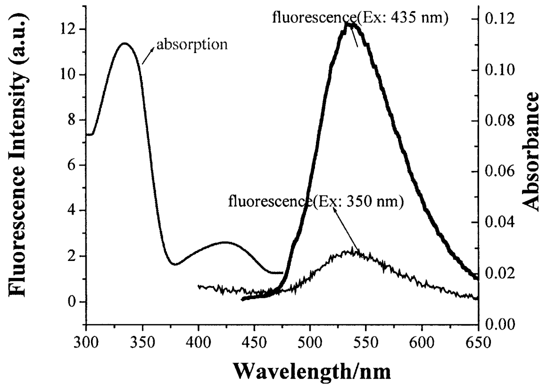


Fig. 5. Absorption and fluorescence spectra of ***lin*-NADA** in methanol (10^{-5} M).

NA, ***lin*-NA**and **MNA** shows that they are nearly identical, indicating that no coupling interaction exists between the two naphthalimide chromophores in the ground state, since **MNA** is the monomer reference. The intensities of the absorption and fluorescence of compound ***cof*-NA** were nearly exact double high as that of compound **MNA** shown in Fig. 2. According to the prediction of the zero-order molecular [13], dipole–dipole coupling of the transition moments of the monomers will produce two electronic transition upon dimer formation, with the lowest energy electronic transition of the dimer splitting into two bands. They both have a single band at 415 nm and no band shift and/or splitting for ***cof*-NA** suggests that almost no coupling exists between the two naphthalimide in ***cof*-NA**. We can exclude the possibility of intramolecular aggregation due to folding of the face-to-face spacer. The absorption spectra of ***lin*-NA** are alike to that of ***cof*-NA**. If the transition dipoles of two identical chromophores are positioned in a parallel, stacked geometry, the molecular exciton model predicts that coupling of the two transition diploes will cause the lowest energy electronic transition of the dimer to split into two bands, with the higher energy band having all of the oscillator strength [14]. The lack of a significant absorption band-shift and/or splitting for ***cof*-NA** and ***lin*-NA** suggests that they have a relative distance and/or geometry in which exciton coupling is very weak.

However, the dimers ***cof*-NADA** and ***lin*-NADA** exhibited the red shift of 11nm ($\lambda_{\max}=426$ nm) compared with that of monomer model **MNA**($\lambda_{\max}=415$ nm). This indicates an exciton coupling between the transitions in the two naphthalimide moieties (one is the donor, another is the acceptor) and intramolecular photo-induce energy or electron transfer (PET) occurring. Comparison between two compounds with same geometry conformation, ***cof*-NA** and ***cof*-NADA**, the absorption maximum of ***cof*-NA** is 415 nm, around where is the absorption sub-peak of ***cof*-NADA** (426 nm). The maximum absorption of ***cof*-NADA** is in short wavelength region of 324 nm. However, when excited at this maximum absorption wavelength (345 nm), ***cof*-NADA** shows relative weak fluorescence emission compared with that obtained by the excitation at the lower energy band (435 nm, shown in Fig. 4). The same phenomena were observed for the comparison between the linear conformation dimers, i.e. ***lin*-NA** and ***lin*-NADA**. The fluorescence emission of ***lin*-NADA** excited at different energy bands, shown in Fig. 5, can draw the same conclusion as that for ***cof*-NADA**.

As they were strongly fluorescent, we also investigated the fluorescent lifetime of the dimers, as listed in Table 1. The fluorescence lifetime with two components for each compound indicated that there exists an intramolecular interaction between the two chromophores. Comparing the lifetime with heavy weight percentage of ***cof*-NADA**, i.e. 8.55 ns (63.94%), with that of ***cof*-NA** [0.305 ns (85.39%)], the prolongation of the excited state in ***cof*-NADA** may be ascribed to the additional photo-induced electron transfer (PET) process [14–18] from the donor, 2-(3-Amino-4-methyl-phenyl)-6-dimethylamino-benzo[*de*] isoquinoline-1,3-dione to the acceptor, 2-(3-Amino-4-methyl-phenyl)-benzo[*de*]iso-quinoline-1,3-dione. This interaction does not occur in compound ***cof*-NA**. The comparison of fluorescent lifetimes between ***lin*-NA** and ***lin*-NADA** could provide the same conclusion as that discussed above between ***cof*-NA** and ***cof*-NADA**. This conclusion is also consistent with the result from the comparison of the absorption

Table 1
The absorption, fluorescence maximum and relative fluorescence quantum yield (Φ_{fluo} the fluorescence quantum yield of MNA was defined as 1.00) in methanol and the fluorescence lifetimes data (τ, excited at 380 nm) of the dimers in DMSO

Compounds	λ^{Abs}max/nm	λem/nm	Φ_{fluo}	τ_1/ns	τ_2/ns
***cof*-NA**	415	530	2.25	0.31 (85.4%)	6.73 (14.6%)
***Lin*-NA**	417	530	2.18	0.17 (73.9%)	7.56 (26.1%)
***cof*-NADA**	324, 426	530	1.98	0.33 (36.1%)	8.55 (63.9%)
***Lin*-NADA**	336, 424	530	1.95	0.25 (55.6%)	8.69 (44.4%)
MNA [17,18]	407	508	1.00	4.5–4.8	

spectra. Of course, PET process would decrease fluorescent quantum yield of the compounds in generally. Therefore, the relative fluorescent quantum yield of compound ***cof*-NA** is larger than that of compound ***cof*-NADA**. Similar conclusion can be obtained for the comparison between ***lin*-NA** and ***lin*-NADA**, shown in Table 1.

The short-lived exciton state for the cofacial stacked geometry of ***cof*-NA** cannot be explained in terms of exciton coupling [13] which predicts a long-lifetime and contrary to what is observed. Comparison of the fluorescent lifetimes between ***cof*-NA** and ***cof*-NADA**, for the same geometry of the molecules, the intramolecular charge transfer or PET between the donor and acceptor would influence obviously the fluorescent lifetime. For the linear geometry conformation dimers ***lin*-NA** and ***lin*-NADA**, the charge transfer or PET through the space in these systems can be almost neglected. However, the data listed in Table 1 indicated that the interaction between the donor and the acceptor make strong influence on the fluorescent lifetimes. The charge transfer or PET through the bond in these systems dominated the emission properties. In addition, the fluorescence spectra of these dimers in the solid state are very similar to that in the solution except the small red-shift (Fig. 6)

2.2. Geometry of dimers

The face-to-face orientation between the naphthalimide units in dimers was confirmed by the energy-minimized molecular modeling study, using MM2 [19], were shown as Figs. 7–10.

Using MM2, we can easily calculate that the total steric energy of ***cof*-NA** for the face-to-face conformation is 50.6823 kcal/mol, while that for the linear conformation is 54.6120 kcal/mol as shown in Table 2. Then we can conclude that the two naphthalimide of ***cof*-NA** are positioned in a face-to-face geometry. This may be ascribed to the

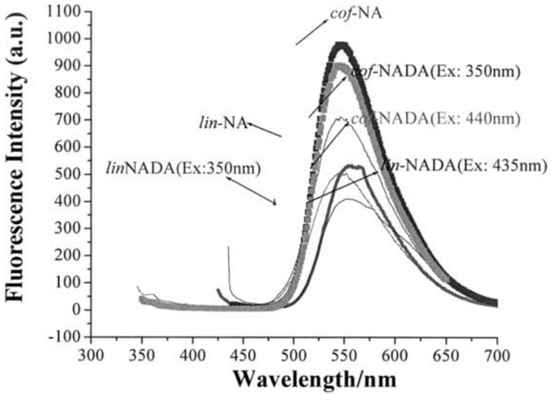


Fig. 6. Solid fluorescence spectra of ***cof*-NA**, ***lin*-NA**, ***cof*-NADA** and ***lin*-NADA.**.

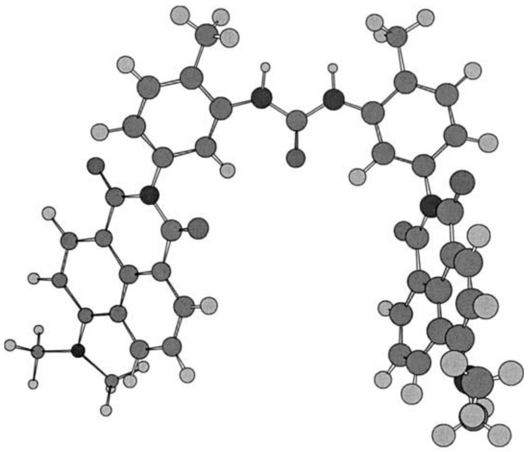


Fig. 7. Energy-minimized molecular modeling of ***cof*-NA**.

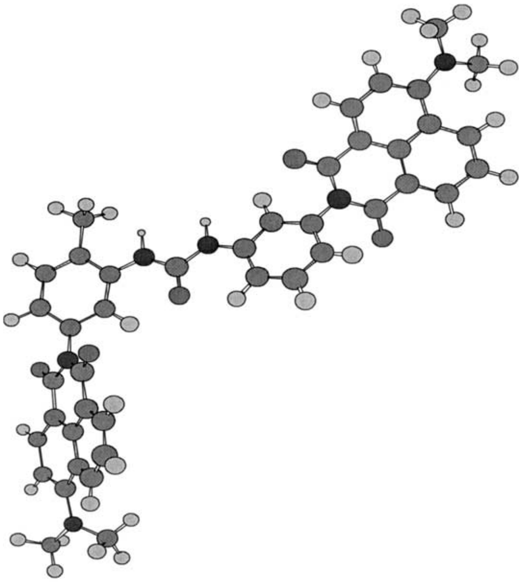


Fig. 8. Energy-minimized molecular modeling of ***lin*-NA.**.

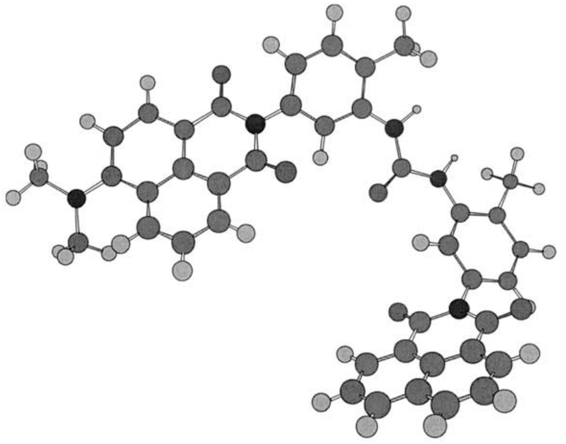


Fig. 9. Energy-minimized molecular modeling of ***cof*-NADA**.

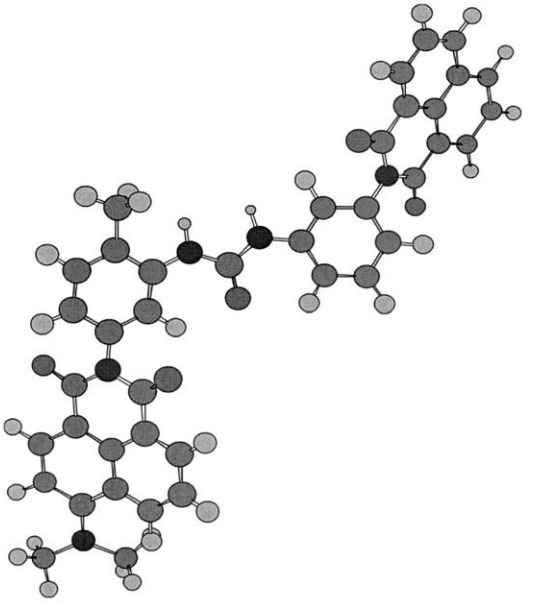


Fig. 10. Energy-minimized molecular modeling of ***lin*-NADA**.

Table 2
The calculated steric energies of the dimers for different conformations

Compounds	Face-to-face conformation (kcal/mol)	Linear conformation (kcal/mol)
***cof*-NA**	50.6823	54.6120
***lin*-NA**	52.1800	49.9006
***cof*-NADA**	34.0095	36.9871
***lin*-NADA**	35.7782	32.7984

steric repulsion between the methyl group and the carbonyl, as shown in Fig. 11. Similarly, comparing 52.1800 kcal/mol for face-to-face orientation with the value of 49.9006 kcal/mol for linear orientation, we can infer that two chromophores of ***lin*-NA** are in a linear geometry, as well as due to no steric repulsion in ***lin*-NA**. ***cof*-NADA** and ***lin*-NADA** have an analogy to ***cof*-NA** and ***lin*-NA**.

2.3. Fluorescence on pH sensitivity

It is well known that the amines quench the fluorescence of the aromatic species via the formation of exciplex which involve some degree of photo-induced electron transfer (PET) [15, 20–23]. Unlike other fluorescent sensors containing amine group, ***cof*-NADA** and ***lin*-NADA** fluorophore series studied here are nearly pH un-sensitive. The fluorescence of the compounds remains nearly unaffected between pH 2 and 11, shown in Fig. 12. The fluorescence emission is directly proportional to the concentration of the compounds (1–100 μM). Therefore, these compounds are not susceptible to self-quenching or to aggregation, at least in the concentration range explored. The fluorescence of ***cof*-NADA** and ***lin*-NADA** dimers almost have no change with pH values, it indicates that although the strong acid and strong base may switch off the PET path from the donor to the acceptor, but the PET processes in these dimers is too weak to influence the fluorescence intensity. Therefore, ***cof*-NADA** and ***lin*-NADA** dimers with partly soluble in water could be useful tools for life sciences. Due that their fluorescence are not affected in a very large pH value range (2–11), the complicate factors on the fluorescent probing resulted from the background of some biological systems can be removed.

The strong acid (pH from 4 to 2) makes protonation on the N, N′-dimethylamino groups of ***cof*-NA** and ***lin*-NA** dimers at the 4-position of 1,8-naphthalimide, and switch off the PET paths from the N,N′-dimethylamino to the fluorophore [15,22]. Then the fluorescence of ***cof*-NA** and ***lin*-NA** dimers are obviously enhanced as shown in Fig. 12. Noticeably, the reverse results were observed on going back from acidic to basic solution and the fluorescence intensity values are

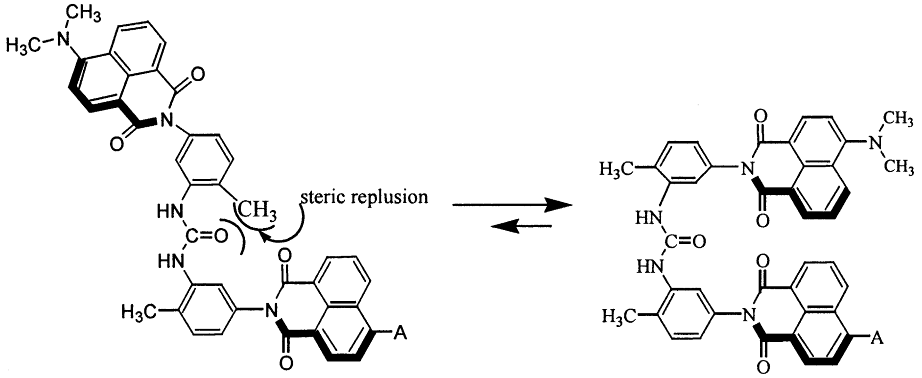


Fig. 11. Conformational equilibrium in the diaryl urea.

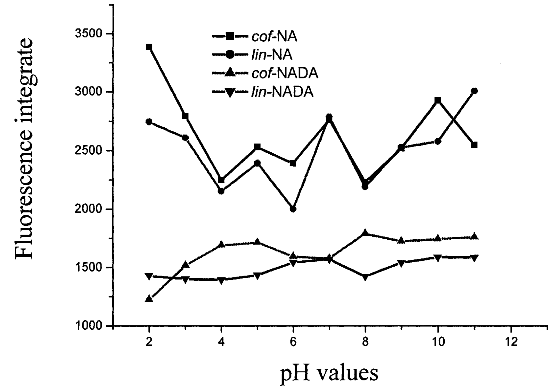


Fig. 12. Variation of integrate of fluorescence emission of ***cof*-NA**, ***lin*-NA**, ***cof*-NADA**, ***lin*-NADA** in methanol and water (v/v = 4:1) with different pH values.

reproducible, at the same pH values, after any change of pH. In the range of pH 5-11, ***cof*-NA** and ***lin*-NA** fluorescent probes are also nearly pH un-sensitive.

3. Conclusions

Four novel "Donor-Bridge-Acceptor" and "Donor-Bridge-Donor" type dimers were synthesized, in which aromatic diaryl urea component was used as "bridge" with a known distance and configuration. Two of them are cofacial configuration, by the steric repulsion between the methyl group and the carbonyl group in the diaryl urea bridge. The fluorescence emission spectra and the lifetimes of these compounds have been measured by a fluorescence spectrometer and single-photon counting technique. The charge separation between two chromophores in a π-stacked configuration has been reported. The influence on the fluorescence, especially on solid state fluorescence, by charge separation or transfer between the two chromophores has been discussed using these model systems. Our results suggest that the cofacial π-stacked configuration in these dimers provides new routes to biomimetic charge separation and to develop new fluorescent materials with high quantum yield in solid state.

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