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Synthesis and fluorescence properties of novel co-facial folded naphthalimide dimers

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Abstract

Two novel co-facial folded naphthalimide dimers were synthesized. Strong exciton coupling was observed in the folded dimers as an absorption maximum blue-shift. The fluorescent quenching of the dimers compared to that of monomers and the solvent polarity effect on the quenching efficiency are discussed. The fluorescence lifetimes of the dimers have been also investigated and discussed.

Keywords: Co-facial folded dimer; Synthesis; Naphthalimide; Fluorescence; Fluorescent lifetimes

Nature relies on large molecules to carry out sophisticated chemical operations, such as catalysis, tight and specific binding, directed flow of electrons, or controlled crystallization of inorganic phase. The molecules entrusted with these crucial tasks, mostly proteins but sometimes RNA, are unique in that they adopt specific folding conformations. Indeed, folding plays a vital role in molecular science [1–5]. Recently, the construction of unnatural molecules that adopt folding conformations is a subject of increasing interest to chemists. Examples include β-peptide folding [6–8], γ-peptide folding [9], δ-peptide folding [10], vinylogous peptide folding [11], and so on. At the same time, design of non-peptide oligomers that fold into well-defined secondary structures also has been attracting much attention [12–14]. Such material might be applicable to the formation of new functional polymers with interesting catalytic or recognition properties. Various approaches to folding structures have been taken, involving primarily the use of hydrogen bonding [15], conformational restriction and π–π interaction [16]. In this paper we report that simple naphthalimide derivatives can be combined to form dimers which take up co-facial structures (Fig. 1), stabilized by π–π interaction. This conformation of the dimers influencing the luminescence properties has been investigated.

The 1,8-naphthalimide derivatives **7a** and **7b** were chosen as monomers owing not only to their excellent properties [17,18], but also to their big π system and rigid planar structures which are beneficial to forming a co-facial structure stabilized by π–π stacking interaction when using a suitable linkage. 1,8-Bis(bromomethyl) anthracene **5** was used as a linkage because when the 1,8-position is substituted by a phenyl group, two phenyl rings become approximately perpendicular to the plane of the anthracene ring and parallel to each other [19]. The syntheses of the two dimers are outlined in Scheme 1.

The folding dimers (**DNPA** and **DNPOA**) exhibit different photochemical properties compared to the monomers (**7a** and **7b**) including the blue-shift of the absorption maximum, the quenching of the fluorescence

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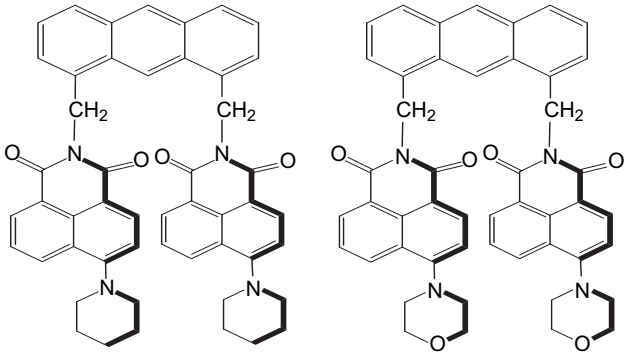


DNP A **DNP OA**

Fig. 1. Structures of naphthalimide dimers.

and the greatly shortened fluorescence lifetimes. The dimers provided a simple but excellent model for further studies on trimers, oligomers, and even aggregation in materials.

1. Experimental

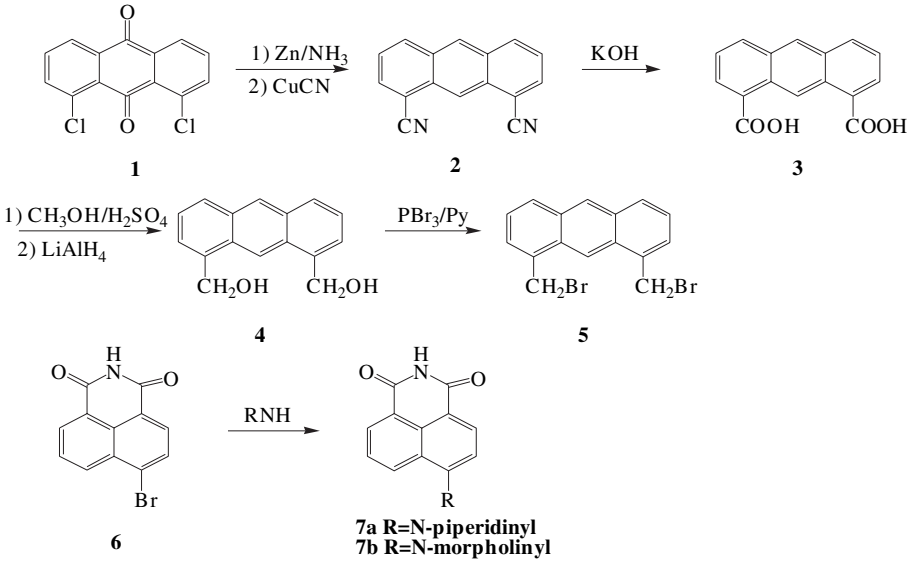
^{1}H NMR spectra were obtained using a Brücker AM 500 spectrometer. Mass spectra (MS) were carried out on an MA1212 instrument. UV–vis spectra were performed on a Varian Cray500 spectrophotometer. Fluorescence spectra were recorded on a Varian Cray Eclipse fluorescence spectrophotometer. The fluorescence lifetime study was performed using 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-square fitting program with deconvolution of the exciting pulse ~200 ps [20]. Compounds **2**–**4** were synthesized according to literature [19,21,22]. 6-Bromo-benzo[*de*]isoquinoline-1,3-dione (**6**) was prepared according to the literature [23] in 85% yield.

*1.1. 1,8-Bis(bromomethyl) anthracene (**5**)*

To a stirred mixture of (**4**) (4.76 g, 20 mmol), pyridine (0.8 g, 10 mmol) and tetrahydrofuran (100 mL), was added a solution of phosphorus tribromide (8.14 g, 30 mmol) in tetrahydrofuran (20 mL) over a period of 20 min. After stirring for another 2 h at room temperature, cracked ice was added to the reaction mixture and yellow precipitate was collected. Recrystallization from benzene gave light yellow needles. M.p. 232–234 °C (decomp.) (lit. [24] 230–232 °C (decomp.)). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 5.16 (s, 4H), 7.44 (dd, J = 8.55, 6.85 Hz, 2H), 7.63 (d, J = 6.85 Hz, 2H), 8.03 (d, J = 8.55 Hz, 2H), 8.54 (s, 1H), 9.01 (s, 1H).

*1.2. 6-Piperidin-1-yl-benzo[de]isoquinoline-1, 3-dione (**7a**)*

6-Bromo-benzo[*de*]isoquinoline-1,3-dione (**6**) (5 g, 18 mmol) was dissolved in 2-methoxyethanol (100 mL) and piperidine (3 g, 36 mmol) was added. The mixture was refluxed for 6 h. After cooling to room temperature,



5 + 7 $\xrightarrow{CH_3ONa}$ **DNPA or DNPOA**

Scheme 1. Synthesis of naphthalimide dimers.

the yellow precipitates were filtered and washed with ethanol (3 × 100 mL) to give pure 6-piperidin-1-yl-benzo[*de*]isoquinoline-1,3-dione (**7a**) (3.46 g, 68%). M.p. 279–280 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 1.67 (m, 2H), 1.85 (m, 4H), 3.20 (t, J = 4.82 Hz, 4H), 7.15 (d, J = 8.14 Hz, 1H), 7.63 (dd, J = 7.96, 7.67 Hz, 1H), 8.35 (d, J = 7.96 Hz, 1H), 8.40 (d, J = 8.14 Hz, 1H), 8.50 (d, J = 7.67 Hz, 1H). Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C 72.84, H 5.75, N 9.99. Found: C 72.68, H 5.86, N 10.05%.

*1.3. 6-Morpholin-4-yl-benzo[de]isoquinoline-1, 3-dione (**7b**)*

6-Bromo-benzo[*de*]isoquinoline-1,3-dione (**6**) (5 g, 18 mmol) was dissolved in 2-methoxyethanol (100 mL) and morpholine (3.13 g, 36 mmol) was added. The mixture was refluxed for 6 h. After cooling to room temperature, the bright yellow precipitates were filtered and washed with ethanol (3 × 100 mL) to give pure 6-piperidin-1-yl-benzo[*de*]isoquinoline-1,3-dione (**7b**) (3.33 g, 65%). M.p. 237–238 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 3.26 (t, J = 4.38 Hz, 4H), 4.00 (t, J = 4.38 Hz, 4H), 7.21 (d, J = 8.10 Hz, 1H), 7.69 (dd, J = 7.92, 7.77 Hz, 1H), 8.45 (d, J = 7.92 Hz, 1H), 8.51 (d, J = 8.10 Hz, 1H), 8.57 (d, J = 7.77 Hz, 1H). Anal. Calcd. for $C_{16}H_{14}N_2O_3$: C 68.07, H 5.00, N 9.92. Found: C 68.29, H 5.24, N 9.78%.

*1.4. Naphthalimide dimer **DNPA***

6-Piperidin-1-yl-benzo[*de*]isoquinoline-1,3-dione (**7a**) (0.1 g, 0.357 mmol) was dissolved in dimethylformamide (20 mL), and methanol sodium (4.10 mg, 0.18 mmol) was added. After stirring at room temperature for 2 h, 1,8-bis(bromomethyl) anthracene (**5**) (0.042 g, 0.12 mmol) was added and stirred for another 6 h. The yellow precipitates were filtered, washed with ethanol and dried. Purification was carried out by column chromatography on a silica gel with $CHCl_3$ as eluent, affording 54 mg of the title compound (yield 38%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 1.66 (m, 4H), 1.84 (m, 8H), 3.18 (t, J = 4.80 Hz, 8H), 6.05 (s, 4H), 7.10 (d, J = 8.04 Hz, 2H), 7.30 (dd, J = 8.10 Hz, 7.15 Hz, 2H), 7.35 (d, J = 7.15 Hz, 2H), 7.61 (dd, J = 7.98 Hz, 7.68 Hz, 2H), 7.80 (d, J = 8.10 Hz, 2H), 8.36 (s, 1H), 8.38 (d, J = 7.98 Hz, 2H), 8.50 (d, J = 8.04 Hz, 2H), 8.52 (d, J = 7.68 Hz, 2H), 9.37 (s, 1H). Anal. Calcd. for $C_{50}H_{42}N_4O_4$: C 78.72, H 5.55, N 7.34. Found: C 78.96, H 5.72, N 7.09%.

*1.5. Naphthalimide dimer **DNPOA***

6-Morpholin-4-yl-benzo[*de*]isoquinoline-1,3-dione (**7b**) (0.1 g, 0.354 mmol) was dissolved in dimethylformamide (20 mL), and methanol sodium (4.01 mg, 0.177 mmol) was added. After stirring at room temperature for 2 h, 1,8-bis(bromomethyl) anthracene (**5**) (0.043 g, 0.12 mmol) was added and stirred for another 6 h. The yellow precipitates were filtered, washed with ethanol and dried. Purification was carried out by column chromatography on a silica gel with $CHCl_3$ as eluent, affording 50 mg of the title compound (yield 35%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 3.25 (t, J = 4.28 Hz, 8H), 4.03 (t, J = 4.28 Hz, 8H), 6.10 (s, 4H), 7.23 (d, J = 8.02 Hz, 2H), 7.33 (dd, J = 8.12 Hz, 7.17 Hz, 2H), 7.40 (d, J = 7.17 Hz, 2H), 7.70 (dd, J = 7.90 Hz, 7.75 Hz, 2H), 7.86 (d, J = 8.12 Hz, 2H), 8.40 (s, 1H), 8.43 (d, J = 7.90 Hz, 2H), 8.57 (d, J = 8.02 Hz, 2H), 8.62 (d, J = 7.75 Hz, 2H), 9.42 (s, 1H). Anal. Calcd. for $C_{48}H_{38}N_4O_6$: C 75.18, H 4.99, N 7.31. Found: C 75.04, H 4.72, N 7.53%.

2. Results and discussion

2.1. Absorption spectra of the dimers

The UV–vis absorption spectra of **7a**, **7b**, **DNPA** and **DNOPA** in $CHCl_3$ are shown in the Figs. 2 and 3. The absorption maximum of monomer **7a** is 414 nm; however, the absorption maximum of **7b** is 394 nm. The difference in their absorption maxima is due to the stronger electron-donating ability of piperidine than that of morpholine substitutes at the 4-position of the naphthalimide ring. The absorption maximum of dimer **DNPA** has two absorption peaks, of which the peak at 390 nm is the absorption of anthracene [25] and the other peak at 408 nm is the absorption of the monomer naphthalimide. While the dimer **DNPOA** has only one maximum absorption peak at 389 nm, this peak may be the sum of the anthracene and the naphthalimide. The red-shift of **DNPA** is also due to the reason discussed above. The intensities of both maximum absorptions of

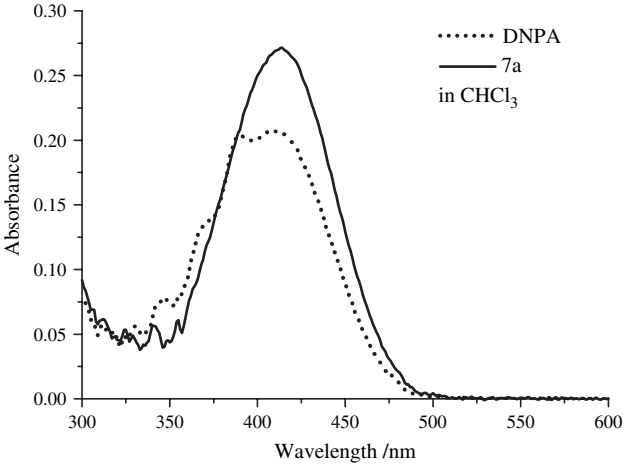


Fig. 2. Absorption spectra of **7a** and **DNPA** in $CHCl_3$ (10^{-5} mol/L).

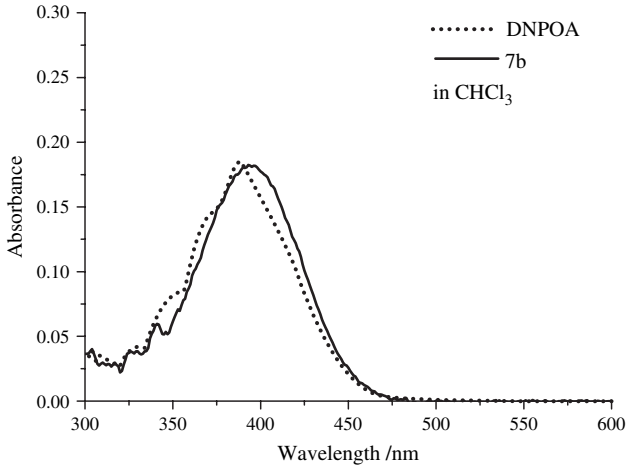


Fig. 3. Absorption spectra of **7b** and **DNPOA** in $CHCl_3$ (10^{-5} mol/L).

DNPA are weaker than that of the monomer **7a**, while the intensity of the maximum absorption of **DNPOA** is almost the same as for monomer **7b**. This also confirmed that the single maximum absorption is the sum of the anthracene and the naphthalimide.

When comparing the absorption maxima of the dimers and the monomers, we could find that the absorption maximum of the dimer **DNPA** (λ = 408 nm) exhibited a slight blue-shift of 5 nm compared to that of monomer **7a** (λ = 413 nm). This indicates a strong exciton coupling between the transition in the two naphthalimides, 6-piperidin-1-yl-benzo[*de*]isoquinoline-1,3-dione (**7a**), adopting a co-facial π-stacked array. According to Kasha's theory [26], when the two monomers in a dimer are arranged in a co-facial conformation, two transitions will occur, one is singlet parallel excitation transition state S_1'', whose energy is allowed from the ground state; and the other is singlet anti-parallel excitation transition state S_1', whose energy is forbidden from the ground state [26] as shown in Fig. 4. The S_1'' transition is a high-energy transition and has all of the oscillator strength, so correspondingly the maximum absorption will be blue-shift. The dimer **DNOPA** also exhibited a similar blue-shift ($\Delta\lambda$ (**7b**–**DNOPA**) = 9 nm) as shown in Fig. 3 compared with the data of the monomer.

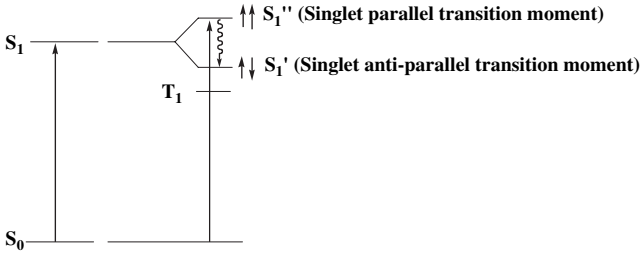


Fig. 4. Excitation energy band diagram of the dimers.

2.2. Fluorescence spectra of the dimers

Fluorescence spectra of the monomers and the dimers in different solvents have been shown in Figs. 5–10. The fluorescence intensity of **7a** is weaker than that of **7b** and the maximum emission peak of **7a** red-shifts compared to **7b** in the same solvent. For example, the fluorescent intensity of **7a** is 7.218 at the maximum emission peak of 517 nm in $CHCl_3$ (Fig. 6), while that of **7b** is 9.154 at 504 nm (Fig. 9). This is attributed to the stronger electron-donating ability of piperidine in **7a**.

The dimers have only one emission peak around 510 nm, which should be the emission of the naphthalimide moiety. No emission peak of anthracene was observed. This is attributed to the overlap between the absorption of monomer naphthalimide (~410 nm) and the emission of anthracene (402 nm) [25] and the effective energy transfer from anthracene to monomer naphthalimide. However, the fluorescence intensities of dimers decrease compared to those of the monomers. Intramolecular energy transfer and face-to-face interaction might be considered simultaneous. The face-to-face interaction of the two monomers in dimers will decrease the energy gap between the singlet state S_1' and the triplet state as shown in Fig. 4 and enhance the formation of triplet state (i.e. S → T intersystem cross increases), consequently decreasing the fluorescence intensity. The fluorescence quenching resulting from the configuration interaction should be stronger than the influence resulting from the intramolecular energy transfer, so the fluorescence of dimers is weaker than that of the monomers.

When the fluorescence intensity of the dimers in the same solvent is compared, **DNPOA** is weaker than **DNPA**. For instance, the fluorescent intensity of **DNPOA** is 0.549 in $CHCl_3$ (Fig. 9), while that of **DNPA** is 2.756 (Fig. 6). The oxygen atom of morpholine of monomer **7b** has bigger electron-attracting ability

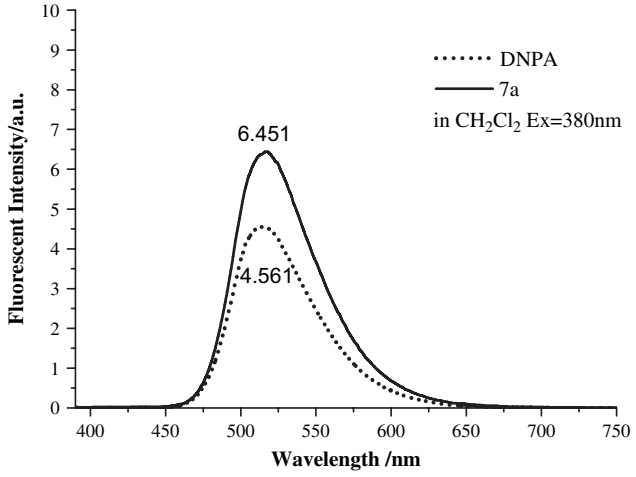


Fig. 5. Fluorescence spectra of **7a** and **DNPA** in CH_2Cl_2 (10^{-5} mol/L).

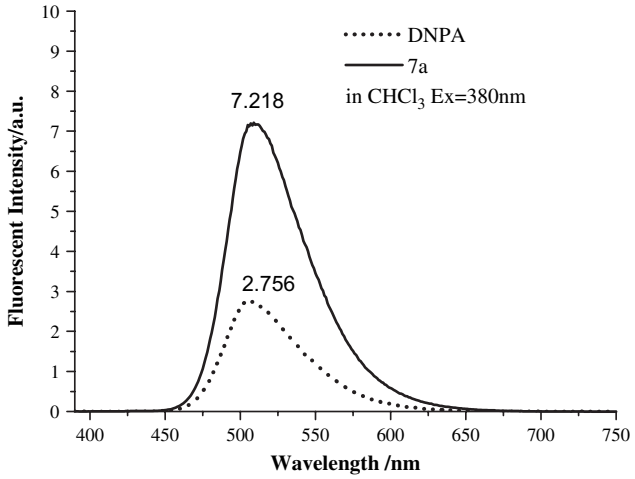


Fig. 6. Fluorescence spectra of **7a** and **DNPA** in $CHCl_3$ (10^{-5} mol/L).

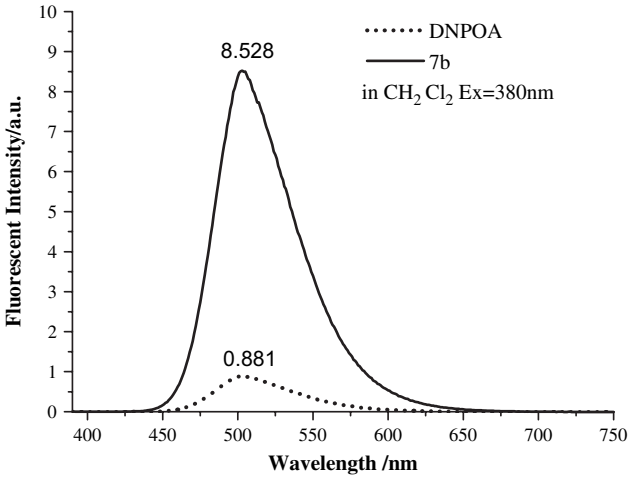


Fig. 8. Fluorescence spectra of **7b** and **DNPOA** in CH_2Cl_2 (10^{-5} mol/L).

than the corresponding position's carbon atom of monomer **7a**. So the rotation of C–N bond at the 4-position of the naphthalimide ring is more difficult in **7b**, which results in (i) the decrease of nonirradiative energy through rotation (therefore, the fluorescence intensity of **7b** is larger than that of **7a**); (ii) the face-to-face interaction of the two monomers containing morpholine is stronger than that of the two monomers containing piperidine in **DNPA**. Correspondingly, the fluorescence intensity of **DNPOA** is weaker than that of **DNPA**. So integrating the above two factors, the fluorescence intensity of the monomer **7a** is stronger than that of **7b**, and the fluorescence intensity of dimer **DNPA** is weaker than that of dimer **DNPOA**. Based on the data in Table 1, it can be deduced that the fluorescence quenching in **DNPOA** relative to **7b** is stronger than that in **DNPA** relative to **7a**.

The polarization of surrounding medium accompanying excitation coupling is an important factor for the luminescence properties in a dimer. In different solvents, the fluorescence quenching ratio for **DNPA** relative to **7a** and for **DNPOA** relative to **7b** is different. Along with the increasing polarity of the solvent, the fluorescence quenching effect decreases. For example, the fluorescence intensity ratio between **DNPA** and **7a** is 0.382 in low polarity solvent $CHCl_3$ (μ = 1.1 D), while the fluorescence intensity ratio between **DNPA** and **7a** is 0.707 in a middle polarity solvent CH_2Cl_2 (μ = 1.5 D) and is 0.780 in a high polarity solvent THF (μ = 1.7 D). Two monomers were coupled to the anthracene through a flexible chain, $-CH_2-$, and their $\pi-\pi$ interaction decreases with increase in medium polarity. So the fluorescence quenching efficiency decreases along with the increasing polarity of solvents. This phenomenon should be used as a new potential polarity sensor of medium by means of fluorescent spectra of the dimers.

2.3. Fluorescence lifetimes of the dimers

The fluorescent lifetimes of the dimers were determined with 380 nm as excitation wavelength and

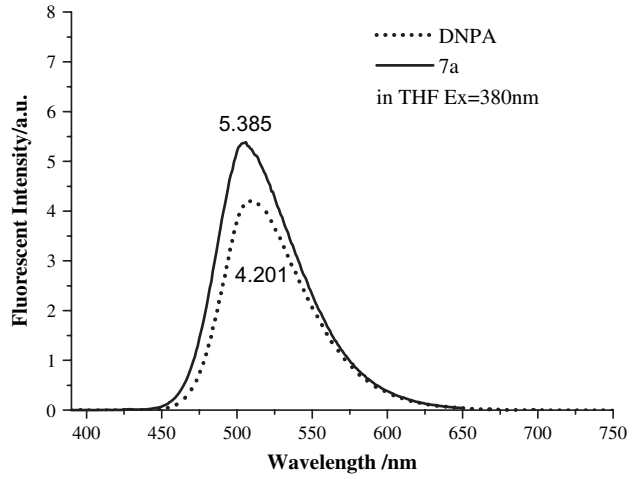


Fig. 7. Fluorescence spectra of **7a** and **DNPA** in THF (10^{-5} mol/L).

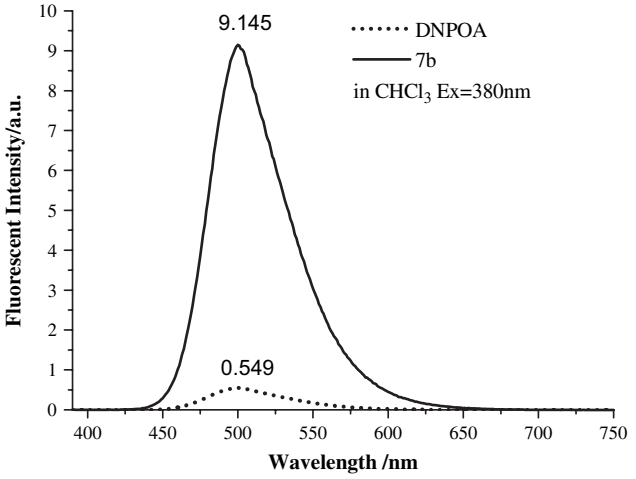


Fig. 9. Fluorescence spectra of **7b** and **DNPOA** in $CHCl_3$ (10^{-5} mol/L).

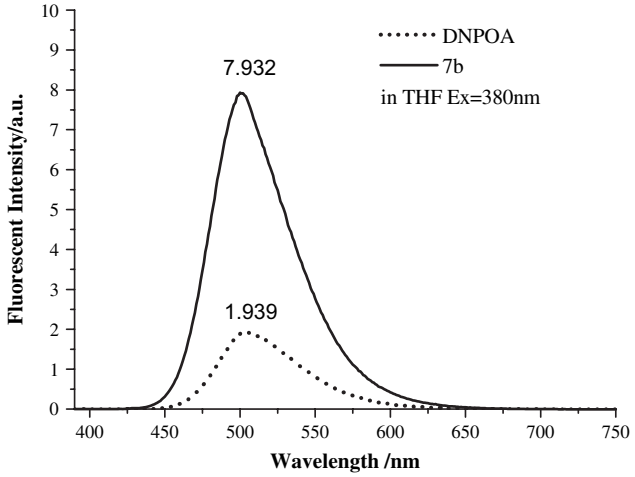


Fig. 10. Fluorescence spectra of **7b** and **DNPOA** in THF (10^{-5} mol/L).

520 nm as the probing emission wavelength; the results are shown in Table 2. The fluorescent lifetimes of the monomers both exhibit single exponential decay kinetics, while those of the two dimers are two-component exponential decay. Since the probing emission wavelength is at 520 nm, no emission of anthracene in the dimers can be detected, as shown in the fluorescence spectra in Figs. 5–10. So the two-component fluorescent lifetimes are expected to belong to the monomer itself and the face-to-face interaction in the dimers, respectively. The longer fluorescent lifetime of the dimer is almost the same as that of the corresponding monomer, while the shorter fluorescent lifetime of the dimer should result from the face-to-face interaction in the dimers. According to the exciton theory, the dimer forms the two singlet transition states as shown in Fig. 4. Very quick intrasystem cross from S_1'' to S_1', as shown in Fig. 4, will decrease the energy gap from S_1' to triplet state. This decreases the fluorescence lifetime correspondingly. Meanwhile, solvent polarities also have different effect on the fluorescent lifetimes of the dimers, as shown in Table 2. For dimer **DNPOA** containing morpholine, the shorter fluorescent lifetimes have more weight percentage along with increasing polarity of solvents. While it is reverse for dimer **DNPA** containing piperidine, i.e. the shorter fluorescent lifetimes in dimer **DNPA** have less weight percentage along with the increasing polarity of solvents. This implies that there exists strong excitation coupling interaction in dimer **DNPOA**. In the same solvent, the shorter fluorescent

Table 1
Fluorescence intensity and the intensity ratios of **7a**, **7b**, **DNPA** and **DNPOA**

	7a	DNPA	DNPA/7a	7b	DNPOA	DNPOA/7b
In $CHCl_3$	7.218	2.756	0.382	9.145	0.549	0.060
In CH_2Cl_2	6.451	4.561	0.707	8.528	0.881	0.103
In THF	5.385	4.201	0.780	7.932	1.939	0.244

Table 2
Fluorescence lifetimes of dimers in $CHCl_3$, CH_2Cl_2 and THF (excited at 380 nm; probed at 520 nm)

	τ (ns)			
	7a	**DNPA**	**7b**	**DNPOA**
In $CHCl_3$	8.862	2.396 (52.48%) 6.845 (47.52%)	8.649	0.955 (31.44%) 7.742 (68.56%)
In CH_2Cl_2	7.023	2.694 (15.27%) 7.293 (84.73%)	8.377	1.246 (56.72%) 7.342 (43.28%)
In THF	7.023	2.687 (14.02%) 6.412 (85.98%)	8.377	1.571 (60.97%) 6.686 (39.03%)

lifetimes of **DNPA** are longer than those of **DNPOA**, for example, in $CHCl_3$ the value is 2.396 ns for **DNPA** and 0.955 ns for **DNPOA**. This also indicates that the face-to-face interaction in **DNPOA** is stronger than that in **DNPA**.

2.4. Geometries of the dimers

The face-to-face orientation between two naphthalimide units in dimers was confirmed by the energy-minimized molecular modeling study, using MM2 [27], as shown in Figs. 11–14. Using MM2, we can easily calculate that the total steric energy of **DNPA** with the front-to-front conformation for the weak coupling between two piperidine units is 39.5585 kcal/mol, while that for the front-to-back conformation with strong coupling is 34.8618 kcal/mol as shown in Figs. 11 and 12, respectively. For dimer **DNPOA** containing morpholine units, the difference in the total steric energy between the front-to-front conformation (weak coupling) and the front-to-back conformation (strong coupling), which are shown in Figs. 13 and 14, is 9.279 kcal/mol. Then we can conclude that the two naphthalimides in the dimers are positioned in the front-to-back geometry (pointed relative position at 4-substitute of naphthalimide ring), which is ascribed to the relative low steric repulsion energy, as shown in Figs. 12

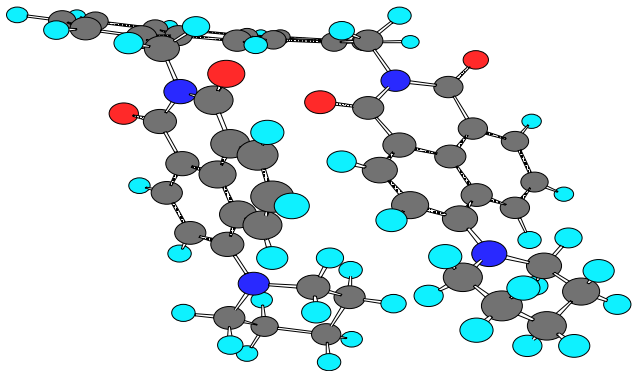


Fig. 11. Energy-minimized molecular modeling of **DNPA** dimer (front-to-front conformation 39.5585 kcal/mol; red color is oxygen, blue is nitrogen atom).

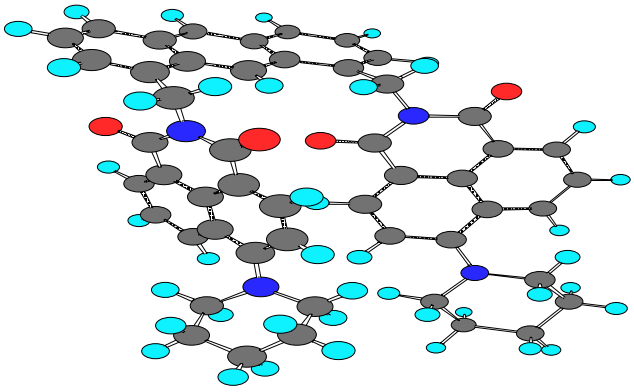


Fig. 12. Energy-minimized molecular modeling of **DNPA** dimer (front-to-back conformation 34.8618 kcal/mol; red color is oxygen, blue is nitrogen atom).

and 14. This also can explain why fluorescent lifetimes of the dimers have been quenched effectively relative to their monomers. In addition, the distance between two naphthalimide units with the front-to-back conformation is obviously smaller than that for the front-to-front conformation because the monomers were coupled to the anthracene through a flexible chain, $-CH_2-$. The energy transfer and coupling interaction between two naphthalimides depend directly upon the distance between two units; therefore, the front-to-back conformation will have strong coupling interaction and more effective energy transfer. The influences on the fluorescent properties including the lifetimes by the polarity of solvents and different electron-donating ability of the substitutes at 4-position of naphthalimide ring might also be explained by means of the geometries of the dimers.

3. Conclusion

Two novel folded naphthalimide dimers were synthesized. The fluorescence emission spectra and the lifetimes of the dimers have been measured by a fluorescence spectrometer and a single-photon counting technique. The absorption maximum blue-shift of the dimers reveals that two chromophores are in a face-to-face folded arrangement. Fluorescence quenching and fluorescence lifetimes in different solvents were reported and discussed. The results provided a good model for further studies of trimers, oligomers, and even aggregation in luminescent materials.

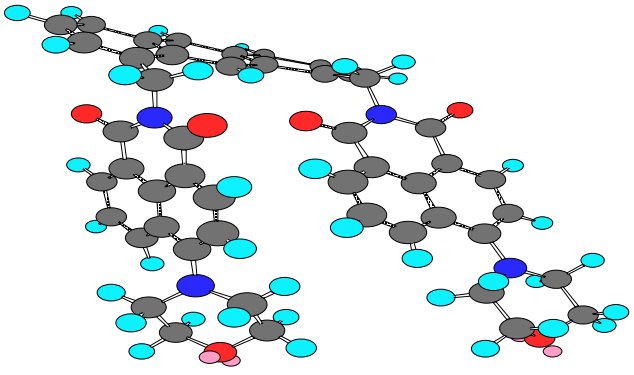


Fig. 13. Energy-minimized molecular modeling of **DNPOA** dimer (front-to-front conformation 53.9657 kcal/mol; red color is oxygen, blue is nitrogen atom).

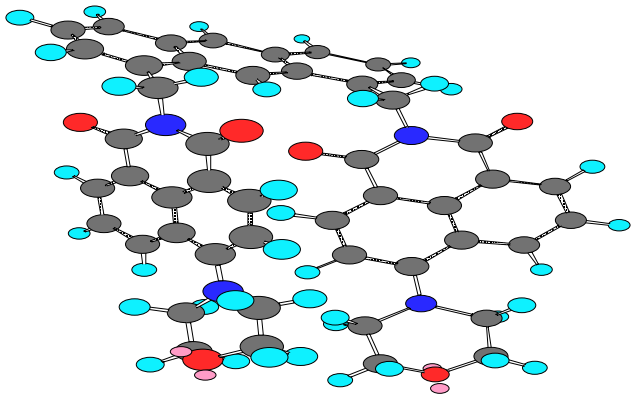


Fig. 14. Energy-minimized molecular modeling of **DNPOA** dimer (front-to-back conformation 44.6867 kcal/mol; red color is oxygen, blue is nitrogen atom).

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