

## Design and Synthesis of a Highly Stable Six-hydrogen-bonded Self-assembly Yellowish Green Electroluminescent Molecular Duplex

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**Abstract:** This paper describes the design, synthesis and characterization of a hydrogen-bonded molecular duplex with 1,8-naphthalimide fluorescent pendants. The two oligoamide molecular strands, with complementary hydrogen bond sequences of DDADAA and AADADD, can form an ultra stable self-assembly duplex. Its molecular structure was confirmed by <sup>1</sup>H NMR and ESI-MS, and its photoluminescence properties were determined. The resulting duplex exhibited a dramatically enhanced photoluminescence (PL) quantum efficiency of 63.7% compared to the corresponding 1,8-naphthalimide segment (32.4%), suggesting that the formation of the duplex with larger molecular weight could successfully inhibit the quenching of the fluorescent pendant. This novel duplex is a prospective candidate for new electroluminescent emitter.

**Keywords:** Selfassembly, H-bond, 1, 8-naphthalimide, photoluminescence, electroluminescence.

Since the first fabrication of thin-layer organic electroluminescent (OEL) device in 1987 by C. W. Tang *et al*<sup>1</sup>, OEL materials had been of ever increasing interest<sup>2,3</sup>. While up to now, full-color display has been commercialized with small molecules having different structures. In general, host-dopant systems are often employed in RGB OLEDs. This procedure, however, would lead to relatively poor performance for OEL devices, because of the easy aggregation and crystallization of the dopants, which would result in the concentration quenching and formation of darkspots<sup>4,5</sup>. Therefore, the design and synthesis of OEL dyes with low aggregation mobility should be the key to the problem.

Currently, there is intense interest in constructing selfassembly systems that may lead to nano-sized, supramolecular structures<sup>6-8</sup>. Compared to the other common ways, such as incorporation of dopants into oligomers, or endcapping of dopants into polymers, which had been reported to diminish the aggregation of dyes, the incorporation of fluorescent dyes into noncovalent-bonded selfassembly systems would present more excellent performance, because they have much better well-defined, good purity, and selfrecognized molecular structures. Herein, we designed and synthesized a novel hydrogen-bonded molecular duplex bearing a fluorescent pendant, the synthetic scheme was shown in **Scheme 1**. The two oligoamide molecular strands, with complementary hydrogen bond sequences of DDADAA and AADADD, can form a self-assembly duplex

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with ultra high dimerization constant in chloroform<sup>9,10</sup>, which may result in the self-assembly and self-recognition, and thus can fix the functional group steadily so that the dye segments could not move easily. 1,8-Naphthalimide was chosen as fluorescent pendant for its good PL efficiency<sup>11</sup>. To our knowledge, this is the first time that the laser dyes were incorporated into the self-assembly system using as EL material. This may pave a new pathway to improve the PL and EL efficiencies of the OEL devices. Furthermore, the oligoamide strands can find its application as fluorescent probe in biological systems due to its self-recognition characteristic.

### Results and Discussion

TLC assay indicated the good purity of the duplex **4·4**, and its MS spectrum convinced the duplex structure. The <sup>1</sup>H NMR spectrum data of the duplex **4·4** are in good coincidence with the similar duplex reported in the literatures<sup>10,12</sup>. The chemical shifts of protons of its amide groups ( $\delta=10.12, 10.11, 9.65$ ) were higher than that of protons of ordinary amide groups ( $\delta=8.54$ ). It indicated that intramolecular hydrogen bonds have formed, and the two strands self-associated successfully<sup>9,10,12</sup>. Because the two oligoamide strands have complementary hydrogen bond sequences of DDADAA and AADADD, which is the same with literature<sup>12</sup>, the resulting duplex **4·4** can be estimated having the same high dimerization constant<sup>9,10</sup> in chloroform of  $> 10^9 \text{ mol}^{-1}$ .

Photoluminescent properties of **4·4** and the acetate of **1d** (**Ac-1d**) are summarized in **Table 1**. They both emit yellowish green fluorescence in solid film and solution, and could be used as OEL emitters. However, **Ac-1d** has much lower PL quantum yield due to its planary molecular structure, which is easily aggregate. An additional examination of doping **Ac-1d** into poly(N-vinylcarbazole) (50% wt.) revealed merely little increase of quantum efficiency (34.1%), indicating the mobility of dyes could not be effectively inhibited in polymer matrix. On the contrary, **4·4** has much higher PL efficiency, indicating the sufficient inhibition of aggregation of the dye segments.

### Experimental

*Instruments:* Finnigan-LCQ ESI-MS; Bruker Advance 600 <sup>1</sup>H NMR instrument; Hitachi 850 fluorescence spectrophotometer; quantum yields were determined with an integrating sphere (IS80 from Labsphere).

Segments **2**, **3** were prepared according to literatures<sup>9,10</sup> *via* multistep synthesis. Intermediates **1a-e** and **1** were synthesized by known methods (**Scheme 1**). Their molecular structures were confirmed by ESI-MS and <sup>1</sup>H NMR.

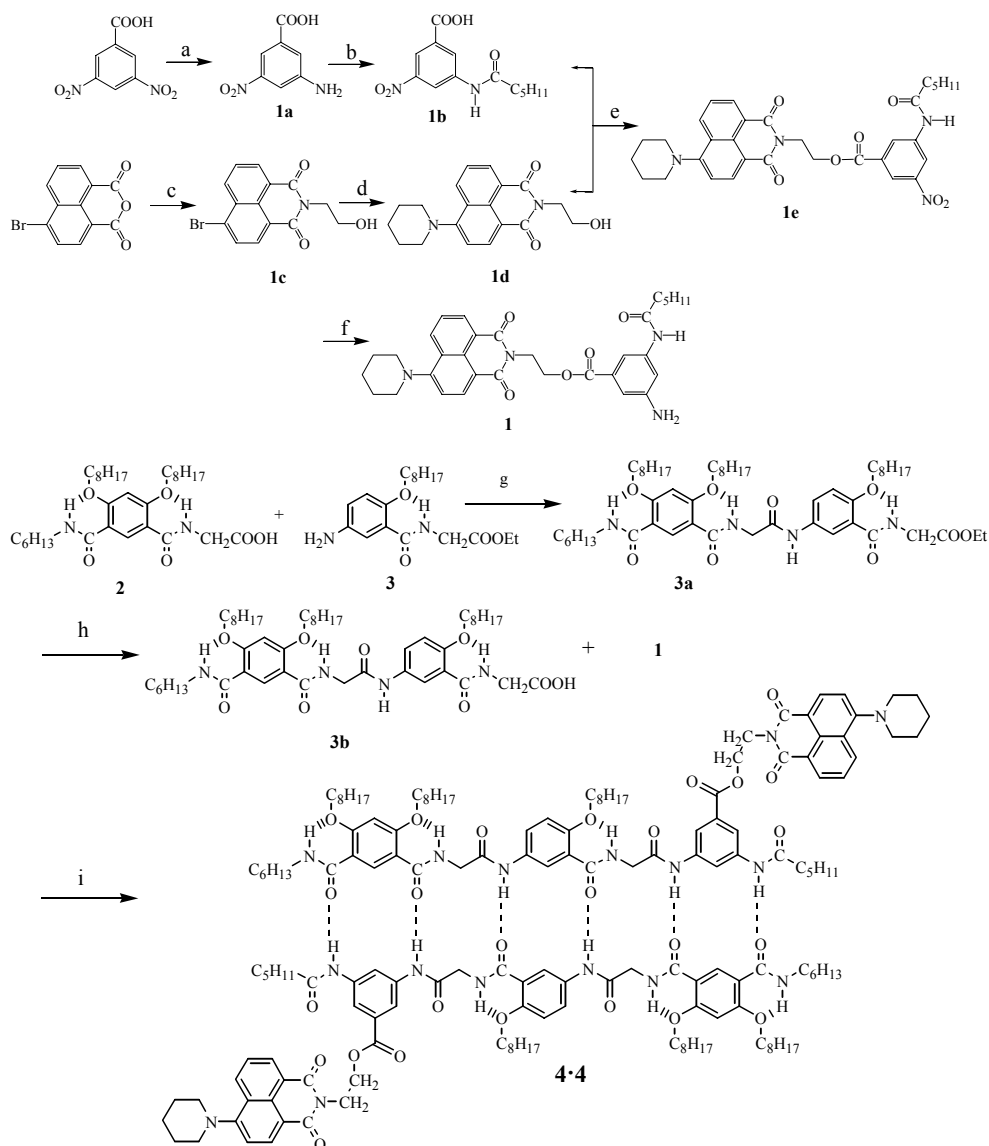
**Table 1** The Photoluminescence properties of the duplex **4·4** and **Ac-1d**

	$\lambda_{EMmax}$ (nm)		FWHM (nm)		Quantum efficiency (Thin film)
	$\lambda_1$	$\lambda_2$	$\lambda_1$	$\lambda_2$	
<b>4·4</b>	515	535	65	60	63.7%
<b>Ac-1d</b>	515	550	65	75	32.4%

( $\lambda_1$ :  $10^{-3}$  mol/L chloroform solution;  $\lambda_2$ : Solid film; FWHM: full width at half maximum)

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**Scheme 1** Synthetic route of the duplex **4·4**



- |                           |  |   |
|---------------------------|--|---|
| a) NaHS, 70%;             | b) C <sub>5</sub> H <sub>11</sub> COCl, 59%; | c) HOCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> , 69%; |
| d) Piperidine, CuCl, 70%; | e) EDC, HOBT, 43%;                           | f) H <sub>2</sub> , Pd/C;                                   |
| g) EDC, HOBT, 89%;        | h) NaOH, DMSO, 85%;                          | i) EDC, HOBT, 75%   |

Synthesis of **3a**: To the solution of **2** (2.64 mmol) in 60 mL DMF was added 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDC) (2.64 mmol) and 1-hydroxybenzotriazole (HOBT) (2.64 mmol), stirring for 30 min., a solution of 2.64 mmol **2** in 50 mL DMF was added under N<sub>2</sub> atmosphere. Then the reactant was stirred overnight, poured into ice-water, and the crude product was recrystallized from methanol

to afford white solid, yield: 89%. M.p. 198-199°C. MS.  $m/z$  894 ( $M^+$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ): 9.02 (s, 1H), 8.95 (s, 1H), 8.70 (t, 1H,  $J=2.8$ ), 8.52 (t, 1H,  $J=2.8$ ), 8.10 (m, 1H), 8.06 (m, 1H), 7.70 (t, 1H,  $J=3.6$ ), 6.96 (d, 1H,  $J=9.2$ ), 6.46 (s, 1H), 4.1-4.4 (m, 12H), 3.42 (m, 2H), 1.9-2.0 (m, 6H), 1.25-1.61 (m, 41H), 0.86 (m, 12H).

**Synthesis of 3b:** To a solution of **3a** (2.23 mmol) in 60 mL hot DMSO was added 9.2 mL of 0.37 mol/L aqueous NaOH. The mixture was refluxed and the reaction was monitored *via* TLC. After the hydrolysis was completed, the mixture was poured into 300 mL of ice-water, and filtered. The filtrate was acidified with conc. HCl, the white precipitate was collected and used without further purification.

**4•4** was synthesized with the similar procedure of **3a**, except for using **1** and **3b** as reactants. The reactant was stirred overnight, poured into ice-water, and the crude product was dissolved in chloroform, then deposited with methanol for several times followed by column chromatography (eluent:  $\text{CH}_2\text{Cl}_2$ ) to afford yellow solid, yield: 75% M.p. 228-229°C. MS.  $m/z$  2809 ( $M^+-1$ ), 1405 ( $M^+/2$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ): 10.2 (s, 1H),  $\delta$ 10.1 (s, 1H), 9.65 (s, 1H), 9.50 (s, 1H), 9.13 (s, 1H), 9.05 (s, 1H), 8.82 (s, 1H), 8.38-8.63 (m, 5H), 8.02 (s, 1H), 7.89 (s, 1H), 7.65 (t, 1H,  $J=3.6$ ), 7.16 (t, 2H,  $J=9.2$ ), 6.93 (s, 1H), 6.51 (s, 1H), 4.62 (m, 4H), 4.16 (m, 4H), 4.14-4.15 (m, 6H), 3.40 (m, 2H), 3.20 (s, 4H), 2.40 (t, 2H,  $J=4.8$ ), 1.17-2.01 (m, 56H), 0.74-0.90 (m, 15H).

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