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Novel four-hydrogen-bond assembled oligoamide dimer with pyrazoline moieties and its photoluminescent properties

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Abstract

In this paper, the synthesis and characterization of a triarylpyrazoline modified four-H-bonded molecular duplex are described. Its molecular structure has been confirmed by ^{1}H NMR and ESI-MS. The duplex emits strong pure blue light peaking at 448 and 452 nm under UV photoexcitation in solution and solid state, respectively, and its relative photoluminescence quantum efficiency in solution is determined as 0.778 using quinine sulfate as reference. In concentration of >40 mmol/L, the duplex can gelate DMSO, and the organogel formed shows good pure blue photoluminescence too. This novel duplex, for its well-defined structure and efficient photoluminescence property, is a prospective candidate for pure blue electroluminescent emitter.

Keywords: Self-assembly; H-bond; Pyrazoline; Photoluminescence; Organogel

Owing to their potential applications in flat panel displays, organic electroluminescent (OEL) materials have attracted much interest all over the world in the past twenty years [1,2]. Among the RGB primary colors in fabrication of full-color display, only the performance of green OEL devices are qualified for industrialization with high efficiencies and durability [3], while that of red and blue OEL devices are relatively low [4,5]. Thus the development of blue-emitting material with high efficiency and good color purity draws much attention, and extensive studies on the design and synthesis of blue light-emitting materials have been demonstrated [5–7].

Generally, the fabrication of light-emitting diodes (LEDs) often involves a doping procedure [3,4,8,9], because it may inhibit the concentration quenching of the small planar dye molecules. This procedure, however, would result in relatively poor device durability, since the dopants may aggregate, stack, and crystallize, thus lead to phase separation under prolonged electric stress and higher working temperature [5,10]. Therefore, a hot issue recently is the design of novel-emitting molecules that have less propensity of concentration quenching, while the most effective way is the construction of dyes with bulky volumes or non-planar structures, which could prevent the fluorophores from the close stacking [5,11,12].

In our previous work, we have reported the successful incorporation of 1,8-naphthalimide segments into oligoamide strand, and the resulting H-bond self-assembly duplex possesses highly improved photoluminescence (PL)

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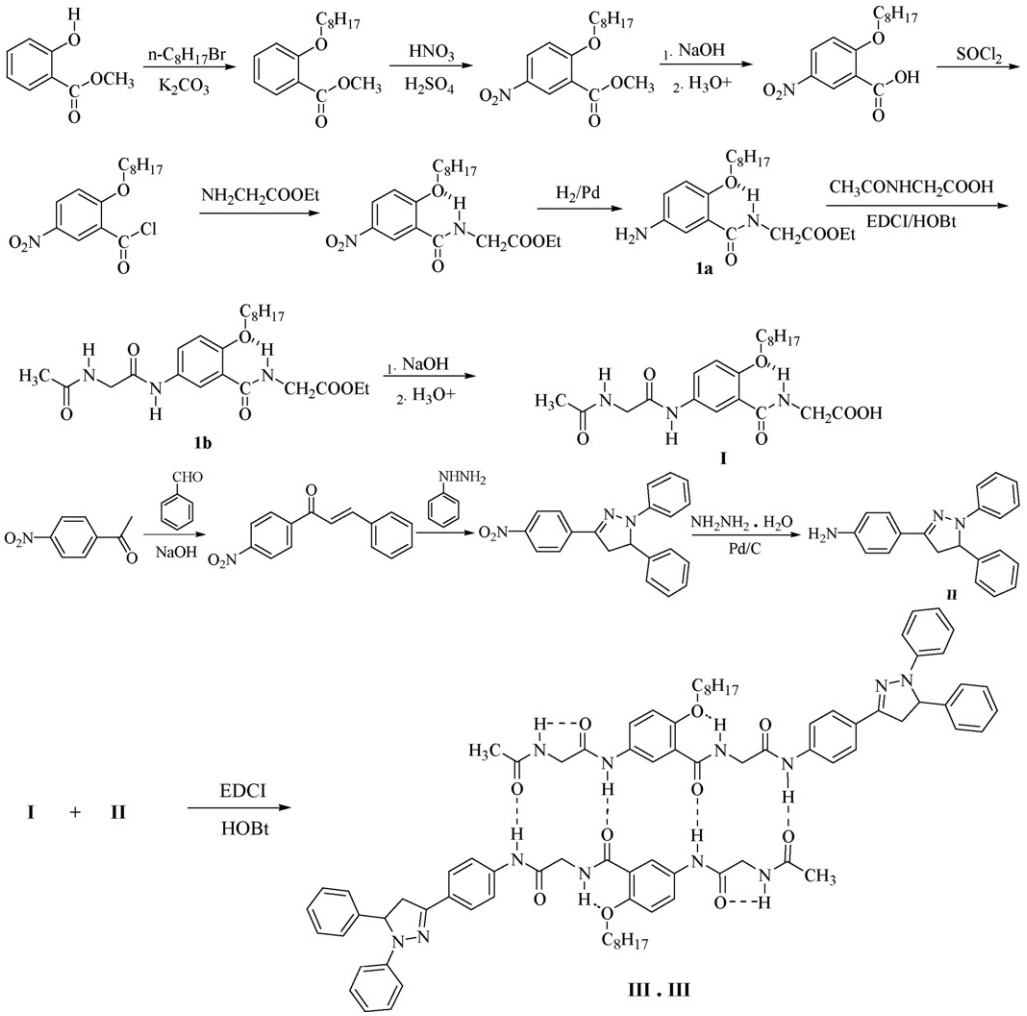

Scheme 1. The synthetic route to the target molecule.

property [13]. Herein, we would describe the design and synthesis of a novel bulky pure blue light-emitting dimmer bearing quadruple H-bonding motif comprising arrays on one edge with complementary H-bond sequences of DADA and ADAD, while the blue fluorophore is a pyrazoline derivative, which has been confirmed to be suitable as pure blue emitter in LEDs before [14,15]. By introduction of bulky and rigid oligoamides into triarylpyrazoline skeleton, the aggregation of chromophore may be diminished effectively.

The synthetic route to the target molecule is outlined in Scheme 1.

1. Experimental

^{1}H NMR spectra were performed on a Bruker AVANCE-II-400. ESI-MS spectra were recorded on a FINNIGAN-LCQ^{DECA}. Photoluminescence spectra were recorded on a HITACHI F-4600 spectrofluorometer. Intermediates **1a** and **II** were prepared according to literatures [16] and [17], respectively.

*1.1. Synthesis of ethyl 2-[5-(2-acetamidoacetamido)-2-(octyloxy)benzamido]acetate (**1b**)*

To a three-neck bottle was added acetyl glycin (5 mmol), 1-ethyl-3-[3-(dimethylamino)propyl] carbodiimide hydrochloride (EDCI) (5 mmol), 1-hydroxybenzotriazole (HOBt) (5 mmol) and 40 mL of DMF. The reactant was mixed for 30 min under argon, then **1a** (5 mmol) was added. After stirring for 6 h at 35 °C, the reactant mixture was

poured into 200 g of cracked ice. The solid was collected, washed with water, and recrystallized from methanol to give white solid. Yield: 76.5%. ESI-MS: *m/z* 449(M^+). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 9.960 (s, 1H), 8.548 (t, 1H, J = 5.6 Hz), 8.192 (t, 1H, J = 5.6 Hz), 8.018 (d, 1H, J = 2.4 Hz), 7.785 (dd, 1H, J = 6.4 Hz, J = 2.8 Hz), 7.142 (d, 1H, J = 8.8 Hz), 4.093–4.165 (m, 6H), 3.830 (d, 2H, J = 6.0 Hz), 1.880 (s, 3H), 1.802 (m, 2H), 1.233–1.433 (m, 13H), 0.850 (t, 3H, J = 6.8 Hz).

*1.2. Synthesis of 2-[5-(2-acetamidoacetamido)-2-(octyloxy)benzamido]acetic acid (**I**)*

To a three-neck bottle was added **1b** (3.5 mmol) and 30 mL of DMSO, and the reactant was heated to 100 °C, then 10 mL of 0.4 mol/L aqueous NaOH was added. After refluxing for 30 min, it was poured into 150 mL of ice water. Acidification with concentrated HCl to pH 2–3 would afford white solid. The crude product was recrystallized from methanol and white crystal was obtained. Yield 81.2%.

*1.3. Synthesis of 5-(2-acetamidoacetamido)-N-{2-[4-(1,5-diphenyl-4,5-dihydro-1H-pyrazole-3-yl)phenylamino]-2-oxoethyl}-2-(octyloxy)benzamide (**III**)*

To a three-neck bottle was added **I** (2 mmol), EDCI (2 mmol), HOBt (2 mmol), and 20 mL of DMF. The reactant was mixed for 30 min under argon, then **II** (2 mmol) was added. After stirring for 6 h at room temperature, the reactant mixture was poured into 150 g of cracked ice. The solid was collected, washed with water, ethanol, acetone to afford yellow solid. It was dissolved in DMSO, then dropped to methanol to remove trace impurities. This procedure was repeated for three times, then the yellowish fiber was collected and purified in a soxhlet extractor from methanol for 48 h. Yield, 62%. ESI-MS: *m/z* 715.31 (60%, M^+-1); 739.45 (60%, M^++Na^+); 1453.29 (100%, $2M^+$+Na^+-2); 1455.27 (65%, $2M^+$+Na^+). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 10.323 (s, 1H), 9.971 (s, 1H), 8.715 (t, 1H, J = 3.6 Hz), 8.198 (t, 1H, J = 4.2 Hz), 8.10 (d, 1H, J = 2.8 Hz), 7.878 (d, 1H, J = 4.4 Hz), 7.815 (d, 1H, J = 2.4 Hz), (d, 1H, J = 0.3 Hz), 7.7 (m, 3H), 7.2–7.5 (m, 5H), 7.15 (m, 2H), 6.985 (d, 2H, J = 4.0 Hz), 6.701 (t, 1H, J = 4.0 Hz), 5.450 (q, 1H, J = 5.4 Hz), 4.225 (d, 2H, J = 4.4 Hz), 4.137 (m, 2H), 3.920 (dd, 1H, J = 12 Hz, J = 5.6 Hz), 3.841 (t, 2H, J = 5.2 Hz), 3.050 (dd, 1H, J = 6.4 Hz, J = 11.2 Hz), 1.874 (m, 5H), 1.220–1.457 (m, 10H), 0.811 (t, 3H, J = 6.8 Hz).

2. Results and discussion

The ^{1}H NMR spectrum of the self-assembly duplex **III·III** (25 mmol/L in DMSO-d_6) shows the existence of two amide NH protons with higher chemical shifts in the region of 9.97 and 10.32 ppm, which confirms the formation of strong H-bond interaction, while the other two amide NH protons, which can form six-member and five-member intramolecular H-bonds, have much lower chemical shifts of 8.72 and 8.20 ppm, respectively. These results imply that there exist intense intermolecular H-bonds between the two strands, which is consistent with those reported in the literatures [16] and [18]. Moreover, the ESI-MS spectrum of **III·III** gives additional evidence confirming the formation of dimmer structure, because the peak of the highest abundance appears at 1453.29, which can be assigned to the molecular ion of $2M^+$+Na^+-2; while another strong signal locates at 1455.27 with a relatively high abundance of 65%, which can be assigned to the molecular ion peak of $2M^+$+Na^+. All these evidences elucidate the successful self-association of the two strands, for the two oligoamide strands have complementary hydrogen-bond sequences of DADA and ADAD, respectively.

Photoluminescent (PL) properties of **III·III** are also investigated. The results indicate that the duplex can emit bright pure blue fluorescence under UV irradiation both in solid states and solution (Fig. 1). In 10^{-6} mol/L DMF solution, its fluorescence peak locates at 448 nm, with full width at half-maximum (FWHM) of 67 nm; while its PL spectrum determined from solid powder is slightly red-shifted (452 nm), with FWHM of 66 nm. The relative PL quantum yield of its solution in 10^{-6} mol/L DMF is determined as 0.778 [(using 4×10^{-6} mol/L quinine sulfate solution as reference (Φ_F = 0.55, excited at 366 nm in 1 mol/L H_2SO_4 at 22 °C)]. All these results suggest that **III·III** is a potential candidate as emitting dye for fabrication of both doped and nondoped pure blue organic LEDs.

Another interesting observation is that when dissolved in DMSO, the resulting solution of the duplex **III·III** shows increased viscosity with increased concentration, and would even form organogel at high concentration of >40 mmol/L at 25 °C, indicating the duplex acts as gelator to form a continuous, three-dimensional and entangled network through noncovalent forces such as hydrogen-bond and π-stacking, and reversible gel–sol transition would be

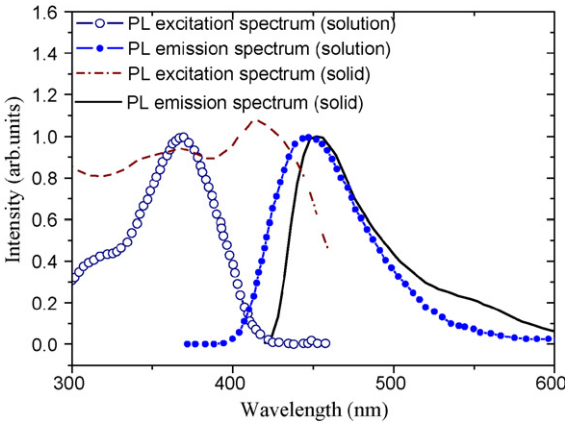

Fig. 1. The photoluminescent excitation and emission spectra of **III**·**III** in solution and solid state.

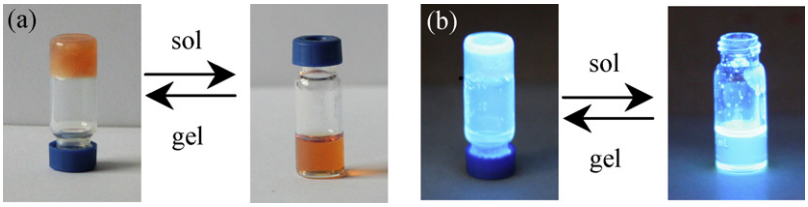

Fig. 2. (a) Sol (55 °C) and gel (25 °C) transition of **III**·**III** (in DMSO, $c = 40$ mmol/L); (b) the fluorescent properties of the sol–gel.

observed when the temperature is 55 °C (Fig. 2(a)). Furthermore, the organogel shows strong pure blue fluorescence too (Fig. 2(b)). These results suggest that the duplex may form unique films with well-defined structure through wet-process, which is beneficial to the efficient carrier transportation inner the LEDs.

Acknowledgments

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