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Aggregation induced emission properties of naphthalimide–coumarin conjugates with various intermolecular linkages

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ABSTRACT

Naphthalimide–coumarin conjugates (NCs **1–5**), possessing various linkages such as ether, thioether, secondary amine, acetylene and C–C single bond between naphthalimide and coumarin moieties, have been synthesized. NCs **1–5** were fully characterized by ^{1}H NMR, ^{13}C NMR and mass spectroscopy. The effects of linkages in NCs **1–5** on the absorption, fluorescence and aggregation induced emission (AIE) were explored. The electronic absorption spectra of the NCs **1–5** show red shifted absorption and fluorescence as compared to 4–bromo-naphthalimide. The secondary amine linked naphthalimide–coumarin (NC) **3** conjugate shows significant red shift in absorption and fluorescence, whereas other NCs show moderate red shifts. Among NCs conjugates, only thioether linked NC **2** clearly showed a significant AIE effect while the other NCs conjugates showed aggregation caused emission quenching.

1. Introduction

The design, synthesis and development of new luminescent materials have been of significant interest, due to their widespread advantages in several fields including sensors, biological and optoelectronics [1–4].1,8–Naphthalimide derivatives containing molecular systems are widely studied as DNA targeting binders [4–6], fluorescent sensors [7], anticancer agents [8], fluorescent cellular imaging agents [4], organic light emitting diodes [9], liquid crystals [10] and organic photovoltaics [11]. Coumarins are interesting heterocycles found in a variety of plant sources [12], and are widely used in various applications, such as laser dyes [13], fluorescent probes [14,15], organic light emitting diodes [16,17], solar cells [18], nonlinear optical chromophores [19], and biomedicines [20,21]. The fluorescence property of 1,8–naphthalimide derivatives can be modulated by changing the substituent at C–4 position [22]. Since, Tang et al., reported the first AIE effects, AIE fluorogens or fluorophores have been developed in the field of various applications, such as, sensing, biomedical, environmental monitoring, optoelectronic and green energy devices [23–29]. Zhu et al., reported the synthesis and AIE properties of an NPI–TPE conjugate (Fig. 1). This conjugate showed approximately 3–fold emission enhancement upon aggregation [30]. Li et al., reported the synthesis of naphthalimide bioprobe organic dye (FD–9) (Fig. 1), which showed AIE effects in methanol: water mixture (1:9 v/v) upon aggregation; its application for the monitoring of cell membranes was also shown [31]. Iyer et al., reported the synthesis and AIE properties of naphthalimide derivatives functionalized with α–naphthol, β–naphthol and 8–hydroxyquinoline (Fig. 1) [32]. Thilagar et al., reported a set of naphthalimide dyes, containing various phenol groups and 1–naphthol substituted at C–4 position of the naphthalimide structure (Fig. 1) [33–35]. 1–Naphthol naphthalimide derivative exhibited a 37.5–fold emission enhancement upon aggregation.

In this context, we focus on the effect of coumarin moiety linked via various intermolecular linkages such as ether, thioether, secondary amine, acetylene and C–C single bond between naphthalimide and coumarin moieties on the AIE properties of 1,8–naphthalimide derivatives. Herein, we report the design and synthesis of five naphthalimide–coumarin conjugates (NCs **1–5**) and their photophysical and AIE properties.

2. Experimental

2.1. Materials

All the chemicals were purchased from commercial sources and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were performed on 400 MHz and 150 MHz Bruker Ultrashield (Avance–III) Nano Bay spectrometer. All the spectra were recorded at 298 K.^{1}H NMR data are reported as follows: s: singlet, d: doublet, t: triplet, bs: broad singlet and coupling constants, *J*, are given in Hz. Chemical shifts in ^{1}H NMR and ^{13}C NMR spectra were reported in parts per million (ppm) with TMS (0 ppm) and $CDCl_3$ (77.00) as standards. TLC analysis was

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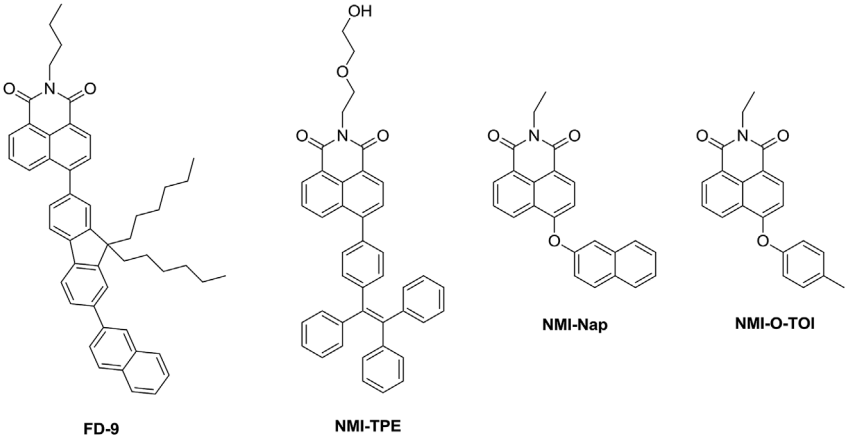

Fig. 1. Structures of previously reported naphthalimide based aggregation induced emission molecules.

carried out using silica gel 60 F_{254} plates. UV–vis absorption spectra of all compounds were recorded in THF on a Jasco V–670 UV–visible spectrophotometer. Dynamic light scattering was measured with Zeta–potential and particle size analyzer Otsuka ELSZ–2000 series. FT–IR spectra were measured with Jasco FT–IR–4000 series. TEM images were collected with a JEOL JEM–1010 filed–emission transmission electron microscope. Melting points were measured with differential scanning calorimetry TA instruments DSC–2010. Emission spectra were taken in a PerkinElmer LS 55 fluorescence spectrophotometer. The excitation and emission slits were 3 nm wide for the emission measurements. All the measurements were done at 298 K. Column chromatography was performed on Merck silica gel (230–400 mesh).

2.2. Synthesis

2.2.1. 2–Butyl–6–((4–methyl–2–oxo–2H–chromen–7–yl)oxy)–1H–benzo [de]isoquinoline–1,3(2H)–dione, 1

6–Bromo–2–butyl–benzo [*de*]isoquinoline–1,3–dione **7** (0.2 g, 0.604 mmol), 7–hydroxy–4–methylcoumarin (0.10 g, 0.604 mmol) and potassium carbonate (0.24 g, 1.81 mmol) were taken in dry *N*, *N*–dimethylformamide (15 mL) and stirred at 90 °C for 3 h. Upon completion of the reaction, the mixture was cooled and *N*, *N*–dimethylformamide was evaporated under vacuum and the obtained crude solid was extracted with chloroform (50 × 2) and dried on sodium sulphate and chloroform was evaporated under vacuum to obtain the residue. Then the residue was purified on silica gel column chromatography employing hexane: ethyl acetate (7:3, V/V). Yield, 48% (0.13 g), m. p. 179 °C. IR (KBr): ν_{max}/cm^{-1} 1721 (νCO), 1691 (νCO). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, 1H, J = 7.2 Hz, aromatic), 8.58 (d, 1H, J = 8.4 Hz, aromatic), 8.52 (d, 1H, J = 8.4 Hz, aromatic), 7.79 (t, 1H, J = 7.2 Hz, aromatic), 7.67 (d, 1H, J = 9.2 Hz, aromatic), 7.12–7.08 (m, 3H, aromatic), 6.28 (d, 1H, J = 1.2 Hz, aromatic), 4.19 (t, 2H, J = 7.6 Hz, CH_2), 1.76–1.69 (m, 2H, CH_2), 1.50–1.41 (m, 2H, CH_2), 0.98 (t, 3H, J = 7.6 Hz, CH_3). ^{13}C (150 MHz, $CDCl_3$) δ 164.17, 163.55, 160.37, 158.39, 157.75, 155.04, 151.87, 132.37, 132.08, 129.78, 128.17, 127.03, 126.45, 124.29, 122.90, 118.31, 117.10, 115.84, 114.20, 112.92, 108.11, 40.27, 30.23, 20.39, 18.80, 13.87.

HRMS (*m/z*): [M + H] calculated for $C_{26}H_{22}NO_5$: 428.1498; Found: 428.1497.

2.2.2. 2–Butyl–6–((4–methyl–2–oxo–2H–chromen–7–yl)thio)–1H–benzo [de]isoquinoline–1,3(2H)–dione, 2

6–Bromo–2–butyl–benzo [*de*]isoquinoline–1,3–dione **7** (0.2 g, 0.604 mmol), 7–mercapto–4–methylcoumarin (0.11 g, 0.604 mmol) and potassium carbonate (0.24 g, 1.81 mmol) were taken in dry *N*, *N*–dimethylformamide (15 mL) and stirred at 90 °C for 3 h. Upon completion of the reaction, the mixture was cooled and *N*, *N*–dimethylformamide was evaporated under vacuum and the obtained crude solid was extracted with chloroform (50 × 2) and dried on sodium sulphate and chloroform was evaporated under vacuum to obtain the residue. Then the residue was purified on silica gel column chromatography employing hexane: ethyl acetate (8:2, V/V). Yield, 74.38% (0.21 g), m. p. 208 °C, IR (KBr): ν_{max}/cm^{-1} 1720 (νCO), 1691 (νCO). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, 1H, J = 7.6 Hz, aromatic), 8.61 (d, 1H, J = 8.4 Hz, aromatic), 8.51 (d, 1H, J = 7.6 Hz, aromatic), 7.80–7.76 (m, 2H, aromatic), 7.53 (d, 1H, J = 8.4 Hz, aromatic), 7.19 (dd, J^{1-2} = 1.6 Hz, J^{1-3} = 8.4 Hz,1H, aromatic), 7.11 (d, 1H, J = 1.6 Hz, aromatic), 6.27 (s, 1H), 4.20 (t, 2H, J = 7.6 Hz, CH_2), 2.45 (s, 3H, CH_3), 1.77–1.69 (m, 2H, CH_2), 1.50–1.41 (m, 2H, CH_2), 0.98 (t, 3H, J = 7.6 Hz, CH_3). ^{13}C (150 MHz, $CDCl_3$) δ163.73, 163.59, 160.02, 153.92, 151.73, 139.59, 139.01, 131.87, 131.63, 131.27, 130.95, 130.72, 128.86, 127.83, 123.48, 122.97, 119.04, 117.90, 115.15, 40.37, 30.18, 20.37, 18.62, 13.85. HRMS (*m/z*): [M + H] calculated for $C_{26}H_{22}NO_4S$: 444.1270; Found: 444.1275.

2.2.3. Synthesis of 2–Butyl–6–((4–methyl–2–oxo–2H–chromen–7–yl) amino)–1H–benzo[de]isoquinoline–1,3(2H)–dione, 3

2–Butyl–6–ethynyl–1*H*–benz [*de*]isoquinoline–1,3(2*H*)–dione **7** (0.2 g, 0.604 mmol) and 7–amino–4–methylcoumarin (0.105 g, 0.604 mmol) were dissolved in toluene and the mixture was deaerated by bubbling with nitrogen gas for 10 min; then, Pd $(dppf)_2Cl_2$ (8.88 mg, 2mol%) and sodium–*tert*–butoxide (0.087 g, 0.906 mmol) were added. The solution was deaerated for further 5 min; after that, the reaction mixture was refluxed at 110 °C under nitrogen atmosphere for overnight. After completion of the reaction, the reaction mixture was cooled to room temperature and the solvent was evaporated. The crude product was dissolved in dichloromethane and purified by using silica gel column chromatography with hexane: ethyl acetate (6:4, v/v %) as eluant. **NC 3** was obtained in 63.8% yield (0.17 g), m. p. 301 °C. IR (KBr): ν_{max}/cm^{-1} 3319 (νNH) 1739 (νCO), 1690 (νCO). ^{1}H NMR (400 MHz, DMSO–d_6) δ 9.71 (s, NH, 1H, D_2O exchanged), 8.75 (d, 1H, J = 8.4 Hz, aromatic), 8.54 (d, 1H, J = 7.6 Hz, aromatic), 8.40 (d, 1H, J = 8.4 Hz, aromatic), 7.87 (t, 1H, J = 8.4 Hz, aromatic), 7.77 (d, 1H, J = 8.4 Hz, aromatic), 7.68 (d, 1H, J = 8.4 Hz, aromatic), 7.36 (d, 1H, J = 8.8 Hz, aromatic), 6.25 (s, 1H), 4.05 (t, 2H, J = 7.6 Hz, CH_2), 2.43 (s, 3H, CH_3), 1.64–1.60 (m, 2H, CH_2), 1.39–1.33 (m, 2H, CH_2), 0.94 (t, 3H, J = 7.6 Hz, CH_3)·^{13}C (150 MHz, $CDCl_3$) δ 163.49, 162.77, 159.99, 154.33, 153.18, 145.31, 144.96, 132.71, 131.14, 129.20, 129.13, 126.50, 125.81, 123.20, 122.20, 115.72, 114.22, 114.00, 112.01, 114.41, 105.45, 39.95, 29.67, 19.75, 18.00, 13.68.

HRMS (*m/z*): [M + H] calculated for $C_{26}H_{23}N_2O_4$: 427.1658; Found: 427.1655.